Complex Atoms

described by orthogonal operators

(to Jørgen, Brian and Ton)

Peter H.M. Uylings

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Complex Atoms

This reference booklet on the machinery and implementation of orthogonal operators as a method to describe complex atoms, would not have existed without the many years of knowledgeable support from Jørgen E Hansen, Brian Judd and Ton Raassen.

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Anton Pannekoek Institute for Astronomy
University of Amsterdam
Science Park 904, 1098 XH Amsterdam
The Netherlands;
E: p.uylings@contact.uva.nl

Cover design and realization: Rob Uylings

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Preface

In atomic systems with their essentially spherical symmetry, quantities of interest may be factorized as the product of a spin-angular and a radial factor. Spin-angular factors can be calculated by Racah algebra while radial factors can be approximated by *ab initio* Hartree-Fock programs that are increasingly capable of performing large-scale, relativistic calculations [Froese Fischer et al., 2016, Jönsson et al., 2017]. On the other hand, given known spin-angular matrices and an accurately enough prediction, radial energy factors may also be treated as parameters and determined semi-empirically. Stimulated by newly developed computer packages, the focus of attention has over the last 50 years shifted much from the spin-angular towards the radial side. To attain the desired degree of accuracy, however, complex spectra are still analyzed semi-empirically either using Cowan's Slater-Condon approach [Cowan, 1981] or orthogonal operators [Judd et al., 1982] as described in the present work. In both these approaches (especially in the last), effective operators are used to account for second and higher orders of perturbation. There is thus a growing gap between the (partially perturbation based) semi-empirical approaches employing the supposedly non-relativistic $SL-$coupling and the present-day large scale (variation based) *ab initio* computations using the relativistic $jj-$coupling. One of the aims of this work is to reconcile the two methods showing how relativistic quantities derived within $jj-$coupling can be fitted into an $SL-$coupled framework.

This booklet is primarily intended as a resource for experimental and theoretical research atomic physicists. Atomic units are used throughout, with only a few exceptions like transition probabilities that are traditionally given in SI. The most common conventions for the reduced matrix elements, the Wigner $nj-$symbols and phases are applied everywhere with the possible exception of the cfp's, where the original Racah phases [Nielson and Koster, 1963] are still used instead of the possibly more principal quasispin phase [Judd, 1967].

In 1975, I followed Bernard Metsch as a master student at the Amsterdam Zeeman Laboratory. Soon, Jørgen Hansen came to support our group theoretically, and it was during his first stay that he handed out some sheets of paper with formulae of practical use. In later years, I have used them that frequently that they worn out and had to be replaced by a LaTeXversion. This LaTeXversion actually became the start of the present work, and the original formulae can still be found in chapters 2 and 3 of Part I; the focus remains on their practical use rather than on the mathematical background.
In the late seventies, John Morrison stayed some years at the Zeeman Laboratory

while finishing his part of the book *Atomic Many-Body Theory* [Lindgren and Morrison, 1982]; he pointed out the possibilities of the graphical approach treated in chapter 4. Soon thereafter, Jørgen Hansen got a permanent position in Amsterdam and became my PhD supervisor on the subject of orthogonal operators: [Newman, 1981, Newman, 1982, Judd et al., 1982] were published and atomic physics had gained a promising new method.

The field of second quantization opened up for me by studying Brian Judd's compact but illuminating monograph *Second Quantization and Atomic Spectroscopy* [Judd, 1967]. Second quantization runs like a thread through this booklet.
In chapter 5, it is used to derive several relations between coefficients of fractional parentage. More importantly, operators are consistently dissected to their underlying bone structure in terms of second quantization; a cooking recipe to do this is given in section 5.3. Any one-particle operator may be written as
$F^{(\kappa k)t} = -S(a,b) \cdot (\mathbf{a}^\dagger \mathbf{b})^{(\kappa k)t}$ with the radial factor $S(a,b) = [\kappa,k]^{-\frac{1}{2}} \langle a \parallel F^{(\kappa k)} \parallel b \rangle$; Hermiticity requires that $\kappa + k + t$ is even. Moreover, it will be shown that an elementary $jj \rightarrow SL$ recoupling suffices to replace $S(a,b)$ by its relativistic analogue $S_R(a,b)$ with the identical spin-angular behavior. Similar expressions apply to two-particle operators. The strength of translating traditional tensor operators into second quantized form is illustrated in chapter 5 by the matrix element calculation of various intricate Breit-Pauli operators. Products of operators are encountered in perturbation theory as well as with inner products: in both cases, second quantization is fruitfully employed to calculate the summations in closed form. Second quantization is also used to derive the transformation of relativistic reduced matrix elements towards the radial factors $S_R(a,b)$ in a quick and transparent way.

The main text of the book is divided into three parts.
Part I outlines the general theory of Racah algebra (chapters 2 and 3), graphical representations (chapter 4) and second quantization (chapter 5), i.e. the technology for performing practical calculations subsequently illustrated in chapters 6 and 7. Chapters 8 and 16 concern some work I did in support of the Zeeman Laboratory laser group. No attempt has been made to include pure quantum-electrodynamical (QED) effects; topics like parity non-conservation (chapter 9) or group theory (chapter 13) are only treated superficially for the sake of completeness.
Part II is devoted to the theory of orthogonal operators in addition to essential supporting subjects like the Hartree-Fock approach, perturbation theory and the use of B-splines therein. The concept of an operator inner product could have been used in the thirties e.g. with [Condon and Shortley, 1935], but it took until the early eighties that the added value of a linear algebra of operators was seen. Orthogonality ensures least correlation between the operators and this increased stability appears to be a powerful tool in reducing the deviations between calculated and experimental energy values in complex spectra ($Z > 20$). Due to its orthogonality, the operator set is stable enough to introduce small (thus far neglected) higher-order magnetic and electrostatic effects in the fitting procedure. By this extension, deviations between calculated and experimental energy values frequently approach experimental accuracy. Also, the linear algebra of operators can fruitfully be used to project

a variety of contributions onto the orthogonal operator set, both analytically and numerically, using the central equation (14.26); this procedure supersedes the often used but incomplete direct proportionality like the Δ–factors in hyperfine structure. It was actually in this way, that the Blume and Watson theory for the spin-orbit interaction [Blume and Watson, 1962] was generalized and corrected [Uylings, 1989] and other contributions than $s \rightarrow d$ excitations to the Trees operator were found.
Part III deals with the application of relativity in atoms and ions. Chapter 19 sets out some of the mathematical machinery of relativistic calculations with the Dirac-Breit Hamiltonian. Expressions for the reduced matrix elements are given in explicit form in chapter 20, together with their relevant non-relativistic limits. This leads e.g. to the slightly surprising result $(\frac{1}{2}lj \parallel \boldsymbol{\alpha} \parallel \frac{1}{2}l'j') \rightarrow -\alpha \left\langle \frac{1}{2}lj \parallel \boldsymbol{p} \parallel \frac{1}{2}l'j' \right\rangle$.
Many authors gave non-relativistic limits of the occurring reduced matrix elements. For a complete comparison, however, the full operator should also possess the correct spin-angular character like $(\mathbf{a}^\dagger \mathbf{b})^{(\kappa k)t}$ or $\left\{ (\mathbf{a}^\dagger \mathbf{c})^{\kappa_1 k_1} (\mathbf{b}^\dagger \mathbf{d})^{\kappa_2 k_2} \right\}^{(\kappa k)t}$.
It is shown in chapter 21 how this can be achieved by a $jj \rightarrow SL$ coupling transformation yielding the correct weighting procedure over j, j'. It should be emphasized that this way of finding the correct non-relativistic limit is not just a formal point of retrieving well known results in an alternative way: precisely this procedure can be used to replace non-relativistic quantities $S(a, b)$ by their relativistic analogues $S_R(a, b)$ thereby implementing full relativity in the SL–framework.
A case in point is the magnetic multipole radiation: while the relativistic integrals are the same, the orbit and spin terms in the SL–framework differ slightly as a result of different j–dependent weighting factors.
Subjects like the Zeeman effect, hyperfine structure and (electric or magnetic multipole) transition probabilities are first treated non-relativistically, indicated by a (1) in chapters 3 and 7; later, their relativistic counterparts are given in chapters 22 and 23, indicated by a (2). The appendices contain supplementary material.
In summary, the followed approach enables one to implement full relativity while adopting the known large body of SL–formulae in full. Double tensors and operators in second quantization like $(\mathbf{a}^\dagger \mathbf{b})^{(\kappa k)t}$ can be maintained without adjustments for the same reason. To define, apply and find the contributions of any operator, one can be content to know the matrix elements in its parent configuration and use the formulae from sections 14.2 and 14.6 to find the necessary N–dependence.

It is a pleasure to work with so many colleagues in the field like (theory) Brian Judd, Charlotte Froese Fischer, Bob Cowan and Jørgen Hansen and (experiment) Jean-François Wyart, Lydia Tchang-Brillet, Vladimir Azarov, Yogi Joshi, Dik van Kleef, Sasha Ryabtsev (with whom Ton and I stayed in contact during our twenty years of absence), and many others. Most of all, I would like to mention my friend and close colleague Ton Raassen: without him, orthogonal operators would hardly be the effective method it is today. I would also like to express my appreciation to Tomas Brage, Alan Hibbert, Gediminas Gaigalas, Michel Godefroid and Sasha Kramida for stimulating our comeback in the field of atomic physics.

Amsterdam, January 2021 Peter Uylings

Part I

General theory

Chapter 1

Hartree atomic units au

Hartree's system of atomic units is based on setting the below constants to one:

- e
- m_e
- $\hbar$
- $4\pi\varepsilon_0 = f^{-1}$

As a result, the Bohr radius $a_0 = \hbar^2/(m_e \cdot fe^2) \to 1$ is the au unit of length.
1 b (=barn)$\to 3.57106483 \cdot 10^{-8}$ in au.

The fine-structure constant $\alpha = fe^2/(\hbar c) \to c^{-1}$, so $c = \alpha^{-1} \approx 137.036$ in au and the (reduced) Compton wavelength of the electron: $\lambda\!\!\!^{-}_e = \alpha \cdot a_0 = \hbar/m_e c$.
Likewise, the Rydberg constant $R_\infty = (m_e e^4 f^2)/(\hbar^3 4\pi c) \to \alpha/4\pi$ in au.

Therefore, the energy Ry= hcR_∞ = 13.605693 eV (often used in spectroscopy) $\to \frac{1}{2}$ in au and thus 1 H = 1 E_h = 2 Ry = $\hbar^2/(m_e a_0^2)$ = 27.21138602 eV is the au of energy.
The well-known non-relativistic formula for the energies of hydrogen thus becomes in au: $\varepsilon_n = -1/(2n^2)$.

1 H = 1 au = 219474.631 cm^{-1} and 1 eV = 8065.54402 cm^{-1}, whereas
1 cm^{-1} = $1.98644561 \times 10^{-23}$ J.

The Bohr magneton in SI: $\mu_B = e\hbar/(2m_e) \to \frac{1}{2}$ in au.
In Gaussian-CGS: $\mu_B = e\hbar/(2m_e c) \to \frac{1}{2}\alpha$ in au.
In SI, the au unit of magnetic field is given by: $\hbar/(ea_0^2) = 2.350517568 \times 10^5$ T.
In Gaussian-CGS: $ef/(a_0^2 c) = 1.71525554 \times 10^3$ T, again differing by a factor α.

Similarly, as $\mu_0\varepsilon_0 = c^{-2}$ [$\to \varepsilon_0 = (4\pi c^2 \times 10^{-7})^{-1}$ in SI], the magnetic constant $\mu_0/4\pi \to \alpha^2$ in au.

Combining the above two formulae, one obtains for the frequently encountered magnetic constant $\mu_0/(2\pi) \cdot \mu_B \to 2\alpha^2 \cdot \frac{1}{2} = \alpha^2$.

1.1 Constants of nature

speed of light	c	=	2.99792458×10^{8}	m s^{-1}
Bohr radius	a_0	=	$5.29177211 \times 10^{-11}$	m
electron charge	e	=	$1.60217663 \times 10^{-19}$	C
electron mass	m_e	=	$9.10938371 \times 10^{-31}$	kg
Planck constant	h	=	$6.62607015 \times 10^{-34}$	J s
reduced Planck constant	$\hbar$	=	$1.05457182 \times 10^{-34}$	J s
Boltzmann constant	k	=	$1.38064900 \times 10^{-23}$	J K^{-1}
Hartree energy a.u.	H	=	$4.35974472 \times 10^{-18}$	J
Hartree energy a.u.	H	=	2.72113860×10^{1}	eV
Hartree energy a.u.	H	=	2.19474631×10^{5}	cm^{-1}
Rydberg constant	R_∞	=	1.09737316×10^{7}	m^{-1}
fine-structure constant	α	=	$7.29735257 \times 10^{-3}$	
Bohr magneton	μ_B	=	$9.27401008 \times 10^{-24}$	J T^{-1}
electron g factor	g_s	=	2.00231930	
electron QED correction	$\frac{1}{2}(g_s - 2)$	=	$1.15965219 \times 10^{-3}$	
proton g factor	g_p	=	5.58569469	
electron-proton mass ratio	m_e/m_p	=	$5.44617021 \times 10^{-4}$	
time a.u.	$m_e a_0^2/\hbar$	=	$2.41888433 \times 10^{-17}$	s
velocity a.u.	αc	=	2.18769126×10^{6}	m s^{-1}

1.2 Some basic mathematics

$$a^x = e^{x \cdot \ln a} \qquad {}^a\log x = \frac{\ln x}{\ln a} \qquad \int_0^\infty (Fg)\,\mathrm{d}r = [FG]_0^\infty - \int_0^\infty (fG)\,\mathrm{d}r$$

$$\int_0^\infty x^k \cdot e^{-mx}\,\mathrm{d}x = \frac{k!}{m^{k+1}} \tag{1.1a}$$

$$\int_0^\infty x^k \cdot e^{-ax^2}\,\mathrm{d}x = \frac{\frac{1}{2} \cdot \left(\frac{k-1}{2}\right)!}{a^{\left(\frac{k+1}{2}\right)}} \text{ with } \left(-\tfrac{1}{2}\right)! = \sqrt{\pi} \tag{1.1b}$$

$$\int_0^\infty \frac{x^k}{e^x - 1}\,\mathrm{d}x = k! \sum_{n=1}^{\infty} n^{-(k+1)} \tag{1.1c}$$

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c})\,\mathbf{b} - (\mathbf{a} \cdot \mathbf{b})\,\mathbf{c} \tag{1.2}$$

$$\boldsymbol{\nabla} \times (\mathbf{a}\phi) = \phi(\boldsymbol{\nabla} \times \mathbf{a}) - \mathbf{a} \times \boldsymbol{\nabla}\phi \qquad \nabla \times \nabla\phi = 0 \tag{1.3}$$

$$\mathbf{a} \cdot (\mathbf{a} \times \mathbf{b}) = \mathbf{b} \cdot (\mathbf{a} \times \mathbf{b}) = 0 \qquad \boldsymbol{\nabla} \cdot (\mathbf{a} \times \mathbf{b}) = \mathbf{b} \cdot (\boldsymbol{\nabla} \times \mathbf{a}) - \mathbf{a} \cdot (\boldsymbol{\nabla} \times \mathbf{b}) \tag{1.4}$$

Chapter 2

nj-symbols

2.1 Basic 3j-symbols

For the $3j$-symbol $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$, every odd permutation of columns or sign reversal of the $m-$values yields a phase $(-1)^{j_1+j_2+j_3}$.
Here, j_1, j_2 and j_3 fulfill the triangular condition $\{j_1 j_2 j_3\}$ and $m_1 + m_2 + m_3 = 0$.

Under the requirement that $g = \frac{1}{2}(l + k + l')$ be an integer, i.e. $l + k + l'$ is even:

$$\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} = (-1)^g \sqrt{\frac{(2g-2l)!(2g-2k)!(2g-2l')!}{(2g+1)!}} \; \frac{g!}{(g-l)!(g-k)!(g-l')!} \tag{2.1}$$

2.2 Sum rules and definitions

$$\sum_{j_3 m_3} [j_3] \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta(m_1, m_1') \cdot \delta(m_2, m_2') \tag{2.2}$$

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = [j_3]^{-1} \cdot \delta(j_3, j_3') \cdot \delta(m_3, m_3') \tag{2.3}$$

The Wigner $6j$-symbol differs from the Racah W-function [Racah, 1942b] in phase only:

$$\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} = (-1)^{a+b+c+d} \cdot W(abcd; ef) \tag{2.4}$$

[Jahn, 1951] gives the alternative U-coefficient:

$$\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} = (-1)^{a+b+c+d} \cdot [e, f]^{-\frac{1}{2}} \cdot U(abcd; ef) \tag{2.5}$$

it follows directly that $U(abcd;ef) = [e,f]^{\frac{1}{2}} \cdot W(abcd;ef)$.

Any of the six possible permutations of its columns leaves a $6j$-symbol invariant:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_2 & j_1 & j_3 \\ j_5 & j_4 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_2 & j_3 & j_1 \\ j_5 & j_6 & j_4 \end{Bmatrix} \tag{2.6}$$

Any two elements in the upper row may be interchanged with the elements underneath:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_4 & j_5 & j_3 \\ j_1 & j_2 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_4 & j_2 & j_6 \\ j_1 & j_5 & j_3 \end{Bmatrix} = \begin{Bmatrix} j_1 & j_5 & j_6 \\ j_4 & j_2 & j_3 \end{Bmatrix} \tag{2.7}$$

There are four triangular conditions to be satisfied:

$$\begin{Bmatrix} \circ & \cdots & \circ & \cdots & \circ \\ & & & & \end{Bmatrix} \quad \begin{Bmatrix} & & \circ & & \\ & \iddots & & \ddots & \\ \circ & & & & \circ \end{Bmatrix}$$
$$\begin{Bmatrix} \circ & & & & \\ & \ddots & & & \\ & & \circ & \cdots & \circ \end{Bmatrix} \quad \begin{Bmatrix} & & & & \circ \\ & & & \iddots & \\ \circ & \cdots & \circ & & \end{Bmatrix} \tag{2.8}$$

2.2.1 Summations

$$\sum_x [x] \begin{Bmatrix} a & b & x \\ a & b & p \end{Bmatrix} = (-1)^{2a+2b} \tag{2.9}$$

$$\sum_x [x](-1)^{-x} \begin{Bmatrix} a & b & x \\ b & a & p \end{Bmatrix} = \delta(p,0)\,(-1)^{a+b}\,[a,b]^{\frac{1}{2}} \tag{2.10}$$

$$\sum_x [x] \begin{Bmatrix} a & b & x \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & x \\ a & b & q \end{Bmatrix} = \frac{\delta(p,q)}{[p]} \tag{2.11}$$

$$\sum_x [x]\,(-1)^{p+q+x} \begin{Bmatrix} a & b & x \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & x \\ b & a & q \end{Bmatrix} = \begin{Bmatrix} c & a & q \\ d & b & p \end{Bmatrix} \tag{2.12}$$

$$\sum_x [x]\,(-1)^{x+p+q+r+a+b+c+d+e+f} \begin{Bmatrix} a & b & x \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & x \\ e & f & q \end{Bmatrix} \begin{Bmatrix} e & f & x \\ b & a & r \end{Bmatrix} = \begin{Bmatrix} p & q & r \\ e & a & d \end{Bmatrix} \begin{Bmatrix} p & q & r \\ f & b & c \end{Bmatrix} \tag{2.13}$$

The $9-j$ symbol is defined as:

$$\begin{Bmatrix} a & f & r \\ d & q & e \\ p & c & b \end{Bmatrix} = \sum_x [x]\,(-1)^{2x} \begin{Bmatrix} a & b & x \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & x \\ e & f & q \end{Bmatrix} \begin{Bmatrix} e & f & x \\ a & b & r \end{Bmatrix} \tag{2.14}$$

Every odd permutation of rows or columns produces a sign change of $(-1)^T$, with $T = a+b+c+d+e+f+p+q+r$ the sum of all nine arguments. Every even permutation of rows and columns, therefore, leaves the symbol unchanged.
Also, rows and columns may be interchanged (transposition):

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix} = \begin{Bmatrix} a & d & g \\ b & e & h \\ c & f & i \end{Bmatrix} = \begin{Bmatrix} i & f & c \\ h & e & b \\ g & d & a \end{Bmatrix} = \begin{Bmatrix} i & h & g \\ f & e & d \\ c & b & a \end{Bmatrix} \tag{2.15}$$

$$\sum_x [x] \begin{Bmatrix} a & b & x \\ d & c & a \\ c & e & b \end{Bmatrix} = [c]^{-1} \tag{2.16}$$

$$\sum_x [x] (-1)^x \begin{Bmatrix} a & b & x \\ c & d & b \\ e & c & a \end{Bmatrix} = [c]^{-1} \cdot (-1)^{2b+e-d} \tag{2.17}$$

$$\sum_x [x] \begin{Bmatrix} a & f & x \\ d & q & e \\ p & c & b \end{Bmatrix} \begin{Bmatrix} a & f & x \\ e & b & \lambda \end{Bmatrix} = (-1)^{2\lambda} \begin{Bmatrix} c & d & \lambda \\ e & f & q \end{Bmatrix} \begin{Bmatrix} a & b & \lambda \\ c & d & p \end{Bmatrix} \tag{2.18}$$

$$\sum_{x,y} [x,y] \begin{Bmatrix} a & f & x \\ d & q & y \\ p & c & b \end{Bmatrix} \begin{Bmatrix} a & f & x \\ d & q & y \\ p' & c' & b \end{Bmatrix} = \delta(p,p')\, \delta(c,c')\, [p,c]^{-1} \tag{2.19}$$

$$\sum_{x,y} [x,y] (-1)^x \begin{Bmatrix} a & d & x \\ b & e & y \\ c & f & g \end{Bmatrix} \begin{Bmatrix} d & a & x \\ b & e & y \\ h & i & g \end{Bmatrix} = (-1)^{a+b+d-e+f+i-g} \begin{Bmatrix} a & b & c \\ e & d & f \\ i & h & g \end{Bmatrix} \tag{2.20}$$

With $R_4 = \sum_{i=1}^4 (j_i + l_i + k_i)$, the 12j-symbol of the first kind is defined as:

$$\begin{Bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{Bmatrix} = \sum_x [x] (-1)^{R_4 - x} \begin{Bmatrix} j_1 & k_1 & x \\ k_2 & j_2 & l_1 \end{Bmatrix} \begin{Bmatrix} j_2 & k_2 & x \\ k_3 & j_3 & l_2 \end{Bmatrix} \times \begin{Bmatrix} j_3 & k_3 & x \\ k_4 & j_4 & l_3 \end{Bmatrix} \begin{Bmatrix} j_4 & k_4 & x \\ j_1 & k_1 & l_4 \end{Bmatrix} \tag{2.21}$$

The symmetric 12j-symbol of the second kind is given by:

$$\begin{bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{bmatrix} = (-1)^{l_1 - l_2 - l_3 + l_4} \sum_x [x] \begin{Bmatrix} k_1 & k_2 & x \\ j_3 & j_1 & l_1 \end{Bmatrix} \begin{Bmatrix} k_3 & k_4 & x \\ j_3 & j_1 & l_2 \end{Bmatrix} \times \begin{Bmatrix} k_1 & k_2 & x \\ j_4 & j_2 & l_3 \end{Bmatrix} \begin{Bmatrix} k_3 & k_4 & x \\ j_4 & j_2 & l_4 \end{Bmatrix} \tag{2.22}$$

$$\sum_x [x] \begin{Bmatrix} l_4 & l_1 & x \\ k_3 & j_1 & l_2 \end{Bmatrix} \begin{Bmatrix} l_4 & l_1 & x \\ k_4 & j_3 & l_2 \end{Bmatrix} \tag{2.23}$$
$$= (-1)^{j_1-j_2-j_3+j_4} \begin{bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{bmatrix}$$

$$\sum_x [x] \begin{bmatrix} x & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{bmatrix} = \delta(l_1,l_2)\,\delta(l_3,l_4)\,\delta(k_1,k_3)\,\delta(k_2,k_4)\,[l_4,k_4]^{-1} \tag{2.24}$$

$$\sum_x [x] (-1)^x \begin{bmatrix} x & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{bmatrix}$$
$$= \delta(k_1,l_2)\,\delta(l_1,k_3)\,(-1)^{l_1+l+2-l_3+l_4}(-1)^{k_2-k_4} \begin{Bmatrix} k_1 & k_4 & j_3 \\ j_2 & l_4 & k_3 \\ l_3 & j_4 & k_2 \end{Bmatrix} \tag{2.25}$$

2.3 Reductions

$$\begin{Bmatrix} a & b & c \\ 0 & c & b \end{Bmatrix} = (-1)^{a+b+c}\,[b,c]^{-\frac{1}{2}} \tag{2.26}$$

$$\begin{Bmatrix} a & b & e \\ c & d & e \\ f & f & 0 \end{Bmatrix} = \begin{Bmatrix} 0 & e & e \\ f & d & b \end{Bmatrix} = \begin{Bmatrix} e & 0 & e \\ c & f & a \end{Bmatrix} = \begin{Bmatrix} f & f & 0 \\ d & c & e \end{Bmatrix} = \begin{Bmatrix} f & b & d \\ 0 & e & e \\ f & a & c \end{Bmatrix} =$$
$$\begin{Bmatrix} a & f & c \\ e & 0 & e \\ b & f & d \end{Bmatrix} = \begin{Bmatrix} b & a & e \\ f & f & 0 \\ d & c & e \end{Bmatrix} = \begin{Bmatrix} e & d & c \\ e & b & a \\ 0 & f & f \end{Bmatrix} = \begin{Bmatrix} c & e & d \\ a & e & b \\ f & 0 & f \end{Bmatrix}$$
$$= (-1)^{b+c+e+f}\,[e,f]^{-\frac{1}{2}} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} \tag{2.27}$$

$$\begin{Bmatrix} a & b & c \\ a & b & c \\ 0 & 0 & 0 \end{Bmatrix} = \begin{Bmatrix} a & a & 0 \\ b & b & 0 \\ c & c & 0 \end{Bmatrix} = [a,b,c]^{-\frac{1}{2}} \tag{2.28}$$

$$\begin{Bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & 0 \\ k_1 & k_2 & k_3 & k_4 \end{Bmatrix} = \delta(j_4,k_1)\cdot\delta(k_4,j_1)\cdot[j_1,k_1]^{-\frac{1}{2}}$$
$$\times \begin{Bmatrix} j_1 & l_1 & j_2 \\ k_3 & k_2 & l_2 \\ l_3 & k_1 & j_3 \end{Bmatrix} \tag{2.29}$$

$$\begin{Bmatrix} j_1 & j_2 & j_3 & 0 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{Bmatrix} = \delta(j_3,l_3)\cdot\delta(k_1,l_4)\cdot[l_3,l_4]^{-\frac{1}{2}}$$
$$\times(-1)^{l_1+l_2+l_3+k_1-j_2-k_2}\cdot\begin{Bmatrix} j_1 & k_1 & k_4 \\ k_2 & j_2 & l_1 \end{Bmatrix}\begin{Bmatrix} j_2 & k_2 & k_4 \\ k_3 & j_3 & l_2 \end{Bmatrix} \tag{2.30}$$

$$\begin{Bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ 0 & k_2 & k_3 & k_4 \end{Bmatrix} = \delta(k_2,l_1)\cdot\delta(j_4,l_4)\cdot[l_1,l_4]^{-\frac{1}{2}}$$
$$\times(-1)^{l_1+l_2+l_3+l_4-j_3-k_3}\cdot\begin{Bmatrix} j_2 & l_1 & j_1 \\ k_3 & j_3 & l_2 \end{Bmatrix}\begin{Bmatrix} j_3 & k_3 & j_1 \\ k_4 & l_4 & l_3 \end{Bmatrix} \tag{2.31}$$

$$\begin{Bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & 0 & k_3 & k_4 \end{Bmatrix} = \delta(k_1,l_1)\cdot\delta(k_3,l_2)\cdot[l_1,l_2]^{-\frac{1}{2}}$$
$$\times(-1)^{l_1+l_2+l_3+l_4-j_4-k_4}\cdot\begin{Bmatrix} j_3 & l_2 & j_2 \\ k_4 & j_4 & l_3 \end{Bmatrix}\begin{Bmatrix} j_4 & k_4 & j_2 \\ j_1 & l_1 & l_4 \end{Bmatrix} \tag{2.32}$$

$$\begin{bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & 0 \end{bmatrix} = \delta(j_4,l_4)\,\delta(j_3,l_2)\,[l_2,l_4]^{-\frac{1}{2}}\,(-1)^{j_1+l_1-j_2-l_3}$$
$$\begin{Bmatrix} l_1 & l_2 & k_2 \\ k_3 & k_1 & j_1 \end{Bmatrix}\begin{Bmatrix} k_2 & l_3 & l_4 \\ j_2 & k_3 & k_1 \end{Bmatrix} \tag{2.33}$$

$$\begin{bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & 0 & k_3 & k_4 \end{bmatrix} = \delta(j_4,l_3)\,\delta(j_3,l_1)\,[l_1,l_3]^{-\frac{1}{2}}\,(-1)^{j_1-j_2+l_2-l_4}$$
$$\begin{Bmatrix} j_2 & k_1 & l_3 \\ k_4 & l_4 & k_3 \end{Bmatrix}\begin{Bmatrix} k_1 & j_1 & l_1 \\ l_2 & k_4 & k_3 \end{Bmatrix} \tag{2.34}$$

$$\begin{bmatrix} j_1 & j_2 & j_3 & j_4 \\ 0 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{bmatrix} = \delta(j_1,k_1)\,\delta(j_3,k_2)\,[j_1,j_3]^{-\frac{1}{2}}\,(-1)^{j_2+k_3-j_4-k_4}$$
$$\begin{Bmatrix} l_2 & l_3 & l_4 \\ j_2 & k_3 & j_1 \end{Bmatrix}\begin{Bmatrix} l_2 & l_3 & l_4 \\ j_4 & k_4 & j_3 \end{Bmatrix} \tag{2.35}$$

2.4 Recoupling identities

Change order of coupling, like in going from $|LS;J\rangle$ to $|SL;J\rangle$:

$$\langle j_1 j_2; J | j_2 j_1; J\rangle = (-1)^{j_1+j_2-J} \tag{2.36}$$

$$\langle J_{12}J_{34}; J \mid J_{13}J_{24}; J\rangle = [J_{12},J_{34},J_{13},J_{24}]^{\frac{1}{2}}\cdot\begin{Bmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{Bmatrix} \tag{2.37}$$

$$\langle J_{12}J_{34};J \mid J_{14}J_{23};J\rangle = (-1)^{j_3+j_4-J_{34}}\,[J_{12},J_{34},J_{23},J_{14}]^{\frac{1}{2}}\cdot\begin{Bmatrix} j_1 & j_2 & J_{12}\\ j_4 & j_3 & J_{34}\\ J_{14} & J_{23} & J\end{Bmatrix} \tag{2.38}$$

A state in a new coupling scheme is found from summing over the quantum numbers of the old coupling scheme that are to be removed:

$$\psi(J_{12}j_3;J) = \sum_{J_{23}} \langle J_{12}j_3;J|j_1J_{23};J\rangle\cdot\psi(j_1J_{23};J) \tag{2.39}$$

$$\langle j_1j_2(J_{12})j_3;J \mid j_1,j_2j_3(J_{23});J\rangle = (-1)^{j_1+j_2+j_3+J}\,[J_{12},J_{23}]^{\frac{1}{2}}\begin{Bmatrix} j_1 & j_2 & J_{12}\\ j_3 & J & J_{23}\end{Bmatrix} \tag{2.40}$$

$$\langle j_1j_3(J_{13})j_2;J \mid j_1j_2(J_{12})j_3;J\rangle = (-1)^{j_2+j_3+J_{12}+J_{13}}\,[J_{12},J_{13}]^{\frac{1}{2}}\begin{Bmatrix} j_1 & j_2 & J_{12}\\ J & j_3 & J_{13}\end{Bmatrix} \tag{2.41}$$

$$\langle j_1,j_2j_3(J_{23});J \mid j_1j_3(J_{13})j_2;J\rangle = (-1)^{J+J_{23}+j_1}\,[J_{23},J_{13}]^{\frac{1}{2}}\begin{Bmatrix} J_{23} & j_2 & j_3\\ J_{13} & j_1 & J\end{Bmatrix} \tag{2.42}$$

$$\langle j_1j_2(J_{12})j_3;J \mid j_2,j_1j_3(J_{13});J\rangle = (-1)^{J_{12}+J+j_3}\,[J_{12},J_{13}]^{\frac{1}{2}}\begin{Bmatrix} J_{12} & J & j_3\\ J_{13} & j_1 & j_2\end{Bmatrix} \tag{2.43}$$

$$\langle j_1j_2(J_{12})j_3;J \mid j_1j_3(J_{13})j_2;J\rangle = (-1)^{J_{12}+j_2+j_3+J_{13}}\,[J_{12},J_{13}]^{\frac{1}{2}}\begin{Bmatrix} J_{12} & J & j_3\\ J_{13} & j_1 & j_2\end{Bmatrix} \tag{2.44}$$

$$\langle j_1j_2(J_{12})j_3;J \mid j_3j_1(J_{13})j_2;J\rangle = (-1)^{2j_3}(-1)^{j_1+j_2+J_{12}}\,[J_{12},J_{13}]^{\frac{1}{2}}\begin{Bmatrix} J_{12} & J & j_3\\ J_{13} & j_1 & j_2\end{Bmatrix} \tag{2.45}$$

$$\begin{aligned}\langle (j_1j_2(J_{12})j_3)\,J_{123},j_4;J \mid j_1,(j_2j_3(J_{23})j_4)\,J_{234};J\rangle &= (-1)^{2J_{12}+2J_{23}+2j_4}\\ \cdot[J_{12},J_{123},J_{23},J_{234}]^{\frac{1}{2}}\cdot(-1)^{j_2+j_3+J_{23}}&\cdot\begin{Bmatrix} J_{12} & J_{123} & j_3\\ J_{23} & j_2 & j_1\end{Bmatrix}\\ \cdot(-1)^{J_{123}+j_4+J}&\cdot\begin{Bmatrix} J_{123} & J & j_4\\ J_{234} & J_{23} & j_1\end{Bmatrix}\end{aligned} \tag{2.46}$$

$$\begin{aligned}\langle j_1,(j_2j_3(J_{23})j_4)\,J_{234};J \mid j_1j_2(J_{12})j_3j_4(J_{34});J\rangle &= (-1)^{j_2+j_3+j_4+J_{234}}\\ \cdot[J_{12},J_{34},J_{23},J_{234}]^{\frac{1}{2}}\cdot(-1)^{j_1+j_2+J_{34}+J}&\cdot\begin{Bmatrix} j_2 & j_3 & J_{23}\\ j_4 & J_{234} & J_{34}\end{Bmatrix}\cdot\begin{Bmatrix} j_1 & j_2 & J_{12}\\ J_{34} & J & J_{234}\end{Bmatrix}\end{aligned} \tag{2.47}$$

$$\begin{aligned}&\langle (j_1,j_2j_3(J_{23}))\,J_{123}\,j_4;J \mid (j_1j_2(J_{12})\,j_4)\,J_{124}\,j_3;J\rangle =\\ &[J_{123},J_{23},J_{12},J_{124}]^{\frac{1}{2}}\cdot(-1)^{j_1+j_2+J_{12}}\cdot\begin{Bmatrix} J_{23} & j_3 & j_2\\ J_{12} & j_1 & J_{123}\end{Bmatrix}\\ &\cdot(-1)^{J_{12}+J_{124}+j_4}\cdot\begin{Bmatrix} j_3 & J & J_{124}\\ j_4 & J_{12} & J_{123}\end{Bmatrix}\end{aligned} \tag{2.48}$$

$$\langle (j_1 j_2(J_{12})\ j_3(J_{123}))\, j_4; J \mid j_1 j_4(J_{14})\ j_2 j_3(J_{23}); J\rangle =$$
$$[J_{12}, J_{123}, J_{14}, J_{23}]^{\frac{1}{2}} \cdot (-1)^{j_2+j_3-J_{23}} \cdot \begin{Bmatrix} j_1 & j_2 & J_{12} \\ j_3 & J_{123} & J_{23} \end{Bmatrix}$$
$$\cdot (-1)^{j_4+J_{14}-j_1} \cdot \begin{Bmatrix} j_1 & j_4 & J_{14} \\ J & J_{23} & J_{123} \end{Bmatrix} \tag{2.49}$$

$$\langle j_1 j_2(J_{12}) j_3 j_4(J_{34}); J \mid (j_1(j_2 j_3) J_{23})\ J_{123},\ j_4; J\rangle = (-1)^{2j_3}$$
$$\cdot [J_{12}, J_{34}, J_{23}, J_{123}]^{\frac{1}{2}} \cdot (-1)^{j_1+j_2+J_{12}} \cdot \begin{Bmatrix} j_3 & J_{23} & j_2 \\ j_1 & J_{12} & J_{123} \end{Bmatrix}$$
$$\cdot (-1)^{J_{123}+j_4+J} \cdot \begin{Bmatrix} j_3 & J_{34} & j_4 \\ J & J_{123} & J_{12} \end{Bmatrix} \tag{2.50}$$

$$\langle (j_1 j_2(J_{12})\ j_3(J_{123}))\, j_4; J \mid j_1 j_3(J_{13})\ j_2 j_4(J_{24}); J\rangle =$$
$$[J_{12}, J_{123}, J_{13}, J_{24}]^{\frac{1}{2}} \cdot (-1)^{J_{123}+j_4+J} \cdot \begin{Bmatrix} j_2 & j_4 & J_{24} \\ J & J_{13} & J_{123} \end{Bmatrix}$$
$$\cdot (-1)^{J_{12}+j_3+J_{123}} \cdot \begin{Bmatrix} J_{12} & J_{123} & j_3 \\ J_{13} & j_1 & j_2 \end{Bmatrix} \tag{2.51}$$

A recoupling identity useful in the manipulation of equivalent creation and annihilation operators:

$$\langle (j_1 j_2) j_{12} (j_3 j_4) j_{34}; 0 |\, (j_1 (j_2 j_3) j_{23})\ j_{123}, j_4; 0\rangle$$
$$= \delta(j_{12}, j_{34}) \delta(j_{123}, j_4) (-1)^{j_1+j_2+j_3+j_4} [j_{12}, j_{23}]^{\frac{1}{2}} \begin{Bmatrix} j_3 & j_{23} & j_2 \\ j_1 & j_{12} & j_4 \end{Bmatrix} \tag{2.52}$$

Chapter 3

Wigner-Eckhart theorem

3.1 CG-coefficients and tensor operators

Clebsch-Gordan (CG) or vector-coupling coefficients $\langle \mathbf{AB}|\mathbf{C}\rangle$ couple the product of two eigenstates $\mathbf{A}$ and $\mathbf{B}$ to a new eigenstate $\mathbf{C}$. They are defined as follows:

$$\mathbf{C}(jm) = \sum_{m_1,m_2} (j_1 m_1\ j_2 m_2|jm)\ \mathbf{A}(j_1 m_1)\mathbf{B}(j_2 m_2) \tag{3.1}$$

The Lithuanian group of Gaigalas, Kaniauskas and Rudzikas uses the notation:

$$(j_1 m_1\ j_2 m_2|jm) = \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} \tag{3.2}$$

Another notation has been used e.g. by [Rose, 1961]:

$$(j_1 m_1\ j_2 m_2|jm) = C(j_1, j_2, j; m_1, m_2, m) = C(j_1, j_2, j; m_1, m_2) \tag{3.3}$$

The CG-coefficients are subject to two orthogonality conditions:

$$\sum_{m_1 m_2} (jm|j_2 m_2\ j_1 m_1)(j_1 m_1\ j_2 m_2|j'm') = \delta_{jj'}\delta_{mm'} \tag{3.4a}$$

and:

$$\sum_{jm} (j_1 m_1\ j_2 m_2|jm)(jm|j_2 m_2'\ j_1 m_1') = \delta_{m_1 m_1'}\delta_{m_2 m_2'} \tag{3.4b}$$

By definition:

$$(j_1 m_1\ j_2 m_2|jm) = (-1)^{j_1 - j_2 + m} \cdot [j]^{\frac{1}{2}} \cdot \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} \tag{3.5}$$

This procedure applies both to eigenstates and to tensor operators, which gives in fact the definition of a spherical tensor operator $T_q^{(k)}$: both eigenstates and tensor operators transform equally under the rotations of the group $\mathcal{R}_3$.
This group-theoretical property underlies the Wigner-Eckart theorem, which can actually be generalized to any group.
The Hermitian adjoint of a spherical tensor operator [as in $\langle\psi|T^\dagger|\psi'\rangle = \langle\psi'|T|\psi\rangle^*$] is - with the [Schwinger, 1952] phase convention - given by [Racah, 1942b, Edmonds, 1957]:

$$T_q^{(k)\dagger} = (-1)^q\ T_{-q}^{(k)} \tag{3.6}$$

$(TU)^\dagger = U^\dagger T^\dagger$. The alternative phase $(-1)^{k-q}$ was used by [Fano and Racah, 1959]. The coupling of a tensor product of two tensor operators to a third tensor operator is performed in a way similar to equation (3.1):

$$\begin{aligned}\left(\mathbf{T}^{(k)}\mathbf{U}^{(k')}\right)^{(K)}_{Q} \equiv \mathbf{V}^{(K)}_{Q} &= \sum_{qq'} (kq\, k'q'|KQ)\, T^{(k)}_q U^{(k')}_{q'} \\ &= \sum_{qq'} (-1)^{k-k'+Q} \cdot [K]^{\frac{1}{2}} \cdot \begin{pmatrix} k & k' & K \\ q & q' & -Q \end{pmatrix} T^{(k)}_q U^{(k')}_{q'} \end{aligned} \tag{3.7}$$

An example is the vector spherical harmonic, defined as:

$$\begin{aligned}\left(Y^{(k)}\mathbf{e}^{(1)}\right)^{(J)}_{M} \equiv \mathbf{Y}_{J\,k\,M} &= \sum_{mq} (km\ 1q|JM)\, Y_{km} e^{(1)}_q \\ &= \sum_{mq} (-1)^{k-1+M} \cdot [J]^{\frac{1}{2}} \cdot \begin{pmatrix} k & 1 & J \\ m & q & -M \end{pmatrix} Y_{km}\, e^{(1)}_q \end{aligned} \tag{3.8}$$

By reverse, any particular product of two tensor operators may be expressed as a series of coupled products. Multiplying both sides of equation (3.7) by $(kq\, k'q'|KQ)$, summing over KQ and applying orthogonality yields:

$$\begin{aligned} T^{(k)}_q U^{(k')}_{q'} &= \sum_{KQ} (kq\, k'q'|KQ) \cdot \left(\mathbf{T}^{(k)}\mathbf{U}^{(k')}\right)^{(K)}_{Q} \\ &= \sum_{KQ} (-1)^{k-k'+Q} \cdot [K]^{\frac{1}{2}} \cdot \begin{pmatrix} k & k' & K \\ q & q' & -Q \end{pmatrix} \left(\mathbf{T}^{(k)}\mathbf{U}^{(k')}\right)^{(K)}_{Q} \end{aligned} \tag{3.9}$$

The spherical vector components $V^{(1)}_q$ are related to their Cartesian counterparts as follows:

$$\begin{aligned} V^{(1)}_0 &= V_z \\ V^{(1)}_{\pm 1} &= \mp \frac{(V_x \pm i V_y)}{\sqrt{2}} \end{aligned}$$

Here, equation (3.6) can be verified explicitly. The normalized spherical unit vector $e^{(1)}_q$ is given by:

$$e^{(1)}_0 = e_z = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{3.10a}$$

$$e^{(1)}_{\pm 1} = \mp\, 1/\sqrt{2}\,(e_x \pm i e_y) = \frac{1}{\sqrt{2}} \begin{pmatrix} \mp 1 \\ -i \\ 0 \end{pmatrix} \tag{3.10b}$$

They satisfy the orthonormality condition $e^{(1)}_\mu \cdot e^{(1)}_\nu = (-1)^\mu\, \delta(\mu, -\nu)$.
For the vector $\vec{r}$, it then follows immediately:

$$r^{(1)}_0 = z \tag{3.11a}$$

$$r^{(1)}_{\pm 1} = \mp\, 1/\sqrt{2}\,(x \pm iy) \tag{3.11b}$$

In fact, every arbitrary vector $\vec{A} = \mathbf{A}$ may be expanded in a spherical basis set as follows:

$$\mathbf{A} = \sum_{q=0,\pm1} (-1)^q \, A^{(1)}_{-q} \, e^{(1)}_q \tag{3.12}$$

The spherical components of a vector operator should not be confused with the related angular momentum shift or ladder operators:

$$J_+ \;=\; J_x + iJ_y \qquad \rightarrow \qquad J^{(1)}_1 = -\frac{1}{\sqrt{2}} \, J_+ \tag{3.13a}$$

$$J_- \;=\; J_x - iJ_y \qquad \rightarrow \qquad J^{(1)}_{-1} = \frac{1}{\sqrt{2}} \, J_- \tag{3.13b}$$

The commutation relations of angular momentum operators yield the below well-known relations:

General states:

$$\begin{cases} \mathbf{J}^2 \, |J\,M\rangle &= J(J+1) \, |J\,M\rangle \\ J_z \, |J\,M\rangle &= M \, |J\,M\rangle \\ J_\pm \, |J\,M\rangle &= \left[J(J+1) - M(M\pm1)\right]^{\frac{1}{2}} \, |J\,M\pm1\rangle \end{cases}$$

Spherical harmonics:

$$\begin{cases} \mathbf{L}^2 \, Y_{LM} &= L(L+1) \, Y_{LM} \\ L_0 \, Y_{LM} &= M \, Y_{LM} \\ L_\pm \, Y_{LM} &= \left[L(L+1) - M(M\pm1)\right]^{\frac{1}{2}} \, Y_{LM\pm1} \end{cases}$$

Irreducible tensor operators, commutation rules:

$$\begin{cases} [\mathbf{J}^2, T^{(k)}_q] &= k(k+1) \, T^{(k)}_q \\ [J_z, T^{(k)}_q] &= q \, T^{(k)}_q \\ [J_\pm, T^{(k)}_q] &= \left[k(k+1) - q(q\pm1)\right]^{\frac{1}{2}} \, T^{(k)}_{q\pm1} \end{cases}$$

By definition, the inner product of two tensors is given by:

$$\left(\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}\right) = \sum_q (-1)^q \, T^{(k)}_q \, U^{(k)}_{-q} = \sum_q \, T^{(k)}_q \, U^{(k)\dagger}_q \tag{3.14}$$

Application of equation (3.7) yields:

$$\begin{aligned} \left(\mathbf{T}^{(k)}\mathbf{U}^{(k)}\right)^{(0)}_0 \;&=\; \sum_q \, (kq\; k{-}q|00) \, T^{(k)}_q U^{(k)}_{-q} \\ &=\; \sum_q \begin{pmatrix} k & k & 0 \\ q & -q & 0 \end{pmatrix} \, T^{(k)}_q U^{(k)}_{-q} = \sum_q \, (-1)^{k+q} \, [k]^{-\frac{1}{2}} \, T^{(k)}_q U^{(k)}_{-q} \end{aligned}$$

Comparison gives now directly:

$$\left(\mathbf{T}^{(k)}\mathbf{U}^{(k)}\right)^{(0)}_0 = (-1)^k \, [k]^{-\frac{1}{2}} \left(\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}\right) \tag{3.15}$$

The inner product $a_x b_x + a_y b_y + a_z b_z$ of two vectors $\mathbf{a}$ and $\mathbf{b}$ is thus given by:

$$\mathbf{a} \cdot \mathbf{b} = -\sqrt{3} \, \cdot \left(a^{(1)} b^{(1)}\right)^{(0)}_0 = -\sqrt{3} \, \cdot [1]^{-\frac{1}{2}} \cdot (-a_z b_z - a_x b_x - a_y b_y) \tag{3.16}$$

Similarly, the common cross product $\begin{pmatrix} a_y b_z - a_z b_y \\ a_z b_x - a_x b_z \\ a_x b_y - a_y b_x \end{pmatrix}$ of two vectors $\mathbf{a}$ and $\mathbf{b}$ is written as:

$$\mathbf{a} \times \mathbf{b} = -i\sqrt{2}\ \left(a^{(1)} b^{(1)}\right)^{(1)} \tag{3.17}$$

This relation may be verified from $\left(a^{(1)} b^{(1)}\right)^{(1)}_Q = \sum_{qq'} (1q\ 1q'|1Q)\ a^{(1)}_q b^{(1)}_{q'}$:

$$\left(a^{(1)} b^{(1)}\right)^{(1)}_Q = \sum_{qq'} \sqrt{3}\,(-1)^Q \begin{pmatrix} 1 & 1 & 1 \\ q & q' & -Q \end{pmatrix} a^{(1)}_q b^{(1)}_{q'} \text{ with } \begin{pmatrix} 1 & 1 & 1 \\ q & q' & -Q \end{pmatrix} = \frac{\pm 1}{\sqrt{6}} \rightarrow$$
$$\left(a^{(1)} b^{(1)}\right)^{(1)}_0 = \frac{1}{\sqrt{2}} \left(a^{(1)}_1 b^{(1)}_{-1} - a^{(1)}_{-1} b^{(1)}_1\right) = \frac{i}{\sqrt{2}} \left(a_x b_y - a_y b_x\right) \tag{3.18}$$

while similarly:

$$\left(a^{(1)} b^{(1)}\right)^{(1)}_{\pm 1} = \frac{\pm 1}{\sqrt{2}} \left(a^{(1)}_{\pm 1} b^{(1)}_0 - a^{(1)}_0 b^{(1)}_{\pm 1}\right) = \tfrac{1}{2} \left[a_z b_x - a_x b_z \pm i \left(a_z b_y - a_y b_z\right)\right] \tag{3.19}$$

From the well-known relation of vector analysis (1.2):

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c})\, \mathbf{b} - (\mathbf{a} \cdot \mathbf{b})\, \mathbf{c} \rightarrow \vec{r} \times \vec{l} = \vec{r} \times (\vec{r} \times \vec{p}) = (\vec{r} \cdot \vec{p})\, \vec{r} - r^2\, \vec{p}$$

and the identities: $\vec{p} = -i\nabla^{(1)}, \vec{r} = rC^{(1)}, \vec{r} \cdot \nabla = r\, \partial/\partial r$, one derives the known formula for the gradient in tensor operator form:

$$-i\sqrt{2}\, r \left(C^{(1)} l^{(1)}\right)^{(1)} = -i\, r^2\, \partial/\partial r\, C^{(1)} - r^2\, \vec{p} \rightarrow$$
$$\vec{p} = -i\, \nabla^{(1)} = -i \left[C^{(1)} \frac{\partial}{\partial r} - \frac{\sqrt{2}}{r}\ \left(C^{(1)} l^{(1)}\right)^{(1)}\right] \tag{3.20}$$

The gradient formula in vector form is given by [Edmonds, 1957], equation 5.9.17; with $\Phi(r) = j_L(kr)$ and $\mathbf{C}^{L\lambda}_M = \left(C^{(\lambda)} \mathbf{e}^{(1)}\right)^{(L)}_M = (4\pi/2\lambda + 1)^{\frac{1}{2}} \cdot \mathbf{Y}_{L\lambda M}$, one obtains:

$$\nabla \left(j_L(kr) C^{(L)}_M\right) = \frac{k}{2L+1} \left\{[L(2L-1)]^{\frac{1}{2}} j_{L-1}(kr) \mathbf{C}^{L\,L-1}_M + [(L+1)(2L+3)]^{\frac{1}{2}} j_{L+1}(kr) \mathbf{C}^{L\,L+1}_M\right\} \tag{3.21}$$

The spherical Bessel functions may be simplified in the long wavelength limit $kr \ll 1$:

$$j_L(kr) \approx \frac{k^L \cdot r^L}{(2L+1)(2L-1)!!} \tag{3.22}$$

which leads to the vector expression:

$$\begin{aligned} \nabla \left(r^L C^{(L)}_M\right) &= r^{L-1} \left\{[L(2L-1)]^{\frac{1}{2}} \mathbf{C}^{L\,L-1}_M + [(L+1)(2L+3)]^{\frac{1}{2}} \frac{(kr)^2}{(2L+1)(2L+3)} \mathbf{C}^{L\,L+1}_M\right\} \\ &\approx [L(2L-1)]^{\frac{1}{2}} \cdot r^{L-1} \cdot \mathbf{C}^{L\,L-1}_M \end{aligned} \tag{3.23}$$

From equations (3.12) and (3.14) it is seen that:

$$\mathbf{C}^{L\lambda}_M \cdot \mathbf{a} = \left(C^{(\lambda)} \mathbf{e}^{(1)}\right)^{(L)}_M \cdot \mathbf{a} = \left(C^{(\lambda)} a^{(1)}\right)^{(L)}_M \tag{3.24}$$

This finally yields an expression often used in the long wavelength limit of multipole expansions:

$$\nabla\left(r^L C_M^{(L)}\right)\cdot\mathbf{a} = [L(2L-1)]^{\frac{1}{2}}\cdot r^{L-1}\cdot\left(C^{(L-1)}a^{(1)}\right)_M^{(L)} \tag{3.25}$$

Denoting the orthonormal unit vectors e_x, e_y and e_z as $e_i\,(i=1,2,3)$, the dyadic form of the juxtaposing (setting side by side) of two vectors $\mathbf{a}$ and $\mathbf{b}$ yields a second order Cartesian tensor $Q_{ij} = a_i b_j$ defined as:

$$\boldsymbol{Q} = \sum_{i,j} Q_{ij}\, e_i e_j = \sum_{i,j} a_i b_j\, e_i e_j \text{ with: } Q_{ij} = Q_{ij}^{(0)} + Q_{ij}^{(1)} + Q_{ij}^{(2)} \tag{3.26}$$

where:

$$Q_{ij}^{(0)} = \delta_{ij}\,\frac{\mathbf{a}\cdot\mathbf{b}}{3} \tag{3.27a}$$

$$Q_{ij}^{(1)} = \frac{a_i b_j - a_j b_i}{2} \tag{3.27b}$$

$$Q_{ij}^{(2)} = \frac{a_i b_j + a_j b_i}{2} - \delta_{ij}\,\frac{\mathbf{a}\cdot\mathbf{b}}{3} \tag{3.27c}$$

The spherical tensor components of these three tensors are found to be:

$$Q_0^{(0)} = \frac{1}{3}\sum_i Q_{ii} \tag{3.28a}$$

$$Q_0^{(1)} = Q_{xy}^{(1)} \tag{3.28b}$$

$$Q_{\pm1}^{(1)} = \mp\frac{1}{\sqrt{2}}\left(Q_{yz}^{(1)} \pm i\,Q_{zx}^{(1)}\right) \tag{3.28c}$$

$$Q_0^{(2)} = Q_{zz}^{(2)} \tag{3.28d}$$

$$Q_{\pm1}^{(2)} = \mp\sqrt{\frac{2}{3}}\left(Q_{zx}^{(2)} \pm i\,Q_{zy}^{(2)}\right) \tag{3.28e}$$

$$Q_{\pm2}^{(2)} = \frac{1}{\sqrt{6}}\left(Q_{xx}^{(2)} - Q_{yy}^{(2)} \pm 2i\,Q_{xy}^{(2)}\right) \tag{3.28f}$$

The according unit dyadic $\boldsymbol{I}$ is then given by:

$$\boldsymbol{I} = \sum_i e_i e_i = -e_{+1}^{(1)}e_{-1}^{(1)} + e_0^{(1)}e_0^{(1)} - e_{+1}^{(1)}e_{-1}^{(1)} \tag{3.29}$$

The double contraction of two dyadics $\boldsymbol{P}$ and $\boldsymbol{Q}$ is:

$$\boldsymbol{P}:\boldsymbol{Q} = \sum_{i,j} P_{ij}Q_{ij} \tag{3.30}$$

In fact, the coupling of two spherical tensors in equation (3.7) can be seen as a dyadic product.

3.2 Baryon magnetic moment calculated from the constituent quarks

From the symmetry properties of the three-quark wavefunction of protons and neutrons, one can calculate the total magnetic moments as vector sums of the individual quark moments. In this, quarks are assumed to behave as point-like Dirac fermions, like the electron. Contributions other than those from the stationary baryon model (such as the currents from virtual quark-antiquark pairs) are neglected.
First, we will build the total angular momentum function of a proton.
The proton is composed of three generation I type quarks, two up- and one down-quark: *(uud)*. We choose to describe a (spin-up) proton as: $|\, J, M_J\rangle = |\, \frac{1}{2}, \frac{1}{2}\rangle$. [1]
In the groundstate, the two equivalent $u-$quarks will be in a (symmetric) triplet spin state $u\uparrow u\uparrow$ designated by: $|\, j_1, m_1\rangle = |\, 1, 0\rangle$ or $|\, 1, \pm 1\rangle$, respectively.
Similarly, the $d-$quark function reads: $|\, j_2, m_2\rangle = |\, \frac{1}{2}, \pm\frac{1}{2}\rangle$. To find the total spin function $|\, J, M_J\rangle$ as eigenfunction of $\vec{J}^2$, we have to form a linear combination by means of Clebsch-Gordan coefficients:

$$|\, (j_1 j_2) J M_J\rangle = \sum_{m_1, m_2} |\, j_1 m_1, j_2 m_2\rangle \;\; (j_1 m_1 \; j_2 m_2 | J M_J)$$

$$\text{where}: \;\; (j_1 m_1 \; j_2 m_2 | J M_J) = (-1)^{j_1 - j_2 + M_J} \; [J]^{\frac{1}{2}} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M_J \end{pmatrix} \tag{3.31}$$

If we abbreviate $|\, 1\; m_1, \frac{1}{2}\; m_2\rangle$ by $|\, m_1, m_2\rangle$, we find:

$$\begin{aligned} |\, \tfrac{1}{2}, \tfrac{1}{2}\rangle &= \sum_{m_1, m_2} (1\, m_1 \; \tfrac{1}{2} \; m_2 | \tfrac{1}{2}, \tfrac{1}{2}) \; |\, m_1, m_2\rangle \\ &= \sqrt{\tfrac{2}{3}} \;\; |\, 1, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{1}{3}} \;\; |\, 0, \tfrac{1}{2}\rangle \end{aligned} \tag{3.32}$$

With $|\, 1, -\frac{1}{2}\rangle$, a magnetic moment $(\mu_u + \mu_u - \mu_d)$ is associated: both $u-$quarks point upward whereas the $d-$quark points downward. In the same way, a magnetic moment μ_d is associated with $|\, 0, \frac{1}{2}\rangle$. Taking expectation values, we finally arrive at:

$$\mu_p = \frac{2}{3}(2\mu_u - \mu_d) + \frac{1}{3}\mu_d = \frac{4}{3}\mu_u - \frac{1}{3}\mu_d. \tag{3.33a}$$

For neutrons, we only have to interchange the labels u and d:

$$\mu_n = \frac{4}{3}\mu_d - \frac{1}{3}\mu_u. \tag{3.33b}$$

To find an expression for the quark magnetic moment, recall that for the electron spin:

$$\vec{\mu}_e = -g_s \frac{e\hbar}{2m_e}\vec{s} = -g_s \; \mu_B \vec{s} \qquad \left[\text{where in au: } \mu_B = \tfrac{1}{2}\right] \tag{3.34}$$

Similarly, the general expression for nuclei is:

$$\vec{\mu}_I = \left(\frac{\mu_I}{I}\right) \; \vec{I} = g_I \left(\frac{m_e}{m_p}\right) \mu_B \; \vec{I} = g_I \; \mu_N \; \vec{I} \tag{3.35}$$

[1] This amounts to stating what was chosen 'upward' in the following; naturally, starting from a spin-down proton would yield the same result.

where $g_I = (\mu_I/I) \cdot \mu_N^{-1}$ is the nuclear g-factor. For our purpose, the above can be generalized to the magnetic moment magnitude of any particle with charge q and mass m_q:

$$|\vec{\mu_q}| = \frac{q\hbar}{2m_q} \tag{3.36}$$

The electric charges of the up- and down quarks being $\frac{2}{3}e$ and $-\frac{1}{3}e$ respectively, it is straightforward to express the quark magnetic moments in terms of the nuclear Bohr magneton $(e\hbar)/(2m_p) = (m_e/m_p)\,\mu_B \equiv \mu_N$.

$$\mu_u = \frac{2}{3}\frac{m_p}{m_u}\mu_N \approx 2\,\mu_N \tag{3.37a}$$

$$\mu_d = -\frac{1}{3}\frac{m_p}{m_d}\mu_N \approx -\mu_N \tag{3.37b}$$

Thus in a very first model, one could substitute $m_u = m_d = 1/3m_p$ into equations 3.37 yielding the above approximate results. Inserting these into equations 3.33a and 3.33b, one finds $\mu_p = 3\mu_N$ and $\mu_n = -2\mu_N$; these numbers should be compared with the experimental result $\mu_p = 2.79\mu_N$ and $\mu_n = -1.91\mu_N$, respectively, with a ratio of −1.46 instead of −1.5.

The spins of a proton and a neutron are both $s = \frac{1}{2}$, so their g-factors $g = \mu/s$ equal twice the above numbers: $g_p = 5.59$ and $g_n = -3.83$; all nuclear g-factors are observed to lie in between those two values: $\forall I : g_n < g_I < g_p$.

A modest improvement can be achieved by a better mass ratio. Several small effects outside the above simple picture affect the mass, like the Coulomb interaction, the magnetic moment interaction (Fermi-contact type) or a mass difference between the $u-$ and the $d-$quark; all these effects are in the order of a few MeV. Using experimental mass values $m_p = 938$ MeV and the effective quark masses $m_u = m_d = 336$ MeV, we arrive at $\mu_p = 2.79\mu_N$ and $\mu_n = -1.86\mu_N$, respectively. Actually, the effective or dressed quark mass is predominantly determined by the binding energy of the gluon field, as the bare mass is much smaller: $m_u \approx 2.3$ MeV and $m_d \approx 4.8$ MeV, respectively.

3.3 Derivation WE theorem

Both the simultaneous rotation of two eigenstates $|j_1 m_1 > |j_2 m_2 >$, and the comparable operator-state combination $T_q^{(k)}|j_1 m_1 >$, are determined by the direct product of the rotation matrices: $\mathcal{D}^{(j_1)} \otimes \mathcal{D}^{(j_2)}$ and $\mathcal{D}^{(k)} \otimes \mathcal{D}^{(j_1)}$, respectively.
Using Clebsch-Gordan coefficients to express the one-electron product in terms of a total angular momentum state:

$$|j_1 m_1\rangle\,|j_2 m_2\rangle = \sum_j (j_1 m_1\; j_2 m_2|jm)\;\; |jm\rangle$$

Similarly, with $m = q + m_2$:

$$T_q^{(k)}\,|j_2 m_2\rangle = \sum_j (kq\; j_2 m_2|jm)\;\Phi(jm)$$

Expansion of the function Φ yields:

$$\begin{aligned}\Phi(jm) &= \sum_{\gamma'} c(\gamma')\ |\gamma' j' m'\rangle \text{ so:}\\ T_q^{(k)}\ |j_2 m_2\rangle &= \sum_{j,\gamma'} (kq\ j_2 m_2|jm)\ c(\gamma')\ |\gamma' j' m'\rangle\end{aligned}$$

Application of the orthogonality constraint $\langle j_1 m_1|j'm'\rangle = \delta(j_1, j')\delta(m_1, m')$ now gives with $(kq\ j_2 m_2|j_1 m_1) = (-1)^{k+j_2-j_1} \cdot (j_2 m_2\ kq|j_1 m_1)$:

$$\begin{aligned}\left\langle \gamma_1 j_1 m_1|T_q^{(k)}|\gamma_2 j_2 m_2\right\rangle &= c(\gamma_1)(kq\ j_2 m_2|j_1 m_1)\\ &\equiv (-1)^{2k} \cdot (j_2 m_2\ kq|j_1 m_1) \quad [j_1]^{-\frac{1}{2}} \cdot \left\langle \gamma_1 j_1 \parallel T^{(k)} \parallel \gamma_2 j_2\right\rangle\\ &= (-1)^{j_1-m_1}\begin{pmatrix} j_1 & k & j_2\\ -m_1 & q & m_2\end{pmatrix} \left\langle \gamma_1 j_1 \parallel T^{(k)} \parallel \gamma_2 j_2\right\rangle \qquad (3.38)\end{aligned}$$

Implicitly defining the reduced matrix element $\langle \gamma_1 j_1 \parallel T^{(k)} \parallel \gamma_2 j_2\rangle$, this relation is called the Wigner-Eckart theorem. [2]
It turns out that every matrix element can be split into a physical part, the reduced matrix element, and a geometrical part containing the rotation dependence in the 3j-symbol, which is thus responsible for the selection rules.
In the absence of any preference direction, the magnetic sublevels become degenerate and the corresponding quantum numbers may be summed over:

$$\sum_{m_1,q,m_2} \left|\left\langle \gamma_1 j_1 m_1|T_q^{(k)}|\gamma_2 j_2 m_2\right\rangle\right|^2 = \left|\left\langle \gamma_1 j_1 \parallel T^{(k)} \parallel \gamma_2 j_2\right\rangle\right|^2$$

$$\begin{aligned}&\left\langle \gamma j_1 j_2\, J\, m_J \mid T_q^{(k)} \mid \gamma' j_1' j_2'\, J'\, m_J'\right\rangle \qquad \text{(Wigner-Eckart theorem, generally:)}\\ &\qquad = (-1)^{J-m_J}\begin{pmatrix} J & k & J'\\ -m_J & q & m_J'\end{pmatrix} \left\langle \gamma j_1 j_2\, J \parallel T^{(k)} \parallel \gamma' j_1' j_2'\, J'\right\rangle \qquad (3.39)\end{aligned}$$

3.4 Applications

$$\begin{pmatrix} j & 0 & j\\ -m & 0 & m\end{pmatrix} = (-1)^{j-m}[j]^{-\frac{1}{2}} \rightarrow \left\langle jm_j|T_Q^{(0)}|j'm_j'\right\rangle = \delta(jj')\,[j]^{-\frac{1}{2}} \left\langle j \parallel T^{(0)} \parallel j\right\rangle \qquad (3.40)$$

$$\begin{aligned}&\begin{pmatrix} j & 1 & j\\ -m & 0 & m\end{pmatrix} = (-1)^{j-m}\frac{m}{\sqrt{j(j+1)(2j+1)}} \text{ (Zeeman effect) } \rightarrow\\ &\left\langle \alpha J m_J|M_0^{(1)}|\alpha J m_J\right\rangle = \frac{m_J}{\sqrt{J(J+1)(2J+1)}} \left\langle \alpha J \parallel M^{(1)} \parallel \alpha J\right\rangle \qquad (3.41)\end{aligned}$$

Tensor operators may be expressed in terms of so-called double tensors, i.e. tensors that carry a rank κ in the spin space as well as a rank k in the orbital space, while

[2] The reduced matrix elements defined by [Brink and Satchler, 1968] differ by a factor $[j_1]^{\frac{1}{2}}$: $\left\langle \gamma_1 j_1 \parallel T^{(k)} \parallel \gamma_2 j_2\right\rangle_{BS} = [j_1]^{-\frac{1}{2}} \left\langle \gamma_1 j_1 \parallel T^{(k)} \parallel \gamma_2 j_2\right\rangle$

κ and k are coupled to a total rank t. By the Wigner-Eckart theorem, the reduced matrix element of a double tensor T is defined as follows:

$$\left\langle \Psi_{SLJM_J} | T^{(\kappa k)t}_Q | \Psi_{S'L'J'M_{J'}} \right\rangle = (-1)^{J-M_J} \begin{pmatrix} J & t & J' \\ -M_J & Q & M_{J'} \end{pmatrix} \left\langle \Psi_{SLJ} \parallel T^{(\kappa k)t} \parallel \Psi_{S'L'J'} \right\rangle$$

$$= (-1)^{J-M_J} \begin{pmatrix} J & t & J' \\ -M_J & Q & M_{J'} \end{pmatrix} [J, J', t]^{\frac{1}{2}} \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & t \end{Bmatrix} \left\langle \Psi_{SL} \parallel T^{(\kappa k)} \parallel \Psi_{S'L'} \right\rangle \tag{3.42}$$

For energy operators with $t = 0$, this reduces to:

$$\left\langle \Psi_{SLJM_J} | T^{(kk)0}_0 | \Psi_{S'L'J'M_{J'}} \right\rangle$$

$$= (-1)^{J-M_J} \begin{pmatrix} J & 0 & J' \\ -M_J & 0 & M_{J'} \end{pmatrix} [J, J', 0]^{\frac{1}{2}} \begin{Bmatrix} S & S' & k \\ L & L' & k \\ J & J' & 0 \end{Bmatrix} \left\langle \Psi_{SL} \parallel T^{(kk)} \parallel \Psi_{S'L'} \right\rangle$$

$$= \delta(J, J')\delta(M_J, M_{J'})(-1)^k [k]^{-\frac{1}{2}} (-1)^{L+S'+J} \begin{Bmatrix} S & L & J \\ L' & S' & k \end{Bmatrix} \left\langle \Psi_{SL} \parallel T^{(kk)} \parallel \Psi_{S'L'} \right\rangle \tag{3.43}$$

With the result for electrostatic operators:

$$\left\langle \Psi_{SLJ} | T^{(00)0} | \Psi'_{S'L'J'} \right\rangle = \delta(J, J')\delta(S, S')\delta(L, L') \cdot [S, L]^{-\frac{1}{2}} \left\langle \Psi_{SL} \parallel T^{(00)} \parallel \Psi'_{SL} \right\rangle$$

It follows immediately:

$$\langle \psi\, SL \parallel \mathbb{1} \parallel \psi'\, S'L' \rangle = \delta(\psi, \psi') \cdot \delta(S, S') \cdot \delta(L, L') \cdot [S, L]^{\frac{1}{2}} \tag{3.44}$$

For the real matrix elements of Hermitian operators, one obtains following the phase convention (3.6):

$$\left\langle \alpha j \parallel T^{(k)} \parallel \alpha' j' \right\rangle = (-1)^{j-j'} \cdot \left\langle \alpha' j' \parallel T^{(k)} \parallel \alpha j \right\rangle \tag{3.45}$$

and correspondingly for double tensors:

$$\left\langle \alpha SL \parallel T^{(\kappa k)} \parallel \alpha' S'L' \right\rangle = (-1)^{(S-S')+(L-L')} \cdot \left\langle \alpha' S'L' \parallel T^{(\kappa k)} \parallel \alpha SL \right\rangle \tag{3.46}$$

Matrix elements of the tensor product of two tensor operators operating on the same system [Edmonds, 1957] (7.1.1 and further):

$$\left\langle \gamma j \parallel X^{(k)} \parallel \gamma' j' \right\rangle = \left\langle \gamma j \parallel \left(T^{(k_1)} U^{(k_2)} \right)^{(k)} \parallel \gamma' j' \right\rangle = [k]^{\frac{1}{2}} \cdot (-1)^{j+j'+k}$$
$$\cdot \sum_{\gamma''} \begin{Bmatrix} k_1 & k_2 & k \\ j' & j & j'' \end{Bmatrix} \left\langle \gamma j \parallel T^{(k_1)} \parallel \gamma'' j'' \right\rangle \left\langle \gamma'' j'' \parallel U^{(k_2)} \parallel \gamma' j' \right\rangle \tag{3.47}$$

A straightforward generalization of this equation to double tensors:

$$\left\langle \psi \parallel \left(T^{(\kappa' k')} U^{(\kappa'' k'')} \right)^{(\kappa k)} \parallel \psi' \right\rangle = [\kappa, k]^{\frac{1}{2}} \cdot (-1)^{S+S'+\kappa} \cdot (-1)^{L+L'+k}$$
$$\cdot \sum_{\psi''} \begin{Bmatrix} \kappa' & \kappa'' & \kappa \\ S' & S & S'' \end{Bmatrix} \cdot \begin{Bmatrix} k' & k'' & k \\ L' & L & L'' \end{Bmatrix} \left\langle \psi \parallel T^{(\kappa' k')} \parallel \psi'' \right\rangle \left\langle \psi'' \parallel U^{(\kappa'' k'')} \parallel \psi' \right\rangle \tag{3.48}$$

For two commuting tensor operators operating on different systems:

$$\begin{aligned}\left\langle \gamma j_1 j_2 J \parallel X^{(k)} \parallel \gamma' j_1' j_2' J' \right\rangle &= \sum_{\gamma''} \left\langle \gamma j_1 \parallel T^{(k_1)} \parallel \gamma'' j_1' \right\rangle \left\langle \gamma'' j_2 \parallel U^{(k_2)} \parallel \gamma' j_2' \right\rangle \\ &\times [J,k,J']^{\frac{1}{2}} \begin{Bmatrix} j_1 & j_1' & k_1 \\ j_2 & j_2' & k_2 \\ J & J' & k \end{Bmatrix} \end{aligned} \tag{3.49}$$

Special cases for k_1, k_2 or k equal to zero:

$$\begin{aligned}&\left\langle \gamma j_1 j_2 J M_J \left| T^{(k)} \cdot U^{(k)} \right| \gamma' j_1' j_2' J' M_J' \right\rangle \\ &= (-1)^{k+J-M_J} [k]^{-\frac{1}{2}} \begin{pmatrix} J & 0 & J' \\ -M_J & 0 & M_J' \end{pmatrix} \left\langle \gamma j_1 j_2 J \parallel \left(T^{(k)} U^{(k)} \right)^{(0)} \parallel \gamma' j_1' j_2' J' \right\rangle \\ &= (-1)^{j_1'+j_2'+J} \delta(J,J') \delta(M_J, M_J') \begin{Bmatrix} j_1' & j_2' & J \\ j_2 & j_1 & k \end{Bmatrix} \sum_{\gamma''} \left\langle \gamma j_1 \parallel T^{(k)} \parallel \gamma'' j_1' \right\rangle \left\langle \gamma'' j_2 \parallel U^{(k)} \parallel \gamma' j_2' \right\rangle \end{aligned} \tag{3.50}$$

$$\begin{aligned}&\left\langle \gamma j_1 j_2 J \parallel T_1^{(k)} \parallel \gamma' j_1' j_2' J' \right\rangle \\ &\qquad = \delta(j_2, j_2') (-1)^{j_1+j_2+J'+k} [J,J']^{\frac{1}{2}} \begin{Bmatrix} J & k & J' \\ j_1' & j_2 & j_1 \end{Bmatrix} \left\langle \gamma j_1 \parallel T_1^{(k)} \parallel \gamma' j_1' \right\rangle \end{aligned} \tag{3.51a}$$

for an operator $T_1^{(k)}$ acting only on part 1.

$$\begin{aligned}&\left\langle \gamma j_1 j_2 J \parallel U_2^{(k')} \parallel \gamma' j_1' j_2' J' \right\rangle \\ &\qquad = \delta(j_1, j_1') (-1)^{j_1'+j_2'+J+k'} [J,J']^{\frac{1}{2}} \begin{Bmatrix} J & k' & J' \\ j_2' & j_1 & j_2 \end{Bmatrix} \left\langle \gamma j_2 \parallel U_2^{(k')} \parallel \gamma' j_2' \right\rangle \end{aligned} \tag{3.51b}$$

for an operator $U_2^{(k')}$ acting only on part 2.
Both equations (3.51a) or (3.51b) can be used to decouple spectator electrons in the calculation.
When the operator ranks k or k' equal zero, as is the case with Coulomb operators, full matrix elements are used. For single zero ranked tensors, this leads analogous to equation (3.44) to:

$$\left\langle J \left| T^{(0)} \right| J' \right\rangle = \delta(J,J') \cdot [J]^{-\frac{1}{2}} \cdot \left\langle J \parallel T^{(0)} \parallel J' \right\rangle \tag{3.52}$$

Using this in both the LHS and RHS of equation (3.51a), it simply follows:

$$\left\langle j_1 j_2 J \left| T_1^{(0)} \right| j_1 j_2' J \right\rangle = \delta(j_2, j_2') \cdot \left\langle j_1 \left| T_1^{(0)} \right| j_1 \right\rangle \tag{3.53}$$

More specifically for SL-coupling, applying the Wigner-Eckart theorem (3.39) twice and inserting the analytical expressions for the 3j- and 6j-symbols, one immediately derives:

$$\left\langle S_1 L_1, S_2 L_2 (SL) \left| C_1^{(00)} \right| S_1 L_1, S_2 L_2 (SL) \right\rangle = \left\langle S_1 L_1 \left| C_1^{(00)} \right| S_1 L_1 \right\rangle \tag{3.54a}$$

for (Coulomb) operators acting only on part 1, and

$$\left\langle S_1 L_1, S_2 L_2 (SL) \left| C_2^{(00)} \right| S_1 L_1, S_2 L_2 (SL) \right\rangle = \left\langle S_2 L_2 \left| C_2^{(00)} \right| S_2 L_2 \right\rangle \tag{3.54b}$$

for (Coulomb) operators acting only on part 2.

For magnetic operators in SL-coupling, decoupling is carried out in the S- and L- space separately, see the below application of equations (3.51a) and (3.51b):

$$\left\langle S_1L_1, S_2L_2(SL) \parallel A_1^{(\kappa k)} \parallel S_1'L_1', S_2'L_2'(S'L') \right\rangle = \delta(S_2,S_2')\delta(L_2,L_2') \cdot \left\langle S_1L_1 \parallel A_1^{(\kappa k)} \parallel S_1'L_1' \right\rangle \cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{S_1+S_2+S'+\kappa} \cdot (-1)^{L_1+L_2+L'+k} \cdot \begin{Bmatrix} S & \kappa & S' \\ S_1' & S_2 & S_1 \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ L_1' & L_2 & L_1 \end{Bmatrix} \tag{3.55a}$$

$$\left\langle S_1L_1, S_2L_2(SL) \parallel A_2^{(\kappa k)} \parallel S_1'L_1', S_2'L_2'(S'L') \right\rangle = \delta(S_1,S_1')\delta(L_1,L_1') \cdot \left\langle S_2L_2 \parallel A_2^{(\kappa k)} \parallel S_2'L_2' \right\rangle \cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{S_1'+S_2'+S+\kappa} \cdot (-1)^{L_1'+L_2'+L+k} \cdot \begin{Bmatrix} S & \kappa & S' \\ S_2' & S_1 & S_2 \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ L_2' & L_1 & L_2 \end{Bmatrix} \tag{3.55b}$$

Subsequently, equation (3.43) has to be applied to incorporate the J-dependence and arrive at the full matrix elements of $A^{(kk)0}$.

3.5 Racah spherical tensors

$C_m^{(k)}(\Omega) = \left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}} Y_{km}(\theta,\phi)$ thus, in view of equations (3.11): (3.56)

$$rY_{1q}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\, r_q^{(1)} \rightarrow \boldsymbol{r} = rC_q^{(1)} \tag{3.57}$$

$$(r_{ij})^{-1} = \sum_k \frac{r_<^k}{r_>^{k+1}} \cdot \left(C_i^{(k)} \cdot C_j^{(k)}\right) \tag{3.58a}$$

$$(r_{ij})^{-3} = \frac{1}{r_>^2 - r_<^2} \sum_k \frac{r_<^k}{r_>^{k+1}} \cdot [k] \cdot \left(C_i^{(k)} \cdot C_j^{(k)}\right) \tag{3.58b}$$

$$(r_{ij})^{-5} = \frac{1}{3(r_>^2 - r_<^2)^3} \sum_k \frac{r_<^k}{r_>^{k+1}} \cdot [k] \cdot \left[(2k+3)r_>^2 - (2k-1)r_<^2\right] \cdot \left(C_i^{(k)} \cdot C_j^{(k)}\right) \tag{3.58c}$$

Table 3.1: Values of $C^{(k)}$

$m =$	0	± 1	± 2
$k = 0$	1	—	—
$k = 1$	$\cos\theta$	$\mp\frac{1}{\sqrt{2}}\sin\theta e^{\pm i\phi}$	—
$k = 2$	$(\frac{3}{2}\cos^2\theta - \frac{1}{2})$	$\mp\sqrt{\frac{3}{2}}\sin\theta\cos\theta e^{\pm i\phi}$	$\sqrt{\frac{3}{8}}\sin^2\theta e^{\pm 2i\phi}$

It follows directly that:

$$C_0^{(k)}(\theta,\phi) = P_k(\cos\theta) \tag{3.59a}$$

$$C_m^{(k)}(0,\phi) = \delta(m,0) \tag{3.59b}$$

The inner product is given by the addition theorem of spherical harmonics:

$$C_1^{(k)} \cdot C_2^{(k)} = P_k(\cos\theta_{12}) \text{ with } \theta_{12} \text{ the angle between } \Omega_1 \text{ and } \Omega_2. \tag{3.60}$$

For the case 1 = 2:

$$\left(C^{(k)}C^{(k')}\right)_Q^{(K)} = \sum_{qq'}(kq\ k'q'|KQ)\ C_q^{(k)}C_{q'}^{(k')} = (k0\ k'0|K0)\ C_Q^{(K)}$$

$$= (-1)^K[K]^{\frac{1}{2}}\begin{pmatrix} k & k' & K \\ 0 & 0 & 0 \end{pmatrix} C_Q^{(K)} \tag{3.61}$$

Notice the application of the above to a dyadic, i.e. a tensor of order 2 formed by two vectors:

$$\left(C^{(1)}C^{(1)}\right)_Q^{(2)} = \sqrt{2/3}\cdot C_Q^{(2)} \tag{3.62}$$

3.6 Reduced matrix elements

$$\left\langle \alpha j \parallel j^{(1)} \parallel \alpha' j' \right\rangle = \delta_{\alpha\alpha'}\delta_{jj'}\sqrt{j(j+1)(2j+1)} \tag{3.63}$$

$$\left\langle l \parallel C^{(k)} \parallel l' \right\rangle = (-1)^l\ [l,l']^{\frac{1}{2}}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \tag{3.64}$$

It follows from equation (2.1) that $l + k + l'$ is even.
For a $3j$-symbol, every odd permutation of columns yields a phase $(-1)^{j_1+j_2+j_3}$.
As a result:

$$\left\langle l \parallel C^{(k)} \parallel l' \right\rangle = (-1)^k \left\langle l' \parallel C^{(k)} \parallel l \right\rangle$$

With the integer g defined as $g = \frac{1}{2}(l + k + l')$:

$$(k = 0, g = l)\ \left\langle l \parallel C^{(0)} \parallel l' \right\rangle = \delta(l,l')\,(-1)^l\ [\,l\,]\begin{pmatrix} l & 0 & l \\ 0 & 0 & 0 \end{pmatrix} = \delta(l,l')\ [\,l\,]^{\frac{1}{2}} \tag{3.65}$$

$$(l' = s, g = l)\ \left\langle s \parallel C^{(l)} \parallel l \right\rangle = [\,l\,]^{\frac{1}{2}}\begin{pmatrix} 0 & l & l \\ 0 & 0 & 0 \end{pmatrix} = (-1)^l \tag{3.66}$$

$$\left\langle l \parallel C^{(1)} \parallel l' \right\rangle = (-1)^{l_>-l}\sqrt{l_>} \quad \text{and} \quad \left\langle l \parallel C^{(2)} \parallel l \right\rangle = -\left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}} \tag{3.67}$$

The second identity results from the below useful recursion relation for $k = 1$:

$$\left\langle l \parallel C^{(k+1)} \parallel l \right\rangle = -\left[\frac{(2l+k+1)(2l-k+1)}{(2l+k+2)(2l-k)}\right]^{\frac{1}{2}} \cdot \frac{k}{k+1} \cdot \left\langle l \parallel C^{(k-1)} \parallel l \right\rangle \tag{3.68}$$

In the more general form:

$$\left\langle l \parallel C^{(k+1)} \parallel l' \right\rangle = -\left[\frac{(l+l'+k+1)(l+l'-k+1)\,(k^2-(l-l')^2)}{(l+l'+k+2)(l+l'-k)\,((k+1)^2-(l-l')^2)}\right]^{\frac{1}{2}} \cdot \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle \tag{3.69}$$

3.7 Zeeman effect(1)

The magnetic moment of a charged particle like an electron may be related to its angular momentum with the Bohr magneton $\mu_B = e\hbar/2m = \frac{1}{2}$ as a proportionality factor (the minus sign applies to negative particles):

$$\vec{\mu}_j = -g_j \cdot \mu_B \cdot \vec{j} \tag{3.70}$$

For atomic electrons, $M^{(1)} = L^{(1)} + g_s \cdot S^{(1)}$ with $g_l = 1$ and $g_s = 2.002319304$.
The spin g-factor is QED corrected by $2 + (g_s - 2) \approx 2 + \alpha/\pi$. Therefore:

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = -\mu_B(\vec{L} + g_s \cdot \vec{S}) = -\mu_B\, M^{(1)} = -\mu_B \left(J^{(1)} + (g_s - 1) \cdot S^{(1)}\right) \tag{3.71}$$

If the atom is exposed to a uniform magnetic field $B_0 = B_z$, the perturbation

$$V_Z = -\vec{\mu} \cdot \vec{B}_0 = \mu_B\, B_0\, M_0^{(1)} = \mu_B\, B_0 \left(J_0^{(1)} + (g_s - 1) \cdot S_0^{(1)}\right)$$

leads to Zeeman splitting. The Zeeman correction to the energy due to V_Z is:

$$\begin{aligned}\Delta E_Z &= \langle \alpha J m_J | V_Z | \alpha J m_J \rangle = \mu_B\, B_0 \left\langle \alpha J m_J | M_0^{(1)} | \alpha J m_J \right\rangle \\ &= m_J \cdot \mu_B \cdot B_0 \cdot \frac{\langle \alpha J \parallel M^{(1)} \parallel \alpha J \rangle}{\sqrt{J(J+1)(2J+1)}} = m_J \cdot \mu_B \cdot B_0 \cdot g_J.\end{aligned} \tag{3.72}$$

where the Wigner-Eckart equation (3.41) is applied in the last step; the last factor implicitly defines the Landé g-factor g_J. As obviously $M^{(1)}$ is a vector, its matrix elements are (by the WE theorem) necessarily proportional to the matrix elements of any other vector, the obvious choice being the vector $J^{(1)}$ for $|Jm_J\rangle$ states:

$$\left\langle \alpha J \parallel M^{(1)} \parallel \alpha J \right\rangle = g_J \cdot \left\langle \alpha J \parallel J^{(1)} \parallel \alpha J \right\rangle \tag{3.73}$$

The Landé g-factor is therefore simply defined as the proportionality factor between the matrix elements of the magnetic moment and the matrix elements of the total angular momentum.
In pure $(SL)J$-coupling, the numerator can be further elaborated with equations (3.63) and (3.51a), e.g.:

$$\begin{aligned}&\left\langle (SL)J \parallel S^{(1)} \parallel (SL)J \right\rangle = (-1)^{S+L+J+1}\,[J] \begin{Bmatrix} J & 1 & J \\ S & L & S \end{Bmatrix} \sqrt{S(S+1)(2S+1)} \\ = \;& (-1)^{S+L+J+1}\,[J]\,(-1)^{S+L+J+1} \frac{S(S+1) + J(J+1) - L(L+1)}{2\sqrt{J(J+1)(2J+1)S(S+1)(2S+1)}} \sqrt{S(S+1)(2S+1)} \\ = \;& \sqrt{\frac{2J+1}{J(J+1)}} \cdot \frac{(S(S+1) + J(J+1) - L(L+1))}{2}\end{aligned}$$

As a result, the Landé g-factor g_J in the $(SL)J$-coupling scheme is given by:

$$g_J(SLJ) = 1 + (g_s - 1) \left(\frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}\right) \tag{3.74}$$

where again $(g_s - 1) = 1.002319$. The Zeeman splitting is now simply given as:

$$\Delta E_Z = \langle \alpha J m_J | V_Z | \alpha J m_J \rangle = m_J \cdot \mu_B \cdot g_J \cdot B_0 = \tfrac{1}{2} m_J \cdot g_J \cdot B_0 \tag{3.75}$$

Actual g-factors are calculated in intermediate coupling from the $(SL)J$ eigenvector percentages; sums of actual and pure g-factors are therefore equal for a given value of J (the Pauli g-sum rule: the sum of the g-factors over a particular J of a configuration should be equal to the sum of the g-factors for all possible LS-basis states in that configuration of that same J). The use of g-factors and all of the above is based on pure, diagonal J-values: the magnetic field should be small enough not to mix different values of J.
For larger fields, calculation of off-diagonal matrix elements may however be performed by straightforward angular momentum techniques, again using the WE theorem:

$$\left\langle (SL)Jm_J|L_0^{(1)}+g_sS_0^{(1)}|(SL)J'm_J\right\rangle = (-1)^{J-m_J}\begin{pmatrix} J & 1 & J' \\ -m_J & 0 & m_J\end{pmatrix}\left\langle (SL)J \parallel L^{(1)}+g_sS^{(1)} \parallel (SL)J'\right\rangle \tag{3.76}$$

NMR (or MRI medical imaging) is based on the nuclear Zeeman effect $V = -\vec{\mu}_p \cdot \vec{B}$ as a result of the interaction of an external magnetic field and the proton magnetic moment, proportional to the nuclear hydrogen spin:

$$\begin{aligned}\vec{\mu}_p &= \vec{\mu}_I = g_I \cdot \frac{e\hbar}{2m_p}\cdot \vec{I} = g_I \cdot \mu_N \cdot \vec{I} \text{ with the Larmor frequency:} \\ \omega &= \frac{g_I \cdot e}{2m_p}\cdot B_0 = \frac{5.5856947 \cdot 1.60218 \times 10^{-19}}{2 \cdot 1.67262 \times 10^{-27}}\cdot B_0 = 2.6752 \times 10^8 \cdot B_0. \end{aligned} \tag{3.77}$$

Therefore, the linear MRI (radio) frequencies are given by: $\nu = 42,58$ MHz T^{-1}. The relaxation of the nuclear magnetization after application of a radiofrequency pulse of Larmor frequency is described by the Bloch equations [Bloch, 1946].
There is some similarity between MRI and (the origin of) the well-known 21 cm line to be discussed in section 7.11. There, the part of the external magnetic field is taken over by the internal magnetic field of the electron spin.

3.8 Hyperfine structure(1)

3.8.1 General theory

To describe the effect of the electronic electromagnetic field at a nucleus of non-zero nuclear spin $\vec{I}$, [Schwartz, 1955] proposed an expansion of inner products of electronic and nuclear spherical tensors:

$$H_{\text{hfs}} = \sum_t T_e^{(t)} \cdot T_n^{(t)} \tag{3.78}$$

The total electronic angular momentum $\vec{J}$ is coupled to the nuclear spin $\vec{I}$: $\vec{J}+\vec{I} = \vec{F}$. Actually, F and I are the only good quantum numbers here and equation (3.50) is used to factor this $F-$dependence out:

$$\left\langle \gamma JIF\left|T_e^{(t)}\cdot T_n^{(t)}\right|\gamma' J'IF\right\rangle = (-1)^{J'+I+F}\cdot\begin{Bmatrix} J' & I & F \\ I & J & t\end{Bmatrix}\cdot\left\langle \gamma J \parallel T_e^{(t)} \parallel \gamma' J'\right\rangle\left\langle I \parallel T_n^{(t)} \parallel I\right\rangle \tag{3.79}$$

Nuclear multipole moments are commonly defined as the (maximized for $m_I = I$) matrix element of the corresponding nuclear tensor: $M_t = \left\langle II|T^{(t)}_{n,0}|II\right\rangle$.
The WE theorem is then used to display this manifestly:

$$\left\langle \gamma JIF \left| T^{(t)}_e \cdot T^{(t)}_n \right| \gamma' J' I F \right\rangle = (-1)^{J'+I+F} \cdot \begin{Bmatrix} J' & I & F \\ I & J & t \end{Bmatrix} \cdot \left\langle \gamma J \parallel T^{(t)}_e \parallel \gamma' J' \right\rangle \frac{M_t}{\begin{pmatrix} I & t & I \\ -I & 0 & I \end{pmatrix}} \tag{3.80}$$

In what follows, the summation over t is restricted to the magnetic dipole interaction ($t = 1$) and the electric quadrupole interaction ($t = 2$). Then, $M_1 = \mu_I$ and $M_2 = \frac{1}{2}Q$; nuclear magnetic dipole and electric quadrupole moments are commonly given in nuclear magnetons ($\mu_N = \frac{1}{2} \cdot m_e/m_p$ in au) and barns, respectively [Stone, 2005]. Equations (C.2) are used to express the 3j-symbol in the denominator explicitly:

$$\frac{M_1}{\begin{pmatrix} I & 1 & I \\ -I & 0 & I \end{pmatrix}} = \frac{\mu_I}{I} \cdot \sqrt{I(I+1)(2I+1)} \tag{3.81a}$$

$$\frac{M_2}{\begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}} = \tfrac{1}{2}Q \cdot \left[\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)} \right]^{\frac{1}{2}} \tag{3.81b}$$

Expanded in terms of single particle double tensors, the electronic hyperfine structure (hfs) tensor is written as: $T^{(t)}_e = \sum_{\kappa k} F^{(\kappa k)t}$.
As $\kappa + k + t$ is even for reasons of Hermiticity, (κk) equals $(01), (12)$ and (10) for magnetic dipole and $(02), (11)$ and (13) for electric quadrupole interactions.
Next, the J–dependence of $\left\langle \gamma J \parallel T^{(t)}_e \parallel \gamma' J' \right\rangle$ is factored out by equation (3.42):

$$\left\langle \gamma SLJ \parallel F^{(\kappa k)t} \parallel \gamma' S' L' J' \right\rangle = [J, J', t]^{\frac{1}{2}} \cdot \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & t \end{Bmatrix} \cdot \left\langle \gamma SL \parallel F^{(\kappa k)} \parallel \gamma' S' L' \right\rangle \tag{3.82}$$

If the hyperfine interaction is weak so that the interaction energy is small compared to the fine-structure separation and J remains a good quantum number, $H^D_{\text{hfs}} + H^Q_{\text{hfs}}$ can be treated in first-order perturbation theory with diagonal matrix elements only. The energy of hyperfine structure multiplets is then given by:

$$E_F = E_J + \tfrac{1}{2}A_J \cdot C + \tfrac{1}{2}B_J \cdot \frac{\frac{3}{4}C(C+1) - J(J+1)I(I+1)}{I(2I-1)J(2J-1)} \tag{3.83}$$

where E_J is the energy of the fine structure level of quantum number J and
$C = F(F+1) - J(J+1) - I(I+1)$.
A_J and B_J are the magnetic dipole and electric quadrupole hyperfine interaction constants proportional to μ_I/I and Q, respectively; they may directly be determined from experiment with equation (3.83).

3.8.2 Magnetic dipole

The electronic part of the magnetic dipole interaction of an electron i with the nucleus is described by the hyperfine magnetic dipole operator $T_i^{(1)}$:

$$\sum_i T_i^{(1)} = \sum_{i,l\neq 0} \left(l_i^{(1)} - (10)^{\frac{1}{2}} \left(sC^{(2)} \right)_i^{(1)} \right) \cdot \left\langle r_i^{-3} \right\rangle + \sum_{i,l=0} s_i^{(1)} \cdot \tfrac{2}{3} \left\langle \delta(r) r^{-2} \right\rangle_i = \sum_i N_i^{(1)} \cdot \left\langle r_i^{-3} \right\rangle \tag{3.84}$$

In a non-relativistic single configuration model, the first two terms of T_i have a common radial factor $\langle r_i^{-3} \rangle$. The description is much improved, however, if $\langle r_i^{-3} \rangle$ is effectively replaced by separate (and different) radial parameters a_{nl}^{01}, a_{nl}^{12} and a_{nl}^{10} for the orbital, spin-dipole and contact terms, respectively. The $a_{nl}^{\kappa k}$ (and $b_{nl}^{\kappa k}$ for the electric quadrupole effects) are effective radial parameters which are treated as adjustable quantities to be fitted to the experimental data in order to take into account relativistic and CI effects.
Again non-relativistically, the dominant a_{nl}^{10} term is only non-vanishing for unpaired s-electrons, in which case the factor $\langle r^{-3} \rangle$ is replaced by the contact term[3] $(8\pi/3) \langle \delta(\boldsymbol{r}) \rangle = \frac{2}{3} \cdot \langle \delta(r) r^{-2} \rangle = \frac{2}{3} \cdot AZ^2$. This contact term, essential for understanding the 21 cm line, is worked out non-relativistically in equation (7.95) for hydrogenic atoms; the general relativistic counterpart is found in equation (22.19h).

Given the electronic part (3.84), it follows:

$$H_{\text{hfs}}^D = \alpha^2 \sum_i T_i^{(1)} \cdot \boldsymbol{\mu}_I = \frac{\alpha^2}{2} \cdot \left(\frac{m_e}{m_p} \right) \cdot \frac{\mu_I}{I} \sum_i T_i^{(1)} \cdot \boldsymbol{I} \tag{3.85}$$

In some earlier publications, [Judd, 1963, Bauche-Arnoult, 1971, Bauche-Arnoult, 1973], the prefactor $2\beta\beta_N = \alpha^2/2 \cdot (m_e/m_p)$ is used.

As mentioned earlier with equation (3.84), the magnetic dipole interaction is effectively replaced by:

$$H_{\text{hfs}}^D = \sum_i \left(a_{nl}^{01} \, l_i^{(1)} - (10)^{\frac{1}{2}} \cdot a_{nl}^{12} \left(s_i C_i^{(2)} \right)^{(1)} + a_{nl}^{10} \, s_i^{(1)} \right) \cdot \boldsymbol{I} \tag{3.86}$$

where the $a_{nl}^{\kappa k}$ parameters are defined as:

$$a_{nl}^{\kappa k} = \frac{\alpha^2}{2} \cdot \left(\frac{m_e}{m_p} \right) \cdot \frac{\mu_I}{I} \cdot \left\langle r^{-3} \right\rangle_{nl}^{\kappa k} = 3.1825571 \times 10^{-3} \cdot \frac{\mu_I}{I} \cdot \left\langle r^{-3} \right\rangle_{nl}^{\kappa k} \tag{3.87}$$

The numerical factor yields parameters in cm^{-1} with $\langle r^{-3} \rangle_{nl}^{\kappa k}$ given in atomic units and μ_I in nuclear magnetons; the spin term $(\kappa k) = (10)$ is multiplied with the additional QED factor $g_s/2$, replacing the numerical factor by 3.1862477×10^{-3}.
Frequently, the hyperfine structure is small enough to treat as a perturbation and only diagonal matrix elements have to be considered. The $F-$dependence is then

[3] Here, the MCHF definition $AZ = \lim_{r\to 0} (\mathrm{d}P_{ns}(r)/\mathrm{d}r)$ is used.

factored out by equations (3.50) and (C.11):

$$\begin{aligned}\left\langle \gamma JIF|N^{(1)}\cdot I^{(1)}|\gamma JIF\right\rangle &= (-1)^{J+I+F}\begin{Bmatrix} J & I & F \\ I & J & 1\end{Bmatrix}\left\langle \gamma J \parallel N^{(1)} \parallel \gamma J\right\rangle \left\langle I \parallel I^{(1)} \parallel I\right\rangle \\ &= \tfrac{1}{2}\cdot(F(F+1)-J(J+1)-I(I+1))\,\frac{\left\langle \gamma J \parallel N^{(1)} \parallel \gamma J\right\rangle}{\left\langle \gamma J \parallel J^{(1)} \parallel \gamma J\right\rangle}\end{aligned} \tag{3.88}$$

Like $M^{(1)}$ in the Zeeman effect discussed in the above, $N^{(1)}$ is proportional to $J^{(1)}$ and one may write $H^D_{\rm hfs} = A_J\,(\boldsymbol{I}\cdot\boldsymbol{J})$. The expectation value $\langle \boldsymbol{I}\cdot\boldsymbol{J}\rangle$ is readily found from considering $(\boldsymbol{F})^2 = (\boldsymbol{I}+\boldsymbol{J})^2 \rightarrow F(F+1) = I(I+1) + 2\langle \boldsymbol{I}\cdot\boldsymbol{J}\rangle + J(J+1) \rightarrow \langle \boldsymbol{I}\cdot\boldsymbol{J}\rangle = \frac{1}{2}C$ where $C = F(F+1) - J(J+1) - I(I+1)$. Therefore:

$$\left\langle \gamma JIF|H^D_{\rm hfs}|\gamma JIF\right\rangle = \Delta E^D_{\rm hfs} = A_J\cdot\tfrac{1}{2}\left(F(F+1)-J(J+1)-I(I+1)\right) = A_J\cdot\tfrac{1}{2}C \tag{3.89}$$

here, A_J is defined as:

$$\begin{aligned}A_J &= \frac{\alpha^2}{2}\cdot\left(\frac{m_e}{m_p}\right)\cdot\frac{\mu_I}{I}\cdot\frac{\sum_i\left\langle \gamma J \parallel T^{(1)}_i \parallel \gamma J\right\rangle}{\left\langle \gamma J \parallel J^{(1)} \parallel \gamma J\right\rangle} \\ &= \frac{\alpha^2}{2}\cdot\left(\frac{m_e}{m_p}\right)\cdot\frac{\mu_I}{I}\cdot \\ &\quad\cdot\ \frac{\sum_{i,l\neq 0}\left\langle \gamma J \parallel \left(l^{(1)}_i - (10)^{\frac{1}{2}}\left(sC^{(2)}\right)^{(1)}_i\right) \parallel \gamma J\right\rangle\cdot\langle r_i^{-3}\rangle + \sum_{i,l=0}\left\langle \gamma J \parallel s^{(1)}_i \parallel \gamma J\right\rangle\cdot\frac{2}{3}\langle\delta(r)r^{-2}\rangle_i}{[J(J+1)(2J+1)]^{\frac{1}{2}}}\end{aligned} \tag{3.90}$$

in its generalized, relativistic formulation:

$$A_J = \frac{\sum_i\left(a^{01}_{nl}\left\langle \gamma J \parallel l^{(1)}_i \parallel \gamma J\right\rangle - (10)^{\frac{1}{2}}\cdot a^{12}_{nl}\left\langle \gamma J \parallel \left(s_i C^{(2)}_i\right)^{(1)} \parallel \gamma J\right\rangle + a^{10}_{nl}\left\langle \gamma J \parallel s^{(1)}_i \parallel \gamma J\right\rangle\right)}{[J(J+1)(2J+1)]^{\frac{1}{2}}} \tag{3.91}$$

As an example, it follows for a single unpaired $s-$electron directly that $A_J = a^{10}_{ns}$. The detailed calculation of the matrix elements $\sum_i\left\langle \gamma J \parallel T^{(1)}_i \parallel \gamma J\right\rangle$ is best carried out in second quantization as outlined in chapter 5 below. If configuration interaction outside the model space is taken into account, additional two- and three-particle hfs operators appear and $T^{(1)} = \sum_{\kappa k} F^{(\kappa k)1}$ is expanded to include these as well, see section 15.6 for further elaboration.

The more general expression for the dipole hyperfine interaction is given by:

$$\begin{aligned}\left\langle \gamma JF|H^D_{\rm hfs}|\gamma' J'F\right\rangle &= \sqrt{I(I+1)(2I+1)}\cdot(-1)^{J'+I+F}\begin{Bmatrix} J' & I & F\\ I & J & 1\end{Bmatrix}\\ &\cdot\frac{\alpha^2}{2}\cdot\left(\frac{m_e}{m_p}\right)\cdot\frac{\mu_I}{I}\cdot\left\langle r^{-3}\right\rangle\cdot\left\langle \gamma J\parallel\sum_i N_i^{(1)}\parallel\gamma' J'\right\rangle\\ &= \sqrt{I(I+1)(2I+1)}\cdot(-1)^{J'+I+F}\begin{Bmatrix} J' & I & F\\ I & J & 1\end{Bmatrix}\\ \cdot\sum_i\Bigg(&a^{01}_{nl}\left\langle\gamma J\parallel l_i^{(1)}\parallel\gamma' J'\right\rangle-(10)^{\frac12}\cdot a^{12}_{nl}\left\langle\gamma J\parallel\left(s_iC_i^{(2)}\right)^{(1)}\parallel\gamma' J'\right\rangle+a^{10}_{nl}\left\langle\gamma J\parallel s_i^{(1)}\parallel\gamma' J'\right\rangle\Bigg)\end{aligned}$$

see equation (5.67a) for the expression in second quantization. (3.92)

3.8.3 Electric quadrupole

Using equation (3.58a), the electrostatic interaction between the individual nucleons and the individual electrons may be expressed as a multipole expansion in terms of Legendre polynomials $P_k(\cos\theta)$. If r is the distance between the two charge distributions, it follows:

$$\frac{1}{r_{12}}=\sum_k\frac{r_<^k}{r_>^{k+1}}\cdot P_k(\cos\theta)=\frac{1}{r_e}+\frac{r_n}{r_e^2}\cdot P_1(\cos\theta)+\frac{r_n^2}{r_e^3}\cdot P_2(\cos\theta)+\cdots \tag{3.93}$$

The first term is the usual nuclear Coulomb attraction and the second vanishes for symmetry reasons. The present focus is therefore on the third (electric quadrupole) term, which is of the form $\left(r_e^{-3}C_e^{(2)}\cdot r_n^2C_n^{(2)}\right)$.
The classical expression for the electric quadrupole moment is given by:

$$Q=\int\left(3z^2-r^2\right)\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\approx\frac25 Z\left(b^2-a^2\right) \tag{3.94}$$

where in the last step, a and b denote the semi-major and semi-minor axes of a homogeneous spheroidal object. Therefore, the nuclear quadrupole moment Q is positive for cigar-shaped objects and negative for flattened objects (like planets).
In its quantummechanical formulation, using table 3.1, this becomes:

$$Q=\left\langle 3z^2-r^2\right\rangle=\left\langle 2r^2\cdot P_2(\cos\theta)\right\rangle=\left\langle 2r^2\cdot C_0^{(2)}\right\rangle \tag{3.95}$$

leading to the definition:

$$\left\langle II|r_n^2\cdot C^{(2)}_{n,0}|II\right\rangle\ =M_2=\tfrac12 Q \tag{3.96}$$

Some care is in order with the above factor $\frac12$, as it occurs in the literature in various other places like in the angular, nuclear or electronic part. In line with the above discussion, the electric quadrupole Hamiltonian is given by:

$$H^Q_{\rm hfs}=-\sum_i C_i^{(2)}\cdot Q^{(2)}\,r_i^{-3} \tag{3.97}$$

From equations (3.80) and (3.81b), the below general expression also valid for off-diagonal matrix elements follows directly:

$$\left\langle \gamma JF|H^Q_{\rm hfs}|\gamma' J'F\right\rangle = -\left\langle r^{-3}\right\rangle \cdot \tfrac{1}{2}Q \cdot \left[\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)}\right]^{\frac{1}{2}} \cdot(-1)^{J'+I+F}\begin{Bmatrix} J' & I & F \\ I & J & 2\end{Bmatrix} \cdot \left\langle \gamma J \parallel \sum_i C^{(2)}_i \parallel \gamma' J'\right\rangle \tag{3.98}$$

The radial parameters are related to the effective expectation values of $\langle r^{-3}\rangle$ (in au) and the nuclear quadrupole moment Q (in barns). To calculate the electronic quadrupole moment $\left\langle JJ|\sum_i C^{(2)}_i|JJ\right\rangle$, one may use the equivalent operator $C^{(2)} \propto 3J_z^2 - J(J+1)$. Similar to the magnetic dipole case, the dominant diagonal contribution $\left\langle \gamma JF|H^Q_{\rm hfs}|\gamma JF\right\rangle = \Delta E^Q_{\rm hfs}$ may thereby be simplified to:

$$\begin{aligned}\Delta E^Q_{\rm hfs} &= \tfrac{1}{2}B_J \cdot \frac{3\left\langle (\boldsymbol{I}\cdot\boldsymbol{J})^2\right\rangle + \frac{3}{2}\left\langle \boldsymbol{I}\cdot\boldsymbol{J}\right\rangle - J(J+1)I(I+1)}{I(2I-1)J(2J-1)} \\ &= \tfrac{1}{2}B_J \cdot \frac{\frac{3}{4}C(C+1) - J(J+1)I(I+1)}{I(2I-1)J(2J-1)}\end{aligned} \tag{3.99}$$

This corresponds exactly to the expression already given by [Casimir, 1935]:

$$\begin{aligned}\Delta E^Q_{\rm hfs} &= -\left\{\overline{\frac{1}{r^3}\,\frac{3\cos^2\theta - 1}{J(2J-1)}}\right\}_{JJ} \cdot \left\{\overline{\frac{3z^2 - r^2}{I(2I-1)}}\right\}_{II} \cdot \left[\tfrac{3}{8}C(C+1) - \tfrac{1}{2}IJ(I+1)(J+1)\right] \\ &= -\left\langle r^{-3}\right\rangle \cdot \left\langle JJ|2C^{(2)}_0|JJ\right\rangle \cdot Q \cdot \tfrac{1}{2} \cdot \frac{\frac{3}{4}C(C+1) - J(J+1)I(I+1)}{I(2I-1)J(2J-1)}\end{aligned} \tag{3.100}$$

where the present notation is used in the second line. Obviously:

$$\tfrac{1}{2}B_J = -\left\langle r^{-3}\right\rangle \cdot Q \cdot \begin{pmatrix} J & 2 & J \\ -J & 0 & J\end{pmatrix} \cdot \left\langle \gamma J \parallel \sum_i C^{(2)}_i \parallel \gamma J\right\rangle \tag{3.101a}$$

Returning to the general expression 3.97 again, one recognizes from equations (C.2) and (C.12) the below equality, symmetric in I and J:

$$\frac{\frac{1}{2}\cdot(-1)^{I+J+F}\begin{Bmatrix} J & I & F \\ I & J & 2\end{Bmatrix}}{\begin{pmatrix} J & 2 & J \\ -J & 0 & J\end{pmatrix} \cdot \begin{pmatrix} I & 2 & I \\ -I & 0 & I\end{pmatrix}} = \frac{\frac{3}{4}C(C+1) - J(J+1)I(I+1)}{I(2I-1)J(2J-1)} \tag{3.101b}$$

Comparison of equations (3.98) and (3.99) yields once more:

$$\tfrac{1}{2}B_J = -\left\langle r^{-3}\right\rangle \cdot Q \cdot \left[\frac{J(2J-1)}{(J+1)(2J+1)(2J+3)}\right]^{\frac{1}{2}} \cdot \left\langle \gamma J \parallel \sum_i C^{(2)}_i \parallel \gamma J\right\rangle \tag{3.101c}$$

In the relativistic approach, radial parameters $b^{\kappa k}_{nl}$ are introduced for $(\kappa k) = 02, 11$ and 13.
With $\langle r^{-3}\rangle^{\kappa k}_{nl}$ in atomic units, $b^{\kappa k}_{nl}$ in cm^{-1} and Q in barns, they are defined as:

$$b^{\kappa k}_{nl} = 7.83758136 \times 10^{-3} \cdot Q \cdot \left\langle r^{-3}\right\rangle^{\kappa k}_{nl} \tag{3.102}$$

Anticipating the development of the theory of second quantization in chapter 5, the complete electronic quadrupole operator is written as a sum over orthogonal operators:

$$\begin{aligned} T_e^{(2)} &= -S_{nl}^{02}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(02)2} - S_{nl}^{11}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(11)2} - S_{nl}^{13}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(13)2} \\ &= -\left\langle r^{-3}\right\rangle_{nl}^{02}\sum_i C_i^{(2)} - \frac{1}{\sqrt{30}}\left\langle r^{-3}\right\rangle_{nl}^{11}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(11)2} - \frac{1}{\sqrt{70}}\left\langle r^{-3}\right\rangle_{nl}^{13}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(13)2} \end{aligned} \tag{3.103}$$

As a result, the relativistic quadrupole interaction is given by:

$$\begin{aligned} &\left\langle \gamma JF|H_{\rm hfs}^{Q}|\gamma' J'F\right\rangle = -\tfrac{1}{2}\left[\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)}\right]^{\frac{1}{2}}\cdot(-1)^{J'+I+F}\begin{Bmatrix} J' & I & F \\ I & J & 2\end{Bmatrix} \\ &\cdot\left(b_{nl}^{02}\left\langle \gamma J \parallel \sum_i C_i^{(2)} \parallel \gamma' J'\right\rangle + \frac{1}{\sqrt{30}}b_{nl}^{11}\left\langle \gamma J \parallel \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(11)2} \parallel \gamma' J'\right\rangle + \frac{1}{\sqrt{70}}b_{nl}^{13}\left\langle \gamma J \parallel \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(13)2} \parallel \gamma' J'\right\rangle\right) \\ &\text{see equation (5.67b) for the complete expression in second quantization.} \end{aligned} \tag{3.104}$$

Realizing from equation (5.58) that $\sum_i C_i^{(2)} = -\sqrt{2/5}\,\langle l \parallel C^{(2)} \parallel l\rangle\cdot\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(02)2}$, all the above reduced matrix elements may be calculated in the SL-coupling scheme from:

$$\left\langle \gamma SLJ \parallel \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)t} \parallel \gamma' S'L'J'\right\rangle = [J,J',t]^{\frac{1}{2}}\begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & t\end{Bmatrix}\left\langle \gamma SL \parallel \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)} \parallel \gamma' S'L'\right\rangle \tag{3.105}$$

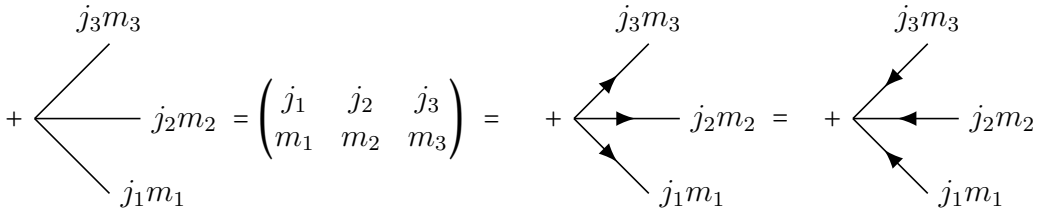
Comparison of equations (3.104) and (3.99) now gives in the relativistic case:

$$\begin{aligned} \tfrac{1}{2}\ \cdot B_J &= -\left[\frac{J(2J-1)}{(J+1)(2J+1)(2J+3)}\right]^{\frac{1}{2}} \\ \cdot\ &\left(b_{nl}^{02}\left\langle \gamma J \parallel \sum_i C_i^{(2)} \parallel \gamma J\right\rangle + \frac{1}{\sqrt{30}}b_{nl}^{11}\left\langle \gamma J \parallel \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(11)2} \parallel \gamma J\right\rangle + \frac{1}{\sqrt{70}}b_{nl}^{13}\left\langle \gamma J \parallel \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(13)2} \parallel \gamma J\right\rangle\right) \end{aligned} \tag{3.106}$$

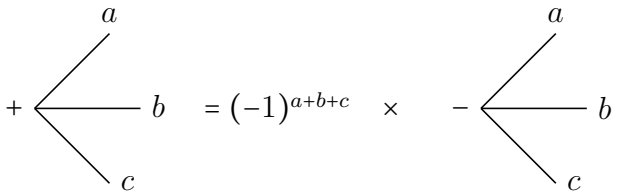
Again, if configuration interaction outside the model space is taken into account, $T^{(2)} = \sum_{\kappa k} F^{(\kappa k)2}$ is to be expanded to include the additional two- and three-particle hfs operators, see section 15.6.

Chapter 4

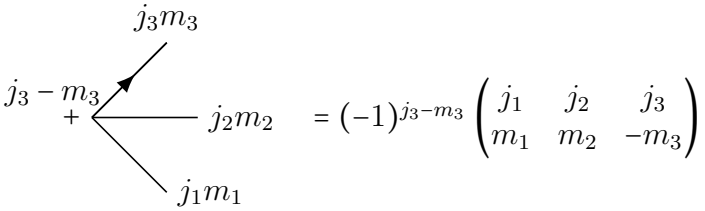
Graphical representations



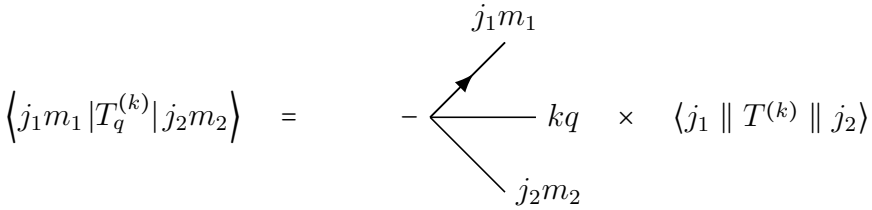
(4.1)



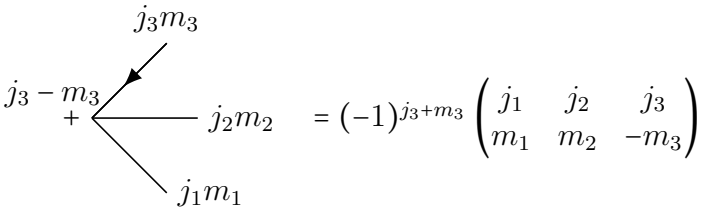
(4.2)



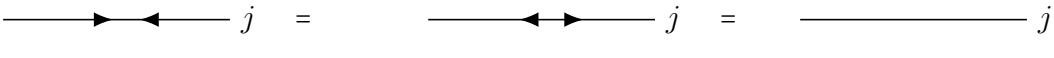
(4.3a)



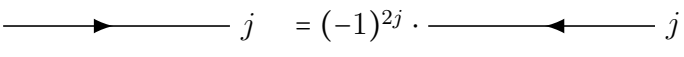
(4.3b)



(4.3c)

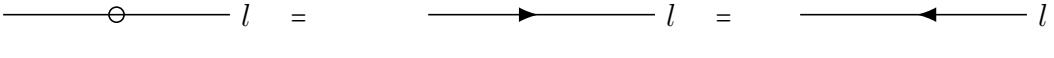


(4.4)

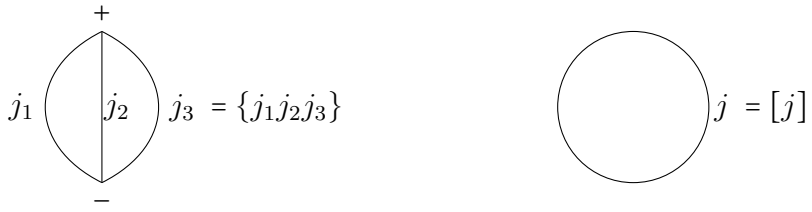


(4.5)

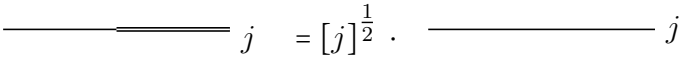
Therefore, an undirected arrow may be used for integer angular momenta:



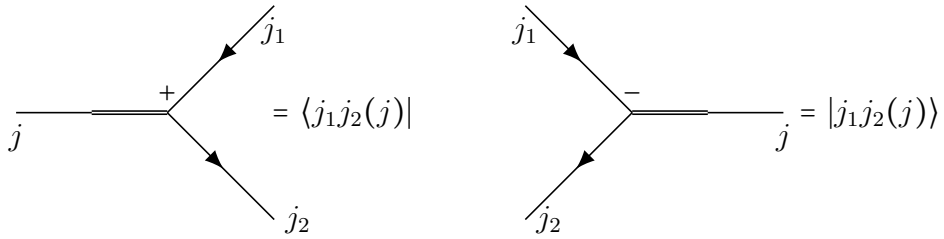
(4.6)



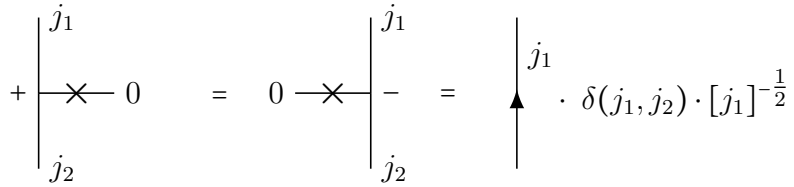
(4.7)



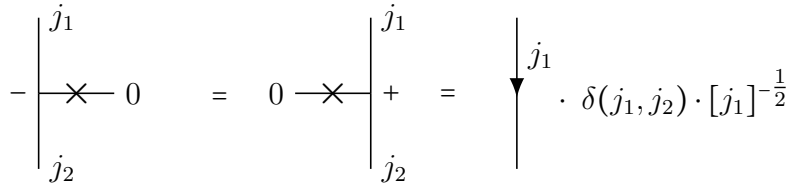
(4.8)



(4.9)



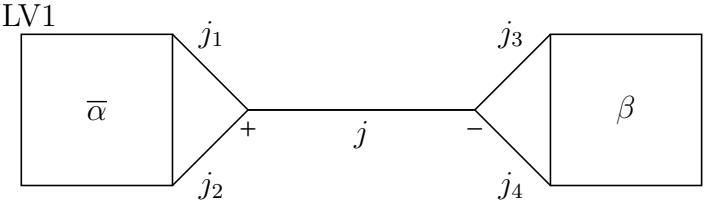
(4.10a)



(4.10b)

4.1 Jucys, Levinson and Vanagas [Jucys et al., 1962]

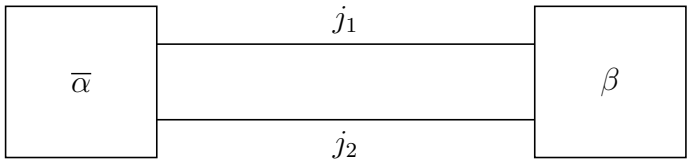
JLV1



$$= \quad \delta(j_1, j_2) \cdot \delta(j_3, j_4) \cdot \delta(j, 0) \cdot [j_1, j_3]^{-\frac{1}{2}} \cdot$$

(4.11)

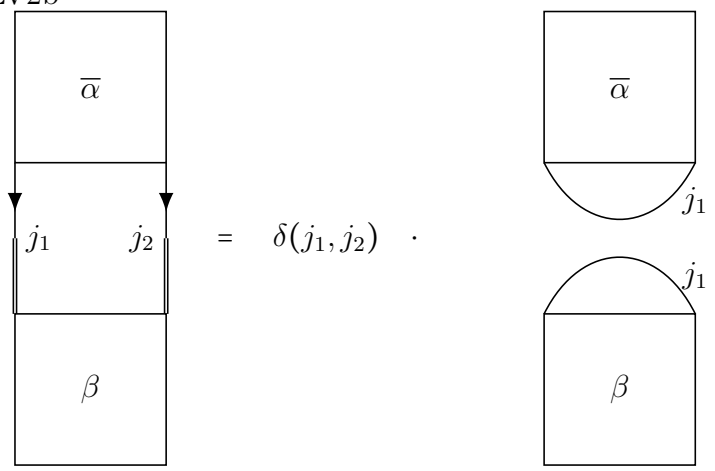
JLV2a



$$= \quad \delta(j_1, j_2) \cdot [j_1]^{-1} \cdot$$

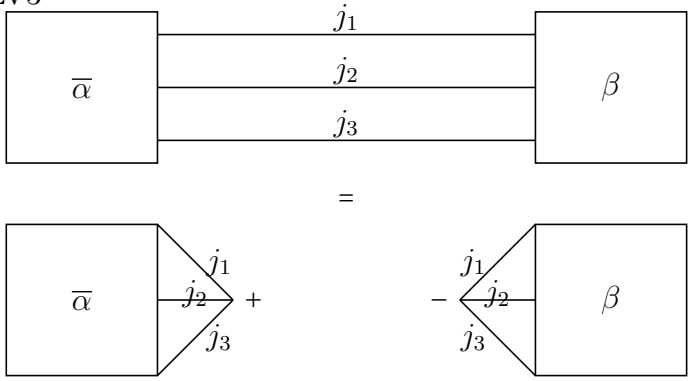
(4.12a)

JLV2b



(4.12b)

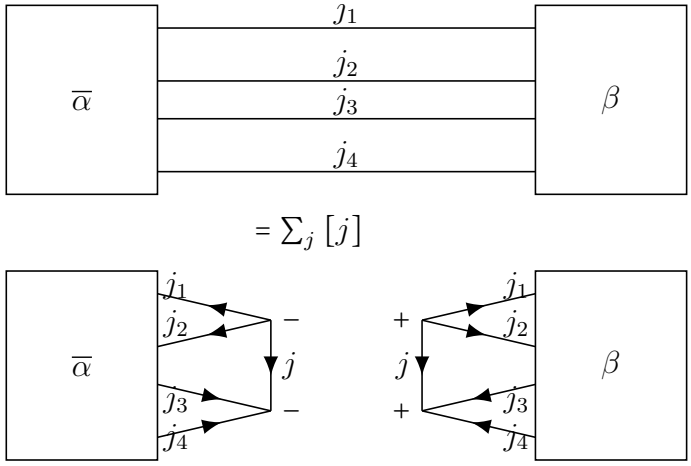
JLV3



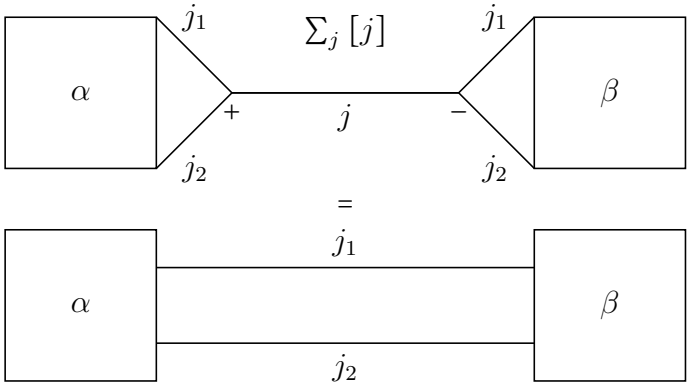
(4.13)

For empty β, JLV3 essentially represents the Wigner-Eckart theorem.

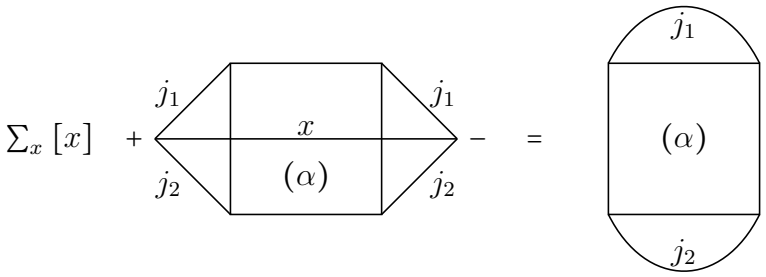
JLV4



(4.14)

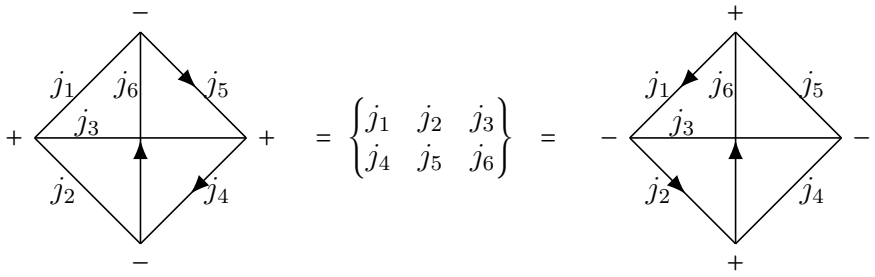


(4.15)

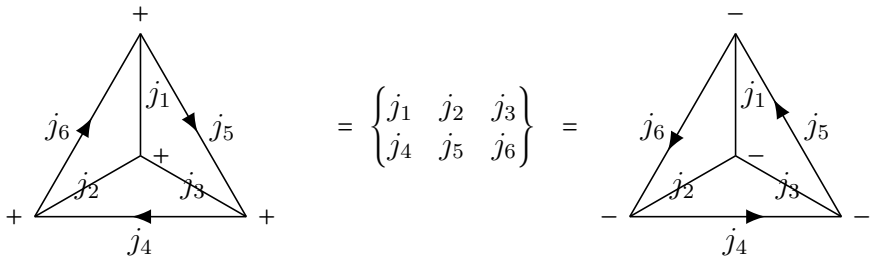


(4.16)

4.2 Basic nj-symbols

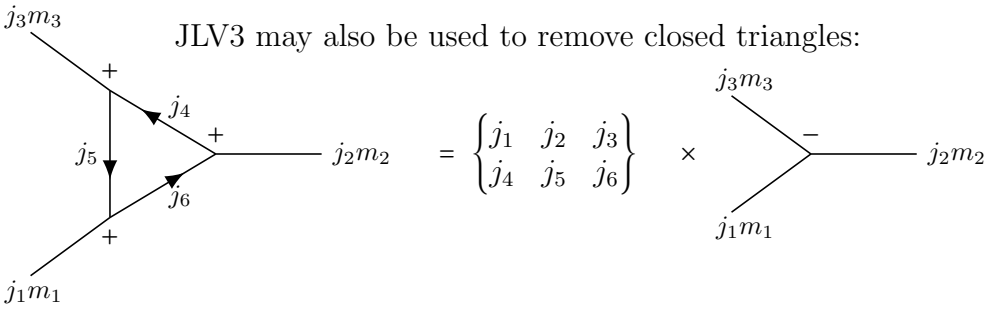


(4.17)

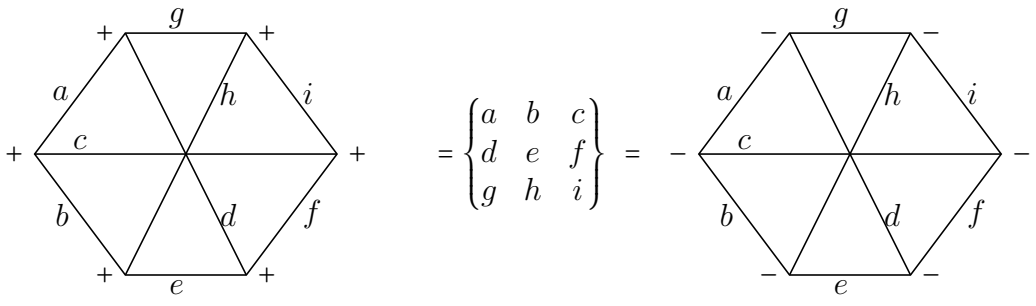


(4.18)

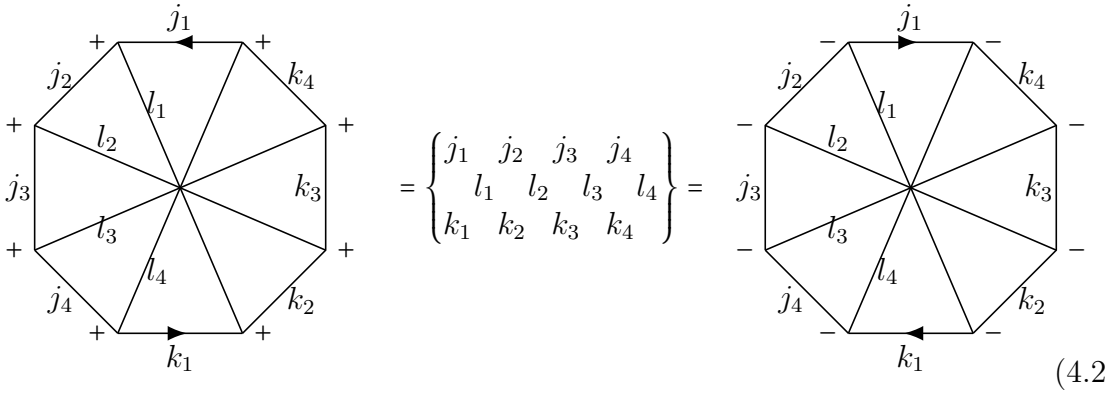
JLV3 may also be used to remove closed triangles:



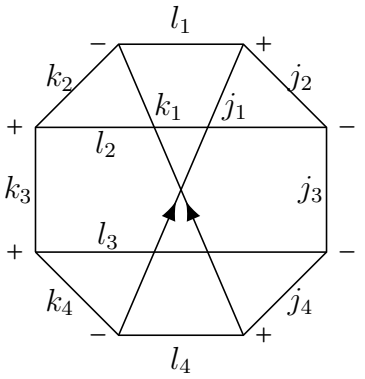
(4.19)



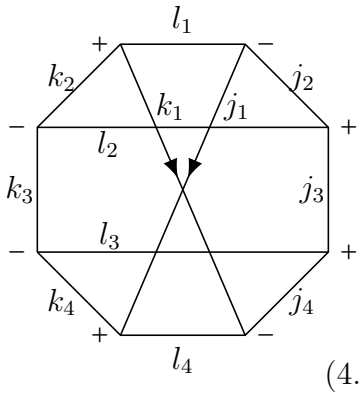
(4.20)



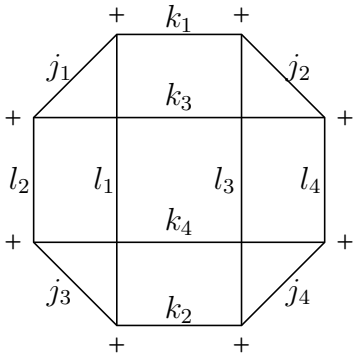
(4.21a)



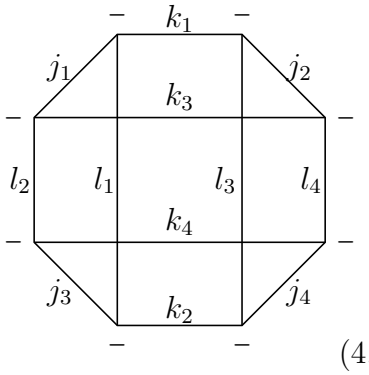
$$= \begin{Bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{Bmatrix} =$$



(4.21b)



$$= (-1)^{(k_1-l_1)-(k_2-l_2)-(k_3-l_3)+(k_4-l_4)} \cdot \begin{bmatrix} j_1 & j_2 & j_3 & j_4 \\ l_1 & l_2 & l_3 & l_4 \\ k_1 & k_2 & k_3 & k_4 \end{bmatrix} =$$



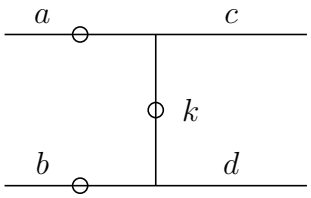
(4.22)

4.3 Interactions

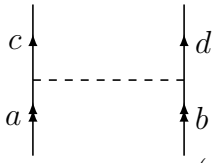
$$V_{\text{elst}} = \sum_k (-1)^k \cdot R^k(ab, cd)$$

$$\cdot \langle a \parallel C^{(k)} \parallel c \rangle \langle b \parallel C^{(k)} \parallel d \rangle \quad \times$$

$$= \sum_k X^k(ab, cd)$$

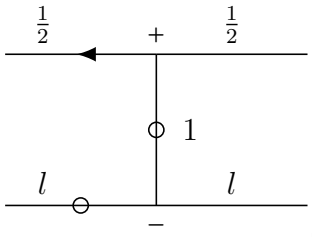


(Feynman) →



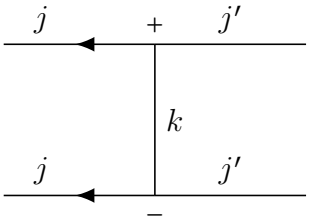
(4.23)

$$V_{\text{magn}} = \qquad (-1) \quad \cdot \left\langle \tfrac{1}{2} \parallel s^{(1)} \parallel \tfrac{1}{2} \right\rangle \cdot \langle l \parallel l^{(1)} \parallel l \rangle \quad \zeta_l \cdot$$



(4.24)

$$T^{(k)} = \qquad \langle j \parallel T^{(k)} \parallel j' \rangle \quad \cdot$$



(4.25)

Chapter 5

Second quantization

[1] Creation and annihilation operators, implicitly defined by $a_\alpha^\dagger |0\rangle = |\alpha\rangle$ and $a_\beta |\beta\rangle = |0\rangle$ while $a_\gamma |0\rangle = 0$, satisfy commutation [] ánd anti-commutation {} rules:

anti-commutation	**commutation**
$a_\xi a_\eta + a_\eta a_\xi = 0$	$\frac{1}{2}[a_\xi, a_\eta] = a_\xi a_\eta$
$a_\xi^\dagger a_\eta^\dagger + a_\eta^\dagger a_\xi^\dagger = 0$	$\frac{1}{2}[a_\xi^\dagger, a_\eta^\dagger] = a_\xi^\dagger a_\eta^\dagger$
$a_\xi^\dagger a_\eta + a_\eta a_\xi^\dagger = \delta(\xi,\eta)$	$\frac{1}{2}[a_\xi^\dagger, a_\eta] = a_\xi^\dagger a_\eta - \frac{1}{2}\delta(\xi,\eta)$

Table 5.1: Commutation relations

While identical operators vanish when placed side by side ($a_\xi a_\xi = 0$ and $a_\xi^\dagger a_\xi^\dagger = 0$), the useful mixed expression $\sum_\xi a_\xi^\dagger a_\xi |\psi\rangle = N |\psi\rangle$ is called the number operator. Expressed in terms of second quantization, single-particle operators F and two-particle operators G become:

$$F = \sum_{\xi,\eta} a_\xi^\dagger \langle \xi | f | \eta \rangle \, a_\eta \tag{5.1a}$$

$$G = \tfrac{1}{2} \sum_{\xi,\eta,\zeta,\lambda} a_\xi^\dagger a_\eta^\dagger \langle \xi_1 \eta_2 | g_{12} | \zeta_1 \lambda_2 \rangle \, a_\lambda a_\zeta \tag{5.1b}$$

One may proceed to collect or couple these operators to form tensor operators:

$$\mathbf{a}^\dagger = \mathbf{a}^{\dagger(sl)}_{m_s m_l}$$
$$\mathbf{a} = (-1)^x \cdot \mathbf{a}^{(sl)}_{-m_s -m_l} \text{ with } x = (s + l - m_s - m_l). \tag{5.2}$$

With $\xi = (nl\, m_s m_l)$ and $\eta = (nl\ -m_s - m_l)$ and $\tilde{a}_\eta = (-1)^x a_\xi$, this leads to e.g.:

$$\left(\mathbf{a}^\dagger \mathbf{a}\right)^{(\kappa k)}_{\pi q} = \sum_{\xi\eta} (sm_{s\xi}\ sm_{s\eta}|\kappa\pi)(lm_{l\xi}\ lm_{l\eta}|kq)\, a_\xi^\dagger \tilde{a}_\eta \tag{5.3}$$

As an example, it follows for the number operator, using $(a\alpha\ b\beta|00) = \delta(a,b)\delta(\alpha,-\beta)\cdot[a]^{-\frac{1}{2}} \cdot (-1)^{a-\alpha}$:

$$(\mathbf{a}^\dagger \mathbf{a})^{(00)} = -\left[\tfrac{1}{2}, l\right]^{-\frac{1}{2}} \sum_\xi a_\xi^\dagger a_\xi \tag{5.4}$$

[1] [Judd, 1967] is used as a overarching reference for much of the basic material of this chapter.

The creation and annihilation operators are related by the anti-linear conjugation operator C obeying $C^\dagger C = C^{-1}C = \mathbb{1}$ and $CiC^{-1} = -i$:

$$C\,\mathbf{a}^\dagger\,C^{-1} = \mathbf{a} \tag{5.5a}$$

$$C\,\mathbf{a}\,C^{-1} = -\mathbf{a}^\dagger \tag{5.5b}$$

while:

$$C\,(\mathbf{a}^\dagger\mathbf{a})^{\kappa k}\,C^{-1} = -(\mathbf{a}\mathbf{a}^\dagger)^{\kappa k} \text{ and: } C\,(\mathbf{a}\mathbf{a}^\dagger)^{\kappa k}\,C^{-1} = -(\mathbf{a}^\dagger\mathbf{a})^{\kappa k} \tag{5.6}$$

Likewise:

$$C\,(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{\kappa k}\,C^{-1} = (\mathbf{a}\mathbf{a})^{\kappa k} \text{ and: } C\,(\mathbf{a}\mathbf{a})^{\kappa k}\,C^{-1} = (\mathbf{a}^\dagger\mathbf{a}^\dagger)^{\kappa k} \tag{5.7}$$

$$\left(\mathbf{a}\mathbf{a}^\dagger\right)^{\kappa k} = (-1)^{\kappa+k}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{\kappa k} + \delta(\kappa,0)\delta(k,0)\,[\tfrac{1}{2},l]^{\frac{1}{2}} \tag{5.8a}$$

$$\left(\mathbf{a}^\dagger\mathbf{a}\right)^{\kappa k} = (-1)^{\kappa+k}\left(\mathbf{a}\mathbf{a}^\dagger\right)^{\kappa k} - \delta(\kappa,0)\delta(k,0)\,[\tfrac{1}{2},l]^{\frac{1}{2}} \tag{5.8b}$$

$$\left(\mathbf{a}\mathbf{a}^\dagger\right)^{00} - \left(\mathbf{a}^\dagger\mathbf{a}\right)^{00} = [\tfrac{1}{2},l]^{\frac{1}{2}} \tag{5.8c}$$

$$\left\{\mathbf{a}\left(\mathbf{a}^\dagger\mathbf{a}^\dagger\right)^{SL}\right\}^{\bar{S}\bar{L}} = (-1)^{\frac{1}{2}+l-(\bar{S}+\bar{L})}\left\{\left(\mathbf{a}^\dagger\mathbf{a}^\dagger\right)^{SL}\mathbf{a}\right\}^{\bar{S}\bar{L}} - 2[S,L]^{\frac{1}{2}}\,[\tfrac{1}{2},l]^{-\frac{1}{2}}\,\delta(\bar{S},\tfrac{1}{2})\delta(\bar{L},l)\,\mathbf{a}^\dagger \tag{5.9a}$$

$$\left\{(\mathbf{a}\mathbf{a})^{SL}\,\mathbf{a}^\dagger\right\}^{\bar{S}\bar{L}} = (-1)^{\frac{1}{2}+l-(\bar{S}+\bar{L})}\left\{\mathbf{a}^\dagger\,(\mathbf{a}\mathbf{a})^{SL}\right\}^{\bar{S}\bar{L}} - 2[S,L]^{\frac{1}{2}}\,[\tfrac{1}{2},l]^{-\frac{1}{2}}\,\delta(\bar{S},\tfrac{1}{2})\delta(\bar{L},l)\,\mathbf{a} \tag{5.9b}$$

$$\begin{aligned}\left\{\left(\mathbf{a}^\dagger\mathbf{a}\right)^{kK}\mathbf{a}^\dagger\right\}^{\bar{S}\bar{L}} &= (-1)^{k+K+\frac{1}{2}+l-(\bar{S}+\bar{L})}\left\{\mathbf{a}^\dagger\left(\mathbf{a}^\dagger\mathbf{a}\right)^{kK}\right\}^{\bar{S}\bar{L}} \\ &\quad - (-1)^{k+K}[k,K]^{\frac{1}{2}}\,[\tfrac{1}{2},l]^{-\frac{1}{2}}\,\delta(\bar{S},\tfrac{1}{2})\delta(\bar{L},l)\,\mathbf{a}^\dagger\end{aligned} \tag{5.9c}$$

$$\begin{aligned}\left\{\mathbf{a}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{kK}\right\}^{\bar{S}\bar{L}} &= (-1)^{k+K+\frac{1}{2}+l-(\bar{S}+\bar{L})}\left\{\left(\mathbf{a}^\dagger\mathbf{a}\right)^{kK}\mathbf{a}\right\}^{\bar{S}\bar{L}} \\ &\quad - (-1)^{k+K}[k,K]^{\frac{1}{2}}\,[\tfrac{1}{2},l]^{-\frac{1}{2}}\,\delta(\bar{S},\tfrac{1}{2})\delta(\bar{L},l)\,\mathbf{a}\end{aligned} \tag{5.9d}$$

$$\begin{aligned}\left\{(\mathbf{a}\mathbf{a})^{S'L'}(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}\right\}^{kK} &= (-1)^{k+K}\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}(\mathbf{a}\mathbf{a})^{S'L'}\right\}^{kK} \\ &\quad + 4\cdot[S,L,S',L']^{\frac{1}{2}}\begin{Bmatrix} S & k & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} L & K & L' \\ l & l & l\end{Bmatrix}(\mathbf{a}^\dagger\mathbf{a})^{kK} \\ &\quad - 2\cdot\delta(k,0)\delta(K,0)\delta(SS')\delta(LL')\cdot[S,L]^{\frac{1}{2}}\end{aligned} \tag{5.10a}$$

$$\begin{aligned}\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}(\mathbf{aa})^{S'L'}\right\}^{kK} &= (-1)^{k+K}\left\{(\mathbf{aa})^{S'L'}(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}\right\}^{kK} \\ &\quad - 4\cdot[S,L,S',L']^{\frac{1}{2}}\begin{Bmatrix} S & k & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} L & K & L' \\ l & l & l\end{Bmatrix}(\mathbf{aa}^\dagger)^{kK} \\ &\quad - 2\cdot\delta(k,0)\delta(K,0)\delta(SS')\delta(LL')\cdot[S,L]^{\frac{1}{2}} \end{aligned} \tag{5.10b}$$

$$\begin{aligned}\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}(\mathbf{aa})^{S'L'}\right\}^{00} &- \left\{(\mathbf{aa})^{S'L'}(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}\right\}^{00} \\ &= \ 2[S,L]^{\frac{1}{2}}\ [\tfrac{1}{2},l]^{-\frac{1}{2}}\left\{(\mathbf{a}^\dagger\mathbf{a})^{(00)} + \mathbf{aa}^\dagger)^{(00)}\right\} \\ &= -8[S,L]^{\frac{1}{2}}\ [\tfrac{1}{2},l]^{-1}\ Q_0 \end{aligned} \tag{5.10c}$$

$$(\mathbf{ba}^\dagger)^{(\kappa K)} = (-1)^{l_a+l_b+\kappa+K}(\mathbf{a}^\dagger\mathbf{b})^{(\kappa K)} + \delta(a,b)\delta(\kappa,0)\delta(K,0)\ [\tfrac{1}{2},l_a]^{\frac{1}{2}} \tag{5.11}$$

For closed shells:

$$\left(\mathbf{c}^\dagger\mathbf{c}\right)^{(\kappa k)} = -\delta(\kappa,0)\ \delta(k,0)\ [\tfrac{1}{2},l_c]^{\frac{1}{2}} \tag{5.12}$$

Applied to two-particle operators:

$$\left\{\left(\mathbf{c}^\dagger\mathbf{c}\right)^{\kappa_1 k_1}\left(\mathbf{a}^\dagger\mathbf{b}\right)^{\kappa_2 k_2}\right\}^{(\kappa k)t} = \delta(\kappa_1,0)\delta(k_1,0)\delta(\kappa_2,\kappa)\delta(k_2,k)\cdot -[\tfrac{1}{2},l_c]^{\frac{1}{2}}\cdot(\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)t} \tag{5.13a}$$

$$\begin{aligned}\left\{\left(\mathbf{c}^\dagger\mathbf{b}\right)^{\kappa_1 k_1}\left(\mathbf{a}^\dagger\mathbf{c}\right)^{\kappa_2 k_2}\right\}^{(\kappa k)t} &= (-1)^{l_a+l_b+\kappa_1+\kappa_2+k_1+k_2+1}\,[\kappa_1,\kappa_2,k_1,k_2]^{\frac{1}{2}} \\ &\times \begin{Bmatrix}\kappa_1 & \kappa_2 & \kappa \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} k_1 & k_2 & k \\ l_a & l_b & l_c\end{Bmatrix}\cdot(\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)t} \end{aligned} \tag{5.13b}$$

For virtual shells:

$$\left(\mathbf{vv}^\dagger\right)^{(\kappa k)} = \delta(\kappa,0)\ \delta(k,0)\ [\tfrac{1}{2},l_v]^{\frac{1}{2}} \tag{5.14}$$

Products of operators expressed in second quantization, as occur in perturbation theory and in the theory of inner products, are reduced as follows:
(i) Creation operators $\mathbf{c}^\dagger$ of a closed shell are coupled to the corresponding annihilation operators $\mathbf{c}$, e.g. $(\mathbf{c}^\dagger\mathbf{c})^{(\kappa k)}$. As one cannot create a new electron in a shell that is filled already, $\mathbf{c}^\dagger$ cannot be interchanged to become the rightmost operator: $\mathbf{c}^\dagger|\,A\alpha\rangle = 0$. As seen from equation (5.12), interchange will produce this null result plus a scalar residue in which all operators $\mathbf{c}^{(\dagger)}$ have disappeared.
(ii) The same argument applies to virtual shells if one replaces creation by annihilation and vice versa by application of equation (5.14).
(iii) With the above, operators referring either to closed or to virtual shells are coupled to zero ranks and subsequently removed. Next, the remaining open shell operators are rearranged to bring the creation operators (coupled together) to the left and the annihilation operators (coupled together) to the right of the expression. The number of either one determines the n-particle character of the final operator, which is now referred to be 'in normal form'. Matrix elements of this operator can

trivially be evaluated as unit operators in their 'parent' configuration, i.e. the configuration with n electrons where the operator appears for the first time. Equation (5.11) provides the key to the algebraical manipulation of operators in second quantized form. However, if we restrict our attention to two-particle operators, we have to deal with $2n$ creation and $2n$ annihilation operators in the n^{th} order of perturbation, which already becomes cumbersome in the second order. For this reason, we take recourse to graphical algebra which allows all recoupling transformations to be carried out simultaneously.
When recoupling creation and annihilation operators, there are three additional operations with respect to recoupling ordinary angular momenta:
(i) Each interchange of operators gives a minus sign, yielding a phase factor $(-1)^P$ for P permutations.
(ii) When a creation and an annihilation operator of the same shell are interchanged, one applies equation (5.11) instead of (i). This gives a branching into an n-particle and an $(n-1)$-particle operator, as the second term has one $\mathbf{a}^\dagger\mathbf{a}$ pair less: interchange of equivalent creation/annihilation operators yields additional residues with a lowered $n-$particle character. Frequently, one is only interested in the operator involving the highest number of electrons and step (ii) can be skipped: in this so-called 'top-of-the-tree' formalism, the residues are not considered and only operators with maximum n are retrieved.
(iii) After the recoupling, one multiplies the expression for the orbital angular momenta with the analogous expression of the spins to obtain the final result.

5.1 Electrostatic unit operators

Operators in second quantization act as unit operators in their parent configuration: if the operators are not coupled to the terms of the bra and the ket respectively, the result will be zero. Example:

$$\left\langle nl\,|(\mathbf{a}^\dagger\mathbf{b})^{(00)0}|\,n'l'\right\rangle = -\delta(l,l')\cdot[\tfrac{1}{2},l]^{-\frac{1}{2}} \tag{5.15}$$

This operator appears in the second quantized form of the electronic potential:

$$U_{AB} = -\delta(l,l')\cdot[\tfrac{1}{2},l]^{\frac{1}{2}}\cdot(\mathbf{a}^\dagger\mathbf{b})^{(00)0}\cdot\langle nl\,|U|\,n'l'\rangle$$

where $\langle nl\,|U|\,n'l'\rangle$ represents the sum over the various average Coulomb interactions between configurations A and B.
For l^N, a convenient choice for the definition of basic one-, two- and three-particle electrostatic operators is given by:

$$H_l = -[\tfrac{1}{2},l]^{\frac{1}{2}}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(00)} \tag{5.16a}$$

$$H_{SL} = -\tfrac{1}{2}[S,L]^{\frac{1}{2}}\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}(\mathbf{aa})^{SL}\right\}^{(00)} \tag{5.16b}$$

$$H^{(S_3L_3)}_{SL,S'L'} = (-1)^{\frac{1}{2}+l-(S_3+L_3)}[S_3,L_3]^{\frac{1}{2}}\left[\left\{\mathbf{a}^\dagger(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}\right\}^{S_3L_3}\left\{(\mathbf{aa})^{S'L'}\mathbf{a}\right\}^{S_3L_3}\right]^{(00)} \tag{5.16c}$$

Their corresponding matrix elements are:

$$\langle l\,|H_l|\,l'\rangle = \delta(l,l') \tag{5.17a}$$

$$\begin{aligned}\left\langle l^2(SL)|H_{SL}|l^2(S'L')\right\rangle &= \delta(SS')\,\delta(LL')\\ \left\langle l^N\,\psi_A|H_{SL}|l^N\,\psi_B\right\rangle &= \tfrac{1}{2}N(N-1)\,\delta(\psi_A,\psi_B)\end{aligned} \tag{5.17b}$$

$$\left\langle l^3(S_3L_3\nu_3)|H^{(S_3L_3)}_{SL,S'L'}|l^3(S_3L_3\nu'_3)\right\rangle = 6\left(l^3(S_3L_3\nu_3)\{|l^2(SL)\right)\left(l^2(S'L')|\}l^3(S_3L_3\nu'_3)\right) \tag{5.17c}$$

A similar example for l^2l' operators:

$$\left\langle l^2(SL)l'(S_3L_3)\left|\left[\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}\mathbf{b}^\dagger\right\}^{(S_3L_3)}\left\{(\mathbf{aa})^{(S'L')}\mathbf{b}\right\}^{(S_3L_3)}\right]^{(00)}\right|l^2(S'L')l'(S_3L_3)\right\rangle = 2\,[S_3,L_3]^{-\frac{1}{2}} \tag{5.18}$$

5.2 Reduced matrix elements in second quantization

$$\left\langle a(\tfrac{1}{2}l)\parallel\mathbf{a}^\dagger\parallel(00)\right\rangle = -[\tfrac{1}{2},l]^{\frac{1}{2}} \tag{5.19a}$$

$$\left\langle(00)\parallel\mathbf{a}\parallel a(\tfrac{1}{2}l)\right\rangle = [\tfrac{1}{2},l]^{\frac{1}{2}} \tag{5.19b}$$

$$\left\langle a(\tfrac{1}{2}l_a)\parallel\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)}\parallel b(\tfrac{1}{2}l_b)\right\rangle = -[\kappa,k]^{\frac{1}{2}} \tag{5.20}$$

Equation (5.20) is a direct application of equations (5.19) and (3.48) with the vacuum state (00) as ψ''. This is standard procedure for calculating reduced matrix elements of operators in normal form, with all creation operators arranged to the left and all annihilation operators to the right.
With $C^{(SL)} = (\mathbf{a}^\dagger_1\mathbf{a}^\dagger_2\cdots\mathbf{a}^\dagger_n)^{(SL)}$ and $A^{(S'L')} = (\mathbf{a}_n\cdots\mathbf{a}_2\mathbf{a}_1)^{(S'L')}$, equation (3.48) reduces to:

$$\begin{aligned}&\left\langle\alpha SL\parallel\left(C^{(SL)}A^{(S'L')}\right)^{(\kappa k)}\parallel\alpha'S'L'\right\rangle\\ &= [\kappa,k]^{\frac{1}{2}}\cdot[S,L,S',L']^{-\frac{1}{2}}\cdot\left\langle\alpha SL\parallel C^{(SL)}\parallel(00)\right\rangle\cdot\left\langle(00)\parallel A^{(S'L')}\parallel\alpha'S'L'\right\rangle\end{aligned} \tag{5.21}$$

In turn, compound expressions $\langle\alpha SL\parallel C^{(SL)}\parallel(00)\rangle$ can always be broken down into the smaller pieces (5.19) by repeated application of equation (3.49):

$$\left\langle SL\parallel C^{(SL)}\parallel(00)\right\rangle = [S,L]^{\frac{1}{2}}\cdot[S_1,L_1,S_2,L_2]^{-\frac{1}{2}}\cdot\left\langle S_1L_1\parallel C_1^{(S_1L_1)}\parallel(00)\right\rangle\cdot\left\langle S_2L_2\parallel C_2^{(S_2L_2)}\parallel(00)\right\rangle \tag{5.22}$$

In the absence of spectator electrons, matrix elements are prefactored by a statistical weighting factor $\sqrt{\Pi_\lambda\,q_\lambda!\cdot\Pi_{\lambda'}\,q_{\lambda'}!}$, where q_λ denotes the occupation number of shell λ.

Reduced matrix elements of operators in second quantization may be reversed by:

$$< \Psi \parallel \mathbf{a}_1^{\pm}\mathbf{a}_2^{\pm}...\mathbf{a}_i^{\pm}...\mathbf{a}_n^{\pm} \parallel \Psi' >= (-1)^P < \Psi' \parallel \mathbf{a}_n^{\mp}...\mathbf{a}_i^{\mp}...\mathbf{a}_2^{\mp}\mathbf{a}_1^{\mp} \parallel \Psi > \tag{5.23a}$$

with the phase:

$$P = (S+L) - (S'+L') \pm (\tfrac{1}{2}+l_1)... \pm (\tfrac{1}{2}+l_i)... \pm (\tfrac{1}{2}+l_n) \tag{5.23b}$$

For the ease of notation, the above + and − superscripts refer to creation and annihilation operators, respectively. As an example:

$$\left\langle ab(SL) \parallel \left(\mathbf{a}^\dagger\mathbf{b}^\dagger\right)^{(SL)} \parallel (00)\right\rangle = (1+\delta_{ab})^{\frac{1}{2}}\ [S,L]^{\frac{1}{2}} \tag{5.24a}$$

$$\left\langle (00) \parallel (\mathbf{ab})^{(SL)} \parallel ab(SL)\right\rangle = -(1+\delta_{ab})^{\frac{1}{2}}\ [S,L]^{\frac{1}{2}} \tag{5.24b}$$

Note that the interchange $(\mathbf{ba})^{(SL)} \rightarrow (\mathbf{ab})^{(SL)}$ removes the complete phase factor $(-1)^P$ except for a minus sign. Equation (5.24a) is found by substituting equation (5.19a) into equation (5.22).

Following equation (3.82), the J−dependence of the reduced matrix elements of double tensor operators $X^{(\kappa k)t}$ like $(\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)t}$ is factored out by:

$$\left\langle \psi\, SLJ \parallel X^{(\kappa k)t} \parallel \psi'\, S'L'J' \right\rangle = [J,J',t]^{\frac{1}{2}} \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & t \end{Bmatrix} \left\langle \psi\, SL \parallel X^{(\kappa k)} \parallel \psi'\, S'L' \right\rangle \tag{5.25}$$

$$\begin{aligned} &\left\langle \psi\, \gamma SLJ | X^{(kk)0} | \psi'\, \gamma' S'L'J' \right\rangle \text{ (here, } k = 0,1,2 \text{ for electrostatic, spin-orbit and spin-spin effects)} \\ &= \delta(JJ') \cdot [J]^{-\frac{1}{2}} \left\langle \psi\, \gamma SLJ \parallel X^{(kk)0} \parallel \psi'\, \gamma' S'L'J' \right\rangle \\ &= \delta(J,J')(-1)^k [k]^{-\frac{1}{2}} (-1)^{L+S'+J} \cdot \begin{Bmatrix} S & L & J \\ L' & S' & k \end{Bmatrix} \left\langle \psi\, SL \parallel X^{(kk)} \parallel \psi'\, S'L' \right\rangle \end{aligned} \tag{5.26}$$

Equation (5.26) is identical to equation (3.44) derived earlier.
Important special cases of equation (5.25):

$$\left\langle \tfrac{1}{2} lj \parallel (\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)t} \parallel \tfrac{1}{2} l'j' \right\rangle = -[j,j']^{\frac{1}{2}} \cdot [\kappa,k,t]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l' & k \\ j & j' & t \end{Bmatrix} \tag{5.27}$$

The adjoint becomes therewith:

$$\left\langle \tfrac{1}{2} l'j' \parallel (\mathbf{b}^\dagger\mathbf{a})^{(\kappa k)t} \parallel \tfrac{1}{2} lj \right\rangle = -[j,j']^{\frac{1}{2}} \cdot [\kappa,k,t]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l' & l & k \\ j' & j & t \end{Bmatrix} \tag{5.28}$$

Hermiticity now requires that $P = \kappa + k + t$ always be even!

$$\begin{aligned} &\left\langle l^N\, SLJ \parallel (\mathbf{a}^\dagger\mathbf{a})^{(0k)k} \parallel l^N\, S'L'J' \right\rangle = \delta(S,S') \cdot N \cdot [\tfrac{1}{2}]^{-\frac{1}{2}} \cdot [k]^{\frac{1}{2}} \cdot [J,J',L,L']^{\frac{1}{2}} \cdot \begin{Bmatrix} J & J' & k \\ L & L' & S \end{Bmatrix} \\ &\cdot (-1)^{J+L'+S+L+l+1} \sum_{\overline{S}\,\overline{L}} (-1)^{\overline{L}} \cdot \begin{Bmatrix} l & l & k \\ L' & L & \overline{L} \end{Bmatrix} \cdot \left(l^N SL\, \{|l^{N-1}\overline{S}\,\overline{L}\right) \left(l^{N-1}\overline{S}\,\overline{L}\,|\}l^N S'L'\right) \end{aligned} \tag{5.29}$$

The SL–dependent reduced matrix element $\langle \psi\, SL \parallel (\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)} \parallel \psi'\, S'L' \rangle$ is calculated from equation (5.20) in combination with equation (3.55a) or (3.55b), e.g.:

$$\left\langle l^2 SL \parallel (\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)} \parallel l^2 S'L' \right\rangle = 2(-1)^{\kappa+k}[\kappa,k]^{\frac{1}{2}} \cdot [S,L,S',L']^{\frac{1}{2}} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & l & l \end{Bmatrix} \quad (5.30)$$

$$\left\langle l^N SL \parallel (\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)} \parallel l^N S'L' \right\rangle = N \cdot [\kappa,k]^{\frac{1}{2}} \cdot [S,L,S',L']^{\frac{1}{2}}$$
$$\cdot \sum_{\overline{S}\,\overline{L}} (-1)^z \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ S' & S & \overline{S} \end{Bmatrix} \cdot \begin{Bmatrix} l & l & k \\ L' & L & \overline{L} \end{Bmatrix} \cdot \left(l^N SL \,\{|l^{N-1}\overline{S}\,\overline{L}\right) \left(l^{N-1}\overline{S}\,\overline{L}\,|\}l^N S'L'\right) \quad (5.31)$$

with $z = S + \kappa + L + k + \overline{S} + \overline{L} - (\frac{1}{2} + l)$.

$$\left\langle ll'SL \parallel (\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)} \parallel ll'S'L' \right\rangle = (-1)^{\kappa+k+l+l'+S'+L'}[\kappa,k]^{\frac{1}{2}} \cdot [S,L,S',L']^{\frac{1}{2}} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & l' & l \end{Bmatrix} \quad (5.32a)$$

$$\left\langle ll'SL \parallel (\mathbf{b}^\dagger\mathbf{b})^{(\kappa k)} \parallel ll'S'L' \right\rangle = (-1)^{\kappa+k+l+l'+S+L}[\kappa,k]^{\frac{1}{2}} \cdot [S,L,S',L']^{\frac{1}{2}} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l' & l & l' \end{Bmatrix} \quad (5.32b)$$

$$\left\langle l^N\, SL \parallel \left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)} \parallel l^{N-1}(S_1L_1)\, l'\, S'L' \right\rangle = -[\kappa,k]^{\frac{1}{2}} \cdot \sqrt{N} \cdot \left(l^N\, SL\{|l^{N-1}\, S_1L_1\right)$$
$$\cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{S_1+\frac{1}{2}+S+\kappa} \cdot (-1)^{L_1+l'+L+k} \cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & S_1 & \frac{1}{2} \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l' & L_1 & l \end{Bmatrix} \quad (5.33)$$

$$\left\langle l^N(S_1L_1)l'\, SL \parallel (\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)} \parallel l^N(S_1'L_1')l''\, S'L' \right\rangle = -N \cdot \delta(l',l'') \cdot [\kappa,k]^{\frac{1}{2}} \cdot [S,L,S',L']^{\frac{1}{2}}$$
$$\cdot [S_1,L_1,S_1',L_1']^{\frac{1}{2}} \cdot \sum_{\overline{S}\,\overline{L}} (-1)^{\overline{L}+l'+L'+l} \begin{Bmatrix} L_1 & L_1' & k \\ L' & L & l' \end{Bmatrix} \begin{Bmatrix} L_1 & L_1' & k \\ l & l & \overline{L} \end{Bmatrix}$$
$$\cdot \left(l^N S_1L_1\{|l^{N-1}\overline{S}\,\overline{L}\right) \left(l^{N-1}\overline{S}\,\overline{L}|\}l^N S_1'L_1'\right) \cdot (-1)^{\overline{S}-S'} \begin{Bmatrix} S_1 & S_1' & \kappa \\ S' & S & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} S_1 & S_1' & \kappa \\ \frac{1}{2} & \frac{1}{2} & \overline{S} \end{Bmatrix} \quad (5.34)$$

$$\left\langle l^N(S_1L_1)l'\, SL \parallel (\mathbf{b}^\dagger\mathbf{c})^{(\kappa k)} \parallel l^N(S_1'L_1')l''\, S'L' \right\rangle = -[\kappa,k]^{\frac{1}{2}} \cdot \delta(S_1,S_1') \cdot \delta(L_1,L_1')$$
$$\cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{S_1+\frac{1}{2}+S+\kappa} \cdot (-1)^{L_1+l''+L+k} \cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & S_1 & \frac{1}{2} \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l'' & L_1 & l' \end{Bmatrix} \quad (5.35)$$

Reduced matrix elements of two-particle operators in coupled second quantized normal form:

$$\left\langle ab(SL) \parallel \{(\mathbf{a}^\dagger\mathbf{b}^\dagger)^{(SL)}(\mathbf{cd})^{(S'L')}\}^{(\kappa k)} \parallel cd(S'L') \right\rangle = -\left((1+\delta_{ab})(1+\delta_{cd})\right)^{\frac{1}{2}} [\kappa,k]^{\frac{1}{2}} \quad (5.36)$$

Equation (5.36) follows directly from equation (5.21) and equations (5.24). Examples:

$$\left\langle l^2(SL) \parallel \{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}(\mathbf{bb})^{(S'L')}\}^{(\kappa k)} \parallel l'^2(S'L') \right\rangle = -2 \cdot [\kappa,k]^{\frac{1}{2}} \quad (5.37)$$

$$\left\langle ab(SL)\left|\{(\mathbf{a}^\dagger\mathbf{b}^\dagger)^{(SL)}(\mathbf{cd})^{(SL)}\}^{(00)}\right|cd(SL)\right\rangle = -\left((1+\delta_{ab})(1+\delta_{cd})\right)^{\frac{1}{2}}\cdot[S,L]^{-\frac{1}{2}} \quad (5.38)$$

In its initial form, two-particle operators are usually found as the coupled product of two one-particle operators:

$$\begin{aligned}\left\langle ab(SL)\parallel\left\{(\mathbf{a}^\dagger\mathbf{c})^{(\kappa_1 k_1)}(\mathbf{b}^\dagger\mathbf{d})^{(\kappa_2 k_2)}\right\}^{(\kappa k)}\parallel cd(S'L')\right\rangle &= \left((1+\delta_{ab})(1+\delta_{cd})\right)^{\frac{1}{2}}\\ \times[\kappa_1,k_1,\kappa_2,k_2,\kappa,k]^{\frac{1}{2}}\cdot[S,L,S',L']^{\frac{1}{2}}&\begin{Bmatrix}\frac{1}{2}&\frac{1}{2}&\kappa_1\\ \frac{1}{2}&\frac{1}{2}&\kappa_2\\ S&S'&\kappa\end{Bmatrix}\begin{Bmatrix}l_a&l_c&k_1\\ l_b&l_d&k_2\\ L&L'&k\end{Bmatrix}\end{aligned} \quad (5.39)$$

For the Coulomb interaction, this specializes to:

$$\begin{aligned}\left\langle ab(SL)\left|\left\{(\mathbf{a}^\dagger\mathbf{c})^{(0k)}(\mathbf{b}^\dagger\mathbf{d})^{(0k)}\right\}^{(00)}\right|cd(SL)\right\rangle &= \left((1+\delta_{ab})(1+\delta_{cd})\right)^{\frac{1}{2}}\\ \times\tfrac{1}{2}\cdot[k]^{\frac{1}{2}}\cdot(-1)^{l_b+l_c+k+L}&\cdot\begin{Bmatrix}l_a&l_c&k\\ l_d&l_b&L\end{Bmatrix}\end{aligned} \quad (5.40)$$

The above may straightforwardly be used to find matrix elements of two-particle operators in more general configurations, e.g.:

$$\begin{aligned}&\left\langle l^N(S_1L_1\nu_1)l'(SL)\parallel\left\{(\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)}(\mathbf{b}^\dagger\mathbf{b})^{(\kappa' k')}\right\}^{(tt)}\parallel l^N(S_1'L_1'\nu_1')l'(S'L')\right\rangle =\\ &N\cdot[t]\cdot[S,L,S',L']^{\frac{1}{2}}\cdot[S_1,S_1',L_1,L_1']^{\frac{1}{2}}\cdot[\kappa,k,\kappa',k']^{\frac{1}{2}}\cdot\begin{Bmatrix}S_1&S_1'&\kappa\\ \frac{1}{2}&\frac{1}{2}&\kappa'\\ S&S'&t\end{Bmatrix}\begin{Bmatrix}L_1&L_1'&k\\ l'&l'&k'\\ L&L'&t\end{Bmatrix}\\ &\cdot\sum_{\overline{S}\,\overline{L}}(-1)^{\overline{S}+\frac{1}{2}+S_1+\kappa}\begin{Bmatrix}S_1&\kappa&S_1'\\ \frac{1}{2}&\overline{S}&\frac{1}{2}\end{Bmatrix}(-1)^{\overline{L}+l+L_1+k}\begin{Bmatrix}L_1&k&L_1'\\ l&\overline{L}&l\end{Bmatrix}\\ &\cdot\left(l^N S_1L_1\nu_1\{|l^{N-1}\overline{S}\,\overline{L}\overline{\nu}\right)\left(l^{N-1}\overline{S}\,\overline{L}\overline{\nu}|\}l^N S_1'L_1'\nu_1'\right)\end{aligned} \quad (5.41)$$

Three-particle operators in normal form are calculated from equation (5.21), e.g.:

$$\begin{aligned}&\left\langle l^2(SL)l'(S_3L_3)\parallel[\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}\mathbf{b}^\dagger\right\}^{(S_3L_3)}\left\{(\mathbf{aa})^{(S'L')}\mathbf{b}\right\}^{(S_3'L_3')}]^{(\kappa k)}\parallel l^2(S'L')l'(S_3'L_3')\right\rangle\\ &=[\kappa,k]^{\frac{1}{2}}\cdot[S_3,L_3,S_3',L_3']^{-\frac{1}{2}}\cdot\left\langle l^2(SL)l'(S_3L_3)\parallel\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}\mathbf{b}^\dagger\right\}^{(S_3L_3)}\parallel(00)\right\rangle\\ &\quad\cdot\left\langle(00)\parallel\left\{(\mathbf{aa})^{(S'L')}\mathbf{b}\right\}^{(S_3'L_3')}\parallel l^2(S'L')l'(S_3'L_3')\right\rangle\\ &=2\cdot[\kappa,k]^{\frac{1}{2}}\end{aligned} \quad (5.42)$$

the above last line follows directly from application of equations (5.22) and (5.23):

$$\left\langle l^2(SL)l'(S_3L_3)\parallel\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}\mathbf{b}^\dagger\right\}^{(S_3L_3)}\parallel(00)\right\rangle = -\sqrt{2}\cdot[S_3,L_3]^{\frac{1}{2}} \quad (5.43a)$$

$$\left\langle(00)\parallel\left\{(\mathbf{aa})^{(S'L')}\mathbf{b}\right\}^{(S_3'L_3')}\parallel l^2(S'L')l'(S_3'L_3')\right\rangle = -\sqrt{2}\cdot[S_3',L_3']^{\frac{1}{2}} \quad (5.43b)$$

Equation (5.18) is a special case for $(\kappa k)=(00)$ after application of equation (3.44). The reversed order case $(\mathbf{a}^\dagger\mathbf{b}^\dagger\mathbf{b}^\dagger)(\mathbf{abb})$ manifestly yields the identical result:

$$\left\langle l\,l'^2(SL)S_3L_3\parallel[\left\{\mathbf{a}^\dagger(\mathbf{b}^\dagger\mathbf{b}^\dagger)^{(SL)}\right\}^{(S_3L_3)}\left\{\mathbf{a}(\mathbf{bb})^{(S'L')}\right\}^{(S_3'L_3')}]^{(\kappa k)}\parallel l\,l'^2(S'L')S_3'L_3'\right\rangle = 2\cdot[\kappa,k]^{\frac{1}{2}} \quad (5.44)$$

5.3 Operators put in second quantized form

[Feneuille, 1967] defined a unit one-particle double tensor operator as:

$$\left\langle sl \parallel w^{(\kappa k)}(l_a, l_b) \parallel sl' \right\rangle = \delta(l, l_a) \cdot \delta(l', l_b) \cdot [\kappa, k]^{\frac{1}{2}} \tag{5.45}$$

differing from equation (5.20) only by a minus sign. A general one-particle operator may now be factorized in terms of a radial part R and this angular double tensor:

$$F^{(\kappa k)t} = \sum_i R_i \cdot w_i^{(\kappa k)t} \tag{5.46}$$

Operators acting on spin only now become:

$$T_i^{(\kappa)} = [l_i]^{\frac{1}{2}} \, [\kappa]^{-\frac{1}{2}} \left\langle s_i \parallel T^{(\kappa)} \parallel s_i' \right\rangle w_i^{(\kappa 0)\kappa} \tag{5.47a}$$

Whereas operators acting only on orbital angular momenta:

$$A_i^{(k)} = [s_i]^{\frac{1}{2}} \, [k]^{-\frac{1}{2}} \left\langle l_i \parallel A^{(k)} \parallel l_i' \right\rangle w_i^{(0k)k} \tag{5.47b}$$

Note that the reduction of a double tensor with one zero rank differs from the reduction of the corresponding single tensor by the first factors $[l_i]^{\frac{1}{2}}$ and $[s_i]^{\frac{1}{2}}$ in the above equations.
[Racah, 1942b] defined the tensor $u_i^{(k)}$ by:

$$\left\langle l_i \parallel u^{(k)} \parallel l_i' \right\rangle = \delta(l_i, l_i') \rightarrow u_i^{(k)} = [s_i]^{\frac{1}{2}} \, [k]^{-\frac{1}{2}} \, w_i^{(0k)k} \tag{5.48}$$

Spin- and orbital operators can be combined using straightforward angular momentum algebra, e.g. the coupled product of a pure 'spin' and a pure 'orbital' operator yields:

$$\left(T_i^{(\kappa)} A_i^{(k)}\right)^{(t)} = [\kappa, k]^{-\frac{1}{2}} \cdot \left\langle s_i \parallel T^{(\kappa)} \parallel s_{i'} \right\rangle \left\langle l_i \parallel A^{(k)} \parallel l_{i'} \right\rangle w_i^{(\kappa k)t} \tag{5.49}$$

To be compared with:

$$\left(w_i^{(\kappa 0)} w_i^{(0k)}\right)^{(\kappa k)t} = [s_i, l_i]^{-\frac{1}{2}} \cdot w_i^{(\kappa k)t} \tag{5.50}$$

Furthermore:

$$\left(w_i^{(\kappa_1 k_1)} w_j^{(\kappa_2 k_2)}\right)^{(kk)0} = \sum_t (-1)^{k_1+\kappa_2+k} \cdot [k]^{\frac{1}{2}} \cdot \begin{Bmatrix} \kappa_1 & k_1 & t \\ k_2 & \kappa_2 & k \end{Bmatrix} \; w_i^{(\kappa_1 k_1)t} \cdot w_j^{(\kappa_2 k_2)t} \tag{5.51a}$$

with the reverse relation:

$$w_i^{(\kappa_1 k_1)t} \cdot w_j^{(\kappa_2 k_2)t} = \sum_k (-1)^{k_1+\kappa_2+k} \cdot [t] \cdot [k]^{\frac{1}{2}} \cdot \begin{Bmatrix} \kappa_1 & k_1 & t \\ k_2 & \kappa_2 & k \end{Bmatrix} \; \left(w_i^{(\kappa_1 k_1)} w_j^{(\kappa_2 k_2)}\right)^{(kk)0} \tag{5.51b}$$

Keeping in mind the Hermiticity requirement that $\kappa + k + t$ is even, the following basic equality now holds [Judd, 1967]:

$$\sum_i w_i^{(\kappa k)t}(l_a, l_b) = W^{(\kappa k)t} = -\left(\mathbf{a}^\dagger \mathbf{b}\right)^{(\kappa k)t} \tag{5.52}$$

Therefore:

$$F^{(\kappa k)t} = -[\kappa,k]^{-\frac{1}{2}} \left\langle a \parallel F^{(\kappa k)} \parallel b \right\rangle \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(\kappa k)t} \tag{5.53}$$

$$\sum_i T_i^{(k)} \cdot A_i^{(k)} = (-1)^{k+1}[k]^{-\frac{1}{2}} \cdot \left\langle s \parallel T^{(\kappa)} \parallel s' \right\rangle \left\langle l \parallel A^{(k)} \parallel l' \right\rangle \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(kk)0} \tag{5.54}$$

Equation (5.48) thus results in:

$$U^{(k)} = \sum_i u_i^{(k)} = -[s]^{\frac{1}{2}}[k]^{-\frac{1}{2}} \cdot \delta(l,l') \cdot \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(0k)k} \tag{5.55}$$

The reduced matrix elements $\langle l^N SL \parallel U^{(k)} \parallel l^N S'L' \rangle$ are tabulated by [Nielson and Koster, 1963]. Combining the above with equation (5.31) e.g. directly yields:

$$\left\langle l^N SL \parallel U^{(2)} \parallel l^N S'L' \right\rangle = N \cdot \delta(S,S') \cdot [S,L,L']^{\frac{1}{2}} \cdot \sum_{\overline{S}\,\overline{L}} (-1)^{L+l+\overline{L}} \cdot \begin{Bmatrix} l & l & 2 \\ L' & L & l \end{Bmatrix} \cdot \left(l^N SL\{|\, l^{N-1}\, \overline{S}\, \overline{L}\right) \left(l^N S'L'\{|\, l^{N-1}\, \overline{S}\, \overline{L}\right) \tag{5.56}$$

Earlier, [Sandars and Beck, 1965] introduced $U_i^{(\kappa k)t}$ for similar purposes:

$$\sum_i U_i^{(\kappa k)t} = \sum_i [\kappa,k]^{-\frac{1}{2}} \cdot w_i^{(\kappa k)t} = -[\kappa,k]^{-\frac{1}{2}} \cdot \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(\kappa k)t} \tag{5.57}$$

From equation (5.47b), with the single → double tensor reduction implied, one obtains:

$$C_i^{(k)} = [s_i]^{\frac{1}{2}}\, [k]^{-\frac{1}{2}} \cdot \left\langle l_i \parallel C^{(k)} \parallel l_i' \right\rangle \cdot w_i^{(0k)k}$$

Therefore:

$$\sum_i C_i^{(k)} = -[s]^{\frac{1}{2}}\, [k]^{-\frac{1}{2}} \cdot \left\langle l \parallel C^{(k)} \parallel l' \right\rangle \cdot (\mathbf{a}^\dagger \mathbf{b})^{(0k)k} \tag{5.58}$$

$$\sum_i C_i^{(2)} = -\sqrt{2/5} \cdot \left\langle l \parallel C^{(2)} \parallel l' \right\rangle \cdot (\mathbf{a}^\dagger \mathbf{b})^{(02)2} = f^{02} \cdot (\mathbf{a}^\dagger \mathbf{b})^{(02)2} \tag{5.59}$$

Direct comparison learns:

$$\delta(l,l') \cdot \sum_i C_i^{(k)} = \left\langle l \parallel C^{(k)} \parallel l \right\rangle \cdot U^{(k)} \tag{5.60}$$

Some other physically interesting examples are:

$$\sum_i \left(sC^{(k)}\right)_i^{(t)} = -[k,\tfrac{1}{2}]^{-\frac{1}{2}} \cdot \left\langle l \parallel C^{(k)} \parallel l' \right\rangle \cdot (\mathbf{a}^\dagger \mathbf{b})^{(1k)t} \text{ with: } 1+k+t \text{ even.} \tag{5.61}$$

$$\sum_i \left(C^{(k)} l\right)_i^{(t)} = (-1)^{l+t+l'+1}\, [2l'(l'+1)(2l'+1)]^{\frac{1}{2}} \cdot \begin{Bmatrix} l & l' & t \\ 1 & k & l' \end{Bmatrix} \cdot \left\langle l \parallel C^{(k)} \parallel l' \right\rangle \cdot (\mathbf{a}^\dagger \mathbf{b})^{(0t)t} \tag{5.62}$$

where equation (3.47) is used in the above. For $t = k$, from comparison with equation (5.58) and using equation (C.11), one finds:

$$\sum_i \left(C^{(k)}l\right)_i^{(k)} = \frac{l(l+1) - k(k+1) - l'(l'+1)}{2\sqrt{k(k+1)}} \cdot \sum_i C_i^{(k)} \tag{5.63}$$

A related useful reduction formula may be derived from equations (5.62) and (3.69):

$$\left(C^{(k+1)}l\right)_i^{(k)} = \left[\frac{k(2k-1)}{(k+1)(2k+3)}\right]^{\frac{1}{2}} \cdot \left(C^{(k-1)}l\right)_i^{(k)} \tag{5.64}$$

from which e.g.: $\sum_i l_i^{(1)} = (10)^{\frac{1}{2}} \sum_i (C^{(2)}l)_i^{(1)}$, which may also be verified from equations (3.67), (5.62) and (C.13). This unveils a resemblance with the spin-dipole term: $-(10)^{\frac{1}{2}} \sum_i (sC^{(2)})_i^{(1)} = -(10)^{\frac{1}{2}} \sum_i (C^{(2)}s)_i^{(1)}$.

Also, by equation (3.61):

$$\left(C^{(k)}C^{(k')}\right)_i^{(K)} = (-1)^K \cdot [K]^{\frac{1}{2}} \cdot \begin{pmatrix} k & k' & K \\ 0 & 0 & 0 \end{pmatrix} C_i^{(K)} \tag{5.65}$$

Further examples are given below; they are notably relevant to the hyperfine dipole operator: $\sum_i T_i^{(1)} = \sum_i a_i^{01} \cdot l_i^{(1)} - a_i^{12} \cdot (10)^{\frac{1}{2}} (sC^{(2)})_i^{(1)} + a_i^{10} \cdot s_i^{(1)}$ as well as to the atomic dipole moment:
$M_i^{(1)} = l_i^{(1)} + g_s \cdot s_i^{(1)} - 2\,(10)^{\frac{1}{2}}\, a^{12}\, (sC^{(2)})_i^{(1)}$ where $a^{12} \to 0$ in the Pauli limit.
To include relativity and correlation effects, however, it is essential to consider these operators separately:

$$\sum_i l_i^{(1)} = -\delta(l,l') \cdot \left[\frac{2l(l+1)(2l+1)}{3}\right]^{\frac{1}{2}} \cdot (\mathbf{a}^\dagger \mathbf{b})^{(01)1} = f^{01} \cdot (\mathbf{a}^\dagger \mathbf{b})^{(01)1} \tag{5.66a}$$

$$-(10)^{\frac{1}{2}} \sum_i \left(sC^{(2)}\right)_i^{(1)} = \left\langle l \parallel C^{(2)} \parallel l' \right\rangle \quad \cdot \quad (\mathbf{a}^\dagger \mathbf{b})^{(12)1} = f^{12} \cdot (\mathbf{a}^\dagger \mathbf{b})^{(12)1} \tag{5.66b}$$

$$\sum_i s_i^{(1)} = -\delta(l,l') \cdot \left[\frac{2l+1}{2}\right]^{\frac{1}{2}} \cdot (\mathbf{a}^\dagger \mathbf{b})^{(10)1} = f^{10} \cdot (\mathbf{a}^\dagger \mathbf{b})^{(10)1} \tag{5.66c}$$

In terms of second quantization, the complete expression for the hyperfine interaction thus becomes:

$$\left\langle \gamma(SL)JF | H_{\text{hfs}}^D | \gamma'(S'L')J'F \right\rangle = \sqrt{I(I+1)(2I+1)} \cdot (-1)^{J'+I+F} \cdot \begin{Bmatrix} J' & I & F \\ I & J & 1 \end{Bmatrix}$$
$$\cdot \sum_{\kappa k, nl} [J, J', 1]^{\frac{1}{2}} \cdot \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & 1 \end{Bmatrix} \cdot a_{nl}^{\kappa k} \cdot f^{\kappa k} \cdot \left\langle \gamma(SL) \parallel \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(\kappa k)} \parallel \gamma'(S'L') \right\rangle \tag{5.67a}$$

$$\left\langle \gamma(SL)JF|H^Q_{\rm hfs}|\gamma'(S'L')J'F\right\rangle = -\tfrac{1}{2}\left[\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)}\right]^{\frac{1}{2}}\cdot(-1)^{J'+I+F}\cdot\begin{Bmatrix} J' & I & F\\ I & J & 2\end{Bmatrix}$$

$$\cdot\sum_{\kappa k,nl}[J,J',2]^{\frac{1}{2}}\cdot\begin{Bmatrix} S & S' & \kappa\\ L & L' & k\\ J & J' & 2\end{Bmatrix}\cdot b^{\kappa k}_{nl}\cdot f^{\kappa k}\cdot\left\langle\gamma(SL)\parallel\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)}\parallel\gamma'(S'L')\right\rangle \qquad (5.67b)$$

Here, $a^{\kappa k}_{nl}$ and $b^{\kappa k}_{nl}$ are the hfs interaction parameters given in equations (3.87) and (3.102), $f^{\kappa k}$ the RHS prefactors of equations (5.66) and (5.59) (assuming $f^{11}=1/\sqrt{30}$ and $f^{13}=1/\sqrt{70}$) and the reduced matrix elements are calculated straightforwardly using the formulae of section 5.2.

In conclusion, with the definition:

$$S(a,b) \;=\; \int_0^\infty a(r)R(r)b(r)\,{\rm d}r = [\kappa,k]^{-\frac{1}{2}}\left\langle a\parallel F^{(\kappa k)}\parallel b\right\rangle \qquad (5.68)$$

one arrives at the general expression of a one-particle operator in terms of second quantization:

$$F^{(\kappa k)t} = -S(a,b)\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)t} \qquad (5.69)$$

Next, a corresponding procedure may be followed for two-particle operators. Similar to the use of equation (5.46) for one-particle operators, two-particle operators are expressed in terms of unit double tensors as follows:

$$G^{(\kappa k)t} = \sum_{i\neq j}R_{ij}\cdot\left(w_i^{(\kappa_1 k_1)}w_j^{(\kappa_2 k_2)}\right)^{(\kappa k)t} \qquad (5.70)$$

Equation (5.70) also serves to identify the remaining radial factor R_{ij} for each particular operator in question.
The two-particle analog of equation (5.53) becomes in normal form:

$$\begin{aligned} G^{(\kappa k)t} = \;& -\;\left((1+\delta_{ab})(1+\delta_{cd})\right)^{-\frac{1}{2}}[\kappa,k]^{-\frac{1}{2}}\sum_{SL,S'L'}\left\langle ab(SL)\parallel G^{(\kappa k)}\parallel cd(S'L')\right\rangle\\ & \times\;\left\{\left(\mathbf{a}^\dagger\mathbf{b}^\dagger\right)^{SL}(\mathbf{cd})^{S'L'}\right\}^{(\kappa k)t} \end{aligned} \qquad (5.71)$$

In accordance with equation (5.70), however, two-particle operators in their initial form usually appear as coupled products of one-particle operators. Direct use of equation (5.52) may formally contain both one- and two-particle operators if the summation is taken over (i,j) instead of $(i\neq j)$: the residue term of equation (5.11) refers to the case $i=j$. An example for equivalent electrons:

$$\begin{aligned} &\sum_{i,j}\left(w_i^{(\kappa_1 k_1)}w_j^{(\kappa_2 k_2)}\right)^{(\kappa k)} = \left\{(\mathbf{a}^\dagger\mathbf{a})^{(\kappa_1 k_1)}(\mathbf{a}^\dagger\mathbf{a})^{(\kappa_2 k_2)}\right\}^{(\kappa k)}\\ &= (-1)^{\kappa+k}[\kappa_1,k_1,\kappa_2,k_2]^{\frac{1}{2}}\begin{Bmatrix}\kappa_1 & \kappa_2 & \kappa\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} k_1 & k_2 & k\\ l & l & l\end{Bmatrix}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)}\\ &-\sum_{SL,S'L'}[S,L,S',L']^{\frac{1}{2}}\cdot[\kappa_1,k_1,\kappa_2,k_2]^{\frac{1}{2}}\begin{Bmatrix}\kappa_1 & \kappa_1 & \kappa\\ \frac{1}{2} & \frac{1}{2} & S\\ \frac{1}{2} & \frac{1}{2} & S'\end{Bmatrix}\begin{Bmatrix} k_1 & k_1 & k\\ l & l & L\\ l & l & L'\end{Bmatrix}\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}(\mathbf{aa})^{S'L'}\right\}^{(\kappa k)} \end{aligned} \qquad (5.72)$$

Here, the first RHS term refers to $i = j$ and the second to $i \neq j$. As the summation over i and j is implicit in second quantization in the coupled form, the electrons **b** and **c** have to be treated as inequivalent in two-particle operators of the form $\left\{(\mathbf{a}^\dagger\mathbf{c})^{(\kappa_1 k_1)}\,(\mathbf{b}^\dagger\mathbf{d})^{(\kappa_2 k_2)}\right\}^{(\kappa k)}$, even if they are not. This is a minor downside of the use of second quantization in the initial form. Keeping this in mind, however, use of the initial form is the most direct way to find the second quantization expression of physical operators. The Hermitian conjugate becomes: $\left\{(\mathbf{d}^\dagger\mathbf{b})^{(\kappa_2 k_2)}\,(\mathbf{c}^\dagger\mathbf{a})^{(\kappa_1 k_1)}\right\}^{(\kappa k)} = (-1)^{\kappa_1+\kappa_2-\kappa}\cdot(-1)^{k_1+k_2-k}\cdot\left\{(\mathbf{c}^\dagger\mathbf{a})^{(\kappa_1 k_1)}\,(\mathbf{d}^\dagger\mathbf{b})^{(\kappa_2 k_2)}\right\}^{(\kappa k)}$.
With the definition:

$$S(ab,cd) \;=\; \int_0^\infty\int_0^\infty \mathrm{d}r_1\mathrm{d}r_2\; a(1)b(2)R_{12}(r)c(1)d(2) \tag{5.73}$$

and, allowing for $R_{ij} \neq R_{ji}$, one arrives at:

$$\begin{aligned} G^{(\kappa k)t} \;&=\; D\,S(ab,cd)\,\left\{\left(\mathbf{a}^\dagger\mathbf{c}\right)^{\kappa_1 k_1}\left(\mathbf{b}^\dagger\mathbf{d}\right)^{\kappa_2 k_2}\right\}^{(\kappa k)t} \\ &+\; E\,S(ab,dc)\,\left\{\left(\mathbf{a}^\dagger\mathbf{d}\right)^{\kappa_1 k_1}\left(\mathbf{b}^\dagger\mathbf{c}\right)^{\kappa_2 k_2}\right\}^{(\kappa k)t} \\ &+\; (-1)^P D\,S(ba,dc)\,\left\{\left(\mathbf{a}^\dagger\mathbf{c}\right)^{\kappa_2 k_2}\left(\mathbf{b}^\dagger\mathbf{d}\right)^{\kappa_1 k_1}\right\}^{(\kappa k)t} \\ &+\; (-1)^P E\,S(ba,cd)\,\left\{\left(\mathbf{a}^\dagger\mathbf{d}\right)^{\kappa_2 k_2}\left(\mathbf{b}^\dagger\mathbf{c}\right)^{\kappa_1 k_1}\right\}^{(\kappa k)t} \end{aligned} \tag{5.74}$$

$D = (1 - \frac{1}{2}\delta_{ab}\delta_{cd})$ provides the correct weighting factor and $E = (1-\delta_{ab})(1-\delta_{cd})$ excludes exchange terms when bra or ket contain equivalent electrons.
$P = \kappa_1 + k_1 + \kappa_2 + k_2 - (\kappa + k)$ is the permutation phase.
It may be interesting to note that as a result, Hermitian operators with odd P (as occur in the below mutual spin-orbit interactions V_1 and V_3) do not have direct matrix elements within a configuration.
Effects of a closed shell c can immediately be deduced from equations (5.13), that reduce the expressions of equation (5.74) to the general one-particle form $(\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)t}$ from (equation (5.69)). Analogously, virtual shells v are removed by equation (5.14) with a similar result.
If $R_{ij} = R_{ji}$, as is the case with the Coulomb interaction C, the last two terms coincide with the first two. More explicitly:

$$\begin{aligned} C \;&=\; \tfrac{1}{2}\sum_{i\neq j} r_{ij}^{-1} = \sum_{i<j} r_{ij}^{-1} = \sum_{i<j,k}\frac{r_<^k}{r_>^{k+1}}\cdot\left(C_i^{(k)}\cdot C_j^{(k)}\right) \\ &=\; \sum_{i\neq j,k}(-1)^k\,[k]^{-\frac{1}{2}}\,\frac{r_<^k}{r_>^{k+1}}\cdot\left\langle l_i \parallel C^{(k)} \parallel l_i'\right\rangle\left\langle l_j \parallel C^{(k)} \parallel l_j'\right\rangle\cdot\left(w_i^{(0k)}w_j^{(0k)}\right)^{(00)0} \end{aligned} \tag{5.75}$$

Next, identifying R_{ij} from comparison with equation (5.70):

$R_{ij} = \sum_k (-1)^k\,[k]^{-\frac{1}{2}}\cdot\frac{r_<^k}{r_>^{k+1}}\cdot\left\langle l_i \parallel C^{(k)} \parallel l_i'\right\rangle\left\langle l_j \parallel C^{(k)} \parallel l_j'\right\rangle = R_{ji}$ and therefore:

$$\begin{aligned} S(ab,cd) \;&=\; \sum_k (-1)^k\,[k]^{-\frac{1}{2}}\cdot\left\langle l_a \parallel C^{(k)} \parallel l_c\right\rangle\left\langle l_b \parallel C^{(k)} \parallel l_d\right\rangle\cdot R^k(ab,cd) \\ &=\; \sum_k [k]^{-\frac{1}{2}}\cdot X^k(ab,cd) \end{aligned} \tag{5.76}$$

Application of equation (5.74) directly gives:

$$\begin{aligned} C = \;& 2 \sum_k (-1)^k [k]^{-\frac{1}{2}} \cdot D\, R^k(ab,cd) \left\langle l_a \parallel C^{(k)} \parallel l_c \right\rangle \left\langle l_b \parallel C^{(k)} \parallel l_d \right\rangle \left\{ \left(\mathbf{a}^\dagger \mathbf{c}\right)^{0k} \left(\mathbf{b}^\dagger \mathbf{d}\right)^{0k} \right\}^{(00)0} \\ + \;& 2 \sum_{k'} (-1)^{k'} [k']^{-\frac{1}{2}} \cdot E\, R^{k'}(ab,dc) \left\langle l_a \parallel C^{(k')} \parallel l_d \right\rangle \left\langle l_b \parallel C^{(k')} \parallel l_c \right\rangle \left\{ \left(\mathbf{a}^\dagger \mathbf{d}\right)^{0k'} \left(\mathbf{b}^\dagger \mathbf{c}\right)^{0k'} \right\}^{(00)0} \end{aligned} \tag{5.77}$$

As an example for $a = b$ and $c = d$:

$$C = \sum_k (-1)^k [k]^{-\frac{1}{2}} \cdot R^k(aa,bb) \left\langle l_a \parallel C^{(k)} \parallel l_b \right\rangle^2 \left\{ \left(\mathbf{a}^\dagger \mathbf{b}\right)^{0k} \left(\mathbf{a}^\dagger \mathbf{b}\right)^{0k} \right\}^{(00)0} \tag{5.78}$$

For the exchange, a reordering of the ket state is required to apply equation (5.38) or (5.40). For two electrons, $cd\,(SL) \rightarrow dc\,(SL)$ yields an additional phase of $(-1)^1 \cdot (-1)^{\frac{1}{2}+\frac{1}{2}-S} \cdot (-1)^{l_c+l_d-L}$, with the Pauli permutation phase as the first factor. Application of (5.40) in equation (5.77) now automatically yields equation (6.10).

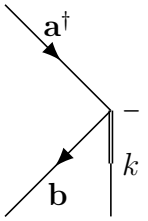
In summary, the conversion of physical operators (like Breit-Pauli Hamiltonian terms) to second quantization generally takes place in a four-step process:

1. The interaction is first written in its original form.
2. Racah algebra is then used to put this into tensor operator form.
3. Equations (5.46) and (5.70) are used to translate to $w_i^{(\kappa_1 k_1)t}$ and/or $w_j^{(\kappa_2 k_2)t}$.
4. Equations (5.69) and (5.74) are used to find the final expression.

5.4 Graphical second quantization

The general one-particle expression (5.69): $F^{(\kappa k)t} = -S(a,b)\left(\mathbf{a}^\dagger \mathbf{b}\right)^{(\kappa k)t}$
may graphically be expressed as:

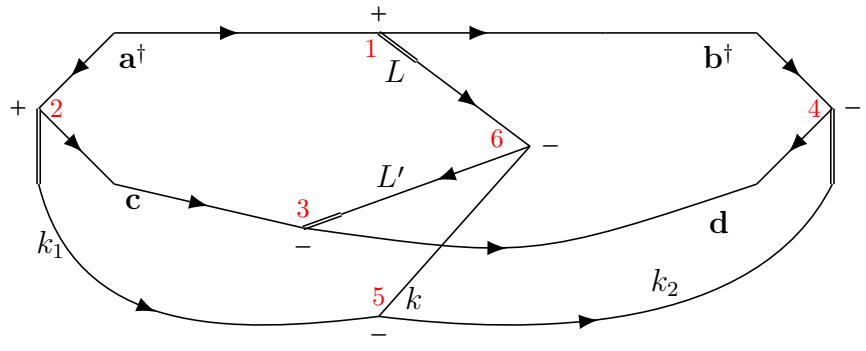
$F^{(\kappa k)t} = -S(a,b) \times$



(5.79)

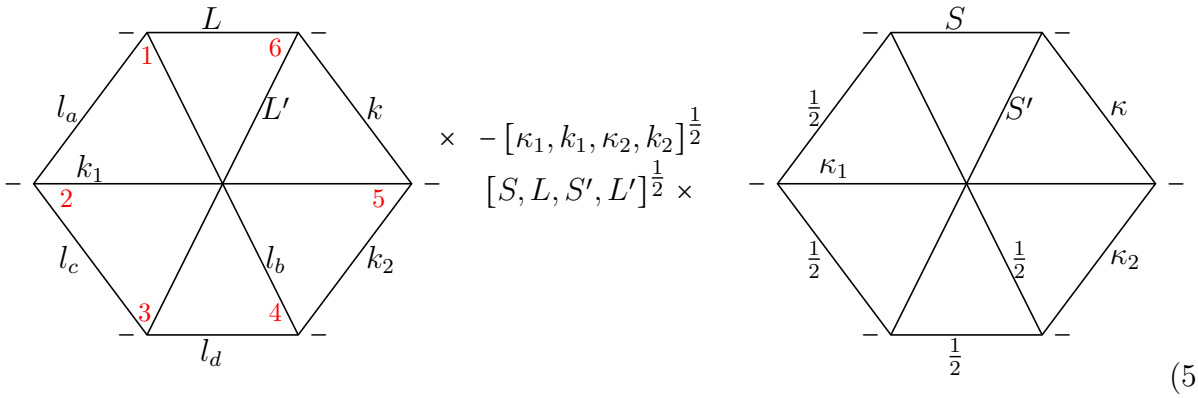
With graphical second quantization, operators are coupled towards expressions (5.36) or (5.38) to find the (reduced) matrix element. The conversion of reduced matrix elements of operators in initial form (5.39) to normal form (5.36) is graphically

shown as follows:



(5.80)

The Hamiltonian line placing all nodes or vertices on the periphery is indicated by consecutive red numbers. The interchange of $\mathbf{b}^\dagger$ and $\mathbf{c}$ (treated as inequivalent!) yields an additional minus sign.



(5.81)

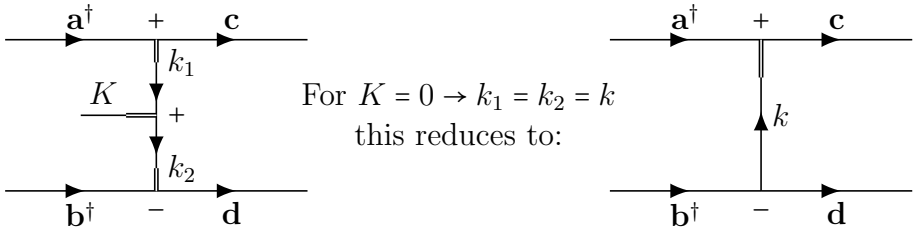
it follows:

$$\left\langle ab(SL) \parallel \left\{(\mathbf{a}^\dagger\mathbf{c})^{(\kappa_1 k_1)}(\mathbf{b}^\dagger\mathbf{d})^{(\kappa_2 k_2)}\right\}^{(\kappa k)} \parallel cd(S'L')\right\rangle = -\left[\kappa_1, k_1, \kappa_2, k_2\right]^{\frac{1}{2}}$$

$$\cdot\left[S, L, S', L'\right]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa_1 \\ \frac{1}{2} & \frac{1}{2} & \kappa_2 \\ S & S' & \kappa \end{Bmatrix} \begin{Bmatrix} l_a & l_c & k_1 \\ l_b & l_d & k_2 \\ L & L' & k \end{Bmatrix} \left\langle ab(SL) \parallel \{(\mathbf{a}^\dagger\mathbf{b}^\dagger)^{(SL)}(\mathbf{cd})^{(S'L')}\}^{(\kappa k)} \parallel cd(S'L')\right\rangle$$

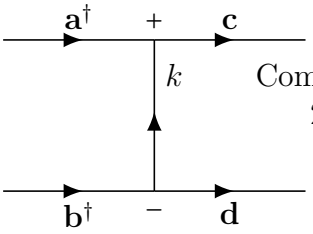
$$= \left((1+\delta_{ab})(1+\delta_{cd})\right)^{\frac{1}{2}} \left[\kappa_1, k_1, \kappa_2, k_2, \kappa, k\right]^{\frac{1}{2}} \cdot \left[S, L, S', L'\right]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa_1 \\ \frac{1}{2} & \frac{1}{2} & \kappa_2 \\ S & S' & \kappa \end{Bmatrix} \begin{Bmatrix} l_a & l_c & k_1 \\ l_b & l_d & k_2 \\ L & L' & k \end{Bmatrix} \tag{5.82}$$

in complete accordance with equation (5.39).
The representation of a two-particle operator in initial form by its graphical coupling scheme is therefore:



(5.83)

As a result, the graphical representation of the direct term of the Coulomb interaction is given below:

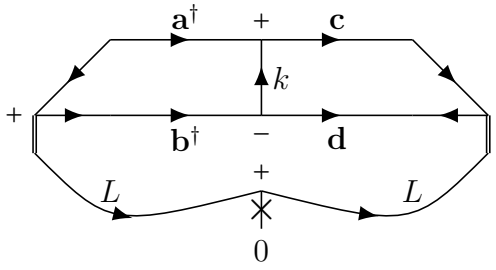


Comparison with equation (5.77) yields the multiplication factor:

$$2\sum_k(-1)^k \cdot D \cdot \langle l_a \parallel C^{(k)} \parallel l_c\rangle \langle l_b \parallel C^{(k)} \parallel l_d\rangle R^k(ab,cd).$$
$$= 2D \cdot \sum_k X^k(ab,cd) \qquad \text{with } D = (1 - \tfrac{1}{2}\delta_{ab}\delta_{cd})$$

(5.84)

To find the two-electron matrix element in this way, the operator is recoupled to equation (5.38), again with an extra minus sign for the interchange of $\mathbf{b}^\dagger$ and $\mathbf{c}$:



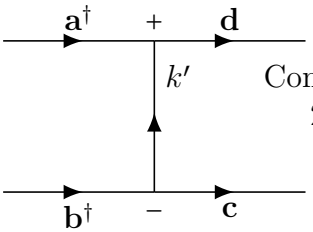
$$= -\tfrac{1}{2} \cdot (-1)^{l_c+l_d+L} \cdot [S,L]^{\frac{1}{2}} \cdot \begin{Bmatrix} L & l_c & l_d \\ k & l_b & l_a \end{Bmatrix}$$

(5.85)

The final result becomes:

$$2D \cdot \sum_k X^k(ab,cd) \cdot -\tfrac{1}{2} \cdot (-1)^{l_c+l_d+L} \cdot [S,L]^{\frac{1}{2}} \cdot \begin{Bmatrix} L & l_c & l_d \\ k & l_b & l_a \end{Bmatrix} \cdot -((1+\delta_{ab})(1+\delta_{cd}))^{\frac{1}{2}} \cdot [S,L]^{-\frac{1}{2}}$$
$$= W \cdot (-1)^{l_c+l_d+L} \cdot \sum_k \begin{Bmatrix} L & l_c & l_d \\ k & l_b & l_a \end{Bmatrix} \cdot X^k(ab,cd) : \text{ exactly the direct term of equation (6.10).}$$

Likewise, the exchange becomes:

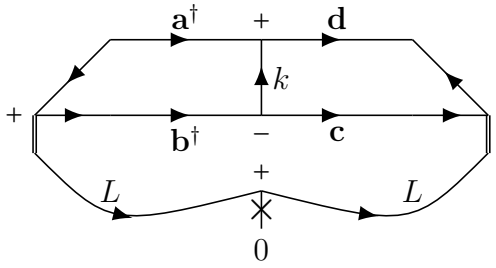


Comparison with equation (5.77) yields the multiplication factor:

$$2 \cdot \sum_{k'}(-1)^{k'} \cdot E \cdot \left\langle l_a \parallel C^{(k')} \parallel l_d\right\rangle \left\langle l_b \parallel C^{(k')} \parallel l_c\right\rangle R^{k'}(ab,dc).$$
$$= 2E \cdot \sum_{k'} X^{k'}(ab,dc) \qquad \text{with } E = (1-\delta_{ab})(1-\delta_{cd})$$

(5.86)

To find the exchange two-electron matrix element, the operator is again recoupled to equation (5.38), with minus signs for the interchange of $\mathbf{b}^\dagger \leftrightarrow \mathbf{d}$ and $c \leftrightarrow d$:



$$= \tfrac{1}{2} \cdot (-1)^{1+S} \cdot [S,L]^{\frac{1}{2}} \cdot \begin{Bmatrix} k' & l_b & l_c \\ L & l_d & l_a \end{Bmatrix}$$

(5.87)

The final result becomes:

$$2E \cdot \sum_{k'} \cdot X^{k'}(ab,dc) \cdot \tfrac{1}{2} \cdot (-1)^{1+S} \cdot [S,L]^{\frac{1}{2}} \cdot \begin{Bmatrix} k' & l_b & l_c \\ L & l_d & l_a \end{Bmatrix} \cdot -\left((1+\delta_{ab})(1+\delta_{cd})\right)^{\frac{1}{2}} \cdot [S,L]^{-\frac{1}{2}}$$

$$= W \cdot (-1)^S \cdot \sum_{k'} \begin{Bmatrix} k' & l_b & l_c \\ L & l_d & l_a \end{Bmatrix} \cdot X^{k'}(ab,dc) : \text{exactly the exchange term of equation (6.10).}$$

5.5 Application to the spin-orbit interaction

The dot product of single-electron operators $\mathbf{A^k}$ (spin type) and $\mathbf{B^k}$ (orbit type) transposes to:

$$\mathbf{A^k} \cdot \mathbf{B^k} = (-1)^{k+1} [k]^{-\frac{1}{2}} \left\langle s \parallel \mathbf{A^k} \parallel s' \right\rangle \left\langle l \parallel \mathbf{B^k} \parallel l' \right\rangle (\mathbf{a^\dagger b})^{(kk)0} \tag{5.88}$$

and thereby the spin-orbit operator becomes:

$$\sum_i \mathbf{s_i} \cdot \mathbf{l_i}\, \zeta(a,b) = \delta(l,l')\ (l(l+1)(2l+1)/2)^{\frac{1}{2}}\ (\mathbf{a^\dagger b})^{(11)0}\, \zeta(a,b) \tag{5.89}$$

The corresponding reduced matrix element becomes thereby:

$$\langle nl \parallel \zeta(a,b) \parallel n'l' \rangle = -3 \cdot \delta(l,l')\ (l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot \boldsymbol{\zeta}(\mathbf{a},\mathbf{b}) \tag{5.90}$$

Analytic formulae for inner products used the theory of the spin-orbit interaction. For l^2:

$$\left[\left\{ (\mathbf{a^\dagger a})^{K_1 k_1} (\mathbf{a^\dagger a})^{K_2 k_2} \right\}^{(11)0} : z(l) \right]$$

$$= (l(l+1)(2l+1)/2)^{\frac{1}{2}} [K_1,k_1,K_2,k_2]^{\frac{1}{2}} \begin{Bmatrix} K_1 & K_2 & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} k_1 & k_2 & 1 \\ l & l & l \end{Bmatrix}$$

$$\times \left((4l+2)\, \delta(K_1,0)\delta(k_1,0) + (4l+2)\delta(K_2,0)\delta(k_2,0) - 2 \right) \tag{5.91}$$

For direct operators in ll':

$$\left[\left\{ (\mathbf{a^\dagger a})^{K_1 k_1} (\mathbf{b^\dagger b})^{K_2 k_2} \right\}^{(11)0} : z(l) \right]$$

$$= -(l(l+1)(2l+1)/2)^{\frac{1}{2}}\ \delta(K_1,1)\delta(k_1,1)\delta(K_2,0)\delta(k_2,0)\,[\tfrac{1}{2},l']^{\frac{1}{2}} \tag{5.92}$$

$$\left[\left\{ (\mathbf{a^\dagger a})^{K_1 k_1} (\mathbf{b^\dagger b})^{K_2 k_2} \right\}^{(11)0} : z(l') \right]$$

$$= -(l'(l'+1)(2l'+1)/2)^{\frac{1}{2}}\ \delta(K_1,1)\delta(k_1,1)\delta(K_2,0)\delta(k_2,0)\,[\tfrac{1}{2},l]^{\frac{1}{2}} \tag{5.93}$$

5.6 Mutual spin-orbit

Following [Blume and Watson, 1962], one may separate the two-electron magnetic interaction into three tractable parts in tensor operator form:

$$H_{\mathrm{MSO}} = \frac{\alpha^2}{2} \sum_{i \neq j} \left(\nabla_i \left(\frac{1}{r_{ij}} \right) \times \mathbf{p}_i \right) \cdot (\mathbf{s}_i + 2\mathbf{s}_j) = -\frac{\alpha^2}{2} \sum_{i \neq j} \left(\frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \right) \cdot (\mathbf{s}_i + 2\mathbf{s}_j) = V_1 + V_2 + V_3 \tag{5.94}$$

Here, $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ and [Innes and Ufford, 1958]:

$$\frac{\mathbf{r}_{ij}}{r_{ij}^3} = \frac{1}{\sqrt{3}} \sum_k (-1)^k \left[\frac{r_i^{k-1}}{r_j^{k+1}} \cdot [k(2k-1)(2k+1)]^{\frac{1}{2}} \cdot \left(C_i^{(k-1)} C_j^{(k)} \right)^{(1)} \cdot \varepsilon(r_j - r_i) \right.$$
$$\left. + \frac{r_j^k}{r_i^{k+2}} \cdot [(k+1)(2k+1)(2k+3)]^{\frac{1}{2}} \cdot \left(C_i^{(k+1)} C_j^{(k)} \right)^{(1)} \cdot \varepsilon(r_i - r_j) \right] \tag{5.95}$$

Further use of equations (3.17) and (3.20) now leads to the tensorial expressions:

$$\begin{aligned} V_1 &= \frac{\alpha^2}{2\sqrt{3}} \sum_{k,i\neq j} (-1)^k \cdot r_j \cdot \frac{r_<^{k-1}}{r_>^{k+2}} \cdot [k(k+1)(2k+1)]^{\frac{1}{2}} \frac{\partial}{\partial r_i} \left(C_j^{(k)} C_i^{(k)} \right)^{(1)} \cdot (\mathbf{s}_i + 2\mathbf{s}_j) \\ &= \frac{\alpha^2}{2} \sum_{k,i\neq j} (-1)^k \cdot r_j \cdot \frac{r_<^{k-1}}{r_>^{k+2}} \cdot \left[\frac{k(k+1)}{2k+1} \right]^{\frac{1}{2}} \frac{\partial}{\partial r_i} \cdot \left\langle l_i \parallel C^{(k)} \parallel l_i' \right\rangle \left\langle l_j \parallel C^{(k)} \parallel l_j' \right\rangle \\ &\quad \cdot \left[\left(w_i^{(1k)} w_j^{(0k)} \right)^{(11)0} + 2 \left(w_i^{(0k)} w_j^{(1k} \right)^{(11)0} \right] \end{aligned} \tag{5.96a}$$

$$\begin{aligned} V_2 &= \frac{\alpha^2}{2\sqrt{3}} \sum_{k,i\neq j} (-1)^k \cdot [k]^{\frac{1}{2}} \left[(2k-1) \frac{r_j^{k-1}}{r_i^{k+2}} \varepsilon(r_i - r_j) \left(C_j^{(k-1)} (C_i^{(k-1)} l_i)^{(k)} \right)^{(1)} \right. \\ &\qquad \left. -(2k+3) \frac{r_i^{k-1}}{r_j^{k+2}} \varepsilon(r_j - r_i) \left(C_j^{(k+1)} (C_i^{(k+1)} l_i)^{(k)} \right)^{(1)} \right] \cdot (\mathbf{s}_i + 2\mathbf{s}_j) \\ &= \frac{\alpha^2}{2} \sum_{k,i\neq j} (-1)^k \cdot [k]^{\frac{1}{2}} \cdot \frac{r_j^{k-1}}{r_i^{k+2}} \varepsilon(r_i - r_j) \cdot [l_i'(l_i'+1)(2l_i'+1)]^{\frac{1}{2}} \cdot \left\langle l_i \parallel C^{(k-1)} \parallel l_i' \right\rangle \cdot \left\langle l_j \parallel C^{(k-1)} \parallel l_j' \right\rangle \\ &\cdot \quad [k-1]^{\frac{1}{2}} \cdot \begin{Bmatrix} k-1 & 1 & k \\ l_i' & l_i & l_i' \end{Bmatrix} \left[\left(w_i^{(1k)} w_j^{(0k-1)} \right)^{(11)0} + 2 \left(w_i^{(0k)} w_j^{(1k-1)} \right)^{(11)0} \right] \\ &- \frac{\alpha^2}{2} \sum_{k,i\neq j} (-1)^k \cdot [k]^{\frac{1}{2}} \cdot \frac{r_i^{k-1}}{r_j^{k+2}} \varepsilon(r_j - r_i) \cdot [l_i'(l_i'+1)(2l_i'+1)]^{\frac{1}{2}} \cdot \left\langle l_i \parallel C^{(k+1)} \parallel l_i' \right\rangle \cdot \left\langle l_j \parallel C^{(k+1)} \parallel l_j' \right\rangle \\ &\cdot \quad [k+1]^{\frac{1}{2}} \cdot \begin{Bmatrix} k+1 & 1 & k \\ l_i' & l_i & l_i' \end{Bmatrix} \left[\left(w_i^{(1k)} w_j^{(0k+1)} \right)^{(11)0} + 2 \left(w_i^{(0k)} w_j^{(1k+1)} \right)^{(11)0} \right] \end{aligned} \tag{5.96b}$$

$$\begin{aligned} V_3 &= \frac{\alpha^2}{2\sqrt{3}} \sum_{k,i\neq j} (-1)^k \cdot [k]^{\frac{1}{2}} \left[k \frac{r_j^k}{r_i^{k+3}} \varepsilon(r_i - r_j) - (k+1) \frac{r_i^{k-2}}{r_j^{k+1}} \varepsilon(r_j - r_i) \right] \\ &\cdot \quad \left(C_j^{(k)} (C_i^{(k)} l_i)^{(k)} \right)^{(1)} \cdot (\mathbf{s}_i + 2\mathbf{s}_j) \\ &= \frac{\alpha^2}{4} \sum_{k,i\neq j} (-1)^k \cdot \left[\frac{k(k+1)}{2k+1} \right]^{\frac{1}{2}} \left[(k+1)^{-1} \frac{r_j^k}{r_i^{k+3}} \varepsilon(r_i - r_j) - k^{-1} \frac{r_i^{k-2}}{r_j^{k+1}} \varepsilon(r_j - r_i) \right] \\ &\quad (l_i(l_i+1) - k(k+1) - l_i'(l_i'+1)) \cdot \left\langle l_i \parallel C^{(k)} \parallel l_i' \right\rangle \left\langle l_j \parallel C^{(k)} \parallel l_j' \right\rangle \\ &\quad \cdot \left[\left(w_i^{(1k)} w_j^{(0k)} \right)^{(11)0} + 2 \left(w_i^{(0k)} w_j^{(1k} \right)^{(11)0} \right] \end{aligned} \tag{5.96c}$$

For the *ab initio* interpretation of one- and two-body magnetic parameters, it is frequently helpful to use explicit formulae for the mutual spin-orbit and spin-spin

interactions. The occurring N^k and W^k integrals, with $M^k(ab) = N^k(ab;ab)$, are defined in accordance with [Godefroid, 1982], equations (3) and (5), respectively:

$$\begin{aligned} N^k(ab;cd) &= \tfrac{1}{4}\alpha^2 \int_0^\infty\int_0^\infty \mathrm{d}r_1\mathrm{d}r_2\, a(1)b(2)\, \frac{r_2^k}{r_1^{k+3}}\, \varepsilon(r_1-r_2)\, c(1)d(2) \\ W^k(ab;cd) &= \tfrac{1}{4}\alpha^2 \int_0^\infty\int_0^\infty \mathrm{d}r_1\mathrm{d}r_2\, a(1)b(2)\, \frac{r_<^k}{r_>^{k+3}}\, r_2\, \frac{\partial}{\partial r_1}\, c(1)d(2) \end{aligned} \tag{5.97}$$

The below further elaboration in terms of second quantization by equation (5.74) is restricted to single configurations only.
For the V_1 and V_3 exchange contributions in ll', $(-1)^P = -1$ and $E = 1$:

$$\begin{aligned} G^{(11)0} = S(ab;ba)\Big[\big\{(\mathbf{a}^\dagger\mathbf{b})^{(1k)}(\mathbf{b}^\dagger\mathbf{a})^{(0k)}\big\}^{(11)0} + 2\big\{(\mathbf{a}^\dagger\mathbf{b})^{(0k)}(\mathbf{b}^\dagger\mathbf{a})^{(1k)}\big\}^{(11)0}\Big] \\ -S(ba;ab)\Big[\big\{(\mathbf{a}^\dagger\mathbf{b})^{(0k)}(\mathbf{b}^\dagger\mathbf{a})^{(1k)}\big\}^{(11)0} + 2\big\{(\mathbf{a}^\dagger\mathbf{b})^{(1k)}(\mathbf{b}^\dagger\mathbf{a})^{(0k)}\big\}^{(11)0}\Big] \end{aligned} \tag{5.98}$$

$$\begin{aligned} V_1 &= 2\,W^{k-1}(ab;ba)\cdot\big\langle l \parallel C^{(k)} \parallel l'\big\rangle^2 \sqrt{\frac{k(k+1)}{2k+1}} \\ &\cdot \Big[\big\{(\mathbf{a}^\dagger\mathbf{b})^{(1k)}(\mathbf{b}^\dagger\mathbf{a})^{(0k)}\big\}^{(11)0} + 2\big\{(\mathbf{a}^\dagger\mathbf{b})^{(0k)}(\mathbf{b}^\dagger\mathbf{a})^{(1k)}\big\}^{(11)0}\Big] \\ &- 2\,W^{k-1}(ba;ab)\cdot\big\langle l' \parallel C^{(k)} \parallel l\big\rangle^2 \sqrt{\frac{k(k+1)}{2k+1}} \\ &\cdot \Big[\big\{(\mathbf{a}^\dagger\mathbf{b})^{(0k)}(\mathbf{b}^\dagger\mathbf{a})^{(1k)}\big\}^{(11)0} + 2\big\{(\mathbf{a}^\dagger\mathbf{b})^{(1k)}(\mathbf{b}^\dagger\mathbf{a})^{(0k)}\big\}^{(11)0}\Big] \end{aligned} \tag{5.99}$$

Using equation (5.39), it is now straightforward to work out the reduced matrix element:

$$\begin{aligned} \langle ll'(SL) \parallel V_1 \parallel ll'(S'L')\rangle = 3\sqrt{2}\sum_k \big\langle l \parallel C^{(k)} \parallel l'\big\rangle^2 \cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{l+l'+L'} \cdot [k(k+1)(2k+1)]^{\frac{1}{2}} \\ \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot \begin{Bmatrix} l & l' & k \\ l' & l & k \\ L & L' & 1 \end{Bmatrix} \cdot \big[W^{k-1}(ab;ba)\big(1+2(-1)^{S+S'}\big) - W^{k-1}(ba;ab)\big((-1)^{S+S'}+2\big)\big] \end{aligned} \tag{5.100}$$

V_1 and V_3 can be taken together after cancellation of non-Hermitian terms, using $K^{k-1}(ab;ba) = kN^k(ab;ba) - (k+1)N^{k-2}(ba;ab) = W^{k-1}(ab;ba) + W^{k-1}(ba;ab)$ as abbreviation:

$$\begin{aligned} \langle ll'(SL) \parallel V_1 + V_3 \parallel ll'(S'L')\rangle = -\frac{36}{\sqrt{2}} \cdot \delta(S,1)\cdot\delta(S',1)\cdot\sum_k [k(k+1)(2k+1)]^{\frac{1}{2}} \big\langle l \parallel C^{(k)} \parallel l'\big\rangle^2 \\ \cdot(-1)^{l+l'+L'} \cdot [L,L']^{\frac{1}{2}} \cdot \begin{Bmatrix} l & l' & k \\ l' & l & k \\ L & L' & 1 \end{Bmatrix} \cdot \left[W^{k-1}(ab;ba) + \frac{l(l+1)-l'(l'+1)-k(k+1)}{2k(k+1)} K^{k-1}(ab;ba)\right] \end{aligned} \tag{5.101}$$

For V_2, $(-1)^P = 1$ so there is both a direct and an exchange contribution:

$$\begin{aligned}
V_{2,\mathrm{DIR}} = D\cdot N^{k-1}(ab;ab)\cdot\Bigg(&\left[k(2l+k+1)(2l-k+1)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k-1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k-1)}\parallel l'\right\rangle\\
&\cdot\left[\left\{(\mathbf{a}^\dagger\mathbf{a})^{(1k)}(\mathbf{b}^\dagger\mathbf{b})^{(0k-1)}\right\}^{(11)0}+2\left\{(\mathbf{a}^\dagger\mathbf{a})^{(0k)}(\mathbf{b}^\dagger\mathbf{b})^{(1k-1)}\right\}^{(11)0}\right]\\
&+\left[(k+1)(2l'+k+2)(2l'-k)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k+1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k+1)}\parallel l'\right\rangle\\
&\cdot\left[\left\{(\mathbf{a}^\dagger\mathbf{a})^{(0k+1)}(\mathbf{b}^\dagger\mathbf{b})^{(1k)}\right\}^{(11)0}+2\left\{(\mathbf{a}^\dagger\mathbf{a})^{(1k+1)}(\mathbf{b}^\dagger\mathbf{b})^{(0k)}\right\}^{(11)0}\right]\Bigg)\\
+D\cdot N^{k-1}(ba;ba)\cdot\Bigg(&\left[k(2l'+k+1)(2l'-k+1)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k-1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k-1)}\parallel l'\right\rangle\\
&\cdot\left[\left\{(\mathbf{a}^\dagger\mathbf{a})^{(0k-1)}(\mathbf{b}^\dagger\mathbf{b})^{(1k)}\right\}^{(11)0}+2\left\{(\mathbf{a}^\dagger\mathbf{a})^{(1k-1)}(\mathbf{b}^\dagger\mathbf{b})^{(0k)}\right\}^{(11)0}\right]\\
&+\left[(k+1)(2l+k+2)(2l-k)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k+1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k+1)}\parallel l'\right\rangle\\
&\cdot\left[\left\{(\mathbf{a}^\dagger\mathbf{a})^{(1k)}(\mathbf{b}^\dagger\mathbf{b})^{(0k+1)}\right\}^{(11)0}+2\left\{(\mathbf{a}^\dagger\mathbf{a})^{(0k)}(\mathbf{b}^\dagger\mathbf{b})^{(1k+1)}\right\}^{(11)0}\right]\Bigg)
\end{aligned}\tag{5.102}$$

Again using equation (5.39), it follows for $l \neq l'$:

$$\begin{aligned}
\langle ll'(SL)\parallel V_{2,\mathrm{DIR}}\parallel ll'(S'L')\rangle = \frac{3}{\sqrt{2}}\cdot[S,L,S',L']^{\frac{1}{2}}\cdot\begin{Bmatrix}S & S' & 1\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\\
\cdot\Bigg[N^{k-1}(ab;ab)\cdot\Bigg(\left[k(2l+k+1)(2l-k+1)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k-1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k-1)}\parallel l'\right\rangle\\
\cdot[k,k-1]^{\frac{1}{2}}\cdot\begin{Bmatrix}l & l & k\\ l' & l' & k-1\\ L & L' & 1\end{Bmatrix}\cdot\left[(-1)^{S'}+2\cdot(-1)^{S}\right]\\
+\left[(k+1)(2l'+k+2)(2l'-k)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k+1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k+1)}\parallel l'\right\rangle\\
\cdot[k,k+1]^{\frac{1}{2}}\cdot\begin{Bmatrix}l & l & k+1\\ l' & l' & k\\ L & L' & 1\end{Bmatrix}\cdot\left[(-1)^{S}+2\cdot(-1)^{S'}\right]\Bigg)\\
+N^{k-1}(ba;ba)\cdot\Bigg(\left[k(2l'+k+1)(2l'-k+1)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k-1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k-1)}\parallel l'\right\rangle\\
\cdot[k,k-1]^{\frac{1}{2}}\cdot\begin{Bmatrix}l & l & k-1\\ l' & l' & k\\ L & L' & 1\end{Bmatrix}\cdot\left[(-1)^{S}+2\cdot(-1)^{S'}\right]\\
+\left[(k+1)(2l+k+2)(2l-k)\right]^{\frac{1}{2}}\left\langle l\parallel C^{(k+1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k+1)}\parallel l'\right\rangle\\
\cdot[k,k+1]^{\frac{1}{2}}\cdot\begin{Bmatrix}l & l & k\\ l' & l' & k+1\\ L & L' & 1\end{Bmatrix}\cdot\left[(-1)^{S'}+2\cdot(-1)^{S}\right]\Bigg)\Bigg]
\end{aligned}\tag{5.103}$$

Within a shell of equivalent electrons there is no exchange and the second quantized form of MSO is reduced to the direct part of V_2 only:

$$\begin{aligned} H_{\mathrm{MSO}} = \sum_k \Big(& [k(2l+k+1)(2l-k+1)]^{\frac{1}{2}} \cdot \left\langle l \parallel C^{(k-1)} \parallel l \right\rangle^2 \\ & \times \left[\left\{ \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(1k)} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(0k-1)} \right\}^{(11)0} + 2 \left\{ \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(0k)} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(1k-1)} \right\}^{(11)0} \right] \\ & + [(k+1)(2l+k+2)(2l-k)]^{\frac{1}{2}} \cdot \left\langle l \parallel C^{(k+1)} \parallel l \right\rangle^2 \\ & \times \left[\left\{ \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(1k)} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(0k+1)} \right\}^{(11)0} + 2 \left\{ \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(0k)} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(1k+1)} \right\}^{(11)0} \right] \Big) N^{k-1}(aa;aa) \end{aligned} \tag{5.104}$$

With equation (5.39), the corresponding reduced matrix element follows directly:

$$\begin{aligned} \left\langle l^2(SL) \parallel H_{\mathrm{MSO}} \parallel l^2(S'L') \right\rangle = \sum_k & \; 3\sqrt{2} \cdot (-1)^S \cdot [S,L,S',L']^{\frac{1}{2}} \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot N^{k-1}(aa;aa) \\ \Bigg(& [k(2l+k+1)(2l-k+1)(2k-1)(2k+1)]^{\frac{1}{2}} \begin{Bmatrix} l & l & k-1 \\ l & l & k \\ L & L' & 1 \end{Bmatrix} \left(1 + 2(-1)^{L+L'}\right) \left\langle l \parallel C^{(k-1)} \parallel l \right\rangle^2 \\ & + [(k+1)(2l+k+2)(2l-k)(2k+1)(2k+3)]^{\frac{1}{2}} \begin{Bmatrix} l & l & k \\ l & l & k+1 \\ L & L' & 1 \end{Bmatrix} \left((-1)^{L+L'} + 2\right) \left\langle l \parallel C^{(k+1)} \parallel l \right\rangle^2 \Bigg) \end{aligned}$$

For the V_2 exchange contribution in ll', $(-1)^P = 1$ and $E = 1$:

$$\begin{aligned} G^{(11)0} = & \; S(ab;ba) \left[\left\{ (\mathbf{a}^\dagger \mathbf{b})^{(1k)} (\mathbf{b}^\dagger \mathbf{a})^{(0k-1)} \right\}^{(11)0} + 2 \left\{ (\mathbf{a}^\dagger \mathbf{b})^{(0k)} (\mathbf{b}^\dagger \mathbf{a})^{(1k-1)} \right\}^{(11)0} \right] \\ & + S(ba;ab) \left[\left\{ (\mathbf{a}^\dagger \mathbf{b})^{(1k)} (\mathbf{b}^\dagger \mathbf{a})^{(0k+1)} \right\}^{(11)0} + 2 \left\{ (\mathbf{a}^\dagger \mathbf{b})^{(0k)} (\mathbf{b}^\dagger \mathbf{a})^{(1k+1)} \right\}^{(11)0} \right] \end{aligned} \tag{5.106}$$

$$\begin{aligned} \left\langle ll'(SL) \parallel V_{2,\mathrm{EXCH}} \parallel ll'(S'L') \right\rangle = & \; \frac{3}{\sqrt{2}} \cdot [S,L,S',L']^{\frac{1}{2}} \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot (-1)^{l+l'-(S'+L')} \\ & \cdot \Bigg[N^{k-1}(ab;ba) \cdot \sqrt{\frac{(l+l'+k+1)(l+l'-k+1)(k^2-(l-l')^2)}{k}} \cdot \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle^2 \\ & \cdot [k,k-1]^{\frac{1}{2}} \cdot \left(\begin{Bmatrix} l & l' & k \\ l' & l & k-1 \\ L & L' & 1 \end{Bmatrix} \cdot \left[(-1)^{S'} + 2 \cdot (-1)^S \right] + \begin{Bmatrix} l & l' & k-1 \\ l' & l & k \\ L & L' & 1 \end{Bmatrix} \cdot \left[(-1)^S + 2 \cdot (-1)^{S'} \right] \right) \\ & + N^{k-1}(ba;ab) \cdot \sqrt{\frac{(l+l'+k+2)(l+l'-k)((k+1)^2-(l-l')^2)}{k+1}} \cdot \left\langle l \parallel C^{(k+1)} \parallel l' \right\rangle^2 \\ & \cdot [k,k+1]^{\frac{1}{2}} \cdot \left(\begin{Bmatrix} l & l' & k \\ l' & l & k+1 \\ L & L' & 1 \end{Bmatrix} \cdot \left[(-1)^{S'} + 2 \cdot (-1)^S \right] + \begin{Bmatrix} l & l' & k+1 \\ l' & l & k \\ L & L' & 1 \end{Bmatrix} \cdot \left[(-1)^S + 2 \cdot (-1)^{S'} \right] \right) \Bigg] \end{aligned} \tag{5.107}$$

The above may be exemplified by the full MSO for the case $ll' = ls$:

$$\langle ls(SL) \parallel H_{\rm MSO} \parallel ls(S'L') \rangle = -36 \sqrt{\frac{l(l+1)}{4l+2}} \cdot \delta(S,1) \cdot \delta(S',1) \cdot W^{l-1}(ls;sl)$$
$$+ 3\sqrt{2} \cdot [l(l+1)(2l+1)]^{\frac{1}{2}} \cdot [S,S']^{\frac{1}{2}} \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot [(-1)^{S'} + 2(-1)^{S}] \cdot N^0(ls;ls) \quad (5.108)$$

5.7 Spin-spin

$$\begin{aligned} H_{ss} &= \frac{\alpha^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}^3} \left(\mathbf{s}_i \cdot \mathbf{s}_j - 3 \frac{(\mathbf{s}_i \cdot \boldsymbol{r}_{ij})(\mathbf{s}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^2} \right) \\ &= \frac{-\alpha^2}{2\sqrt{5}} \sum_{k,i \neq j} (-1)^k \frac{r_j^k}{r_i^{k+3}} \left[\frac{(2k+5)!}{(2k)!} \right]^{\frac{1}{2}} \cdot \varepsilon(r_i - r_j) \cdot \left(C_i^{(k+2)} C_j^{(k)} \right)^{(2)} \cdot (s_i s_j)^{(2)} \\ &= \frac{-\alpha^2}{2} \sum_{k,i \neq j} (-1)^k \frac{r_j^k}{r_i^{k+3}} [(k+1)(k+2)(2k+3)]^{\frac{1}{2}} \cdot \varepsilon(r_i - r_j) \\ &\quad \cdot \left\langle l_i \parallel C^{(k+2)} \parallel l_i' \right\rangle \left\langle l_j \parallel C^{(k)} \parallel l_j' \right\rangle \left(w_i^{(1k+2)} w_j^{(1k)} \right)^{(22)0} \end{aligned} \quad (5.109)$$

As an illustration of equation (5.74), we give the full expression for the spin-spin interaction below (replacing $k \to k-1$ for symmetry purposes):

$$\begin{aligned} H_{ss} &= 2 \sum_k (-1)^k \left(k(k+1)(2k+1) \right)^{\frac{1}{2}} \\ &\times \Big(D\, N^{k-1}(ab;cd) \left\langle l_a \parallel C^{(k+1)} \parallel l_c \right\rangle \left\langle l_b \parallel C^{(k-1)} \parallel l_d \right\rangle \left\{ \left(\mathbf{a}^\dagger \mathbf{c} \right)^{(1k+1)} \left(\mathbf{b}^\dagger \mathbf{d} \right)^{(1k-1)} \right\}^{(22)0} \\ &+ E\, N^{k-1}(ab;dc) \left\langle l_a \parallel C^{(k+1)} \parallel l_d \right\rangle \left\langle l_b \parallel C^{(k-1)} \parallel l_c \right\rangle \left\{ \left(\mathbf{a}^\dagger \mathbf{d} \right)^{(1k+1)} \left(\mathbf{b}^\dagger \mathbf{c} \right)^{(1k-1)} \right\}^{(22)0} \\ &+ D\, N^{k-1}(ba;dc) \left\langle l_a \parallel C^{(k-1)} \parallel l_c \right\rangle \left\langle l_b \parallel C^{(k+1)} \parallel l_d \right\rangle \left\{ \left(\mathbf{a}^\dagger \mathbf{c} \right)^{(1k-1)} \left(\mathbf{b}^\dagger \mathbf{d} \right)^{(1k+1)} \right\}^{(22)0} \\ &+ E\, N^{k-1}(ba;cd) \left\langle l_a \parallel C^{(k-1)} \parallel l_d \right\rangle \left\langle l_b \parallel C^{(k+1)} \parallel l_c \right\rangle \left\{ \left(\mathbf{a}^\dagger \mathbf{d} \right)^{(1k-1)} \left(\mathbf{b}^\dagger \mathbf{c} \right)^{(1k+1)} \right\}^{(22)0} \Big) \end{aligned} \quad (5.110)$$

With equation (5.39), the reduced matrix element for ll' then becomes:

$$\begin{aligned}\langle ll'(SL) \parallel H_{ss} \parallel ll'(S'L')\rangle = 10 \cdot \delta(S,1) \cdot \delta(S',1)[L,L']^{\frac{1}{2}} \sum_k (-1)^k \left[k(k+1)(2k-1)(2k+1)(2k+3)\right]^{\frac{1}{2}} \\ \cdot \Bigg[N^{k-1}(ab;ab) \cdot \langle l \parallel C^{(k+1)} \parallel l\rangle \langle l' \parallel C^{(k-1)} \parallel l'\rangle \begin{Bmatrix} l & l & k+1 \\ l' & l' & k-1 \\ L & L' & 2 \end{Bmatrix} \\ + N^{k-1}(ab;ba) \cdot (-1)^{l+l'-(S'+L')} \cdot \langle l \parallel C^{(k+1)} \parallel l'\rangle \langle l' \parallel C^{(k-1)} \parallel l\rangle \begin{Bmatrix} l & l' & k+1 \\ l' & l & k-1 \\ L & L' & 2 \end{Bmatrix} \\ + N^{k-1}(ba;ba) \cdot \langle l \parallel C^{(k-1)} \parallel l\rangle \langle l' \parallel C^{(k+1)} \parallel l'\rangle \begin{Bmatrix} l & l & k-1 \\ l' & l' & k+1 \\ L & L' & 2 \end{Bmatrix} \\ + N^{k-1}(ba;ab) \cdot (-1)^{l+l'-(S'+L')} \cdot \langle l \parallel C^{(k-1)} \parallel l'\rangle \langle l' \parallel C^{(k+1)} \parallel l\rangle \begin{Bmatrix} l & l' & k-1 \\ l' & l & k+1 \\ L & L' & 2 \end{Bmatrix} \Bigg]\end{aligned} \tag{5.111}$$

A simple example for illustration:

$$\langle ls(SL) \parallel H_{ss} \parallel ls(S'L')\rangle = 10\sqrt{6} \sqrt{\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}} \cdot \delta(S,1) \cdot \delta(S',1) \cdot N^0(ls;ls) \tag{5.112}$$

For a shell of equivalent electrons the interaction H_{ss} simplifies to:

$$\begin{aligned} H_{ss} &= 2 \sum_{k=0,2(l-1)} (-1)^{k+1} \cdot \left[(k+1)(k+2)(2k+3)\right]^{\frac{1}{2}} \cdot N^k(aa;aa) \\ &\times \langle l \parallel C^{(k)} \parallel l\rangle \langle l \parallel C^{(k+2)} \parallel l\rangle \left\{ \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(1k)} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(1k+2)} \right\}^{(22)0} \end{aligned} \tag{5.113}$$

Again using equation (5.39), the corresponding reduced matrix element becomes:

$$\begin{aligned}\left\langle l^2(SL) \parallel H_{ss} \parallel l^2(S'L')\right\rangle = 60 \cdot \sum_{k=0,2(l-1)} [S,L,S',L']^{\frac{1}{2}} \langle l \parallel C^{(k)} \parallel l\rangle \langle l \parallel C^{(k+2)} \parallel l\rangle \cdot N^k(aa;aa) \\ (-1)^{k+1} \cdot \left[(k+1)(k+2)(2k+1)(2k+3)(2k+5)\right]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ S & S' & 2 \end{Bmatrix} \cdot \begin{Bmatrix} l & l & k \\ l & l & k+2 \\ L & L' & 2 \end{Bmatrix}\end{aligned} \tag{5.114}$$

The fact that there are no closed-shell effects of the spin-spin interaction becomes obvious from application of equations (5.13): $(\mathbf{a}^\dagger \mathbf{b})^{(22)}$ cannot exist as two electrons cannot couple to spin 2.

5.8 Spin-spin-contact and two-body Darwin

In addition to the electrostatic energy, only the spin-spin-contact, the two-body Darwin and the orbit-orbit interactions carry ranks $(\kappa k) = (00)$ in the Breit-Pauli

Hamiltonian and may therefore contribute to the average energy of the system. The dependence on the number of electrons and the partial cancellation of the first and second term have not always been taken into account properly.

$$\text{With the } k\text{–independent integral: } A(ab;cd) = \tfrac{1}{4}\alpha^2 \int_0^\infty \mathrm{d}r\; r^{-2}\, P_a(r)P_b(r)P_c(r)P_d(r) \tag{5.115}$$

the spin-spin-contact and the two-body Darwin terms are written as follows:

$$\begin{aligned}
H_{\mathrm{ssc}} &= -\frac{2\alpha^2}{3}\sum_{i<j}(\boldsymbol{s}_i\cdot\boldsymbol{s}_j)\,4\pi\,\delta(\boldsymbol{r}_i-\boldsymbol{r}_j) = -\frac{2\alpha^2}{3}\sum_{i<j,k}(\mathbf{s}_i\cdot\mathbf{s}_j)\,\frac{\delta(r_{ij})}{r_i^2}\cdot[k]\cdot\left(C_i^{(k)}\cdot C_j^{(k)}\right)\\
&= \tfrac{1}{4}\alpha^2\cdot r^{-2}\cdot\frac{2}{\sqrt{3}}\sum_{i\neq j,k}\delta(r_{ij})(-1)^k\cdot[k]^{\frac{1}{2}}\cdot\left\langle l_i\parallel C^{(k)}\parallel l_i'\right\rangle\left\langle l_j\parallel C^{(k)}\parallel l_j'\right\rangle\left(w_i^{(1k)}w_j^{(1k)}\right)^{(00)0}\\
&= \frac{4}{\sqrt{3}}A(ab;cd)\sum_k(-1)^k[k]^{\frac{1}{2}}\cdot D\left\langle l_a\parallel C^{(k)}\parallel l_c\right\rangle\left\langle l_b\parallel C^{(k)}\parallel l_d\right\rangle\left\{\left(\mathbf{a}^\dagger\mathbf{c}\right)^{1k}\left(\mathbf{b}^\dagger\mathbf{d}\right)^{1k}\right\}^{(00)0}\\
&+ \frac{4}{\sqrt{3}}A(ab;dc)\sum_{k'}(-1)^{k'}[k']^{\frac{1}{2}}\cdot E\left\langle l_a\parallel C^{(k')}\parallel l_d\right\rangle\left\langle l_b\parallel C^{(k')}\parallel l_c\right\rangle\left\{\left(\mathbf{a}^\dagger\mathbf{d}\right)^{1k'}\left(\mathbf{b}^\dagger\mathbf{c}\right)^{1k'}\right\}^{(00)0}
\end{aligned} \tag{5.116a}$$

$$\begin{aligned}
H_{\mathrm{D2}} &= -\frac{\alpha^2}{4}\sum_{i<j}4\pi\,\delta(\boldsymbol{r}_i-\boldsymbol{r}_j) = -\frac{\alpha^2}{4}\sum_{i<j,k}\frac{\delta(r_{ij})}{r_i^2}\cdot[k]\cdot\left(C_i^{(k)}\cdot C_j^{(k)}\right)\\
&= \tfrac{1}{4}\alpha^2\cdot r^{-2}\sum_{i\neq j,k}\delta(r_{ij})(-1)^{k+1}\cdot[k]^{\frac{1}{2}}\cdot\left\langle l_i\parallel C^{(k)}\parallel l_i'\right\rangle\left\langle l_j\parallel C^{(k)}\parallel l_j'\right\rangle\left(w_i^{(0k)}w_j^{(0k)}\right)^{(00)0}\\
&= 2A(ab;cd)\sum_k(-1)^{k+1}[k]^{\frac{1}{2}}\cdot D\left\langle l_a\parallel C^{(k)}\parallel l_c\right\rangle\left\langle l_b\parallel C^{(k)}\parallel l_d\right\rangle\left\{\left(\mathbf{a}^\dagger\mathbf{c}\right)^{0k}\left(\mathbf{b}^\dagger\mathbf{d}\right)^{0k}\right\}^{(00)0}\\
&+ 2A(ab;dc)\sum_{k'}(-1)^{k'+1}[k']^{\frac{1}{2}}\cdot E\left\langle l_a\parallel C^{(k')}\parallel l_d\right\rangle\left\langle l_b\parallel C^{(k')}\parallel l_c\right\rangle\left\{\left(\mathbf{a}^\dagger\mathbf{d}\right)^{0k'}\left(\mathbf{b}^\dagger\mathbf{c}\right)^{0k'}\right\}^{(00)0}
\end{aligned} \tag{5.116b}$$

Equation (6.38) from [Brink and Satchler, 1968] is used in the above to retrieve the tensor operator form:

$$4\pi\,\delta(\boldsymbol{r}_i-\boldsymbol{r}_j) = \frac{\delta(r_i-r_j)}{r_i^2}\sum_k[k]\,C_i^{(k)}\cdot C_j^{(k)}\quad\left(\text{compare with: } 4\pi\,\delta(\boldsymbol{r}) = \frac{\delta(r)}{r^2}\right) \tag{5.117}$$

For the second line of both equations, straight recoupling gives e.g.:

$$[k]\;(\mathbf{s}_i\cdot\mathbf{s}_j)\left(C_i^{(k)}\cdot C_j^{(k)}\right) = -\tfrac{1}{2}\sqrt{3}(-1)^k[k]^{\frac{1}{2}}\left\langle l_i\parallel C^{(k)}\parallel l_i'\right\rangle\left\langle l_j\parallel C^{(k)}\parallel l_j'\right\rangle\left(w_i^{(1k)}w_j^{(1k)}\right)^{(00)0}$$

In order to be able to project these operators onto an orthogonal basis, and thus account for their effects, one has to find their matrix elements in the pertinent two-electron configurations, l^2 and ll'. Radial integrals are defined in accordance with [Dankwort, 1977]; for relations between them, we refer to this paper. Although the spin-spin-contact term H_{ssc} and the two-body Darwin term H_{D2} differ both in tensorial character and in origin (H_{ssc} derives from the transverse Breit correction

and H_{D2} from the relativistic part of the Coulomb interaction), their matrix elements are quite similar.
Comparison with equation (3.58a) learns that the angular matrices of both H_{ssc} and H_{D2} are proportional to a sum over angular Coulomb matrix elements.
Denoting the spherical tensor expansion of the Coulomb interaction as $\sum_k c_k$, its sum can be carried out by the following lemma:

$$\sum_k [k]\ \langle l_a l_b(SL)\,|c_k|\,l_c l_d(SL)\rangle = W(1+(-1)^S E)(-1)^{l_a+l_c}\left\langle l_a \parallel C^{(L)} \parallel l_b\right\rangle\left\langle l_c \parallel C^{(L)} \parallel l_d\right\rangle \tag{5.118}$$

where $W = ((1+\delta_{ab})(1+\delta_{cd}))^{1/2}(1-\frac{1}{2}\delta_{ab}\delta_{cd})$ gives the weighting factor and $E = (1-\delta_{ab})(1-\delta_{cd})$ vanishes if bra or ket contain equivalent electrons.
Adding direct and exchange terms, one obtains for H_{ssc} and H_{D2}:

$$\langle ll'(SL)|H_{\mathrm{ssc}}|ll'(SL)\rangle = \left(2-\tfrac{4}{3}S(S+1)\right)(1+(-1)^S E)\left\langle l \parallel C^{(L)} \parallel l'\right\rangle^2 A(ab;ab) \tag{5.119a}$$

$$\langle ll'(SL)|H_{\mathrm{D2}}|ll'(SL)\rangle = -(1+(-1)^S E)\left\langle l \parallel C^{(L)} \parallel l'\right\rangle^2 A(ab;ab) \tag{5.119b}$$

The matrix elements are only non-zero for $S=0$, so that effectively $H_{\mathrm{ssc}} = -2H_{\mathrm{D2}}$, a result that is generally valid. Thus, one may express the combined action of the spin-spin-contact term and the two-body Darwin term for both $a=b$ and $a\neq b$ as:

$$\langle ll'(SL)|H_{\mathrm{ssc}}+H_{\mathrm{D2}}|ll'(SL)\rangle = (1+(-1)^S E)\left\langle l \parallel C^{(L)} \parallel l'\right\rangle^2 A(ab;ab) \tag{5.120}$$

To obtain the average energy contribution from equation (5.120), we use the relation: $\sum_L [L]\langle l \parallel C^{(L)} \parallel l'\rangle^2 = (2l+1)(2l'+1)$ (orthonormality of 3j-symbols) to derive the simple expression:

$$E_{\mathrm{av}}(\mathrm{ssc}+\mathrm{D2}) = \sum_a \binom{N}{2}\frac{2l+1}{4l+1}A(aa;aa) + \sum_{a<b}\tfrac{1}{2}NN'\cdot A(ab;ab) \tag{5.121}$$

where $N(N')$ are the occupation numbers of the shell a(b). [Hartmann and Clementi, 1964] treated only closed shells; they did not include intershell cases and their expression (11) does not contain $\mathrm{H_{D2}}$.

5.9 Orbit-orbit interaction

The orbit-orbit interaction is usually neglected, but is interesting in its own right by its resemblance to the relativistic Breit interaction: it requires similar techniques to translate these expressions to tensor operators.

$$\begin{aligned} H_{\mathrm{oo}} &= -\frac{\alpha^2}{2}\sum_{i<j}\left(\frac{\boldsymbol{p}_i\cdot\boldsymbol{p}_j}{r_{ij}}+\frac{(\boldsymbol{r}_{ij}\cdot\boldsymbol{p}_i)(\boldsymbol{r}_{ij}\cdot\boldsymbol{p}_j)}{r_{ij}}\right) \\ &= -\frac{\alpha^2}{2}\sum_{i<j}\left(-\frac{4}{\sqrt{3}}\left(p_i^{(1)}p_j^{(1)}\right)^{(0)}r_{ij}^{-1}+\sqrt{5}\left\{\left(r_{ij}^{(1)}r_{ij}^{(1)}\right)^{(2)}r_{ij}^{-3}\left(p_i^{(1)}p_j^{(1)}\right)^{(2)}\right\}^{(0)}\right) \end{aligned} \tag{5.122}$$

Here, equation (3.16) is used in the second line.

$$\left(r_{ij}^{(1)}r_{ij}^{(1)}\right)^{(2)}\cdot r_{ij}^{-3}=\sum_k(-1)^k\frac{r_<^k}{r_>^{k+1}}\cdot[k]^{\frac12}\cdot\left[\left(\frac{8k(k+1)}{15(2k-1)(2k+3)}\right)^{\frac12}\left(C_<^{(k)}C_>^{(k)}\right)^{(2)}\right.$$
$$\left.-\left(\frac{k(k-1)(2k-3)}{5(2k-1)}\right)^{\frac12}\left(C_<^{(k-2)}C_>^{(k)}\right)^{(2)}+\left(\frac{(k+1)(k+2)(2k+5)}{5(2k+3)}\right)^{\frac12}\left(C_<^{(k)}C_>^{(k+2)}\right)^{(2)}\right] \tag{5.123}$$

The first three of the four separate terms of the intricate orbit-orbit interaction cancel for direct matrix elements, leaving the following relatively simple expression valid for both ll' and l^2:

$$\langle ll'(SL)|H_{oo,\mathrm{DIR}}|ll'(SL)\rangle=\sum_{k>0}\frac{-2k}{k+1}(-1)^{L+l+l'}\begin{Bmatrix}l' & l & L\\ l & l' & k\end{Bmatrix}$$
$$\times\left[(2l+k+1)(2l-k+1)(2l'+k+1)(2l'-k+1)\right]^{\frac12}$$
$$\times\left\langle l\parallel C^{(k-1)}\parallel l\right\rangle\left\langle l'\parallel C^{(k-1)}\parallel l'\right\rangle\cdot\tfrac12\cdot\left(N^{k-1}(ab;ab)+N^{k-1}(ba;ba)\right). \tag{5.124}$$

There is therefore no contribution to the average energy except when $a=b$; in the latter case one can find the expression for equivalent electrons by replacing $(-1)^L\begin{Bmatrix}l & l & L\\ l & l & k\end{Bmatrix}$ by $-N(N-1)/(4l+2)(4l+1)$:

$$E_{\mathrm{av}}(oo)=\sum_a\binom{N}{2}\frac{1}{(2l+1)(4l+1)}\frac{2k}{k+1}(2l+k+1)(2l-k+1)$$
$$\times\left\langle l\parallel C^{(k-1)}\parallel l\right\rangle^2\cdot N^{k-1}(aa;aa) \tag{5.125}$$

The exchange, however, involves all four terms; again, use can be made of the properties of the radial integrals to establish some cancellation between them.

The final result can be written:

$$
\begin{aligned}
&\langle ll'(SL)|H_{oo,\mathrm{EXCH}}|ll'(SL)\rangle \\
&= (-1)^S \sum_{k>0} \Bigg[\Bigg((k+1)(k+2) \begin{Bmatrix} l & l' & L \\ l & l' & k+1 \end{Bmatrix} \left\langle l \parallel C^{(k+1)} \parallel l' \right\rangle^2 \\
&\qquad\qquad -k(k-1) \begin{Bmatrix} l & l' & L \\ l & l' & k-1 \end{Bmatrix} \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle^2 \Bigg) \\
&\quad \times \left(2T^k(ab;ba) + \frac{(k-1)(k+2)}{2k+1} N^{k-1}(ab;ba) \right) \\
&\quad + 2\left(l(l+1) - l'(l'+1)\right) \Bigg(\begin{Bmatrix} l & l' & L \\ l & l' & k+1 \end{Bmatrix} \left\langle l \parallel C^{(k+1)} \parallel l' \right\rangle^2 \\
&\quad - \begin{Bmatrix} l & l' & L \\ l & l' & k-1 \end{Bmatrix} \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle^2 \Bigg) \\
&\quad \times \left(U^k(ab;ba) + \frac{(k-1)(k+2)}{2k+1} N^{k-1}(ab;ba) \right) \\
&\quad + \left(l(l+1) - l'(l'+1)\right)^2 \Bigg(\frac{k-1}{k+1} \begin{Bmatrix} l & l' & L \\ l & l' & k+1 \end{Bmatrix} \left\langle l \parallel C^{(k+1)} \parallel l' \right\rangle^2 \\
&\quad - \frac{k+2}{k} \begin{Bmatrix} l & l' & L \\ l & l' & k-1 \end{Bmatrix} \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle^2 \Bigg) \frac{N^{k-1}(ab;ba)}{2k+1} \\
&\quad - \frac{2}{k(k+1)} (l+l'+k+1)(l+l'-k+1)\left(k^2 - (l-l')^2\right) \\
&\quad \times \begin{Bmatrix} l & l' & L \\ l & l' & k \end{Bmatrix} \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle^2 N^{k-1}(ab;ba) \Bigg].
\end{aligned}
\tag{5.126}
$$

Note that much of the interaction would vanish if the radial integrals were independent of k.

The contribution to the average energy can be found straightforwardly by replacing all factors $(-1)^S \begin{Bmatrix} l & l' & L \\ l & l' & k \end{Bmatrix}$ with $-2NN'/(4l+2)(4l'+2)$, yielding the expression of [Dankwort, 1977], which is therefore not repeated.

5.10 Quasispin and conjugation

Originally, the quasispin formalism was introduced in 1958 to study superconductivity. Next, the idea of a quasispin operator $\mathbf{Q}$ was fruitfully adapted and elaborated for use in nuclear and atomic physics [Flowers and Szpikowski, 1964a, Flowers and Szpikowski, 1964b, Judd, 1967]:

$$Q_+ = \tfrac{1}{2} \cdot \left[\tfrac{1}{2}, l\right]^{\frac{1}{2}} \left(\mathbf{a}^\dagger \mathbf{a}^\dagger\right)^{(00)} \tag{5.127a}$$

$$Q_- = -\tfrac{1}{2} \cdot \left[\tfrac{1}{2}, l\right]^{\frac{1}{2}} \left(\mathbf{a}\mathbf{a}\right)^{(00)} \tag{5.127b}$$

$$Q_0 = -\tfrac{1}{4} \cdot \left[\tfrac{1}{2}, l\right]^{\frac{1}{2}} \left[\left(\mathbf{a}^\dagger \mathbf{a}\right)^{(00)} + \left(\mathbf{a}\mathbf{a}^\dagger\right)^{(00)}\right] \tag{5.127c}$$

With $\xi = (nl\, m_s m_l)$, $\xi* = (nl\, -m_s - m_l)$, $x = (s + l - m_s - m_l)$ and the relations:

$$(\mathbf{a}^\dagger \mathbf{a}^\dagger)^{(00)} = (-1)^x [\tfrac{1}{2}, l]^{-\frac{1}{2}} \sum_\xi a^\dagger_\xi a^\dagger_{\xi *} \tag{5.128a}$$

$$(\mathbf{aa})^{(00)} = (-1)^x [\tfrac{1}{2}, l]^{-\frac{1}{2}} \sum_\xi a_\xi a_{\xi *} \tag{5.128b}$$

$$(\mathbf{a}^\dagger \mathbf{a})^{(00)} = -[\tfrac{1}{2}, l]^{-\frac{1}{2}} \sum_\xi a^\dagger_\xi a_\xi \tag{5.128c}$$

$$(\mathbf{a a}^\dagger)^{(00)} = +[\tfrac{1}{2}, l]^{-\frac{1}{2}} \sum_\xi a_\xi a^\dagger_\xi \tag{5.128d}$$

from which:

$$Q_+ = (-1)^x \cdot \tfrac{1}{2} \sum_\xi a^\dagger_\xi a^\dagger_{\xi *} \tag{5.129a}$$

$$Q_- = (-1)^{x+1} \cdot \tfrac{1}{2} \sum_\xi a_\xi a_{\xi *} \tag{5.129b}$$

$$Q_0 = \tfrac{1}{4} \sum_\xi \left(a^\dagger_\xi a_{\xi *} - a_\xi a^\dagger_\xi \right) \tag{5.129c}$$

it follows from table (5.1) that the quasispin operators obey commutation relations identical to those for S_+, S_- and S_0:

$$[Q_+, Q_-] = 2Q_0 \tag{5.130a}$$

$$[Q_0, Q_-] = Q_+ \tag{5.130b}$$

$$[Q_-, Q_0] = Q_- \tag{5.130c}$$

The operation of the (likewise anti-linear) time reversal operator T, implicitly defined by $T\,|\xi\rangle = (-1)^{s+l-m_s-m_l}\,|\xi*\rangle \rightarrow TLT^{-1} = -L$ and $TST^{-1} = -S$ now has the analogy:

$$C\, Q_+\, C^{-1} = -Q_- \tag{5.131a}$$

$$C\, Q_0\, C^{-1} = -Q_0 \tag{5.131b}$$

$$C\, Q_-\, C^{-1} = -Q_+ \tag{5.131c}$$

Eigenvalues M_Q of Q_0 are given by:

$$M_Q = -\tfrac{1}{2}(2l + 1 - N) \tag{5.132}$$

with the result that the conjugation $N \rightarrow 4l + 2 - N$ implies $M_Q \rightarrow -M_Q$, compare:

$$C|\psi\, QM_Q\rangle = (-1)^{Q-M_Q}\,|\psi\, Q - M_Q\rangle \text{ to:}$$
$$T|\psi\, SLM_S M_L\rangle = (-1)^{S+L-M_S-M_L}\,|\psi\, SL - M_S - M_L\rangle$$

It follows [Judd, 1967] that time-reversal is to spin what conjugation is to quasispin.

For $\overline{S}\,\overline{L} = 00$, states of the same seniority are connected by the operator Q_+ introduced in the above. Such a string of states begins in nl^ν and ends in $nl^{4l+2-\nu}$. Therefore, the maximum $M_Q = Q$ is given by: $Q = \frac{1}{2}(2l+1-\nu)$. A quasispin multiplet

extends across the l shell from this maximum M_Q, of $\frac{1}{2}(2l+1-\nu)$ to a minimum of $-\frac{1}{2}(2l+1-\nu)$. At each step two electrons are added or subtracted.
As put forward by [Lawson and Macfarlane, 1965, Judd, 1967]:
quasispin is merely another way of regarding seniority: the specification (QM_Q) carries the same information as (νN).
There is, however, a very useful extension: operators can be classified according to their quasispin rank K. The quasispin rank of an operator is useful in determining the behavior of matrix elements under conjugation, that is, the interchange of electron states with hole states. We can also regard conjugation as a kind of reflection in the half-filled shell, since it corresponds to $M_Q \to -M_Q$.
Conjugation of two-particle operators follows:

$$\left\langle l^N\ \psi\ |G|\ l^N\ \psi' \right\rangle = \left\langle l^{4l+2-N}\ \psi\ |G|\ l^{4l+2-N}\ \psi' \right\rangle - (2l+1-N)(4l+1)\left\langle G \right\rangle_{l^2} \tag{5.133}$$

Here, the last factor on the RHS denotes the average energy of the operator G in the l^2 configuration; [Judd, 1967] adds the quasispin phase factor $(-1)^{\frac{1}{2}(\nu'-\nu)}$ to the first term on the RHS to deal with particles rather than holes in the second half of a shell.
Though less straightforward, this concept may be extended to mixed shell configurations as well. If the two l electrons of l^2l' are replaced by two l holes, the configuration $l^{4l}l'$ is obtained.
All two- and three-particle operators with even quasispin ranks K_l possess matrix elements in $l^{4l}l'$ that are unchanged from the corresponding ones in l^2l' if the states of l^2 appearing in the bra and ket are both ^1S or if neither of them is ^1S. If one ^1S term appears, the matrix element changes sign. If K_l is odd, however, the opposite is true: namely, the matrix elements reverse their signs if the terms of l^2 appearing in the bra and ket are both ^1S or neither ^1S; while if one ^1S term appears, the sign of the matrix element is preserved. By group-theoretical inspection, the quasispin ranks K_p and K_d can be assigned to all the two- and three-particle operators.
However, there are several operators that correspond to mixtures of both even and odd quasispin ranks. Because of this, their matrix elements do not possess the simple property of either preserving or reversing their signs under all kinds of conjugation.

5.11 Triple tensors

[Lawson and Macfarlane, 1965] found that the operators $a^\dagger_\xi$ and $\tilde{a}_\xi$ commute with $\mathbf{Q}$ as a rank $\frac{1}{2}$ tensor with $m_q = \frac{1}{2}$ and $-\frac{1}{2}$, respectively. This allows one to form a triple tensor $\mathbf{a}^{(qsl)}$ for $q = s = \frac{1}{2}$ with $[q, s, l]$ components, in which both $\mathbf{a}^\dagger$ and $\mathbf{a}$ are subsumed. Also, with $\lambda = (m_q m_s m_l)$, $\mu = (m'_q m'_s m'_l)$ and $x = q+s+l+m_q+m_s+m_l$, all anti-commutation relations may now be given in one single equation ([Judd, 1967], equation (39)):

$$a^{(qsl)}_\lambda a^{(qsl)}_\mu + a^{(qsl)}_\mu a^{(qsl)}_\lambda = (-1)^{x+1}\ \delta(m_q, -m'_q)\delta(m_s, -m'_s)\delta(m_l, -m'_l) \tag{5.134}$$

with the properties:

$$\begin{aligned} C\ a^{(qsl)}_{uvw}\ C^{-1} &= (-1)^{q-u}\ a^{(qsl)}_{-uvw} \\ T\ a^{(qsl)}_{uvw}\ T^{-1} &= (-1)^{s+l-v-w}\ a^{(qsl)}_{u-v-w} \\ CT\ a^{(qsl)}_{uvw}\ T^{-1}C^{-1} &= (-1)^{q+s+l-u-v-w}\ a^{(qsl)}_{-u-v-w} \end{aligned} \tag{5.135}$$

The coupling of two triple tensors $\mathbf{a}^{(qsl)}$ gives the compound tensor ([Judd, 1967]):

$$\begin{aligned} \mathbf{X}^{(K\kappa k)} &= \left(\mathbf{a}^{(qsl)}\mathbf{a}^{(qsl)}\right)^{(K\kappa k)} \quad \leftrightarrow \\ X^{(K\kappa k)}_{\rho\pi q} &= \sum_{\xi,\eta}(qm_{q\xi}\ qm_{q\eta}|K\rho)(sm_{s\xi}\ sm_{s\eta}|\kappa\pi)(lm_{l\xi}\ lm_{l\eta}|kq)\ a^{(qsl)}_{m_q m_s m_l,\xi}\ a^{(qsl)}_{m_q m_s m_l,\eta} \end{aligned} \tag{5.136}$$

Naturally:

$$C \quad X^{(K\kappa k)}_{\rho\pi q}\ C^{-1} = (-1)^{K-\rho} \quad X^{(K\kappa k)}_{-\rho\pi q} \tag{5.137}$$

Interesting special cases are:

$$\begin{aligned} \mathbf{X}^{(100)} &= -2[l]^{-\frac{1}{2}}\ \mathbf{Q} \\ \mathbf{X}^{(010)} &= -2[l]^{-\frac{1}{2}}\ \mathbf{S} &&= \sqrt{2}\ (\mathbf{a}^\dagger\mathbf{a})^{(10)} \\ \mathbf{X}^{(001)} &= -3^{\frac{1}{2}}\ (l(l+1)(2l+1))^{-\frac{1}{2}}\ \mathbf{L} &&= \sqrt{2}\ (\mathbf{a}^\dagger\mathbf{a})^{(01)} \end{aligned} \tag{5.138}$$

The above equalities may readily be found from equation (5.136) and the CG-coefficients from table (5.2). In particular, $X^{(100)}_{\rho 00} = -2[l]^{-\frac{1}{2}}\ Q_\rho$ as:

$$X^{(100)}_{100} = -\sqrt{2}\ (\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(00)} \quad \text{and} \quad X^{(100)}_{-100} = \sqrt{2}\ (\mathbf{aa})^{(00)} \quad \text{while:}$$

$$X^{(100)}_{000} = \sum(\tfrac{1}{2}\pm\tfrac{1}{2}\,,\ \tfrac{1}{2}\mp\tfrac{1}{2}|10)\ (\mathbf{a}^\pm\mathbf{a}^\mp)^{(00)} = \tfrac{1}{2}\sqrt{2}\left[\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(00)} + \left(\mathbf{aa}^\dagger\right)^{(00)}\right] = -2[l]^{-\frac{1}{2}}\ Q_0.$$

Table 5.2: Relevant CG-coefficients

CG-coefficient	Value
$(l\ m \quad l-m\|00)$	$(1)^{l-m}[l]^{-\frac{1}{2}}$
$(\frac{1}{2}-\frac{1}{2} \quad \frac{1}{2}\ \frac{1}{2}\|00)$	$-(2)^{-\frac{1}{2}}$
$(\frac{1}{2}\ \frac{1}{2} \quad \frac{1}{2}-\frac{1}{2}\|00)$	$(2)^{-\frac{1}{2}}$
$(\frac{1}{2}-\frac{1}{2} \quad \frac{1}{2}\ \frac{1}{2}\|10)$	$(2)^{-\frac{1}{2}}$
$(\frac{1}{2}\ \frac{1}{2} \quad \frac{1}{2}-\frac{1}{2}\|10)$	$(2)^{-\frac{1}{2}}$
$(\frac{1}{2}\ \frac{1}{2} \quad \frac{1}{2}\ \frac{1}{2}\|11)$	1
$(\frac{1}{2}-\frac{1}{2} \quad \frac{1}{2}-\frac{1}{2}\|1\ -1)$	1

Application of equation (5.136) to $X^{(K\kappa k)}_{0\pi q}$ for the two cases $K = 0, 1$ gives:

$K = 0 \to 2^{-\frac{1}{2}}\left[(\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)}_{\pi q} - (\mathbf{aa}^\dagger)^{(\kappa k)}_{\pi q}\right] \quad K = 1 \to 2^{-\frac{1}{2}}\left[(\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)}_{\pi q} + (\mathbf{aa}^\dagger)^{(\kappa k)}_{\pi q}\right]$, therefore:

$$X_{0\pi q}^{(K\kappa k)} = 2^{-\frac{1}{2}}\left[(\mathbf{a}^\dagger\mathbf{a})_{\pi q}^{(\kappa k)} - (-1)^K\cdot(\mathbf{a}\mathbf{a}^\dagger)_{\pi q}^{(\kappa k)}\right]$$

Subsequent use of equation (5.8a) then yields finally:

$$X_{0\pi q}^{(K\kappa k)} = 2^{-\frac{1}{2}}\cdot\left\{1-(-1)^{K+\kappa+k}\right\}(\mathbf{a}^\dagger\mathbf{a})_{\pi q}^{(\kappa k)} - (-1)^K[l]^{\frac{1}{2}}\cdot\delta(\kappa,0)\cdot\delta(k,0) \tag{5.139}$$

Non-trivial operators exist only for odd $K+\kappa+k$, as for even $K+\kappa+k$, the above simplifies to a constant [Judd, 1967]:

$$\mathbf{X}^{(K\kappa k)} = -[l]^{\frac{1}{2}}\cdot\delta(K,0)\cdot\delta(\kappa,0)\cdot\delta(k,0) \tag{5.140}$$

Manipulation with CC^{-1} and $C^{-1}C$ leads to [Judd, 1967]:

$$\left\langle\psi\ QM_Q|X_{0\pi q}^{(K\kappa k)}|\psi'\ Q'M_Q\right\rangle = (-1)^x\cdot\left\langle\psi\ Q\ -M_Q|X_{0\pi q}^{(K\kappa k)}|\psi'\ Q'\ -M_Q\right\rangle \tag{5.141}$$

with $x = Q-M_Q+K+Q'-M_Q$.
[Judd, 1967] also introduced a complementarity operator R satisfying $R^\dagger R = \mathbb{1}$ that interchanges spin and quasispin spaces:

$$R\,a_{m_q m_s m_l}^{(qsl)}R^{-1} = a_{m_s m_q m_l}^{(sql)} \text{ and } R\,X_{\rho\pi q}^{(K\kappa k)}R^{-1} = X_{\pi\rho q}^{(\kappa K k)} \tag{5.142}$$

The Wigner-Eckart theorem (3.39) in quasispin space may be put to use to find the explicit $N-$dependence of matrix elements contained in $M_Q = -\frac{1}{2}(2l+1-N)$:

$$\begin{aligned}\left\langle\psi\ QM_Q|X_{0\pi q}^{(K\kappa k)}|\psi'\ Q'M_Q\right\rangle = (-1)^{Q-M_Q}\cdot\begin{pmatrix}Q & K & Q'\\ -M_Q & 0 & M_Q\end{pmatrix}\cdot\left\langle\psi\ QSL|||X^{(K\kappa k)}|||\psi'Q'S'L'\right\rangle\\ \cdot(-1)^{S-M_s}\cdot(-1)^{L-M_L}\cdot\begin{pmatrix}S & \kappa & S'\\ -M_S & \pi & M_S\end{pmatrix}\cdot\begin{pmatrix}L & k & L'\\ -M_L & q & M_L\end{pmatrix}\end{aligned} \tag{5.143}$$

5.12 Coefficients of fractional parentage

To uncouple an electron from a shell of equivalent electrons while preserving the required Pauli restrictions, additional factors called coefficients of fractional parentage are needed e.g. in the CG coefficients (4.9). Assuming $\psi = l^N(SL)$ and $\overline{\psi} = l^{N-1}(\overline{S}\,\overline{L})$, coefficients of fractional parentage are (implicitly) defined by:

$$|l^N(SL)\rangle = \sum_{\overline{\psi}}|l^{N-1}(\overline{S}\,\overline{L}),l\ (SL)\rangle\cdot\left(\overline{\psi}\ |\}\psi\right) \tag{5.144a}$$

$$\langle l^N(SL)| = \sum_{\overline{\psi}}\left(\psi\ \{|\overline{\psi}\right)\cdot\langle l^{N-1}(\overline{S}\,\overline{L}),l\ (SL)| \tag{5.144b}$$

Combining the two above equations yields the cfp completeness condition when summed over parents:

$$\sum_{\overline{\psi}}\left(\psi\ \{|\overline{\psi}\right)\left(\overline{\psi}\ |\}\psi\right) = 1 \tag{5.145}$$

Or, more explicitly:

$$\sum_{\overline{\psi}}\left(\nu SL\ \{|\overline{\psi}\right)\left(\overline{\psi}\ |\}\nu' SL\right) = \delta(\nu,\nu') \tag{5.146}$$

Creation and annihilation operators are closely related to coefficients of fractional parentage:

$$\left\langle \psi \parallel \mathbf{a}^\dagger \parallel \overline{\psi} \right\rangle = (-1)^N \cdot \sqrt{N} \cdot [S,L]^{\frac{1}{2}} \cdot \left(\psi \, \{ | \overline{\psi} \right) \tag{5.147a}$$

From equations (5.23) it follows:

$$\left\langle \psi \parallel \mathbf{a}^\dagger \parallel \overline{\psi} \right\rangle = (-1)^{(S+L)-(\overline{S}+\overline{L})+(\frac{1}{2}+l)} \cdot \left\langle \overline{\psi} \parallel \mathbf{a} \parallel \psi \right\rangle$$

combining the two above equations gives:

$$\left\langle \overline{\psi} \parallel \mathbf{a} \parallel \psi \right\rangle = (-1)^{N+\overline{S}+\overline{L}-(\frac{1}{2}+S)-(l+L)} \cdot \sqrt{N} \cdot [S,L]^{\frac{1}{2}} \cdot \left(\overline{\psi} \, | \} \psi \right) \tag{5.147b}$$

One way to appreciate (5.145) algebraically, is to start from the matrix element of the number operator using equation (5.4):

$$\left\langle \psi | (\mathbf{a}^\dagger \mathbf{a})^{(00)0} | \psi' \right\rangle = -N \cdot \delta(\psi, \psi') \cdot [\tfrac{1}{2}, l]^{-\frac{1}{2}} = [S,L]^{-\frac{1}{2}} \left\langle \psi \parallel (\mathbf{a}^\dagger \mathbf{a})^{(00)} \parallel \psi' \right\rangle \tag{5.148}$$

With equation (5.31) one arrives at:

$$\left\langle \psi \parallel (\mathbf{a}^\dagger \mathbf{a})^{(00)} \parallel \psi' \right\rangle = -N \cdot \delta(\psi, \psi') \cdot [S,L]^{\frac{1}{2}} \cdot [\tfrac{1}{2}, l]^{-\frac{1}{2}} \sum_{\overline{S}\,\overline{L}} (\psi \{ | \overline{\psi}) (\overline{\psi} | \} \psi') \tag{5.149}$$

Inserting the reduced matrix element into the number operator now gives the required cfp sum rule.

Coefficients of fractional parentage all vanish except for $\overline{\nu} = \nu \pm 1$ ([Racah, 1943], equation (58a)).
With $\overline{\nu} = \nu \pm 1$, one derives the below conjugation relation between cfp's [Racah, 1943, Judd, 1967], with $z = S + L + \overline{S} + \overline{L} - (\frac{1}{2} + l) + \frac{1}{2}(\nu + \overline{\nu} + 1)$. Using holes rather than particles for the second half of a shell, Racah omits the last term in z, i.e. the quasispin phase.

$$\left(l^N \, \psi \, \{ | l^{N-1} \, \overline{\psi} \right) = (-1)^z \left(\frac{(4l+3-N)[\overline{S},\overline{L}]}{N \qquad [S,L]} \right)^{\frac{1}{2}} \left(l^{4l+2-N} \, \psi \, | \} \, l^{4l+3-N} \, \overline{\psi} \right) \tag{5.150}$$

It follows immediately:

$$\left(l^{4l+1} \, {}^2l \, \{ | \, l^{4l} \, SL \right) = [S,L]^{\frac{1}{2}} \cdot ((2l+1)(4l+1))^{-\frac{1}{2}} \tag{5.151}$$

Combining equations (5.145) and (5.150), a second sum rule for the summation[2] over daughters can be derived:

$$\sum_{\psi} [S,L]\left(\overline{\psi}\,|\}\psi\right)\left(\psi\,\{|\overline{\psi'}\right) = \delta(\overline{\psi},\overline{\psi'})\cdot[\overline{S},\overline{L}]\cdot\frac{(4l+3-N)}{N} \tag{5.152}$$

The same result may be found by considering $\left\langle\overline{\psi}\parallel(\mathbf{aa}^\dagger)^{(00)}\parallel\overline{\psi'}\right\rangle$ twice:

$$\left\langle\overline{\psi}\parallel(\mathbf{aa}^\dagger)^{(00)}\parallel\overline{\psi'}\right\rangle = N\cdot[\overline{S},\overline{L},\tfrac{1}{2},l]^{-\frac{1}{2}}\cdot\delta(\overline{\psi},\overline{\psi'})\cdot\sum_{\psi}[S,L](\overline{\psi}|\}\psi)(\psi\{|\overline{\psi'}) \tag{5.153}$$

As: $C\,(\mathbf{aa}^\dagger)^{\kappa k}\,C^{-1} = -(\mathbf{a}^\dagger\mathbf{a})^{\kappa k}$, it also follows after using equation (5.31):

$$\begin{aligned}\left\langle\overline{\psi}\,l^{N-1}\parallel(\mathbf{aa}^\dagger)^{(00)}\parallel\overline{\psi'}\,l^{N-1}\right\rangle &= -\left\langle\overline{\psi}\,l^{4l+3-N}\parallel(\mathbf{a}^\dagger\mathbf{a})^{(00)}\parallel\overline{\psi'}\,l^{4l+3-N}\right\rangle\\ &= (4l+3-N)\cdot[\overline{S},\overline{L}]^{\frac{1}{2}}\cdot[\tfrac{1}{2},l]^{-\frac{1}{2}}\cdot\delta(\overline{\psi},\overline{\psi'})\end{aligned} \tag{5.154}$$

Equating the two above equations now yields the cfp 'sum-over-daughters' rule again. A third alternative derivation starts from equation (5.8c):

$$\left\langle\overline{\psi}\parallel(\mathbf{aa}^\dagger)^{(00)}\parallel\overline{\psi'}\right\rangle - \left\langle\overline{\psi}\parallel(\mathbf{a}^\dagger\mathbf{a})^{(00)}\parallel\overline{\psi'}\right\rangle = [\tfrac{1}{2},l]^{\frac{1}{2}}\cdot\left\langle\overline{\psi}\parallel\mathbb{1}\parallel\overline{\psi'}\right\rangle = \delta(\overline{\psi},\overline{\psi'})\cdot[\tfrac{1}{2},l]^{\frac{1}{2}}\cdot[\overline{S},\overline{L}]^{\frac{1}{2}} \tag{5.155}$$

Setting $x = \sum_\psi[S,L](\overline{\psi}|\}\psi)(\psi\{|\overline{\psi'})$ and using equation (5.153) plus:

$$\left\langle\overline{\psi}\parallel(\mathbf{a}^\dagger\mathbf{a})^{(00)}\parallel\overline{\psi'}\right\rangle = -(N-1)\cdot[\overline{S},\overline{L}]^{\frac{1}{2}}\cdot[\tfrac{1}{2},l]^{-\frac{1}{2}}\cdot\delta(\overline{\psi},\overline{\psi'}) \tag{5.156}$$

it follows:

$$x = \delta(\overline{\psi},\overline{\psi'})\frac{\left([\tfrac{1}{2},l]^{\frac{1}{2}} - (N-1)[\tfrac{1}{2},l]^{-\frac{1}{2}}\right)[\overline{S},\overline{L}]^{\frac{1}{2}}}{N[\overline{S},\overline{L}]^{-\frac{1}{2}}\cdot[\tfrac{1}{2},l]^{-\frac{1}{2}}} = \delta(\overline{\psi},\overline{\psi'})\cdot[\overline{S},\overline{L}]\cdot\frac{(4l+3-N)}{N} \tag{5.157}$$

The below derivation of Redmond's [Redmond, 1954] cfp recursion formula is due to [Judd, 1967].

As a first step, the operators of equation (5.8a) are set between the states $\left\langle\overline{\psi}\right|$ and $\left|\overline{\psi'}\right\rangle$. This gives:

$$\left\langle\overline{\psi}\parallel(\mathbf{aa}^\dagger)^{\kappa k}\parallel\overline{\psi'}\right\rangle = (-1)^{\kappa+k}\left\langle\overline{\psi}\parallel(\mathbf{a}^\dagger\mathbf{a})^{\kappa k}\parallel\overline{\psi'}\right\rangle + \delta(\kappa,0)\delta(k,0)\delta(\overline{\psi},\overline{\psi'})\,[\overline{S},\overline{L},\tfrac{1}{2},l]^{\frac{1}{2}} \tag{5.158}$$

[2]Here it should be remembered that with equivalent electrons, S and L may not be summed over independently as not all SL combinations are allowed by the Pauli principle.
A simple example to illustrate this point:

$$\sum_{S,L}[S,L] = \binom{4l+2}{N} \to \sum_{d^2}[S,L] = 45 \text{ but } \sum_S[S]\cdot\sum_L[L] = 100$$

For l^2, the restriction that $S+L$ is even can be implemented by multiplying with the factor $\frac{1}{2}\left[1+(-1)^{S+L}\right]$. This then yields the correct result:

$$\sum_{d^2}[S,L] = \tfrac{1}{2}\sum_S[S]\cdot\sum_L[L] + \tfrac{1}{2}\sum_S(-1)^S[S]\cdot\sum_L(-1)^L[L] = 50-5 = 45$$

Next, equations (3.48) and (5.147) are used to calculate both reduced matrix elements:

$$\left\langle \overline{\psi} \parallel (\mathbf{a}\mathbf{a}^\dagger)^{\kappa k} \parallel \overline{\psi'} \right\rangle = N \cdot [\kappa, k]^{\frac{1}{2}} \cdot \sum_{\psi} (-1)^x \cdot [S, L] \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ \overline{S'} & \overline{S} & S \end{Bmatrix} \cdot \begin{Bmatrix} l & l & k \\ \overline{L'} & \overline{L} & L \end{Bmatrix} \cdot \left(\overline{\psi} \,|\}\psi\right)\left(\psi \,\{|\overline{\psi'}\right) \tag{5.159a}$$

with $x = \kappa + k + \overline{S'} + \overline{L'} + \frac{1}{2} + l + S + L$.
Similarly, application of equation (5.31) gives:

$$\left\langle \overline{\psi} \parallel (\mathbf{a}^\dagger\mathbf{a})^{\kappa k} \parallel \overline{\psi'} \right\rangle = (N-1) \cdot [\kappa, k]^{\frac{1}{2}} \cdot [\overline{S}, \overline{L}, \overline{S'L'}]^{\frac{1}{2}} \cdot \sum_{\psi''} (-1)^y \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ \overline{S'} & \overline{S} & S'' \end{Bmatrix} \cdot \begin{Bmatrix} l & l & k \\ \overline{L'} & \overline{L} & L'' \end{Bmatrix} \cdot \left(\overline{\psi} \,\{|\psi''\right)\left(\psi'' \,|\}\overline{\psi'}\right) \tag{5.159b}$$

with $y = \overline{S} + \overline{L} + \kappa + k + S'' + L'' - (\frac{1}{2} + l)$.

Next, both sides of equation (5.158) are multiplied with:
$\sum_{\kappa,k}[\kappa, k]^{\frac{1}{2}}(-1)^{-x} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ \overline{S'} & \overline{S} & S \end{Bmatrix} \begin{Bmatrix} l & l & k \\ \overline{L'} & \overline{L} & L \end{Bmatrix}$ and the summations are carried out by application of equations (2.11) and (2.12). This yields:

$$N \sum_{\psi} \left(\overline{\psi} \,|\}\psi\right)\left(\psi \,\{|\overline{\psi'}\right) = \delta(\overline{\psi}, \overline{\psi'}) \;+\; (N-1) \cdot [\overline{S}, \overline{L}, \overline{S'}, \overline{L'}]^{\frac{1}{2}}$$
$$\cdot \sum_{\psi''} (-1)^{\overline{S}+\overline{L}+\overline{S'}+\overline{L'}} \cdot \begin{Bmatrix} \overline{S'} & \frac{1}{2} & S \\ \overline{S} & \frac{1}{2} & S'' \end{Bmatrix} \cdot \begin{Bmatrix} \overline{L'} & l & L \\ \overline{L} & l & L'' \end{Bmatrix} \cdot \left(\overline{\psi} \,\{|\psi''\right)\left(\psi'' \,|\}\overline{\psi'}\right) \tag{5.160}$$

The LHS may be written as $N'\,(\overline{\psi}|\}\psi) = N'\,(\overline{\psi}|\}\nu' SL)$,
where the normalization factor N' is determined by:

$$N'^2 = N^2 \sum_{\nu} (\nu SL\{|\overline{\psi'})^2 \text{[Judd, 1967]} \tag{5.161a}$$

or alternatively [Hassitt, 1955] by:

$$N'^2 = N\left[1 + (N-1) \sum_{\psi''} (-1)^{2\overline{S'}} \cdot [\overline{S'}, \overline{L'}] \cdot \begin{Bmatrix} \overline{S'} & \frac{1}{2} & S \\ \overline{S'} & \frac{1}{2} & S'' \end{Bmatrix} \cdot \begin{Bmatrix} \overline{L'} & l & L \\ \overline{L'} & l & L'' \end{Bmatrix} \cdot \left(\overline{\psi'} \,\{|\psi''\right)^2\right] \tag{5.161b}$$

The final result is the known Redmond cfp recursion formula [Redmond, 1954]:

$$\left(\overline{\psi} \,|\}\psi\right) = 1/N'\left[\delta(\overline{\psi}, \overline{\psi'}) \;+\; (N-1) \cdot [\overline{S}, \overline{L}, \overline{S'}, \overline{L'}]^{\frac{1}{2}}\right.$$
$$\left. \cdot \sum_{\psi''} (-1)^{\overline{S}+\overline{L}+\overline{S'}+\overline{L'}} \cdot \begin{Bmatrix} \overline{S'} & \frac{1}{2} & S \\ \overline{S} & \frac{1}{2} & S'' \end{Bmatrix} \cdot \begin{Bmatrix} \overline{L'} & l & L \\ \overline{L} & l & L'' \end{Bmatrix} \cdot \left(\overline{\psi} \,\{|\psi''\right)\left(\psi'' \,|\}\overline{\psi'}\right)\right] \tag{5.162}$$

Each choice of godparent $\overline{\psi'}$ now involves a different value of N'.

The (N, ν)–dependence of cfp's is found by taking them as (proportional to the)

reduced matrix elements of the triple tensor $\mathbf{a}^{(qsl)}$ after application of equation (5.147a), the Wigner-Eckart theorem and equation (C.5).
For $\overline{\nu} = \nu - 1$:

$$\begin{aligned}
&\left(l^N\psi\{|l^{N-1}\overline{\psi}\right) = (-1)^N \cdot N^{-\frac{1}{2}} \cdot [S,L]^{-\frac{1}{2}} \cdot \left\langle \psi \parallel \mathbf{a}^{(qsl)}_{1/2} \parallel \overline{\psi} \right\rangle \\
= \;& (-1)^N \cdot N^{-\frac{1}{2}} \cdot [S,L]^{-\frac{1}{2}} \cdot (-1)^{2l+1-\frac{1}{2}(N+\nu)} \cdot \begin{pmatrix} \frac{1}{2}(2l+1-\nu) & \frac{1}{2} & \frac{1}{2}(2l+2-\nu) \\ \frac{1}{2}(2l+1-N) & \frac{1}{2} & -\frac{1}{2}(2l+2-N) \end{pmatrix} \left\langle \psi|||\mathbf{a}^{(qsl)}|||\overline{\psi} \right\rangle \\
= \;& (-1)^{4l+2-\nu} \cdot [S,L]^{-\frac{1}{2}} \cdot \left[\frac{(4l+4-N-\nu)}{2N(2l+3-\nu)(2l+2-\nu)} \right]^{\frac{1}{2}} \left\langle \psi|||\mathbf{a}^{(qsl)}|||\overline{\psi} \right\rangle
\end{aligned} \tag{5.163a}$$

whereas for $\overline{\nu} = \nu + 1$:

$$\begin{aligned}
&\left(l^N\psi\{|l^{N-1}\overline{\psi}\right) = (-1)^N \cdot N^{-\frac{1}{2}} \cdot [S,L]^{-\frac{1}{2}} \cdot \left\langle \psi \parallel \mathbf{a}^{(qsl)}_{1/2} \parallel \overline{\psi} \right\rangle \\
= \;& (-1)^N \cdot N^{-\frac{1}{2}} \cdot [S,L]^{-\frac{1}{2}} \cdot (-1)^{2l+1-\frac{1}{2}(N+\nu)} \cdot \begin{pmatrix} \frac{1}{2}(2l+1-\nu) & \frac{1}{2} & \frac{1}{2}(2l-\nu) \\ \frac{1}{2}(2l+1-N) & \frac{1}{2} & -\frac{1}{2}(2l+2-N) \end{pmatrix} \left\langle \psi|||\mathbf{a}^{(qsl)}|||\overline{\psi} \right\rangle \\
= \;& (-1)^{2l+1-\nu} \cdot [S,L]^{-\frac{1}{2}} \cdot \left[\frac{(N-\nu)}{2N(2l+2-\nu)(2l+1-\nu)} \right]^{\frac{1}{2}} \left\langle \psi|||\mathbf{a}^{(qsl)}|||\overline{\psi} \right\rangle
\end{aligned} \tag{5.163b}$$

Here, the completely (fully) reduced matrix elements $\left\langle \psi|||\mathbf{a}^{(qsl)}|||\overline{\psi} \right\rangle = \left\langle l\ SL\nu|||\mathbf{a}^{(qsl)}|||l\ \overline{SL\nu} \right\rangle$ or RCFPs are independent of the occupation number N.
They have been tabulated for the $p-$, $d-$ and $f-$shell [Gaigalas et al., 1998].
Equation (58b) from [Racah, 1943] is retrieved by using (5.163a) twice with $N = \nu$ in the denominator:

$$\frac{\left(l^N\psi\{|l^{N-1}\overline{\psi}\right)}{\left(l^\nu\psi\{|l^{\nu-1}\overline{\psi}\right)} = \left[\frac{(4l+4-N-\nu)\nu)}{2N(2l+2-\nu)} \right]^{\frac{1}{2}} \tag{5.164}$$

The example from [Judd, 1967] for $\overline{\nu} = \nu + 1$, found with [Racah, 1943] equation (58c), employs (5.163b) twice with $N = \nu + 2$ in the denominator:

$$\frac{\left(l^N\psi\{|l^{N-1}\overline{\psi}\right)}{\left(l^{\nu+2}\psi\{|l^{\nu+1}\overline{\psi}\right)} = \left[\frac{(N-\nu)(\nu+2)}{2N} \right]^{\frac{1}{2}} \tag{5.165}$$

Continuing using second quantization, one may also define coefficients of fractional grandparentage in terms of creation and annihilation operators:

$$\left\langle \psi \parallel (\mathbf{a}^\dagger\mathbf{a}^\dagger)^{\overline{S}\,\overline{L}} \parallel \psi' \right\rangle = \sqrt{N(N-1)} \cdot [S,L]^{\frac{1}{2}} \cdot \left(\psi\ \{|\psi', l^2(\overline{S}\,\overline{L})\right) \tag{5.166a}$$

$$\left\langle \psi' \parallel (\mathbf{aa})^{\overline{S}\,\overline{L}} \parallel \psi \right\rangle = (-1)^{(S+L)+1-(S'+L')} \cdot \sqrt{N(N-1)} \cdot [S,L]^{\frac{1}{2}} \cdot \left(\psi', l^2(\overline{S}\,\overline{L})\ |\}\psi\right) \tag{5.166b}$$

The so-called coefficients of (fractional) grandparentage introduced in equations (5.166) are found from:

$$\left(l^N(SL)\ \{|l^{N-2}(S_1L_1), l^2(S_2L_2)\right) = \sum_{\overline{S}\,\overline{L}} (-1)^{S_1+1+S} \cdot (-1)^{L_1+L} \cdot [\overline{S}, \overline{L}, S_2, L_2]^{\frac{1}{2}}$$
$$\cdot \begin{Bmatrix} S_1 & \frac{1}{2} & \overline{S} \\ \frac{1}{2} & S & S_2 \end{Bmatrix} \cdot \begin{Bmatrix} L_1 & l & \overline{L} \\ l & L & L_2 \end{Bmatrix} \cdot \left(l^N(SL)\ \{|l^{N-1}(\overline{S}\,\overline{L})\right) \cdot \left(l^{N-1}(\overline{S}\,\overline{L})\ \{|l^{N-2}(S_1L_1)\right) \tag{5.167}$$

With $S_2L_2 = 00 = {}^1S$, one obtains [Racah, 1943]:

$$\left(l^N(SL\nu)\ \{|l^{N-2}(SL\nu), l^2({}^1S)\right) = \left[\frac{(N-\nu)(4l+4-N-\nu)}{(4l+2)(N-1)N}\right]^{\frac{1}{2}} \tag{5.168}$$

The idea may be extended to non-equivalent electrons:

$$\left(l^{N-1}(S_2L_2\nu_2), l'(S_1L_1)|\}l^N(SL\nu), l'(S'L')\right) = (-1)^{S+L+1+l+l'+S_1+L_1}$$
$$\cdot [S, L, S_1, L_1]^{\frac{1}{2}} \cdot \left(l^{N-1}(S_2L_2\nu_2)|\}l^N(SL\nu)\right) \cdot \begin{Bmatrix} S & S' & \frac{1}{2} \\ S_1 & S_2 & \frac{1}{2} \end{Bmatrix} \cdot \begin{Bmatrix} L & L' & l' \\ L_1 & L_2 & l \end{Bmatrix} \tag{5.169}$$

Chapter 6

Matrix element calculation

6.1 Algebraical scheme

1. Find the statistical weighting factor:

$$|W| = (1 - \tfrac{1}{2}\delta_{ab}\delta_{cd}) \cdot \frac{\sqrt{\prod_\lambda q_\lambda! \prod_{\lambda'} q_{\lambda'}!}}{\prod_{\bar{\lambda}} q_{\bar{\lambda}}!} \text{ \& permutation phase} \tag{6.1}$$

   As an example[1]:

$$\begin{aligned}
&\left\langle p^6 d^8 p' \,|C|\, p^5 d^{10} \right\rangle \rightarrow W = \frac{\sqrt{6!\ 8!\ 1!\ 5!\ 10!}}{5!\ 8!} = +6\sqrt{15} \\
&\left\langle s\, p^4 \,|C|\, s^2\, p^2\, d \right\rangle \ \rightarrow W = +2\sqrt{6} \\
&\left\langle l'^{4l'+2}\, l^{N-2}\, l'' \right| C \left|\, l'^{4l'+1}\, l^N \right\rangle \ \rightarrow W = (-1)^N \cdot \sqrt{(4l'+2)N(N-1)}
\end{aligned} \tag{6.2}$$

2. Recouple bra and ket, in SL-coupling for spin and orbital part independently, to couple both operator- and spectator-electrons separately.

3. If the total operator rank $t \neq 0$, uncouple S and L from J.

4. Decouple the part that is not relevant to the operator.

5. Sum over intermediary quantum numbers and write down direct and exchange contributions separately.

6. The final result is expressed as the product of an angular matrix and the corresponding Slater integrals.

As mentioned with equation (3.58a) and (5.77), the Coulomb interaction may be written as:

$$\frac{1}{r_{12}} = \sum_k \frac{r_<^k}{r_>^{k+1}}\, C_1^{(k)} \cdot C_2^{(k)} = \sum_k (-1)^k [k]^{\frac{1}{2}} \frac{r_<^k}{r_>^{k+1}} \left(C_1^{(k)} C_2^{(k)} \right)_0^{(0)} \tag{6.3}$$

[1] see also subsection A.9

where equation (3.15) is used in the last step. The Slater integral is defined as:

$$\begin{aligned} R^k(ab,cd) &= \int_0^\infty\int_0^\infty P_a(r_1)P_b(r_2)\,\frac{r_<^k}{r_>^{k+1}}\,P_c(r_1)P_d(r_2)\,\mathrm{d}r_1\mathrm{d}r_2 \\ &= \int_0^\infty P_a(r)P_c(r)\,\frac{1}{r}\,Y_k(bd,r)\,\mathrm{d}r \end{aligned} \tag{6.4}$$

Some related symmetries:

$$\begin{aligned} &R^k(ab,cd) = R^k(ba,dc) = R^k(cd,ab) = R^k(dc,ba) \\ &R^k(ab,ab) = F^k(a,b) = R^k(ba,ba) \\ &R^k(ab,ba) = G^k(a,b) = R^k(aa,bb) = R^k(ba,ab) = G^k(b,a) \end{aligned} \tag{6.5}$$

To avoid large denominators, [Condon and Shortley, 1935] redefined the F^k- and G^k- Slater integrals in terms of reduced radial integrals F_k and G_k such that $F_k = F^k/D_k$ and $G_k = F^k/D_k$. Here, $D_0(ll) = 1$.
These so-called Slater denominators $D_k(ll')$ are listed below:

$D_1(sp) = 3$	$D_2(pp) = 25$	$D_2(dd) = 49$	$D_2(ff) = 225$
$D_2(sd) = 5$	$D_1(pd) = 15$	$D_4(dd) = 441$	$D_4(ff) = 1089$
$D_3(sf) = 7$	$D_2(pd) = 35$	$D_1(df) = 35$	$D_6(ff) = 184041/25$
	$D_3(pd) = 245$	$D_2(df) = 105$	
	$D_2(pf) = 175$	$D_3(df) = 315$	
	$D_4(pf) = 189$	$D_4(df) = 693$	
		$D_5(df) = 7623/5$	

(6.6)

The electrostatic inter-electronic repulsion in d^n configurations may also be described by the Racah parameters A, B and C defined as:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 1 & 0 & -49 \\ 0 & 1 & -5 \\ 0 & 0 & 35 \end{pmatrix} \begin{pmatrix} F_0 \\ F_2 \\ F_4 \end{pmatrix} \tag{6.7}$$

$$\begin{pmatrix} F_0 \\ F_2 \\ F_4 \end{pmatrix} = \begin{pmatrix} F^0 \\ F^2/49 \\ F^4/441 \end{pmatrix} \rightarrow \begin{pmatrix} F^0 \\ F^2 \\ F^4 \end{pmatrix} = \begin{pmatrix} A + 7C/5 \\ 49B + 7C \\ 63C/5 \end{pmatrix} \tag{6.8}$$

Similarly for f^n configurations:

$$\begin{pmatrix} E^0 \\ 9E^1 \\ 9E^2 \\ 3E^3 \end{pmatrix} = \begin{pmatrix} 1 & -10 & -33 & 286 \\ 0 & 70 & 231 & 2002 \\ 0 & 1 & -3 & 7 \\ 0 & 5 & 6 & -91 \end{pmatrix} \begin{pmatrix} F_0 \\ F_2 \\ F_4 \\ F_6 \end{pmatrix} \tag{6.9}$$

Table 6.1: Reduced matrix elements of the $C^{(k)}$ tensor

$\langle l \parallel C^{(k)} \parallel l' \rangle$	Value	$\langle l \parallel C^{(k)} \parallel l' \rangle$	Value
$\langle s \parallel C^{(0)} \parallel s \rangle$	1	$\langle s \parallel C^{(1)} \parallel p \rangle$	-1
$\langle p \parallel C^{(0)} \parallel p \rangle$	$\sqrt{3}$	$\langle s \parallel C^{(2)} \parallel d \rangle$	1
$\langle p \parallel C^{(2)} \parallel p \rangle$	$-\sqrt{\frac{6}{5}}$	$\langle s \parallel C^{(3)} \parallel f \rangle$	-1
$\langle d \parallel C^{(0)} \parallel d \rangle$	$\sqrt{5}$	$\langle p \parallel C^{(1)} \parallel d \rangle$	$-\sqrt{2}$
$\langle d \parallel C^{(2)} \parallel d \rangle$	$-\sqrt{\frac{10}{7}}$	$\langle p \parallel C^{(3)} \parallel d \rangle$	$\sqrt{\frac{9}{7}}$
$\langle d \parallel C^{(4)} \parallel d \rangle$	$\sqrt{\frac{10}{7}}$	$\langle p \parallel C^{(2)} \parallel f \rangle$	$\sqrt{\frac{9}{5}}$
$\langle f \parallel C^{(0)} \parallel f \rangle$	$\sqrt{7}$	$\langle p \parallel C^{(4)} \parallel f \rangle$	$-\sqrt{\frac{4}{3}}$
$\langle f \parallel C^{(2)} \parallel f \rangle$	$-2\sqrt{\frac{7}{15}}$	$\langle d \parallel C^{(1)} \parallel f \rangle$	$-\sqrt{3}$
$\langle f \parallel C^{(4)} \parallel f \rangle$	$\sqrt{\frac{14}{11}}$	$\langle d \parallel C^{(3)} \parallel f \rangle$	$\sqrt{\frac{4}{3}}$
$\langle f \parallel C^{(6)} \parallel f \rangle$	$-10\sqrt{\frac{7}{429}}$	$\langle d \parallel C^{(5)} \parallel f \rangle$	$-\sqrt{\frac{50}{33}}$

6.2 Nielson & Koster term order

The below term order given by [Nielson and Koster, 1963] is used:

Table 6.2: Terms in the p^N shell

p^2	${}^3_2P$	${}^1_0S$	${}^1_2D$
p^3	${}^4_3S$	${}^2_1P$	${}^2_3D$

Table 6.3: Terms in the d^N shell

d^2	${}^3_2P$	${}^3_2F$	${}^1_0S$	${}^1_2D$	${}^1_2G$							
d^3	${}^4_3P$	${}^4_3F$	${}^2_3P$	${}^2_{1,3}D_2$	${}^2_3F$	${}^2_3G$	${}^2_3H$					
d^4	${}^5_3D$	${}^3_{2,4}P_2$	${}^3_4D$	${}^3_{2,4}F_2$	${}^3_4G$	${}^3_4H$	${}^1_{0,4}S_2$	${}^1_{2,4}D_2$	${}^1_4F$	${}^1_{2,4}G_2$	${}^1_4I$	
d^5	${}^6_5S$	${}^4_3P$	${}^4_5D$	${}^4_3F$	${}^4_5G$	${}^2_5S$	${}^2_3P$	${}^2_{1,3,5}D_3$	${}^2_{3,5}F_2$	${}^2_{3,5}G_2$	${}^2_3H$	${}^2_5I$

Next, the total angular momenta for spin S_t and orbit L_t are ordered from low to high. Primary for S_t, with L_t increasing for every value of S_t. This leads to, e.g.:

ds : ${}^1D,{}^3D$

dp : ${}^1P,{}^1D,{}^1F,{}^3P,{}^3D,{}^3F$

pf : ${}^1D,{}^1F,{}^1G,{}^3D,{}^3F,{}^3G$

d^2s : $({}^3P)^2P, ({}^3P)^4P, ({}^3F)^2F, ({}^3F)^4F, ({}^1S)^2S, ({}^1D)^2D, ({}^1G)^2G$

p^2d : $({}^3P)^2PDF, ({}^3P)^4PDF, ({}^1S)^2D, ({}^1D)^2SPDFG$ (12 terms in total)

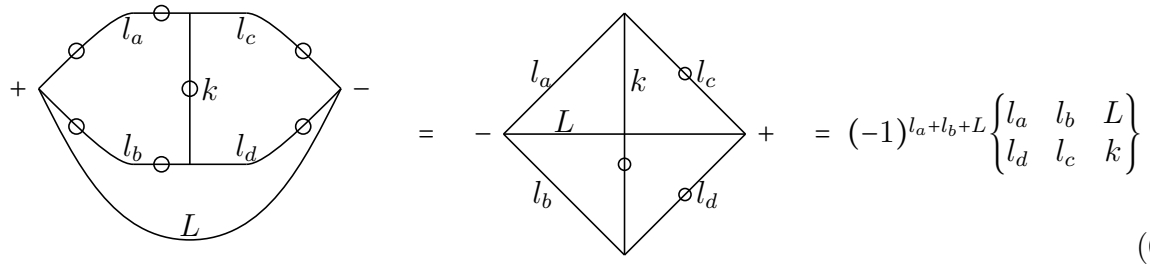
p^3d : $({}^4S)^3D, ({}^4S)^5D, ({}^2P)^1PDF, ({}^2P)^3PDF, ({}^2D)^1SPDFG, ({}^2D)^3SPDFG$ (18 terms)

6.3 Coulomb matrix elements

6.3.1 $l_a l_b \leftrightarrow l_c l_d$

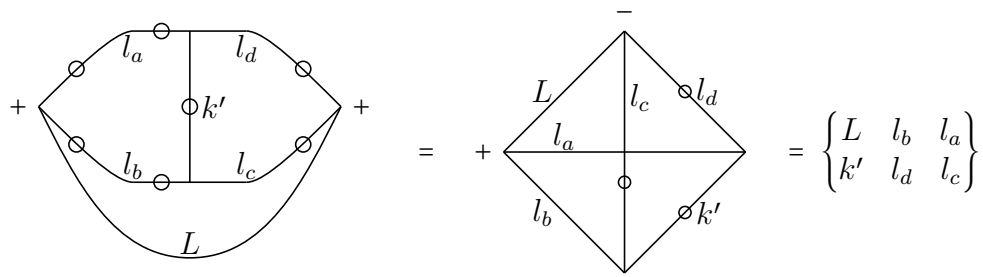
$$\begin{aligned}\langle l_a l_b(SL)\,|\,C\,|\,l_c l_d(SL)\rangle = W\Bigg(&\sum_k (-1)^k \left\langle l_a \parallel C^{(k)} \parallel l_c\right\rangle \left\langle l_b \parallel C^{(k)} \parallel l_d\right\rangle \\ &\cdot \mathbf{R^k(ab,cd)} \cdot (-1)^{l_c+l_d+L} \cdot \begin{Bmatrix} k & l_b & l_d \\ L & l_c & l_a \end{Bmatrix} \\ &+E\sum_{k'} \left\langle l_a \parallel C^{(k')} \parallel l_d\right\rangle \left\langle l_c \parallel C^{(k')} \parallel l_b\right\rangle \\ &\cdot \mathbf{R^{k'}(ab,dc)} \cdot (-1)^S \cdot \begin{Bmatrix} k' & l_b & l_c \\ L & l_d & l_a \end{Bmatrix}\Bigg)\end{aligned} \tag{6.10}$$

$W = (1 - \frac{1}{2}\delta_{ab}\delta_{cd})((1+\delta_{ab})(1+\delta_{cd}))^{\frac{1}{2}} = 1$ except when $a = b$ and $c \neq d$ or vice versa, in which case $W = \sqrt{2}$.
$E = (1-\delta_{ab})(1-\delta_{cd})$ excludes exchange if bra and/or ket contains equivalent electrons.
The direct angular factor after $\mathbf{R^k(ab,cd)}$ is graphically given as:



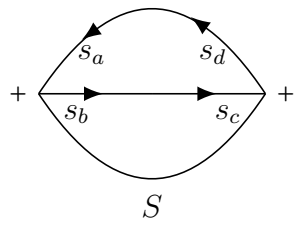
(6.11)

The exchange angular factor after $\mathbf{R^{k'}(ab,dc)}$ is given by:



(6.12)

The exchange produces, in addition to the recoupling, an extra minus sign as permutation phase.
Here, this Pauli exchange minus is included in the spin symbol $(-1)^{1+S}$:



(6.13)

Some important examples; in the case $\langle ll'(SL)\,|\,C\,|\,ll'(SL)\rangle$, vanishing reduced matrix elements may optionally be set to 1 to introduce effective, illegal-k operators.

$$\langle ll'(SL)\,|\,C\,|\,ll'(SL)\rangle = \sum_k \left\langle l \parallel C^{(k)} \parallel l\right\rangle \left\langle l' \parallel C^{(k)} \parallel l'\right\rangle \cdot \mathbf{F^k}(\mathbf{ll'}) \cdot (-1)^{l+l'+L} \cdot \begin{Bmatrix} k & l' & l' \\ L & l & l \end{Bmatrix} + \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l'\right\rangle^2 \cdot \mathbf{G^{k'}}(\mathbf{ll'}) \cdot (-1)^S \cdot \begin{Bmatrix} k' & l' & l \\ L & l' & l \end{Bmatrix} \tag{6.14a}$$

$$\left\langle l^2(SL)\,|\,C\,|\,l'^2(SL)\right\rangle = \sum_k (-1)^k \left\langle l \parallel C^{(k)} \parallel l'\right\rangle^2 \cdot \mathbf{R^k}(\mathbf{l^2}, \mathbf{l'^2}) \cdot (-1)^L \cdot \begin{Bmatrix} k & l & l' \\ L & l' & l \end{Bmatrix} \tag{6.14b}$$

$$\left\langle s^2(SL)\,|\,C\,|\,l^2(SL)\right\rangle = \delta(S,0)\delta(L,0) \cdot (-1)^l \cdot [l]^{-\frac{1}{2}} \cdot \mathbf{R^l}(\mathbf{s^2}, \mathbf{l^2}) \tag{6.14c}$$

$$\left\langle l^2(SL)\,|\,C\,|\,l'l''(SL)\right\rangle = \sqrt{2} \sum_k (-1)^k \left\langle l \parallel C^{(k)} \parallel l'\right\rangle \left\langle l \parallel C^{(k)} \parallel l''\right\rangle \cdot \mathbf{R^k}(\mathbf{l^2}, \mathbf{l'l''}) \cdot (-1)^L \cdot \begin{Bmatrix} k & l & l'' \\ L & l' & l \end{Bmatrix} \tag{6.14d}$$

$$\left\langle l^2(SL)\,|\,C\,|\,ss'(SL)\right\rangle = \sqrt{2} \cdot \delta(S,0)\delta(L,0) \cdot (-1)^l \cdot [l]^{-\frac{1}{2}} \cdot \mathbf{R^l}(\mathbf{l^2}, \mathbf{ss'}) \tag{6.14e}$$

6.3.2 $l^N \leftrightarrow l^{N-1}l'$

$$\begin{aligned} \left\langle l^N(SL)\,|\,C\,|\,l^{N-1}(S'_1L'_1)\,l'(S'L')\right\rangle = {} & (N-1)\sqrt{N}\,\delta(SS')\delta(LL') \\ \sum_k (-1)^k \left\langle l \parallel C^{(k)} \parallel l\right\rangle \left\langle l \parallel C^{(k)} \parallel l'\right\rangle \cdot \mathbf{R^k}(\mathbf{ll}, \mathbf{ll'}) \cdot \sum_{S_1L_1} \delta(S_1, S'_1) \cdot [L_1, L'_1]^{\frac{1}{2}} \\ \cdot \left(l^N\, SL\{|l^{N-1} S_1 L_1\right) \cdot \sum_{S_2L_2} \left(l^{N-1}\, S_1L_1\{|l^{N-2} S_2L_2\right) \left(l^{N-1}\, S'_1L'_1\{|l^{N-2} S_2L_2\right) \\ \cdot (-1)^{L+L_1+L'_1+L_2} \cdot \begin{Bmatrix} l & k & l \\ L'_1 & L_2 & L_1 \end{Bmatrix} \cdot \begin{Bmatrix} l & k & l' \\ L'_1 & L & L_1 \end{Bmatrix} \end{aligned} \tag{6.15}$$

For the Brillouin excitation $nl \to n'l$, there is a contribution of the potential as well:

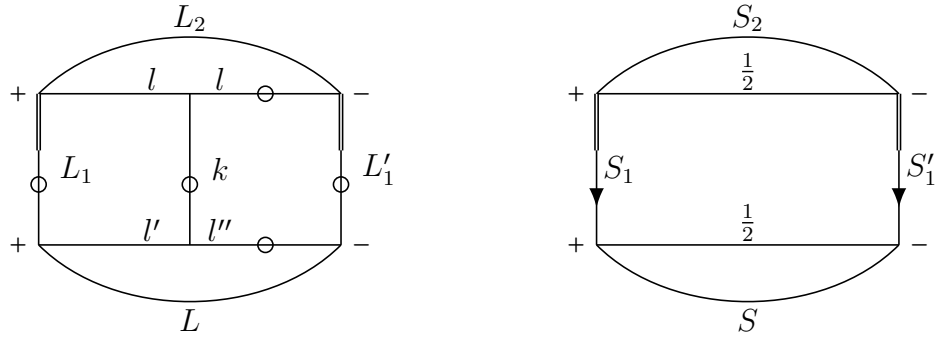
$$\begin{aligned} \left\langle l^N(SL)\,|\,U\,|\,l^{N-1}(S'_1L'_1)\,l'(S'L')\right\rangle &= \delta(l,l') \cdot \delta(\psi_1, \psi'_1) \cdot \sqrt{N} \cdot \left(l^N\, SL\{|l^{N-1} S_1 L_1\right) \cdot \langle nl|U|n'l'\rangle \\ = \delta(l,l') \cdot \delta(\psi_1, \psi'_1) \cdot (N-1)\sqrt{N} \cdot \left(l^N\, SL\{|l^{N-1} S_1 L_1\right) \cdot \left[\mathbf{R^0}(\mathbf{ll}, \mathbf{ll'}) - \sum_{k>0} \frac{\langle l \parallel C^{(k)} \parallel l\rangle^2}{(2l+1)(4l+1)} \mathbf{R^k}(\mathbf{ll}, \mathbf{ll'})\right] \end{aligned} \tag{6.16}$$

See equation (15.4b) further on for the potential matrix element. As to be expected, this cancels the $\mathbf{R^0}(\mathbf{ll}, \mathbf{ll'})$ term exactly and adds corrections to the remaining terms.

6.3.3 $l^N l' \leftrightarrow l^N l''$

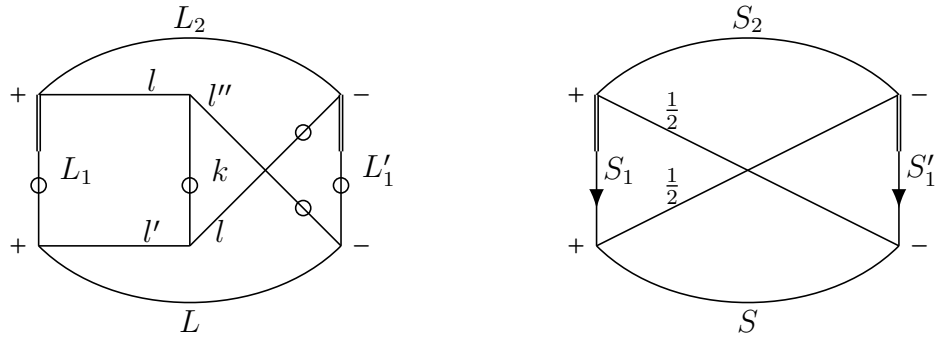
$$\begin{aligned}
&\left\langle l^N(S_1L_1)\,l'(SL)\,|\,C\,|\,l^N(S_1'L_1')\,l''(S'L')\right\rangle = N\cdot\delta(SS')\cdot\delta(LL')\cdot\delta(S_1,S_1')\\
&\sum_k \left\langle l\parallel C^{(k)}\parallel l\right\rangle\left\langle l'\parallel C^{(k)}\parallel l''\right\rangle\cdot\mathbf{R^k}(\mathbf{ll'},\mathbf{ll''})\cdot(-1)^{l+l'+L_1+L_1'+L}\cdot[L_1,L_1']^{\frac12}\cdot\begin{Bmatrix}L_1 & k & L_1'\\ l'' & L & l'\end{Bmatrix}\\
&\cdot\sum_{S_2L_2}(-1)^{L_2}\begin{Bmatrix}L_1 & k & L_1'\\ l & L_2 & l\end{Bmatrix}\cdot\left(l^N\,S_1L_1\{|l^{N-1}S_2L_2\right)\left(l^N\,S_1'L_1'\{|l^{N-1}S_2L_2\right)\\
&+N\cdot\delta(SS')\cdot\delta(LL')\cdot\sum_{k'}\left\langle l\parallel C^{(k')}\parallel l''\right\rangle\left\langle l'\parallel C^{(k')}\parallel l\right\rangle\cdot\mathbf{R^{k'}}(\mathbf{ll'},\mathbf{l''l})\cdot(-1)^{l''+l+S_1+S_1'}\\
&\cdot[S_1,S_1',L_1,L_1']^{\frac12}\sum_{S_2L_2}\begin{Bmatrix}\frac12 & S_2 & S_1'\\ \frac12 & S & S_1\end{Bmatrix}\begin{Bmatrix}L_2 & l & L_1'\\ l & k' & l''\\ L_1 & l' & L\end{Bmatrix}\cdot\left(l^N\,S_1L_1\{|l^{N-1}S_2L_2\right)\left(l^N\,S_1'L_1'\{|l^{N-1}S_2L_2\right)
\end{aligned}\tag{6.17}$$

This is graphically represented below. For the direct Coulomb interaction:



(6.18)

and for the exchange:



(6.19)

For $l' = l''$, one rather calculates $C - U$ with the additional potential contribution:

$$\begin{aligned}
&\left\langle l^N(S_1L_1)\,l'(SL)\,|\,U\,|\,l^N(S_1'L_1')\,l''(SL)\right\rangle = \delta(l',l'')\cdot\delta(\psi_1,\psi_1')\cdot\langle n'l'|U|n''l''\rangle\\
&= \delta(l',l'')\cdot\delta(\psi_1,\psi_1')\cdot N\cdot\left[\mathbf{R^0}(\mathbf{ll'},\mathbf{ll''}) - \tfrac12\sum_{k'}[l,l']^{-1}\left\langle l\parallel C^{(k')}\parallel l'\right\rangle^2\mathbf{R^{k'}}(\mathbf{ll'},\mathbf{l''l})\right]
\end{aligned}\tag{6.20}$$

This exactly cancels the $\mathbf{R^0}(\mathbf{ll'},\mathbf{ll''})$ term and corrects the exchange contributions.

6.4 Magnetic matrix elements

For energy operators with $k \neq 0$, it is customary to use reduced instead of full matrix elements, with the J–dependence decoupled by means of equation 3.43.
An important case is the spin-orbit interaction with $k = 1$:

$$\langle \Psi_{SLJ} |\, \zeta \,| \Psi_{S'L'J} \rangle = -\frac{1}{\sqrt{3}} \cdot (-1)^{L+S'+J} \begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix} \langle \Psi_{SL} \parallel \zeta \parallel \Psi_{S'L'} \rangle \tag{6.21}$$

Examples of such reduced matrix elements (appearing e.g. in EL-SO, see section (15.5)) are:

$$\begin{aligned} \langle l \parallel \zeta \parallel l \rangle &= -3\,(l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot \zeta_l \\ \rightarrow \langle l \mid \zeta \mid l \rangle &= \sqrt{3} \cdot (l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot (-1)^{\frac{1}{2}+l+j} \cdot \begin{Bmatrix} \frac{1}{2} & l & j \\ l & \frac{1}{2} & 1 \end{Bmatrix} \cdot \zeta_l \end{aligned} \tag{6.22}$$

$$\begin{aligned} \left\langle l^2(SL) \parallel \zeta_l \parallel l^2(S'L') \right\rangle &= 6 \cdot [S, L, S', L']^{\frac{1}{2}} \\ &\cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & L' & 1 \\ l & l & l \end{Bmatrix} (l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot \zeta_l \end{aligned} \tag{6.23}$$

$$\begin{aligned} \langle ll'(SL) \parallel \zeta_l \parallel ll'(S'L') \rangle &= 3 \cdot (-1)^{S'+L'+l+l'} \cdot [S, L, S', L']^{\frac{1}{2}} \\ &\cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & L' & 1 \\ l & l & l' \end{Bmatrix} (l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot \zeta_l \end{aligned} \tag{6.24}$$

$$\begin{aligned} \langle ll'(SL) \parallel \zeta_{l'} \parallel ll'(S'L') \rangle &= 3 \cdot (-1)^{S+L+l+l'} \cdot [S, L, S', L']^{\frac{1}{2}} \\ &\begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & L' & 1 \\ l' & l' & l \end{Bmatrix} (l'(l'+1)(2l'+1)/2)^{\frac{1}{2}} \cdot \zeta_{l'} \end{aligned} \tag{6.25}$$

$$\begin{aligned} \left\langle ll'(SL) \parallel \zeta_{ab} \parallel l^2(S'L') \right\rangle &= \delta(l,l') \cdot 3\sqrt{2} \cdot (-1)^{S+L} \cdot [S, L, S', L']^{\frac{1}{2}} \\ &\begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & L' & 1 \\ l & l & l \end{Bmatrix} (l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot \zeta_{ab} \end{aligned} \tag{6.26}$$

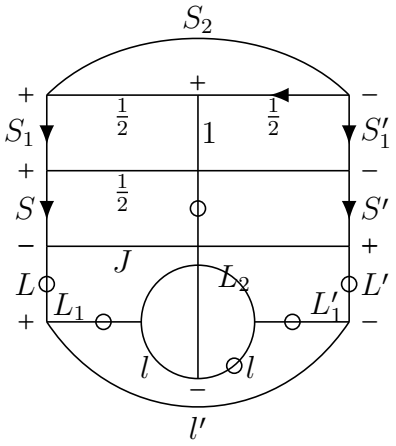
For higher values N of l^N, the matrix elements can either be calculated directly or with chain formulae starting from its parent configuration.
An example of a direct calculation using equations (5.31) and (5.89):

$$\begin{aligned} \left\langle l^N SL \parallel \zeta_l \parallel l^N S'L' \right\rangle &= 3N \cdot (l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot \zeta_l \cdot [S, L, S', L']^{\frac{1}{2}} \\ \cdot \sum_{\overline{S}\,\overline{L}} (-1)^{S+L-\left(\frac{1}{2}+l\right)+\overline{S}+\overline{L}} &\cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ S & S' & \overline{S} \end{Bmatrix} \cdot \begin{Bmatrix} l & l & 1 \\ L & L' & \overline{L} \end{Bmatrix} \cdot \left(l^N SL \,\{|l^{N-1}\overline{S}\,\overline{L}\right) \left(l^N S'L' \,\{|l^{N-1}\overline{S}\,\overline{L}\right) \end{aligned} \tag{6.27}$$

An example in a mixed configuration:

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'(SL)\;\|\;\zeta_l\;\|\;l^N(S_1'L_1')\,l'(S'L')\right\rangle &= -3N\cdot\left(l(l+1)(2l+1)/2\right)^{\frac{1}{2}}\cdot\zeta_l\\ \cdot(-1)^{l'+l}\cdot[S,S',S_1,S_1',L,L',L_1,L_1']^{\frac{1}{2}}\cdot&\begin{Bmatrix}L_1 & 1 & L_1'\\ L' & l' & L\end{Bmatrix}\cdot\begin{Bmatrix}S_1 & 1 & S_1'\\ S' & \frac{1}{2} & S\end{Bmatrix}\\ \cdot\sum_{\overline{S}\,\overline{L}}(-1)^{\overline{S}+\overline{L}+L'-S'}\cdot&\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & 1\\ S_1 & S_1' & \overline{S}\end{Bmatrix}\cdot\begin{Bmatrix}l & l & 1\\ L_1 & L_1' & \overline{L}\end{Bmatrix}\cdot\left(l^N\,S_1L_1\{|l^{N-1}\overline{S}\,\overline{L}\right)\left(l^N\,S_1'L_1'\{|l^{N-1}\overline{S}\,\overline{L}\right)\end{aligned} \tag{6.28}$$

The latter may graphically be represented as:



(6.29)

Chapter 7

Transition probabilities(1)

Einstein related the spontaneous emission ($A_{2\to1}$), absorption ($B_{1\to2}$) and stimulated emission (B_{21}) coefficients as follows (SI):

$$B_{21} = \frac{g_1}{g_2} B_{12} \tag{7.1a}$$

$$A_{21} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{21} \tag{7.1b}$$

The combined transition probability $\sum_f A_{if}$ of an upper level $|i\rangle$ to all lower levels $|f\rangle$ is closely related to the lifetime τ_i of level $|i\rangle$:

$$\tau_i = \left(\sum_f A_{if} \right)^{-1} = \left(\sum_{E_f<E_i} A_{if} \right)^{-1} \tag{7.2}$$

With the degeneracy factor $g = 2j + 1$ and $k = \omega/c$, Fermi's golden rule gives for electric dipole transitions:

$$g_2 \cdot A_{21} = \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{4}{3} \cdot \frac{k^3}{\hbar} \cdot \left|\langle \psi_2 \,|\, \vec{r} \,|\, \psi_1 \rangle\right|^2 \text{(SI)} = \frac{4}{3} \cdot (2\pi\sigma)^3 \cdot \left|\langle \psi_2 \,|\, \vec{r} \,|\, \psi_1 \rangle\right|^2 \text{(au)} \tag{7.3}$$

Here, $g_2 \cdot A_{21} = g_1 \cdot A_{12}$ and the rate of energy loss $-\mathrm{d}W/\mathrm{d}t = A_{21} \cdot \hbar\omega$.

It is customary here to use atomic units where $e = \hbar = m_e = 1/4\pi\varepsilon_0 \equiv 1$ and $k = 2\pi\sigma$, so one arrives at the well-known form of the Einstein coefficient for spontaneous electric dipole emission:

$$g_2 \cdot A_{21}(\gamma J, \gamma' J') = \frac{32\pi^3\sigma^3}{3} \cdot \left|\left\langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \right\rangle\right|^2 = \frac{32\pi^3\sigma^3}{3} \cdot S_{21}(\gamma J, \gamma' J') \tag{7.4}$$

The pertinent one-electron integral is:

$$\left\langle nl \parallel rC^{(1)} \parallel n'l' \right\rangle = \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \int_0^\infty P_{nl}\, r\, P_{n'l'}\, \mathrm{d}r \tag{7.5}$$

The physical line strengths are calculated in intermediate coupling by transforming the SL value with the eigenvectors of the actual atomic states:

$$S_{if} = \left| \sum_{SL\nu S'L'\nu'} (i|SL\nu\, J)\; S^{\frac{1}{2}}(SL\nu\, J, S'L'\nu'\, J')\; (S'L'\nu'\, J'|f) \right|^2 \tag{7.6}$$

7.1 Electric dipole transitions(1)

For a transition from an 'upper' state 2 to a 'lower' state 1 with $g_2 = 2J_2 + 1$ and $g_1 = 2J_1 + 1$, one finds[1] for the **transition probability**, with A_{E1} in s^{-1} and σ in cm^{-1}:

$$g_2\, A_{E1} = 2.0261269 \times 10^{-6} \cdot \sigma^3 \cdot \left|\left\langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \right\rangle\right|^2 \tag{7.7}$$

The **oscillator strength**, on the other hand, may be seen as the quantum efficiency of an atomic absorption (or emission) w.r.t. the absorption (or emission) rate Γ of 3 classical single electron oscillators at the same frequency ω_{21}.

The radial electric field component $E_\perp$ of an electron decreases as r^{-2}; the tangential component $E_\parallel$ vanishes at constant speed. With an electron acceleration $\ddot{r}$, the finite speed of light causes a retardation effect and continuity of the electric field then yields a tangential component as well:

$$\frac{E_\parallel}{E_\perp} = \ddot{r}\,\frac{t\sin\theta}{c} = \ddot{r}\,\frac{r\sin\theta}{c^2} \rightarrow \vec{E}_\parallel = \frac{e\,\vec{\ddot{r}}\sin\theta}{4\pi\varepsilon_0 c^2 r} \text{ with } f = \frac{1}{4\pi\varepsilon_0} \text{ and } E_\perp = f\frac{e}{r^2} \tag{7.8}$$

The Poynting vector $\mathbf{S} = \mu_0^{-1}(\mathbf{E}\times\mathbf{B})$ then becomes $\mathbf{S} = \varepsilon_0 c E_\parallel^2\,\mathbf{e}_r = (e^2\ddot{r}^2\sin^2\theta)/(16\pi^2\varepsilon_0 r^2 c^3)\,\mathbf{e}_r$. The corresponding radiated power through a spherical shell at distance r yields Larmor's formula:

$$P = \int \mathbf{S}\cdot \mathrm{d}\boldsymbol{\sigma} = \int_0^\pi S\cdot 2\pi r^2 \sin\theta \mathrm{d}\theta = \frac{e^2\ddot{r}^2}{6\pi\varepsilon_0 c^3} = \frac{e^2\omega^4 r^2}{6\pi\varepsilon_0 c^3} \text{ using } \int_0^\pi \sin^3\theta\,\mathrm{d}\theta = \frac{4}{3} \tag{7.9}$$

The damped, oscillating electron is now described classically by $\ddot{r} + \Gamma\dot{r} + \omega^2 r = 0$. Small radiation losses ($\Gamma \ll \omega$) imply harmonic motion $\ddot{r} \approx -\omega^2 r$. Solving for F_{rad} from $P = -F_{\mathrm{rad}}\dot{r}$ after averaging over one cycle, $\ddot{r} + \omega^2 r = -\Gamma\dot{r} = F_{\mathrm{rad}}/m \rightarrow P = \Gamma m\dot{r}^2$ and $\dot{r} = \omega r$, finally yields:

$$\Gamma = \frac{e^2\,\omega^2}{6\,\pi\,\varepsilon_0\,m\,c^3} \tag{7.10}$$

With the above expression for Γ, the actual definition of oscillator strength in SI becomes from: $-\mathrm{d}W/\mathrm{d}t = A_{21}\cdot\hbar\omega = \Gamma\cdot(-3f_{21}\cdot\hbar\omega)$ and $g_1\cdot f_{12} = -g_2\cdot f_{21}$ (absorption oscillator strengths assumed positive):

$$g_1\cdot f_{12} = \frac{g_2\cdot A_{21}}{3\,\Gamma} = \frac{2\pi\varepsilon_0\, mc^3}{e^2\,\omega^2}\cdot g_2\cdot A_{21} \;\text{ (or in au:) }\; g_1\cdot f_{12} = \frac{\lambda^2}{8\pi^2\alpha}\cdot g_2\cdot A_{21} \tag{7.11}$$

It thus follows:

$$g_1\cdot f_{12} = \frac{2}{3}\cdot\frac{mc}{\hbar}\cdot k\cdot S = \frac{4\pi\, mc}{3\hbar}\cdot\sigma\cdot S \tag{7.12}$$

Similar to equation (7.7), the oscillator strength is in practice calculated with[2]:

$$g_1\cdot f_{E1} = 3.037556835\times 10^{-6}\cdot\sigma\cdot\left|\left\langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \right\rangle\right|^2 \tag{7.13}$$

With the immediate consequence:

$$g_1\cdot f_{12} = \frac{1.4991938}{\sigma^2}\cdot g_2\cdot A_{21} \tag{7.14}$$

[1] The constant corresponds to the SI value of $fe^2/\hbar\cdot 4/3\cdot(2\pi)^3\cdot 10^6\cdot a_0^2$ with $f = (4\pi\varepsilon_0)^{-1}$. The factor 10^6 translates m^{-3} into cm^{-3}, and a_0^2 converts the linestrength S_{if} from SI to au.

[2] Here, the constant corresponds to the SI value of $(4\pi\, mc/3\hbar)\cdot 10^2\cdot a_0^2$.

As the oscillator strength f_{ij} indicates the fraction of oscillator energy emitted into each channel $j \to i$, the f-sum rule follows $\sum_j f_{ij} = 1$ if i is the lowest level. If i is an excited level, the f-sum (or Thomas-Reiche-Kuhn) rule reads:

$$\sum_{j,k} (f_{ij} + f_{ik}) = 1 \tag{7.15}$$

By definition, summing the oscillator strength over all possible (bound and continuum) transitions will yield the number N of active electrons:

$$\sum\!\!\!\!\!\!\int_j f_{ij} = N \tag{7.16}$$

7.1.1 Some electric dipole line strengths

Calculation of $S^{\frac{1}{2}}(SLJ, S'L'J') = \langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \rangle$ with $T^{(1)} = rC^{(1)}$ is required to apply equations (7.6) and (7.7). As $T^{(1)} = -\sqrt{2/3} \cdot \langle l \parallel C^{(1)} \parallel l' \rangle (\mathbf{a}^\dagger \mathbf{b})^{(01)1} \cdot r$, equation (3.82) -or (5.25)- is used to find the $J-$dependence:

$$\left\langle \gamma SLJ \parallel T^{(1)} \parallel \gamma' S'L'J' \right\rangle = \delta(S,S') \cdot \sqrt{2/3} \cdot (-1)^{J+L'+S} \cdot [J,J']^{\frac{1}{2}} \cdot [S]^{-\frac{1}{2}} \cdot \begin{Bmatrix} J & 1 & J' \\ L' & S & L \end{Bmatrix}$$
$$\cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \int_0^\infty P_{nl}\, r\, P_{n'l'} \mathrm{d}r \cdot \left\langle \gamma SL \parallel (\mathbf{a}^\dagger \mathbf{b})^{(01)} \parallel \gamma' S'L' \right\rangle \tag{7.17}$$

To calculate $\langle \gamma SL \parallel (\mathbf{a}^\dagger \mathbf{b})^{(01)} \parallel \gamma' S'L' \rangle$, bra and ket are decoupled into a spectator factor $S_1 L_1$ and an active part $\langle a \parallel (\mathbf{a}^\dagger \mathbf{b})^{(01)} \parallel b \rangle = -\sqrt{3}$ to apply equation (3.55a) or (3.55b). Some relevant examples:

$$\begin{aligned} \left\langle \tfrac{1}{2} l j \parallel T^{(1)} \parallel \tfrac{1}{2} l' j' \right\rangle &= (-1)^{j+l+\frac{1}{2}} [j,j']^{\frac{1}{2}} \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \begin{Bmatrix} j & 1 & j' \\ l' & \frac{1}{2} & l \end{Bmatrix} \int_0^\infty P_{nl}\, r\, P_{n'l'} \mathrm{d}r \\ &= (-1)^{j'-\frac{1}{2}} \cdot [j,j']^{\frac{1}{2}} \cdot \begin{pmatrix} j & j' & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \int_0^\infty P_{nl}\, r\, P_{n'l'} \mathrm{d}r \end{aligned} \tag{7.18}$$

where identity (C.52) from [Brink and Satchler, 1968], Appendix II is used in the last line. Equations (3.55b), (5.20) and (7.17) are used to find:

$$\left\langle l^N (S_1 L_1) l' (SLJ) \parallel T^{(1)} \parallel l^N (S_1 L_1) l'' (S'L'J') \right\rangle = \delta(S,S') \cdot (-1)^{J+L'+S} \cdot [J,J',L,L']^{\frac{1}{2}}$$
$$\cdot \left\langle l' \parallel C^{(1)} \parallel l'' \right\rangle \cdot \int_0^\infty P_{n'l'}\, r\, P_{n''l''} \mathrm{d}r \cdot \begin{Bmatrix} J & 1 & J' \\ L' & S & L \end{Bmatrix} \cdot (-1)^{L_1+l''+L} \cdot \begin{Bmatrix} L & 1 & L' \\ l'' & L_1 & l' \end{Bmatrix} \tag{7.19}$$

$$\left\langle l^N (SLJ) \parallel T^{(1)} \parallel l^{N-1} (S_1 L_1) l' (S'L'J') \right\rangle = \delta(S,S') \cdot \sqrt{N} \cdot (-1)^{J+L'+S} \cdot [J,J',L,L']^{\frac{1}{2}}$$
$$\left(l^N\, SL\{|l^{N-1}\, S_1 L_1\right) \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \int_0^\infty P_{nl}\, r\, P_{n'l'} \mathrm{d}r \cdot \begin{Bmatrix} J & 1 & J' \\ L' & S & L \end{Bmatrix} \cdot (-1)^{L_1+l'+L} \cdot \begin{Bmatrix} L & 1 & L' \\ l' & L_1 & l \end{Bmatrix} \tag{7.20}$$

Obviously, equations (7.19) and (7.20) both reduce to equation (7.18) for $N = 0$ and $N = 1$, respectively.

7.1.2 Hyperfine transitions and sum rule

If hyperfine structure is involved, equation (3.51a) is used to uncouple the nuclear quantum numbers and subsequently proceed as in the above:

$$\left\langle \gamma JIF \parallel T^{(1)} \parallel \gamma' J' I F' \right\rangle = (-1)^{J+I+F'+1} [F,F']^{\frac{1}{2}} \begin{Bmatrix} F & 1 & F' \\ J' & I & J \end{Bmatrix} \left\langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \right\rangle \quad (7.21)$$

Obviously for $I = 0$, equation (7.21) reduces to $\langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \rangle$ again.
Summed over the total angular momenta F and F', the line strength becomes:

$$\begin{aligned} \sum_{F,F'} S(JIF, J'IF') &= \sum_{F,F'} \left| \left\langle \gamma JIF \parallel T^{(1)} \parallel \gamma' J' I F' \right\rangle \right|^2 \\ &= \sum_{F,F'} [F,F'] \cdot \begin{Bmatrix} F & 1 & F' \\ J' & I & J \end{Bmatrix}^2 \cdot \left| \left\langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \right\rangle \right|^2 \\ &= [I] \cdot \left| \left\langle \gamma J \parallel T^{(1)} \parallel \gamma' J' \right\rangle \right|^2 \end{aligned} \quad (7.22)$$

It follows that hyperfine structure merely distributes the original line strength with weighting factors:

$$\frac{[F,F']}{[I]} \cdot \begin{Bmatrix} F & 1 & F' \\ J' & I & J \end{Bmatrix}^2$$

7.1.3 Cross sections

In the following, it is assumed that the line shape function is peaked sharply enough: $L(\omega) \approx \delta(\omega - \omega_{21})$ to warrant the replacement $\omega \to \omega_{21}$. The photoionization cross section (PICS) in Mb of an atom in a state i by a photon of energy $\hbar\omega$ is proportional to the line strength S as given by the formula:

$$\begin{aligned} \sigma &= \hbar\omega_{21} \cdot \frac{B_{12}^{\omega}}{c} = \frac{\hbar\omega}{g_1 \cdot c} \cdot \frac{\pi^2 c^3}{\hbar\omega^3} \cdot g_2 \cdot A_{21} = \frac{1}{4} \cdot \left(\frac{g_2}{g_1} \right) \cdot \lambda_{21}^2 \cdot A_{21} \\ &= \frac{\hbar\omega}{g_1 \cdot c} \cdot \frac{\pi^2 c^3}{\hbar\omega^3} \cdot \frac{4}{3} \cdot \frac{\omega^3}{\hbar c^3} \cdot S = \frac{4\pi^2 \alpha\omega}{3g_1} \cdot S(\text{au}) \end{aligned} \quad (7.23)$$

To convert the last expression from au to the SI unit Mb, one multiplies by a_0^2:

$$\sigma_{PI} = \frac{4\pi^2 \cdot \alpha \cdot a_0^2 \cdot \omega}{3g_1} \cdot S \quad (7.24)$$

Given in terms of the differential oscillator strength:

$$\sigma_{PI}(E) = \frac{\pi h e^2}{mc} \cdot \frac{\mathrm{d}f}{\mathrm{d}E}(SI) = 4\pi^2 \cdot \alpha \cdot a_0^2 \cdot \frac{\mathrm{d}f}{\mathrm{d}E} \quad (7.25)$$

Remember that hcR_∞ =Ry=13.6 eV= $\frac{1}{2}$ in au.

The electron density n_e equals:

$$n_e = \rho \cdot \frac{Z}{m_{\text{at}}} = \rho \cdot \frac{Z}{M \cdot u} \quad (7.26)$$

with M the molecular (atomic) mass. Therefore, the number of absorbing electrons in a volume of area S_A and depth $\mathrm{d}x$ becomes: $N = n_e \cdot S_A \cdot \mathrm{d}x$. The absorbed intensity is by definition:

$$I_{\text{abs}} = -\mathrm{d}I = \frac{N \cdot \sigma}{S_A} I = (n_e \cdot \sigma \cdot \mathrm{d}x)\, I \rightarrow \frac{\mathrm{d}I}{\mathrm{d}x} = -n_e \cdot \sigma \cdot I = -\mu I \rightarrow I = I_0 \cdot \exp(-\mu \cdot x). \tag{7.27}$$

The relation between the absorption coefficient μ and the cross section σ is called the optical theorem: $\mu = n_e \cdot \sigma$; the quantity $(\mu \cdot x)$ is the optical depth or optical thickness. It follows directly:

$$\sigma = \frac{1}{n_e \cdot x} \cdot \ln\left(\frac{I_0}{I}\right) \tag{7.28}$$

The above can be compared with an expression, in Mb, for the experimental atomic cross section:

$$\sigma = 0.1035 \cdot \left(\frac{T}{p \cdot x}\right) \cdot \ln\left(\frac{I_0}{I}\right) \tag{7.29}$$

with T the temperature in K, p the pressure in Torr and x the absorption path length in cm, and in SI: $kT/p = 1/n_e$.
The absorption coefficient is directly related to the half-width by:

$$d_{\frac{1}{2}} = \frac{\ln 2}{\mu} = \frac{\ln 2}{n_e \cdot \sigma} \tag{7.30}$$

In LTE, the relation between the specific electron density n_e^i of the initial state $|i\rangle$ and the total electron density n_e of the specimen reads:

$$\frac{n_e^i}{n_e} = \frac{g_i \cdot \exp(-E_i/kT)}{\sum_j g_j \cdot \exp(-E_j/kT)} \tag{7.31}$$

where the sum in the partition function in the denominator runs over all relevant atomic states.
Elastic scattering of radiation by a free electron is described the Thomson cross section, derived from the related classical radius of the electron $r_e = \alpha \cdot \lambda\!\!\!^{-}_e$:

$$\frac{fe^2}{r_e} = mc^2 \rightarrow r_e = \frac{fe^2}{mc^2} = \alpha^2 a_0 = 2.818 \cdot 10^{-15}\ \text{m} \rightarrow \sigma_T = \frac{8\pi}{3} r_e^2 = 6.6525 \cdot 10^{-29}\ \text{m}^2 \tag{7.32}$$

with r_e and σ_T the classical electron radius and the Thomson cross section.

7.2 Length and velocity

For quite general operators U, the below commutator relation with the Hamiltonian $\mathcal{H}$ holds:

$$\langle f \,|\, U \,|\, i \rangle = (\varepsilon_i - \varepsilon_f)^{-1}\ \langle f \,|\, [U, \mathcal{H}] \,|\, i \rangle \ \text{ with } \omega = \varepsilon_f - \varepsilon_i. \tag{7.33}$$

For the dipole transition operator, it follows:

$$\langle f \,|\, \vec{r} \,|\, i \rangle = \frac{\langle f \,|\, \nabla \,|\, i \rangle}{\varepsilon_i - \varepsilon_f} \tag{7.34}$$

In SI, as $-i\hbar\,\nabla\Phi = \vec{p}\,\Phi$, this relation reads:

$$\left\langle \psi_f \right| \sum_j \vec{r}_j \left| \psi_i \right\rangle = \frac{i\hbar}{m(\varepsilon_i - \varepsilon_f)} \left\langle \psi_f \right| \sum_j \vec{p}_j \left| \psi_i \right\rangle = \frac{\hbar^2}{m\Delta\varepsilon} \left\langle \psi_f \right| \sum_j \nabla_j \left| \psi_i \right\rangle$$

7.2.1 Commutation[a]

The traditional single electron Hamiltonian is written in atomic units as:

$$\mathcal{H} = -\tfrac{1}{2}\left\{ r^{-1}\frac{\partial^2}{\partial r^2} r - \frac{\mathcal{L}^2}{r^2} \right\} - \frac{Z}{r} + V(r)$$

where $\vec{r} = rC^{(1)}$ and $\mathcal{L}$ represents the one-electron angular momentum operator. The commutator now becomes:

$$[\vec{r}, \mathcal{H}] = -\tfrac{1}{2}\left[rC^{(1)} \left\{ r^{-1}\frac{\partial^2}{\partial r^2} r - \frac{\mathcal{L}^2}{r^2} \right\} - \left\{ r^{-1}\frac{\partial^2}{\partial r^2} r - \frac{\mathcal{L}^2}{r^2} \right\} rC^{(1)} \right]$$

The usual substitution $R_{nl} = P_{nl}/r$ is made. After summation over the degenerate magnetic sublevels and using the WE theorem, the following reduced matrix element appears for the first term:

$$\begin{aligned} \left\langle nl \parallel C^{(1)} \frac{\partial^2}{\partial r^2} r - C^{(1)} \frac{\mathcal{L}^2}{r^2} \parallel n'l' \right\rangle &= \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \left\langle r^{-1} P_{nl} \left| \frac{\partial^2}{\partial r^2} r - \frac{l'(l'+1)}{r} \right| r^{-1} P_{n'l'} \right\rangle \\ &= \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \int_0^\infty P_{nl} \left[\frac{\partial^2}{\partial r^2} r - \frac{l'(l'+1)}{r} \right] P_{n'l'} \, \mathrm{d}r \end{aligned}$$

Here, before factorizing the angular part $\langle l \parallel C^{(1)} \parallel l' \rangle$, $\mathcal{L}^2$ first operates to the right. In the second term, $\mathcal{L}^2$ first operates to the left:

$$\left\langle nl \parallel -r^{-1}\frac{\partial^2}{\partial r^2} r^2 C^{(1)} + \frac{\mathcal{L}^2}{r} C^{(1)} \parallel n'l' \right\rangle = \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \int_0^\infty P_{nl} \left[-\frac{\partial^2}{\partial r^2} r - 2\frac{\partial}{\partial r} + \frac{l(l+1)}{r} \right] P_{n'l'} \, \mathrm{d}r$$

Collecting terms:

$$\begin{aligned} \left\langle nl \parallel rC^{(1)} \parallel n'l' \right\rangle &= \frac{\langle nl \parallel [rC^{(1)}, \mathcal{H}] \parallel n'l' \rangle}{\varepsilon_{n'} - \varepsilon_n} \\ &= \frac{\langle l \parallel C^{(1)} \parallel l' \rangle}{\varepsilon_{n'} - \varepsilon_n} \left\langle r^{-1} P_{nl} \left| \frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r} \right| r^{-1} P_{n'l'} \right\rangle \\ &= \frac{\langle l \parallel C^{(1)} \parallel l' \rangle}{\varepsilon_{n'} - \varepsilon_n} \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r} \right] P_{n'l'} \, \mathrm{d}r \end{aligned} \tag{7.35}$$

In terms of the pertinent integrals, the correspondence thereby becomes finally:

$$\begin{aligned} \left\langle nl \parallel rC^{(1)} \parallel n'l' \right\rangle &= \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \int_0^\infty P_{nl}\, r\, P_{n'l'} \, \mathrm{d}r \\ &= \frac{\langle l \parallel C^{(1)} \parallel l' \rangle}{\varepsilon_{n'} - \varepsilon_n} \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r} \right] P_{n'l'} \, \mathrm{d}r \end{aligned} \tag{7.36}$$

Note that: $(l - l')(l + l' + 1) = l(l+1) - l'(l'+1)$.

7.2.2 Gradient formula[b]

Another route towards the same result is directly calculating the reduced matrix element $\langle \psi_f \parallel \nabla \parallel \psi_i \rangle$ in spherical coordinates:

$$\begin{aligned}\nabla &= \left[\sin\theta\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}\right]\boldsymbol{i} \\ &+ \left[\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta}\right]\boldsymbol{j} \\ &+ \left[\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right]\boldsymbol{k} \end{aligned} \tag{7.37}$$

The $x-$ and $y-$ components are linear combinations of the spherical components ± 1. Fortunately, the preferred $z-$ component (or the equivalent spherical component 0) is simplest. Application of the Wigner-Eckart theorem yields:

$$\left\langle \gamma j \parallel T^{(k)} \parallel \gamma' j' \right\rangle = \frac{\left\langle \gamma j\, 0 \left| T_0^{(k)} \right| \gamma' j'\, 0 \right\rangle}{(-1)^j \begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix}}$$

and therefore for the case at hand:

$$\left\langle nl \parallel \nabla^{(1)} \parallel n'l' \right\rangle = \frac{\left\langle nl\, 0 \left| \nabla_0^{(1)} \right| n'l'\, 0 \right\rangle}{(-1)^l \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}} \tag{7.38}$$

Only two possibilities for l are allowed by the 3j-symbol: $l = l' \pm 1$, the largest of the two called $l_>$. The 3j-symbol may be reduced to:

$$\begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{l_>}\sqrt{l_>}\ [l,l']^{-\frac{1}{2}} \tag{7.39}$$

Remains the calculation of:

$$\left\langle nl\, 0 \left| \nabla_0^{(1)} \right| n'l'\, 0 \right\rangle = \left\langle R_{nl}(r)Y_0^l \left| \left[\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right] \right| R_{n'l'}(r)Y_0^{l'} \right\rangle$$

Therefore, the following two basic properties of spherical harmonics are required:

$$\begin{aligned}\cos\theta\, Y_0^l(\theta,\phi) &= \frac{l+1}{\sqrt{(2l+1)(2l+3)}}\, Y_0^{l+1} + \frac{l}{\sqrt{(2l-1)(2l+1)}}\, Y_0^{l-1} \\ \sin\theta\frac{\partial}{\partial\theta}Y_0^l(\theta,\phi) &= \frac{l(l+1)}{\sqrt{(2l+1)(2l+3)}}\, Y_0^{l+1} - \frac{l(l+1)}{\sqrt{(2l-1)(2l+1)}}\, Y_0^{l-1}\end{aligned}$$

As a result of the orthogonality, either the first or the second term of the above will drop out. After closure with the bra, the $\partial/\partial r$ and the $-1/r$ terms yield:

$$\left\{\frac{\mathrm{d}}{\mathrm{d}r}\cdot\frac{l_>}{[l,l']^{\frac{1}{2}}}\right\} \text{ and } \left\{-\frac{1}{r}\cdot(-1)^{l_>-l'+1}\cdot\frac{l'(l'+1)}{[l,l']^{\frac{1}{2}}}\right\} \text{ respectively.}$$

This can be seen from inspection of the possibilities $l = l' \pm 1$ separately. In conclusion:

$$\left\langle nl\,0 \left| \nabla_0^{(1)} \right| n'l'\,0 \right\rangle = \int_0^\infty R_{nl}(r) \left\{ \frac{\mathrm{d}}{\mathrm{d}r} \cdot \frac{l_>}{[l,l']^{\frac{1}{2}}} + \frac{1}{r} \cdot (-1)^{l_>-l'} \cdot \frac{l'(l'+1)}{[l,l']^{\frac{1}{2}}} \right\} R_{n'l'}(r)\, r^2 \mathrm{d}r \tag{7.41}$$

Only the radial integration is left. As can be seen from equations (7.38) and (7.39), the RHS has to be multiplied with the additional factor $(-1)^{l+l_>}(l_>)^{-\frac{1}{2}}\,[l,l']^{\frac{1}{2}}$:

$$(-1)^{l+l_>}(l_>)^{\frac{1}{2}} \int_0^\infty R_{nl}(r) \left\{ \frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r} \cdot (-1)^{l_>-l'} \cdot \frac{l'(l'+1)}{l_>} \right\} R_{n'l'}(r)\, r^2 \mathrm{d}r$$

Remember that $(-1)^{l+l_>} \cdot (l_>)^{\frac{1}{2}} = \langle l \parallel C^{(1)} \parallel l' \rangle$.
Substitution $P_{nl}/r = R_{nl}$ removes the factor r^2 from the integrand, and due to the action of $\mathrm{d}/\mathrm{d}r$ gives an additional contribution of $\int_0^\infty P_{nl}(r)\,(-1/r)\,P_{n'l'}(r)\,\mathrm{d}r$, so:

$$\int_0^\infty r^2\, R_{nl}\, \frac{\mathrm{d}}{\mathrm{d}r}\, R_{n'l'}\, \mathrm{d}r = \int_0^\infty P_{nl} \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r} \right) P_{n'l'}\, \mathrm{d}r \tag{7.42}$$

Finally:

$$\begin{aligned} \left\langle nl \parallel \nabla^{(1)} \parallel n'l' \right\rangle &= \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \int_0^\infty P_{nl}(r) \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r} \left\{ 1 - \frac{(-1)^{l_>-l} \cdot l'(l'+1)}{l_>} \right\} \right] P_{n'l'}(r)\mathrm{d}r \\ &= \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \int_0^\infty P_{nl}(r) \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r} \right] P_{n'l'}(r)\mathrm{d}r \end{aligned} \tag{7.43}$$

The last step may be verified by explicit use of $l = l' \pm 1$; division by ΔE directly returns equation (7.36).

7.2.3 Gradient formula[c]

A more direct route employs the spherical tensor expression, derived from the expression for the linear momentum $\vec{p}$, equation (3.20):

$$\nabla^{(1)} = C^{(1)}\, \frac{\partial}{\partial r} - \frac{\sqrt{2}}{r} \left(C^{(1)}\, l^{(1)} \right)^{(1)} \tag{7.44}$$

Thereby:

$$\begin{aligned} \left\langle nl \parallel \nabla^{(1)} \parallel n'l' \right\rangle = &\left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \int_0^\infty r^2\, R_{nl}\, \frac{\mathrm{d}}{\mathrm{d}r}\, R_{n'l'}\, \mathrm{d}r \\ &-\sqrt{2} \left\langle l \parallel \left(C^{(1)}\, l^{(1)} \right)^{(1)} \parallel l' \right\rangle \cdot \int_0^\infty r^2\, R_{nl}\, \frac{1}{r}\, R_{n'l'}\, \mathrm{d}r \end{aligned} \tag{7.45}$$

From equations (3.47) and (C.11), one deduces the below identity, directly related to equation (5.63):

$$\left\langle l \parallel \left(C^{(k)}\, l^{(1)} \right)^{(k)} \parallel l' \right\rangle = \frac{l(l+1) - k(k+1) - l'(l'+1)}{2\sqrt{k(k+1)}} \cdot \left\langle l \parallel C^{(k)} \parallel l' \right\rangle \tag{7.46}$$

Using this for $k = 1$ plus equation (7.42), one arrives at:

$$\begin{aligned}\left\langle nl \parallel \nabla^{(1)} \parallel n'l' \right\rangle &= \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \left[\int_0^\infty P_{nl} \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r} \right) P_{n'l'} \, \mathrm{d}r \right. \\ &- \left. \int_0^\infty \left(P_{nl} \, \frac{l(l+1) - 2 - l'(l'+1)}{2r} \, P_{n'l'} \right) \mathrm{d}r \right] \\ &= \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r} \right] P_{n'l'} \, \mathrm{d}r \quad (7.47)\end{aligned}$$

Obviously, equations (7.36), (7.43) and (7.47) are all identical.

7.2.4 Example hydrogen

The relation between the length and velocity operator, for a transition from an upper state b to a lower state a with $\omega = E_b - E_a$, thereby becomes:

$$L(a,b) = -\frac{V(a,b)}{\omega} \rightarrow \omega L(a,b) = \omega L(b,a) = V(b,a) = -V(a,b) \quad (7.48)$$

A simple demonstration is found with the hydrogenic $2p \rightarrow 1s$ transition matrix element: $\langle 2p \parallel rC^{(1)} \parallel 1s \rangle$. In atomic units, one has $\varepsilon_n = -1/(2n^2)$ and:

$$P(1s) = 2r \cdot \exp(-r) \quad (7.49a)$$

$$P(2p) = \frac{1}{2\sqrt{6}} \cdot r^2 \cdot \exp\left(-\tfrac{1}{2}r\right) \quad (7.49b)$$

$$P(3d) = \frac{4}{81\sqrt{30}} \cdot r^3 \cdot \exp\left(-\tfrac{1}{3}r\right) \quad (7.49c)$$

In the length formulation, this yields, with $\langle p \parallel C^{(1)} \parallel s \rangle = 1$:

$$\left\langle 2p \parallel rC^{(1)} \parallel 1s \right\rangle = \int_0^\infty \frac{\sqrt{6} \cdot r^4 \cdot \exp(-3r/2)}{6} \, \mathrm{d}r = \frac{128\sqrt{6}}{243}$$

The velocity formulation, on the other hand, gives:

$$\begin{aligned}\left\langle 2p \parallel rC^{(1)} \parallel 1s \right\rangle &= \frac{1}{\varepsilon_{1s} - \varepsilon_{2p}} \int_0^\infty P(2p) \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1(1+1) - 0(0+1)}{2r} \right] P(1s) \, \mathrm{d}r \\ &= \frac{1}{\varepsilon_{1s} - \varepsilon_{2p}} \int_0^\infty P(2p) \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r} \right] P(1s) \, \mathrm{d}r = -\frac{8}{3} \cdot -\frac{16\sqrt{6}}{81} = \frac{128\sqrt{6}}{243}\end{aligned}$$

Both two terms of the integral yield identical contributions $-8\sqrt{6}/81$, while the energy coefficient gives $-8/3$. So, as expected, length and velocity formulations yield identical results in the hydrogenic case.
N.B.: from the Leibniz theorem, one deduces:

$$P_{1s}^{(n)} = 2 \cdot Z^{n+\frac{1}{2}} \cdot \exp(-Zr) \cdot (-1)^n \cdot (Zr - n)$$

In fact, the use of the operator $\vec{r}$ instead of ∇ is an example of 'distributed' operators. Although mathematically identical for exact wavefunctions, a different (broader) range of integration is used, which may be more accurate in the case of approximate wavefunctions. Relativistically, this corresponds to different gauge choices.

7.3 Sum rules

$$\begin{aligned}\sum_{J'} S(SLJ;S'L'J') &= \sum_{J'} \delta(SS')\cdot[J,J']\cdot\left|\begin{Bmatrix} L & J & S \\ J' & L' & 1\end{Bmatrix}\right|^2 \cdot S(SL;S'L') \\ &= \delta(SS')\cdot[J]\cdot[L]^{-1}\cdot S(SL;S'L') \end{aligned} \tag{7.50}$$

As $\sum_J [J] = [S,L]$, it follows:

$$\sum_{JJ'} S(SLJ;S'L'J') = \delta(SS')\cdot[S]\cdot S(SL;S'L') \tag{7.51}$$

$$\sum_{JJ'} \frac{S(SLJ;S'L'J')}{J_{\rm up}} = \delta(SS')\cdot\frac{\min([S],[L_{\rm up}])}{[L_{\rm up}]}\cdot S(SL;S'L') \tag{7.52}$$

where $J_{\rm up}$ refers to the upper level: $E(J_{\rm up}) = E(J) > E(J')$.

$$\sum_{JJ'} A_{ki}(jj') = \delta(SS')\cdot\min([S],[L_{\rm up}])\cdot A(SL;S'L') \tag{7.53}$$

The Thomas-Reiche-Kuhn sum rule, sum of the oscillator strengths (positive for absorption) equals the number of active electrons in the system:

$$\sum\!\!\!\!\!\!\int_j \overline{f}_{ij} = N \tag{7.54}$$

In the absence of external fields, the initial states $(\gamma J M_J)$ are degenerate with respect to the $(2J+1)$ magnetic substates. A similar argument holds for the final states $(\gamma' J' M'_J)$. Therefore, the average oscillator strength is used:

$$\overline{f}(\gamma' J', \gamma J) = \frac{1}{(2J+1)}\sum_{M_J, M_{J'}} f(\gamma' J' M_{J'}, \gamma J M_J) \tag{7.55}$$

From the asymmetry between the initial and the final state, it follows that:

$$(2J+1)\overline{f}(\gamma' J', \gamma J) = (2J'+1)\overline{f}(\gamma J, \gamma' J')$$

7.4 Selection rules

Not every pair of states 1 and 2 is allowed to make a transition to one another through electric dipole radiation!
Therefore, it has to be investigated when $|<\Psi_2\,|\vec{r}|\,\Psi_1>|^2 \neq 0$. First:
Parity conservation: as every reflection is the result of the product of a point reflection and a rotation, one may limit the study to a point reflection at the origin $\vec{r} \to -\vec{r}$. In spherical coordinates, this implies: $(r,\theta,\phi) \to (r,\pi-\theta,\phi+\pi)$

Because $\Psi(\vec{r}) = R(r)\,Y_\ell^{m_\ell}(\theta,\phi)$ and : $Y_\ell^{m_\ell}(\pi-\theta,\phi+\pi) = (-1)^\ell\, Y_\ell^{m_\ell}(\theta,\phi)$

$\mathcal{H}$ carries no permanent dipole moment, the expectation value vanishes:

$<\Psi \mid \vec{r} \mid \Psi> = <(-1)^\ell\Psi \mid -\vec{r} \mid (-1)^\ell\Psi> = -<\Psi \mid \vec{r} \mid \Psi> = 0!$

Here, $(-1)^\ell$ is the so-called 'parity' of the state; for configurations with more than one electron, parity is given by: $(-1)^{\Sigma\ell}$. With the same line of thought, one obtains:

$$<\Psi_2 \mid \vec{r} \mid \Psi_1> = (-1)^{\ell_2+\ell_1} <\Psi_2 \mid -\vec{r} \mid \Psi_1>$$

it follows that $(-1)^{\ell_2+\ell_1} = -1$, so $\ell_2 + \ell_1$ should necessarily be odd!
From the vectorial character of $\vec{r}$, it turns out that for dipole radiation: $\boxed{\Delta\ell = \pm 1}$, as for $z = r\cos\theta$ one may use:

$$\cos\theta\, Y_\ell^{m_\ell} = \cdots Y_{\ell+1}^{m_\ell} + \cdots Y_{\ell-1}^{m_\ell}$$

$$\rightarrow <\Psi_2 \mid z \mid \Psi_1> = \cdots < Y_{\ell_2}^{m_\ell^2} \mid Y_{\ell_1+1}^{m_\ell^1} > + \cdots < Y_{\ell_2}^{m_\ell^2} \mid Y_{\ell_1-1}^{m_\ell^1} >$$

so either $\ell_2 = \ell_1 + 1$, or $\ell_2 = \ell_1 - 1$. Same for x and y.

If one wants to observe selection rules for $m_2 \leftrightarrow m_1$, the spatial degeneracy in m, i.e. the isotropy, has to be lifted, e.g. by a homogeneous B-field. Only then axes (like the 'z-axis') get a meaning because atoms will orient themselves in such a field with a well-defined external direction. The $\phi-$dependence of $\Psi(\vec{r})$ suffices for the selection:

$$\Psi(\vec{r}) = R(r)Y_\ell^{m_\ell}(\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \text{ with } \Phi(\phi) = e^{im_\ell\phi} \tag{7.56}$$

If the electric vector $\vec{E}$ of the radiation field (both for incoming photons: absorption, stimulated emission, as for outgoing photons: spontaneous emission) lies in one particular well-defined (say z-)direction, this is called linear polarization.
If $\vec{E}_{\text{laser field}} \,//\, \vec{B}$, then:

$$\rightarrow z = r\cos\theta \rightarrow I \sim \left| \int_0^{2\pi} e^{i(m_\ell^2 - m_\ell^1)\phi} \mathrm{d}\phi \right|^2 \neq 0, \text{ only if } m_\ell^2 - m_\ell^1 = 0.$$

So: $\boxed{\Delta m = 0.}$ This is called $\pi-$polarization.

Now assume the $\vec{E}$ to lie in the $x-$ or the $y-$direction (calculating $<\Psi_2 \mid \vec{E}\cdot\vec{r} \mid \Psi_1>$, one selects the $x-$ or the $y-$component of the dipole-operator.)

$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \end{cases} \rightarrow x \pm iy = r\sin\theta e^{\pm i\phi}$. Now we are concerned with $<\Psi_2 \mid x \pm iy \mid \Psi_1>$:

$$I \sim \left| r\sin\theta \int_0^{2\pi} e^{-im_\ell^2\phi} \cdot e^{\pm i\phi} \cdot e^{im_\ell^1\phi} \mathrm{d}\phi \right|^2 \sim \left| \cdots \int_0^{2\pi} e^{(m_\ell^1 - m_\ell^2 \pm 1)i\phi} \mathrm{d}\phi \right|^2 \rightarrow$$

$\boxed{\Delta m \pm 1.}$ This is called circular or $\sigma-$polarization. The electric vector describes a helix (screw-like movement) about $\vec{k}$: σ^+ is called right-handed or clockwise, as seen in the negative $z-$direction, i.e. the light is observed against the propagation direction, and σ^- is called left-handed (or counter-clockwise) accordingly. This is the 'optical convention': the rotation is considered positive if it produces a *clockwise* rotation when the observer looks *into* the light source.
N.B.: m is the quantum number associated with the spatial quantization of an angular momentum. Every angular momentum j (where j corresponds to an integral

or (spin!) half-integral quantum number) has a magnitude $\sqrt{j(j+1)}\hbar$ and $(2j+1)$ spatial orientations m_j where m_j runs from $-j, -j+1, \cdots 0, 1, \cdots j$.
With spatial degeneracy, there are $(2j+1)$ m_j–states that all contribute equally:

$\sum_{m_1} |< \Psi_2\ m_2 \mid e\vec{r} \mid \Psi_1\ m_1 >|^2$ is independent from m_2

and implies that $g_2 A_{2\to1} = g_1 A_{1\to2}$: the initial state 2 is weighed with $(2j_2+1) = g_2$.

7.5 Line broadening

The light emitted by an atom is, as a result of natural or radiation damping, not strictly monochromatic any more. The word 'damping' derives from the analogy with the classical damped harmonic oscillator, with a damping factor $\Gamma = 2\gamma$.
The average lifetime in an excited state i is given by:

$$\Delta t = \tau_i = \frac{1}{\sum_{\omega_j<\omega_i} A_{ij}} \tag{7.57}$$

The excited state i in this equation may in principle decay to several, lower lying energy states j. This phenomenon is called branching, and thereby the ratio between the corresponding values A_{ij} the 'branching ratio'.
According to the Heisenberg uncertainty principle $\Delta E \cdot \Delta t \geq \hbar$ is the order of magnitude of the corresponding spread in energy:

$$\Delta E = \frac{h}{2\pi\Delta t} \tag{7.58}$$

consequently:

$$\Delta\omega = \frac{1}{\Delta t} := \Gamma = \frac{1}{\tau} \tag{7.59}$$

Therefore, one may associate the damping factor with the natural linewidth. When in an excited state, the atom has a finite lifetime τ and will decay exponentially from this state. An important approximation is the so-called Rotating Wave Approximation (RWA) assuming $|\omega - \omega_0| \ll \omega$, as a result of which the fastest oscillations with frequency $\omega + \omega_0$ may be neglected: $(\omega+\omega_0)^{-1} \ll (\omega-\omega_0)^{-1}$. The emission spectrum will then exhibit a symmetrical, so-called Lorentzian profile:

$$L(\omega) = \frac{\gamma}{\pi}\frac{1}{(\omega_0-\omega)^2+\gamma^2} \tag{7.60}$$

Where:

$$\int_{-\infty}^{\infty} L(\omega)\mathrm{d}\omega = 1 \tag{7.61}$$

Here, $\Gamma = 2\gamma$ is known as the Lorentzian width or the damping factor, i.e. the halfwidth of the line profile. The natural line width is an intrinsic property of the atom and can not be reduced experimentally. This in contrast with linewidth broadening mechanisms like Doppler broadening (low temperature) or collisional

broadening (low pressure). The limit for a stable or stationary state: $\tau = \infty \rightarrow \gamma \approx 0$ yields the well known Dirac delta function:

$$\lim_{\gamma \to 0} \frac{\gamma/\pi}{(\omega - \omega_0)^2 + \gamma^2} = \delta(\omega - \omega_0)$$

In a number of cases, the shape of the absorption profile becomes relevant. This is particularly true when narrowband light sources are used, e.g. with modulation techniques. The reason is that the signal from such techniques not only is affected by the strength of the absorption feature but also strongly depends on its shape. The Lorentzian profile, which applies to the case when the sample is either predominantly broadened by the natural lifetime (i.e. spontaneous emission) or by collisions, and the Gaussian profile, which dominates when the transition is mainly Doppler broadened, are two well-known profiles. In the intermediate case, the transitions have a Voigt profile, which is a convolution of the two.

7.6 Transformation to bi-orthonormality

Two separately optimized configuration spaces of opposite parity are represented by two sets $\{\psi_i\}$ and $\{\phi_j\}$ of mutually non-orthogonal orbitals: orbital relaxation yields more reliable results. Each calculation generates its own orthonormal orbital basis and as a result, the Gram overlap matrix $\langle \psi_i \,|\, \phi_j \rangle = S_{ij}$ or $\langle \psi \,|\, \phi \rangle = \boldsymbol{S}$ of the spectator orbitals differs from a unit matrix [3]. This fact, however, violates the implicit assumption made in the above Racah algebra derivation of transition probabilities. The problem can be solved by transforming the wave functions to a new bi-orthonormal radial basis that does meet the requirement of orthonormality $\left\langle \overline{\psi} \,|\, \overline{\phi} \right\rangle = \mathbb{1}$ [Moshinsky and Seligman, 1971, Olsen et al., 1995]:

$$\left\langle \overline{\psi}_i \,|\, \overline{\phi}_j \right\rangle = \delta_{ij} \quad \text{with: } \overline{\psi} = \psi\, \boldsymbol{C}_\psi \text{ and: } \overline{\phi} = \phi\, \boldsymbol{C}_\phi \tag{7.62a}$$

or equivalently in terms of second quantization:

$$\overline{\mathbf{a}}_\psi{}^\dagger = \mathbf{a}_\psi{}^\dagger\, \boldsymbol{C}_\psi \text{ and: } \overline{\mathbf{a}}_\phi{}^\dagger = \mathbf{a}_\phi{}^\dagger\, \boldsymbol{C}_\phi \tag{7.62b}$$

Apparently: $\boldsymbol{C}_\psi^\dagger\, \boldsymbol{S}\, \boldsymbol{C}_\phi = \mathbb{1}$ or equivalently:

$$\boldsymbol{C}_\phi \cdot \boldsymbol{C}_\psi^\dagger = \boldsymbol{S}^{-1} \tag{7.62c}$$

Evidently, if $\{\psi_i\}$ and $\{\phi_j\}$ would coincide as the same orthonormal basis, $\boldsymbol{S} = \mathbb{1}$ and $\boldsymbol{C}_\psi$ and $\boldsymbol{C}_\phi$ are pure rotations with det($\boldsymbol{C}$)=1.
The overlap matrix $\boldsymbol{S}$ is block-diagonal due to the sorting in $l-$value, though the blocks are not necessarily square as the bra state $\langle \Psi_1| = \sum_i c_i \langle \psi_i| = \sum_{i'} \bar{c}_{i'} \left\langle \overline{\psi}_{i'} \right|$ and the ket state $|\Psi_2\rangle = \sum_j c_j |\phi_j\rangle = \sum_{j'} \bar{c}_{j'} \left| \overline{\phi}_{j'} \right\rangle$ may be composed of different correlation orbitals.
The creation and annihilation operators associated with the non-orthogonal basis $\{\psi, \phi\}$ do not obey the usual anti-commutation rules given in table 5.1, as:

$$a_m^\dagger a_n + a_n a_m^\dagger = S_{nm} \neq \delta_{nm} \tag{7.63}$$

[3] Using common spin-angular functions, only radial overlap integrals for the same orbital l-symmetry have to be considered while common closed shells may be discarded.

A new annihilation operator counteracting the above may now be invoked, defined by $\hat{\mathbf{a}} = S^{-1}\mathbf{a}$; this yields directly:

$$a_m^\dagger \hat{a}_n + \hat{a}_n a_m^\dagger = \delta_{nm} \qquad \text{(this corresponds to: } \boldsymbol{S} \to \mathbb{1}\text{)} \tag{7.64}$$

Retaining the original creation operators for the ket states and using the new annihilation operators for the bra states, a so-called bi-orthonormal basis is defined:

$$\langle n|m\rangle = \left\langle 0\left|\hat{a}_n a_m^\dagger\right|0\right\rangle = \delta_{nm} \tag{7.65}$$

[Moshinsky and Seligman, 1971] showed that single-particle operators F and two-particle operators G again satisfy equations 5.1, with all annihilation operators a_n now replaced by $\hat{a}_n$. Actually, this is true only if the sets of operators $a_m^\dagger$ and $\hat{a}_n$ span the same space, i.e. the bra and ket states $\langle\Psi_1|$ and $|\Psi_2\rangle$ satisfy the 'closure under de-excitation' property for all Brillouin excitations $P_{nl} \to P_{n'l}$ with $n' < n$. Next, the action of the excitation operator $a_m^\dagger \hat{a}_n$ on the ket (and similarly for the bra) is calculated from:

$$a_m^\dagger \hat{a}_n \left|\phi_\nu\right\rangle = \sum_\mu A_{mn}^{\mu\nu} \left|\phi_\mu\right\rangle \tag{7.66}$$

Equation 5.4 in its off-diagonal form reads:

$$\sum_{m,n} a_m^\dagger \hat{a}_n = -\delta(l,l') \left[\tfrac{1}{2},l\right]^{\frac{1}{2}} (\mathbf{a}^\dagger \mathbf{b})^{(00)} \tag{7.67}$$

The coefficients $A_{mn}^{\mu\nu}$ are therefore identical to the spin-angular coefficients prefacing $\langle a|U|b\rangle$ [or $\langle a|H_{BN}|b\rangle = I(a,b)$] in the off-diagonal potential [or bare nuclear] matrix elements $\left\langle \phi_\mu \left|U_{AB}\right| \phi_\nu \right\rangle$ [or $\left\langle \phi_\mu \left|H_{BN}\right| \phi_\nu \right\rangle$], as e.g. by equations 3.44 and 5.53:

$$U_{AB} = -\delta(l,l') \left[\tfrac{1}{2},l\right]^{\frac{1}{2}} (\mathbf{a}^\dagger \mathbf{b})^{(00)0} \ \langle a|U|b\rangle \tag{7.68}$$

An upper-triangular orbital transformation matrix can be understood as a finite sequence of single-orbital transformations, each of which expresses a new orbital as the sum over lower-numbered orbitals only. With this construction, both transformation matrices $\boldsymbol{C}_\psi$ and $\boldsymbol{C}_\phi$ will be upper-triangular. As all matrices $\boldsymbol{S}$ and $\boldsymbol{C}$ are well behaved, standard linear algebra LU factorization gives: $\boldsymbol{S} = \boldsymbol{l} \cdot \boldsymbol{u}$; with $\boldsymbol{U} = \boldsymbol{u}^{-1}$ and $\boldsymbol{L} = \boldsymbol{l}^{-1}$ one obtains $\boldsymbol{S}^{-1} = \boldsymbol{U} \cdot \boldsymbol{L}$. From equation 7.62c it follows directly that:

$$\boldsymbol{C}_\phi \cdot \boldsymbol{C}_\psi^\dagger = \boldsymbol{U} \cdot \boldsymbol{L} = \boldsymbol{S}^{-1} \tag{7.69}$$

As a result, a standard upper-lower decomposition of the inverse overlap matrix $\boldsymbol{S}^{-1}$ suffices to find the required transformation matrices. Equation 7.62c also enables an orbital-by-orbital recursive calculation starting from $\boldsymbol{C}_\phi = \mathbb{1}$. The process is generalized and worked out in detail by [Malmqvist, 1986, Olsen et al., 1995] as a finite sequence of single orbital transformations.

7.7 Electric multipole radiation(1)

The electron charge distribution expanded in multipoles, interacts with the electromagnetic field giving rise to electric multipole transitions.
The electric multipole field has the well-defined parity $(-1)^k$, so that $l+l'+k$ is even.
Using equation (5.58), the corresponding single electron operator is simply:

$$T^{(k)} = \sum_i r_i^k \cdot C_i^{(k)} = -\sqrt{\frac{2}{2k+1}} \cdot \left\langle nl \parallel r^k C^{(k)} \parallel n'l' \right\rangle \cdot \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(0k)k} \tag{7.70}$$

The velocity counterpart of the transition integral $L_{NR}^{(k)} = \int_0^\infty P_{nl}\, r^k\, P_{n'l'} \mathrm{d}r$ is best derived from the relativistic theory; it is given in equation (23.41):

$$V_{NR}^{(k)} = \omega^{-1} \cdot \left[k \int_0^\infty P_1 P_2' \cdot r^{k-1} \mathrm{d}r - \tfrac{1}{2}\left[l(l+1) - l'(l'+1) - k(k-1) \right] \int_0^\infty P_1 P_2 \cdot r^{k-2} \mathrm{d}r \right] \tag{7.71}$$

The complete interaction operator is $c_k^e \cdot T^{(k)}$, where the j–independent EM field factor is given by $c_k^e = i^k \cdot (2\pi\sigma)^k/(2k-1)!! \cdot \sqrt{(k+1)/k}$ in the long wavelength approximation. The value of c_k^e is derived from a more complete theory of electric and magnetic multipole radiation, worked out later in the relativistic framework in chapter 23.
By Fermi's golden rule, the electric multipole transition probability in atomic units now becomes:

$$\begin{aligned} g_2 \cdot A_{21} &= \frac{4\pi\sigma}{2k+1} \cdot \left| c_k^e \cdot \left\langle j_1 \parallel T^{(k)} \parallel j_2 \right\rangle \right|^2 \\ &= \left(\frac{2(k+1) \cdot (2\pi)^{2k+1}}{k(2k+1)(2k-1)!!(2k-1)!!} \right) \cdot \sigma^{2k+1} \cdot \left| \left\langle j_1 \parallel T^{(k)} \parallel j_2 \right\rangle \right|^2 \end{aligned} \tag{7.72}$$

In actual calculations, A_{21} is given in s^{-1} and σ in cm^{-1}. This conversion requires an additional factor $fe^2/\hbar \cdot a_0^{2k} \cdot 10^{4k+2}$ on the RHS; in all cases, equation 7.14 may be used to convert $g_2 \cdot A_{21}$ to the oscillator strength $g_1 \cdot f_{12}$.
As the transition probability is proportional to the square of the transition amplitude: $g_2 A_{Ek} \propto \left| \langle \gamma J \parallel T^{(k)} \parallel \gamma' J' \rangle \right|^2$, it remains to calculate the matrix elements $\langle \gamma SLJ \parallel T^{(k)} \parallel \gamma' S' L' J' \rangle \propto \left\langle \gamma SLJ \parallel \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(0k)k} \parallel \gamma' S' L' J' \right\rangle$:

$$\begin{aligned} &\left\langle \gamma SLJ \parallel T^{(k)} \parallel \gamma' S' L' J' \right\rangle = -\sqrt{2} \cdot \delta(S,S') \cdot (-1)^{J+L'+S+k} \cdot [J,J']^{\frac{1}{2}} \cdot [S,k]^{-\frac{1}{2}} \\ &\cdot \begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix} \cdot \left\langle l \parallel C^{(k)} \parallel l' \right\rangle \cdot \int_0^\infty P_{nl}\, r^k\, P_{n'l'} \mathrm{d}r \cdot \left\langle \gamma SL \parallel \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(0k)} \parallel \gamma' S' L' \right\rangle \end{aligned} \tag{7.73}$$

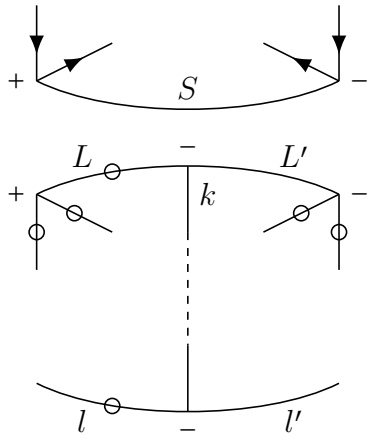
$$\begin{aligned}
&\left\langle l_1^N(S_1L_1)\, l_2^M(S_2L_2)S_{12}L_{12}\, l_3^K(S_3L_3)\, SLJ \parallel T^{(k)} \parallel l_1^N(S_1'L_1')\, l_2^M(S_2'L_2')S_{12}'L_{12}'\, l_3^K(S_3'L_3')\, S'L'J' \right\rangle \\
&= N\cdot\delta(S,S')\cdot\delta(S_1,S_1')\cdot\delta(S_{12},S_{12}')\cdot\delta(n_2,n_2')\cdot\delta(n_3,n_3')\cdot(-1)^{S+J}\cdot[J,J',L,L']^{\frac{1}{2}} \\
&\cdot(-1)^{L_2+l_1+L_{12}+L_{12}'+L_3}\cdot[L_1,L_1',L_{12},L_{12}']^{\frac{1}{2}}\cdot\begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix}\cdot\begin{Bmatrix} L & k & L' \\ L_{12}' & L_3 & L_{12} \end{Bmatrix}\cdot\begin{Bmatrix} L_{12} & k & L_{12}' \\ L_1' & L_2 & L_1 \end{Bmatrix} \\
&\cdot\sum_{\overline{S}_1\overline{L}_1}\left(l_1^N S_1L_1\{|l_1^{N-1}\overline{S}_1\overline{L}_1\right)\cdot\left(l_1^N S_1'L_1'\{|l_1^{N-1}\overline{S}_1\overline{L}_1\right)(-1)^{\overline{L}_1}\cdot\begin{Bmatrix} L_1 & k & L_1' \\ l_1 & \overline{L}_1 & l_1 \end{Bmatrix}\cdot\left\langle n_1l_1 \parallel r^k\, C^{(k)} \parallel n_1l_1\right\rangle \\
&+\ M\cdot\delta(S,S')\cdot\delta(S_2,S_2')\cdot\delta(S_{12},S_{12}')\cdot\delta(n_1,n_1')\cdot\delta(n_3,n_3')\cdot(-1)^{S+J}\cdot[J,J',L,L']^{\frac{1}{2}} \\
&\cdot(-1)^{L_1+L_2+L_2'+l_2+L_3}\cdot[L_2,L_2',L_{12},L_{12}']^{\frac{1}{2}}\cdot\begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix}\cdot\begin{Bmatrix} L & k & L' \\ L_{12}' & L_3 & L_{12} \end{Bmatrix}\cdot\begin{Bmatrix} L_{12} & k & L_{12}' \\ L_2' & L_1 & L_2 \end{Bmatrix} \\
&\cdot\sum_{\overline{S}_2\overline{L}_2}\left(l_2^M S_2L_2\{|l_2^{M-1}\overline{S}_2\overline{L}_2\right)\cdot\left(l_2^M S_2'L_2'\{|l_2^{M-1}\overline{S}_2\overline{L}_2\right)(-1)^{\overline{L}_2}\cdot\begin{Bmatrix} L_2 & k & L_2' \\ l_2 & \overline{L}_2 & l_2 \end{Bmatrix}\cdot\left\langle n_2l_2 \parallel r^k\, C^{(k)} \parallel n_2l_2\right\rangle \\
&+\ K\cdot\delta(S,S')\cdot\delta(n_1,n_1')\cdot\delta(n_2,n_2')\cdot\delta(S_{12},S_{12}')\cdot\delta(L_{12},L_{12}')\cdot(-1)^{S+J}\cdot[J,J',L,L']^{\frac{1}{2}} \\
&\cdot(-1)^{L+L'+L_3+L_3'+l_3+L_{12}}\cdot[L_3,L_3']^{\frac{1}{2}}\cdot\begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix}\cdot\begin{Bmatrix} L & k & L' \\ L_3' & L_{12} & L_3 \end{Bmatrix} \\
&\cdot\sum_{\overline{S}_3\overline{L}_3}\left(l_3^K S_3L_3\{|l_3^{K-1}\overline{S}_3\overline{L}_3\right)\cdot\left(l_3^K S_3'L_3'\{|l_3^{K-1}\overline{S}_3\overline{L}_3\right)(-1)^{\overline{L}_3}\cdot\begin{Bmatrix} L_3 & k & L_3' \\ l_3 & \overline{L}_3 & l_3 \end{Bmatrix}\cdot\left\langle n_3l_3 \parallel r^k\, C^{(k)} \parallel n_3l_3\right\rangle
\end{aligned} \tag{7.74}$$

$$\begin{aligned}
&\left\langle l_1^N(S_1L_1)\, l_2^{M-1}(S_2L_2)S_{12}L_{12}\, l^K(S_3L_3)\, SLJ \parallel T^{(k)} \parallel l_1^{N-1}(S_1'L_1')\, l_2^M(S_2'L_2')S_{12}'L_{12}'\, l^K(S_3L_3)\, S'L'J' \right\rangle \\
&= (-1)^{M-1}\cdot\sqrt{N\cdot M}\cdot\delta(S,S')\cdot[J,J',L,L']^{\frac{1}{2}}\cdot(-1)^{S+J}\cdot\begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix}\cdot\left\langle n_1l_1 \parallel r^k\, C^{(k)} \parallel n_2l_2\right\rangle \\
&\cdot[L_{12},L_{12}']^{\frac{1}{2}}\cdot[S_1,L_1,S_2',L_2']^{\frac{1}{2}}\cdot\delta(S_{12},S_{12}')\cdot(-1)^{l_2+L_3+L_{12}'+L_1+L_1'}\cdot\begin{Bmatrix} L & k & L' \\ L_{12}' & L_3 & L_{12} \end{Bmatrix}\cdot\begin{Bmatrix} L_1 & l_1 & L_1' \\ L_2 & l_2 & L_2' \\ L_{12} & k & L_{12}' \end{Bmatrix} \\
&\cdot(-1)^{S_1'+S_2'+S_{12}}\cdot\begin{Bmatrix} S_1 & S_{12} & S_2 \\ S_2' & \frac{1}{2} & S_1' \end{Bmatrix}\cdot\left(l_1^N(S_1L_1)\{|l_1^{N-1}(S_1'L_1')\right)\cdot\left(l_2^M(S_2'L_2')\{|l_2^{M-1}(S_2L_2)\right)
\end{aligned} \tag{7.75a}$$

$$\begin{aligned}
&\left\langle l^K(S_3L_3)\, l_1^N(S_1L_1)\, S_{12}L_{12}\, l_2^{M-1}(S_2L_2)\, SLJ \parallel T^{(k)} \parallel l^K(S_3L_3)\, l_1^{N-1}(S_1'L_1')\, S_{12}'L_{12}'\, l_2^M(S_2'L_2')\, S'L'J' \right\rangle \\
&= (-1)^{M-1}\cdot\sqrt{N\cdot M}\cdot\delta(S,S')\cdot[J,J',L,L']^{\frac{1}{2}}\cdot\begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix}\cdot\left\langle n_1l_1 \parallel r^k\, C^{(k)} \parallel n_2l_2\right\rangle \\
&\cdot[S_{12},L_{12},S_{12}',L_{12}']^{\frac{1}{2}}\cdot[S_1,L_1,S_2',L_2']^{\frac{1}{2}}\cdot(-1)^{L_1'+L_3+L_{12}'+L}\cdot\begin{Bmatrix} L_1 & L_1' & l_1 \\ L_{12}' & L_{12} & L_3 \end{Bmatrix}\cdot\begin{Bmatrix} L_{12} & l_1 & L_{12}' \\ L_2 & l_2 & L_2' \\ L & k & L' \end{Bmatrix} \\
&\cdot(-1)^{S_{12}+S_3+\frac{1}{2}+S_1'+J-S_2'-S_{12}'}\cdot\begin{Bmatrix} S_1 & S_1' & \frac{1}{2} \\ S_{12}' & S_{12} & S_3 \end{Bmatrix}\cdot\begin{Bmatrix} S & S_2' & S_{12}' \\ \frac{1}{2} & S_{12} & S_2 \end{Bmatrix} \\
&\cdot\left(l_1^N(S_1L_1)\{|l_1^{N-1}(S_1'L_1')\right)\cdot\left(l_2^M(S_2'L_2')\{|l_2^{M-1}(S_2L_2)\right)
\end{aligned} \tag{7.75b}$$

$$\begin{aligned}&\left\langle l_1^N(S_1L_1)\,l^K(S_3L_3)\,S_{12}L_{12}\,l_2^{M-1}(S_2L_2)\,SLJ \parallel T^{(k)} \parallel l_1^{N-1}(S_1'L_1')\,l^K(S_3L_3)\,S_{12}'L_{12}'\,l_2^M(S_2'L_2')\,S'L'J'\right\rangle\\ &= (-1)^K\cdot(-1)^{S_1-S_{12}-S_1'+S_{12}'}\cdot(-1)^{L_1-L_{12}-L_1'+L_{12}'}\\ &\cdot\left\langle l^K(S_3L_3)\,l_1^N(S_1L_1)\,S_{12}L_{12}\,l_2^{M-1}(S_2L_2)\,SLJ \parallel T^{(k)} \parallel l^K(S_3L_3)\,l_1^{N-1}(S_1'L_1')\,S_{12}'L_{12}'\,l_2^M(S_2'L_2')\,S'L'J'\right\rangle\end{aligned} \tag{7.75c}$$

Again in the SL-coupling scheme, the action of $T^{(0k)k}$ is graphically represented by:



$$\cdot\,\delta(S,S') \qquad \cdot W\cdot[J,J',L,L']^{\frac{1}{2}}\cdot(-1)^{S+L+J}\cdot\begin{Bmatrix}J & k & J'\\ L' & S & L\end{Bmatrix}\cdot\langle nl \parallel r^kC^{(k)} \parallel n'l'\rangle \tag{7.76}$$

7.8 Electric quadrupole radiation(1)

Here, the complete transition probability, again with $g_2 = [J_2] = 2J_2+1$ for the upper state, becomes[4]:

$$g_2\,A_{E2} = 1.1199500\times10^{-22}\cdot\sigma^5\cdot\left|\left\langle\gamma J \parallel T^{(2)} \parallel \gamma' J'\right\rangle\right|^2 \tag{7.77}$$

For $P_1 \neq P_2$, the velocity formulation (23.50) of the integral $L_{NR}^{(2)} = \int_0^\infty P_1\,r^2P_2\,\mathrm{d}r$ is:

$$V_{NR}^{(2)} = \frac{2}{\omega}\cdot\int_0^\infty P_1\left(\frac{\mathrm{d}}{\mathrm{d}r}+a\right)P_2\,\mathrm{d}r \text{ with } a=\tfrac{1}{2}(l'=l),\ a=l+2(l'=l+2) \text{ and } a=1-l(l'=l-2) \tag{7.78}$$

These velocity formulations were derived in an alternative way using the hypervirial theorem by [Godefroid, 1978].

For $E2$ radiation, the square root of the line strength is e.g. given by:

$$\begin{aligned}S_{E2}^{\frac{1}{2}} = \left\langle l^N\,SL\nu\,J \parallel T^{(2)} \parallel l^N\,S'L'\nu'\,J'\right\rangle &= N\cdot\delta(S,S')\cdot(-1)^{S+L'+J+l+L}\cdot[J,J',L,L']^{\frac{1}{2}}\\ &\cdot\begin{Bmatrix}J & 2 & J'\\ L' & S & L\end{Bmatrix}\left\langle l \parallel C^{(2)} \parallel l\right\rangle\int_0^\infty P_{nl}\,r^2P_{nl}\,\mathrm{d}r\sum_{\overline{S}\,\overline{L}\,\overline{\nu}}(-1)^{\overline{L}}\cdot\begin{Bmatrix}L & 2 & L'\\ l & \overline{L} & l\end{Bmatrix}\\ &\cdot\left(l^{N-1}(\overline{S}\,\overline{L}\,\overline{\nu})|\}l^N(SL\nu)\right)\cdot\left(l^{N-1}(\overline{S}\,\overline{L}\,\overline{\nu})|\}l^N(S'L'\nu')\right)\end{aligned} \tag{7.79}$$

Evidently, this is just a a special case of equation (7.74) for $k=2$ and $M=0$.

[4]The constant corresponds to the SI value of $fe^2/\hbar\cdot1/15\cdot(2\pi)^5\cdot10^{10}\cdot a_0^4$. The factor 10^{10} translates m^{-5} into cm^{-5}, and a_0^4 converts the linestrength S_{if} from SI to au.

7.9 Magnetic multipole radiation(1)

Here, the EM field factor is given by $c_k^m = \alpha/2 \cdot i^{k+1} \cdot (2\pi\sigma)^k/(2k-1)!! \cdot \sqrt{k+1)/k}$ with the complete interaction operator equal to $c_k^m \cdot M^{(k)}$.
By Fermi's golden rule, the magnetic multipole transition probability is in a.u.:

$$\begin{aligned} g_2 \cdot A_{21} &= \frac{4\pi\sigma}{2k+1} \cdot \left| c_k^m \cdot \left\langle j_1 \parallel M^{(k)} \parallel j_2 \right\rangle \right|^2 \\ &= \left(\frac{\alpha}{2}\right)^2 \cdot \left(\frac{2(k+1) \cdot (2\pi)^{2k+1}}{k(2k+1)(2k-1)!!(2k-1)!!} \right) \cdot \sigma^{2k+1} \cdot \left| \left\langle j_1 \parallel M^{(k)} \parallel j_2 \right\rangle \right|^2 \end{aligned} \tag{7.80}$$

The reader is again referred to chapter 23 for a more complete theory of multipole radiation. Here also, A_{21} is customarily given in s^{-1} and σ in cm^{-1}, requiring an additional prefactor $fe^2/\hbar \cdot a_0^{2k} \cdot 10^{4k+2}$ on the RHS; as with electric multipole radiation, equation 7.14 is used to convert to oscillator strength.
Neglecting QED corrections[5], the generalized magnetic moment operator for all multipolarities 2^k [De-Shalit and Talmi, 1963] is given in the long wavelength limit using equation (3.25) by:

$$\begin{aligned} M^{(k)} &= \frac{2}{k+1} \cdot \sum_i \nabla \left(r_i^k C_i^{(k)} \right) \cdot \left[\mathbf{l}_i + (k+1)\, \mathbf{s}_i \right] \\ &= \frac{2}{k+1} \cdot [k(2k-1)]^{\frac{1}{2}} \sum_i r_i^{k-1} \left[\left(C_i^{(k-1)} l_i \right)^{(k)} + (k+1) \left(C_i^{(k-1)} s_i \right)^{(k)} \right] \end{aligned} \tag{7.81}$$

Naturally, this reduces for $k = 1$ to the atomic magnetic moment $M^{(1)}$ given in equation (3.71). The magnetic multipole field has the well-defined parity $(-1)^{k+1}$, so $l + l' + k$ is odd.
The two RHS operators may subsequently be converted to second quantized form with equations (5.62) and (5.61):

$$\sum_i \left(C_i^{(k-1)} l_i \right)^{(k)} = [2l'(l'+1)(2l'+1)]^{\frac{1}{2}} \cdot \begin{Bmatrix} l & l' & k \\ 1 & k-1 & l' \end{Bmatrix} \cdot \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle \cdot \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(0k)k} \tag{7.82a}$$

$$\sum_i \left(C_i^{(k-1)} s_i \right)^{(k)} = -[2(2k-1)]^{-\frac{1}{2}} \cdot \left\langle l \parallel C^{(k-1)} \parallel l' \right\rangle \cdot \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(1k-1)k} \tag{7.82b}$$

Equation (5.25) is then used to factor out the J–dependence:

$$\begin{aligned} \left\langle \psi\, SLJ \parallel \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(0k)k} \parallel \psi'\, S'L'J' \right\rangle &= \delta(S,S') \cdot (-1)^{J+L'+S+k} \cdot [J,J']^{\frac{1}{2}} \cdot [S]^{-\frac{1}{2}} \\ &\cdot \begin{Bmatrix} J' & J & k \\ L & L' & S \end{Bmatrix} \cdot \left\langle \psi\, SL \parallel \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(0k)} \parallel \psi'\, S'L' \right\rangle \end{aligned} \tag{7.83a}$$

$$\begin{aligned} \left\langle \psi SLJ \parallel \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(1k-1)k} \parallel \psi' S'L'J' \right\rangle &= [J,J',k]^{\frac{1}{2}} \cdot \begin{Bmatrix} S & S' & 1 \\ L & L' & k-1 \\ J & J' & k \end{Bmatrix} \\ &\cdot \left\langle \psi\, SL \parallel \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(1k-1)} \parallel \psi'\, S'L' \right\rangle \end{aligned} \tag{7.83b}$$

Thus, for $\Delta S \neq 0$ transitions, only the second term effectively remains.

[5] A first complement would be multiplication of the spin term by $g_s/2$ in eq. (7.81).

7.10 Magnetic dipole radiation(1)

As with $E1$ radiation, the square roots of the line strengths for $M1$ and $E2$ radiation are first calculated in the SLJ coupling scheme and subsequently transformed to the actual states using equation (7.6).
With $g_2 = 2J_2 + 1$ referring to the upper state, the complete $M1$ transition probability becomes[6]:

$$g_2 A_{M1} = 2.6973500 \times 10^{-11} \cdot \sigma^3 \cdot \left|\left\langle \gamma J \parallel M^{(1)} \parallel \gamma' J' \right\rangle\right|^2 \tag{7.84}$$

The diagonal reduced matrix elements of the magnetic dipole operator $M^{(1)} = L^{(1)} + g_s S^{(1)}$ have already been given in equations (3.73) and (3.74) in connection with the Zeeman effect. Assuming $g_s \approx 2$ for $M1$ radiation, the general expression becomes:

$$S^{\frac{1}{2}}_{M1}(SLJ, S'L'J') = \left\langle SLJ \parallel M^{(1)} \parallel S'L'J' \right\rangle = \delta(SS') \cdot \delta(LL') \cdot (-1)^{S+L+1} \cdot [J, J']^{\frac{1}{2}} \cdot \left[(-1)^J \begin{Bmatrix} J & 1 & J' \\ L & S & L \end{Bmatrix} \sqrt{L(L+1)(2L+1)} + 2(-1)^{J'} \begin{Bmatrix} J & 1 & J' \\ S & L & S \end{Bmatrix} \sqrt{S(S+1)(2S+1)} \right] \tag{7.85}$$

Simplifying the $6j$-symbols, the square root of the line strength in SLJ coupling is thus given by:

$$S^{\frac{1}{2}}_{M1}(SL\nu\, J, SL\nu\, J) = \frac{1}{2}\left[\frac{2J+1}{J(J+1)}\right]^{\frac{1}{2}} \left[S(S+1) - L(L+1) + 3J(J+1)\right] \tag{7.86a}$$

and similarly:

$$\begin{aligned} S^{\frac{1}{2}}_{M1}(SL\nu\, J-1, SL\nu\, J) &= -S^{\frac{1}{2}}_{M1}(SL\nu\, J, SL\nu\, J-1) \\ &= \frac{1}{2}\left\{\frac{[J^2 - (L-S)^2][(S+L+1)^2 - J^2]}{J}\right\}^{\frac{1}{2}} \end{aligned} \tag{7.86b}$$

All other matrix elements are zero, which implies the selection rules:
$\Delta\nu = \Delta S = \Delta L = 0$ and $\Delta J = 0, \pm 1$ with $J = 0 \rightarrow J = 0$ strictly forbidden.

7.11 Application: 21 cm hydrogen line

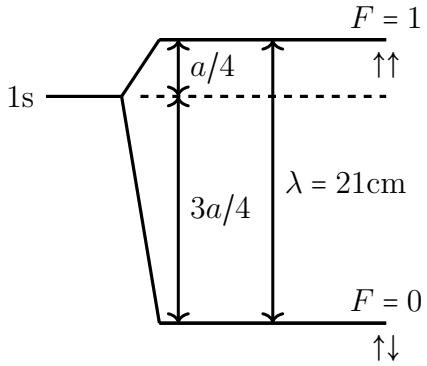
Interstellar clouds of density $\rho \approx 10^3$ m^{-3} mainly consist of neutral atomic hydrogen at $T \approx 100$ K. The two possible hyperfine energy levels in the $1s$ groundstate are: $(F = 1, \uparrow\uparrow)$ with electron and proton spins parallel, and $(F = 0, \uparrow\downarrow)$ with the spins anti-parallel. Each of these levels has $2F + 1$ magnetic sublevels: $F = 1 \rightarrow$ m_F= -1, 0, 1 and for $F = 0$ only m_F=0. As the Boltzmann factor $\exp(-\Delta E/kT) \approx 1$ at $E = 9.42 \times 10^{-25} J$, all these magnetic sublevels are equally populated. Therefore, 75% of the atoms are in the $F = 1$ level and 25% in the $F = 0$ level.

[6]The constant corresponds to the SI value of $fe^2/\hbar \cdot 4/3 \cdot (2\pi)^3 \cdot 10^6 \cdot a_0^2 \cdot (\alpha/2)^2$ $= (8\pi^3 e^2 \hbar)/(3m_e^2) \cdot 10^{-7} \cdot 10^6$ where $f = c^2 \cdot 10^{-7}$ and the factor 10^6 translates m^{-3} into cm^{-3}.

The lifetime of the upper level $F = 1$ of a completely isolated atom is determined by the magnetic dipole $1 \to 0$ transition probability:

$g\,A_{M1} = 2.6973 \times 10^{-11} \times \sigma^3 \times S_{M1} \to 3\,A_{M1} = 2.6973 \times 10^{-11} \times 0.04738^3 \times 3$

Yielding: $A_{M1} = 2.87 \times 10^{-15}\ \mathrm{s}^{-1} \to \tau = A_{M1}^{-1} = 3.5 \times 10^{14}\ \mathrm{s} \approx 11 \times 10^6$ year.



Because on average there is one collision with another H-atom each century with a transition efficiency of 25%, a particular H-atom actually radiates one 21 cm photon every 400 year. Due to the vast dimensions of interstellar clouds, this radiation is readily observable.

The contact interaction between the proton spin **I** and the electron spin **s** can be described as the potential energy of the proton magnetic moment in the magnetic field of the electron:

$$H^D_{\mathrm{hfs}} = -\,\boldsymbol{\mu}_I \cdot \mathbf{B}_s = a_{ns}\ \mathbf{I}\cdot\mathbf{s}. \tag{7.87}$$

Due to symmetry, one could also have chosen the equivalent converse expression:

$$H^D_{\mathrm{hfs}} = -\boldsymbol{\mu}_s \cdot \mathbf{B}_I = a_{ns}\ \mathbf{s}\cdot\mathbf{I}. \tag{7.88}$$

From $F^2 = (\mathbf{I}+\mathbf{s})^2$ one derives:

$$\langle \mathbf{I}\cdot\mathbf{s}\rangle = \tfrac{1}{2}\left[F(F+1) - I(I+1) - s(s+1)\right] = \tfrac{1}{2}\left[F(F+1) - \tfrac{3}{2}\right] \tag{7.89}$$

It follows that:

$$\Delta E = E_{(F=1)} - E_{(F=0)} = a_{ns}\cdot\left(\tfrac{1}{4} - \left(-\tfrac{3}{4}\right)\right) = a_{ns} \tag{7.90}$$

Non-relativistically, the magnetic field of the s-electron at the nucleus is given in SI by:

$$\vec{B}(0) = \frac{8\pi}{3}\cdot\frac{\mu_0}{4\pi}\cdot|\Psi(0)|^2\cdot\mu_s\,\vec{k} \tag{7.91}$$

$\vec{\mu}_s = \mu_s\,\vec{k} = -g_s\cdot\mu_B\cdot\vec{s}$ and, according to equation (3.35):

$$\vec{\mu}_I = g_I\cdot\mu_B\cdot\left(\frac{m_e}{m_p}\right)\cdot\vec{I} \tag{7.92}$$

Therefore, in au the magnetic s-electron field at nucleus is written as:

$$\vec{B}(0) = -\alpha^2 \cdot \frac{8\pi}{3} \cdot |\Psi(0)|^2 \cdot \tfrac{1}{2} g_s \cdot \vec{s} = -\alpha^2 \cdot \tfrac{1}{2} g_s \cdot \frac{2}{3} \cdot \left\langle \frac{\delta(r)}{r^2} \right\rangle \vec{s} \tag{7.93}$$

The second step results from: $\delta(\vec{r}) = \delta(\boldsymbol{r}) = \dfrac{1}{4\pi}\dfrac{\delta(r)}{r^2}$ with: $\langle \delta(\boldsymbol{r}) \rangle = |\Psi(0)|^2$

Once again:

$$H^D_{\text{hfs}} = -\vec{\mu}_I \cdot \vec{B}(0) \tag{7.94}$$

For non-relativistic hydrogenic systems, one has $|\Psi(0)|^2 = Z^3/(\pi n^3 a_0^3)$, finally yielding:

$$a_{ns} = \frac{8\pi}{3} \cdot \frac{\mu_0}{4\pi} \cdot \mu_B^2 \cdot \left(\frac{m_e}{m_p}\right) \cdot g_I \cdot g_s \cdot \frac{Z^3}{\pi n^3 a_0^3} \tag{7.95}$$

In au, this becomes:

$$a_{ns} = \frac{8\pi}{3} \cdot \alpha^2 \cdot \left(\frac{m_e}{m_p}\right) \cdot \tfrac{1}{2} g_I \cdot \tfrac{1}{2} g_s \cdot \frac{Z^3}{\pi n^3} = \tfrac{2}{3}\alpha^2 \cdot \left(\frac{m_e}{m_p}\right) \cdot g_I \cdot g_s \cdot \left(\frac{Z}{n}\right)^3 \tag{7.96}$$

Substituting known constants, the final result becomes: $a_{1s} = 9.432 \times 10^{-25}$ J, to be compared with the experimental result 9.412×10^{-25} J $\rightarrow \lambda = hc/a_{1s} = 21$ cm.

7.12 Magnetic quadrupole radiation(1)

Just like $E1$ radiation, $M2$ radiation involves a parity change. Here, the complete transition probability, again with $g_2 = [J_2] = 2J_2 + 1$ for the upper state, becomes[7]:

$$g_2\, A_{M2} = 1.4909714 \times 10^{-27} \cdot \sigma^5 \cdot \left|\left\langle \gamma J \parallel M^{(2)} \parallel \gamma' J' \right\rangle\right|^2 \tag{7.97}$$

where $M^{(2)}$ is given by:

$$\begin{aligned} M^{(2)} &= 2/3 \cdot \sqrt{6} \cdot \sum_i r_i \left[\left(C_i^{(1)} l_i \right)^{(2)} + 3 \left(C_i^{(1)} s_i \right)^{(2)} \right] \\ &= 2/3 \cdot \int_0^\infty P_{nl}\, r P_{n'l'}\, \mathrm{d}r \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \left[2\sqrt{3}\, [l'(l'+1)(2l'+1)]^{\frac{1}{2}} \cdot \begin{Bmatrix} l & l' & 2 \\ 1 & 1 & l' \end{Bmatrix} \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(02)2} \right. \\ &\qquad \left. -3 \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(11)2} \right] \end{aligned} \tag{7.98}$$

$$\begin{aligned} \left\langle l^N (SLJ) \parallel \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(02)2} \parallel l^{N-1} (S_1 L_1)\, l'\, (S' L' J') \right\rangle &= -\sqrt{\tfrac{5}{2}} \cdot \sqrt{N} \cdot \delta(S, S') \cdot \left(l^N\, SL \{ | l^{N-1}\, S_1 L_1 \right) \\ \cdot (-1)^{J+L'+S} \cdot [J, J']^{\frac{1}{2}} \cdot \begin{Bmatrix} J' & J & 2 \\ L & L' & S \end{Bmatrix} &\cdot (-1)^{L_1+l'+L} \cdot [L, L']^{\frac{1}{2}} \cdot \begin{Bmatrix} L & 2 & L' \\ l' & L_1 & l \end{Bmatrix} \end{aligned} \tag{7.99a}$$

[7] The constant corresponds to the SI value of $fe^2/\hbar \cdot 1/15 \cdot (2\pi)^5 \cdot 10^{10} \cdot a_0^4 \cdot (\alpha/2)^2$.
The $M1(M2)$ constants are equal to the $E1(E2)$ constants $\times\, (\alpha/2)^2$.
The $M2(E2)$ constants are equal to the $M1(E1)$ constants $\times\, \left(1/20 \cdot 10^4 \cdot (2\pi)^2 \cdot a_0^2\right)$.

$$\left\langle l^N(SLJ) \parallel \left(\mathbf{a}^\dagger\mathbf{b}\right)^{(11)2} \parallel l^{N-1}(S_1L_1)\, l'\,(S'L'J')\right\rangle = -3\sqrt{N}\cdot\left(l^N\, SL\{|l^{N-1}\, S_1L_1\right)\cdot[J,J',2]^{\frac{1}{2}}$$
$$\cdot\begin{Bmatrix} S & S' & 1\\ L & L' & 1\\ J & J' & 2\end{Bmatrix}\cdot[S,L,S',L']^{\frac{1}{2}}\cdot(-1)^{S_1+\frac{1}{2}+S+1}\cdot(-1)^{L_1+l'+L+1}\cdot\begin{Bmatrix} S & 1 & S'\\ \frac{1}{2} & S_1 & \frac{1}{2}\end{Bmatrix}\cdot\begin{Bmatrix} L & 1 & L'\\ l' & L_1 & l\end{Bmatrix} \tag{7.99b}$$

$$\left\langle l^N(S_1L_1)l'\,(SLJ) \parallel \left(\mathbf{a}^\dagger\mathbf{b}\right)^{(02)2} \parallel l^N(S_1L_1)\, l''\,(S'L'J')\right\rangle = -\sqrt{\tfrac{5}{2}}\cdot\delta(S,S')$$
$$\cdot(-1)^{J+L'+S}\cdot[J,J']^{\frac{1}{2}}\cdot\begin{Bmatrix} J' & J & 2\\ L & L' & S\end{Bmatrix}\cdot(-1)^{L_1+l''+L}\cdot[L,L']^{\frac{1}{2}}\cdot\begin{Bmatrix} L & 2 & L'\\ l'' & L_1 & l'\end{Bmatrix} \tag{7.99c}$$

$$\left\langle l^N(S_1L_1)l'\,(SLJ) \parallel \left(\mathbf{a}^\dagger\mathbf{b}\right)^{(11)2} \parallel l^N(S_1L_1)\, l''\,(S'L'J')\right\rangle = -3\cdot[J,J',2]^{\frac{1}{2}}$$
$$\cdot\begin{Bmatrix} S & S' & 1\\ L & L' & 1\\ J & J' & 2\end{Bmatrix}\cdot[S,L,S',L']^{\frac{1}{2}}\cdot(-1)^{S_1+\frac{1}{2}+S+1}\cdot(-1)^{L_1+l''+L+1}\cdot\begin{Bmatrix} S & 1 & S'\\ \frac{1}{2} & S_1 & \frac{1}{2}\end{Bmatrix}\cdot\begin{Bmatrix} L & 1 & L'\\ l'' & L_1 & l'\end{Bmatrix} \tag{7.99d}$$

Chapter 8

Light-matter interactions

Most elementary concepts can be understood from the interaction of a two-level atom with monochromatic light. We call the ground state $|g\rangle$, the excited state $|e\rangle$, and their energy difference $\hbar\omega_0$. This atom interacts with a (strong) monochromatic laser with frequency ω and wavevector $k_L = \omega/c$. We define the detuning as $\delta = \omega - \omega_0$. Although the atom is taken at rest, a moving atom can in many cases be described by including a Doppler shift in the detuning: $\delta \to \delta - k_L v$.

8.1 Frequencies vs. angular frequencies

Equations usually look better when angular frequencies are used. In the following, all varieties of ω, δ and γ denote angular frequencies, i.e. the corresponding oscillation is something like $\cos\omega t$ or $e^{-i\omega t}$ and the corresponding period is $2\pi/\omega$, etc. Confusion can be avoided, e.g., as follows: $\omega/2\pi = 1$ MHz, or $\omega = 2\pi \times 1$ MHz.

For linewidths the situation is as follows: if an excited state has a $1/e$-decay time of τ, then $\Gamma = 1/\tau$ is an angular frequency. The full width at half height (FWHM) of the corresponding Lorentzian line is then Γ in rad/s, or $\Gamma/2\pi$ in normal frequency units (Hertz, cycles per second). The usually quoted 'natural linewidth' is thus equal to $(2\pi\tau)^{-1}$. For example, for Rb the natural linewidth is 6 MHz, $\Gamma = 2\pi \times 6$ MHz and $\tau = 26.5$ ns.

However, the rate at which an atom can scatter photons is $\Gamma/2 = 1/2\tau$, in photons/s. So for the scattering rate we do *not* divide Γ by 2π, but for the linewidth (in Hz) we *do* (!).

8.1.1 Rabi frequency

In calculations we usually need the Rabi frequency. However, in the lab we usually measure the intensity of a laser beam. Here's a shortcut to calculate the Rabi frequency Ω_1 if the intensity I is given:

$$2\left(\frac{\Omega_1}{\Gamma}\right)^2 = \frac{I}{I_0}, \tag{8.1}$$

where I_0 is the saturation intensity:

$$I_0 = \frac{\pi hc}{3\lambda^3}\Gamma. \tag{8.2}$$

Here the internal structure (angular momentum) of an atomic level has been ignored, i.e. it is assumed that the Clebsch-Gordan coefficient is 1. Beware for alternative definitions in the literature. In particular an extra factor 2 in the saturation intensity is frequently used.

For resonant excitation ($\delta = 0$), in the absence of spontaneous emission, the Rabi frequency is the frequency at which the population oscillates between the ground and excited state. So, starting in $|g\rangle$ at $t = 0$, the population is entirely transferred to $|e\rangle$ at $t = \pi/\Omega_1$ and back to $|g\rangle$ at $t = 2\pi/\Omega_1$ (full cycle).

It is useful to define the saturation coefficient s:

$$s = \frac{\Omega_1^2/2}{\delta^2 + \Gamma^2/4} = \frac{I/I_0}{1 + 4\delta^2/\Gamma^2}. \tag{8.3}$$

Again, beware alternative definitions, such as I/I_0.

8.2 Two-level atom plus monochromatic laser

8.2.1 Light shift

The term 'light shift' is jargon for what is sometimes called 'dynamic Stark shift' or 'AC Stark shift'. It is also synonymous with 'dipole potential', with its spatial derivative the 'dipole force'. Not all optical forces are dipole forces. The term 'dipole force' is frequently used to distinguish it from radiation pressure, which is also called (spontaneous) scattering force. A simple derivation for the light shift is obtained in the dressed-level picture.

Dressed states are combined states of the atom and the radiation field. The uncoupled dressed states are $|g, N+1\rangle$ and $|e, N\rangle$, where N is the number of laser photons. These two uncoupled dressed states are nearly degenerate, their energy difference is $\hbar\delta$:

$$E(|g, N+1\rangle) - E(|e, N\rangle) = (N+1)\hbar\omega - (N\hbar\omega + \hbar\omega_0) = \hbar\delta.$$

The coupling strength of the atom-light interaction is described by the Rabi frequency Ω_1. In the presence of coupling, the eigenstates are linear superpositions of $|g, N+1\rangle$ and $|e, N\rangle$. The energy of the coupled dressed states are the eigenvalues of

$$\hbar \begin{pmatrix} \omega & \Omega_1/2 \\ \Omega_1/2 & \omega_0 \end{pmatrix}. \tag{8.4}$$

Note that the common energy of N photons, $N\hbar\omega$ has been left out. The eigenvalues of this matrix are

$$E_{1,2} = \frac{\hbar\omega + \hbar\omega_0}{2} \pm \frac{\hbar\Omega}{2} = \frac{\hbar\omega + \hbar\omega_0}{2} \pm \frac{\hbar}{2}\sqrt{\delta^2 + \Omega_1^2}.$$

The splitting $\Omega = \sqrt{\delta^2 + \Omega_1^2}$ is sometimes called the *generalized Rabi frequency.*

The eigenstates are

$$|1(N)\rangle = \sin\theta\,|g, N+1\rangle + \cos\theta\,|e, N\rangle \tag{8.5}$$

$$|2(N)\rangle = \cos\theta\,|g, N+1\rangle - \sin\theta\,|e, N\rangle \tag{8.6}$$

where the angle θ is defined by

$$\tan 2\theta = -\frac{\Omega_1}{\delta}. \tag{8.7}$$

For detunings large compared to the Rabi frequency, $|\delta| \gg \Omega_1$, we have $|\theta| \ll 1$, so $|\sin\theta| \ll 1$ and the dressed states approach the uncoupled states. In this case the effect of the interaction is mostly a level shift: the light shift. For the ground state the light shift (expressed as a frequency) is

$$\frac{\Delta E_g}{\hbar} = \frac{E_1}{\hbar} - \omega \approx \frac{\Omega_1^2}{4\delta} \approx \delta\frac{s}{2}. \tag{8.8}$$

In the last approximation it has been assumed that $|\delta| \gg \Gamma$ (which is usually the case).

8.2.2 Photon scattering rate

The photon scattering rate is determined by the population of the excited state. This is found by solving for the steady-state solution of the optical Bloch equations. This steady-state population is given by:

$$\sigma_{ee}^{st} = \frac{1}{2}\left(\frac{s}{1+s}\right). \tag{8.9}$$

Note that this population never exceeds $\frac{1}{2}$. For the photon scattering rate $\gamma_{\rm sc}$ we simply multiply by the decay rate of the excited state Γ:

$$\gamma_{\rm sc} = \frac{\Gamma}{2}\left(\frac{s}{1+s}\right). \tag{8.10}$$

Scattering force

An atom excited by a single laser beam receives one photon momentum $\hbar k_L$ per scattered photon, so the force is

$$F = \hbar k_L \cdot \gamma_{\rm sc} = \hbar k_L \cdot \frac{\Gamma}{2}\left(\frac{s}{1+s}\right). \tag{8.11}$$

The maximum scattering force, for large saturation, $s \gg 1$, is thus given by

$$F_{\rm max} = \hbar k_L \cdot \frac{\Gamma}{2}. \tag{8.12}$$

For rubidium, $F_{\rm max}/m \approx 10^5$ m s^{-2} $\approx 10^4\ g$.

8.2.3 Far off-resonance limit, low saturation

Of considerable experimental interest is the situation where the laser is intense, $I \gg I_0$, and far detuned, $|\delta| \gg \Gamma$. Due to the large detuning the saturation parameter

can be very small, $s \ll 1$, even for very high intensity. In this situation the following simplifications are useful. Saturation parameter:

$$s \approx \frac{I/I_0}{4(\delta/\Gamma)^2}. \tag{8.13}$$

The lightshift is proportional to I/δ:

$$\frac{\Delta E_g}{\hbar} = \frac{I/I_0}{2\delta/\Gamma}\ \frac{\Gamma}{4} \approx \frac{s}{2}\delta. \tag{8.14}$$

The photon scattering rate is proportional to I/δ^2:

$$\gamma_{\rm sc} = \frac{\Gamma}{2}\frac{s}{s+1} \approx \frac{I/I_0}{4\delta^2/\Gamma^2}\ \frac{\Gamma}{2} = \frac{s}{2}\Gamma. \tag{8.15}$$

Note that the ratio of light shift to scattering rate is δ/Γ.

8.3 Parameters for ^{87}Rb

resonance wavelength	λ_1	795	nm (D_1)	
	λ_2	780	nm (D_2)	
lifetime	τ	27	ns ($p_{3/2}$; D_2)	
linewidth	$\Gamma/2\pi$	6.0	MHz ($p_{3/2}$; D_2)	$\equiv (2\pi\tau)^{-1}$
saturation intensity	I_0	1.6	mW/cm^2 (D_2)	
polarizability	$\alpha/4\pi\epsilon_0$	48	Å^3	
Van der Waals coefficient	C_6	4700	a.u.	
Doppler temperature	T_D	140	μK	$\equiv \hbar\Gamma/2k_B$
Doppler capture	Γ/k_L	4.6	m/s	
typ. velocity @ T_D	v_D	16	cm/s	$\equiv \sqrt{2k_BT_D/m}$
recoil velocity	v_R	5.8	mm/s	$\equiv \hbar k_L/m$
recoil temperature	T_R	362	nK	$\equiv \hbar^2k_L^2/mk_B = 2E_R/k_B$
recoil frequency	ω_R	$2\pi \times 3.8$	kHz	$\equiv \hbar k_L^2/2m = E_R/\hbar$
gravity	mg/k_B	1	mK/cm	
	mg/h	21	MHz/cm	
	mg/μ_B	15	G/cm	
De-Broglie wavelength	Λ	16	nm @ T_D	$\equiv h/\sqrt{2\pi mk_BT}$
		311	nm @ T_R	
s-wave scattering length	$a_{2,2}$	109	a_0	

8.4 Quantum beats, isotope-selective ionization.

Quantum beats of magnetic and hyperfine structure substates can be used to selectively photoionize isotopes. E.g. in Cd-like systems, an initially unpolarized ground state $|i\rangle = {}^1S_0$ is excited to a final state $|f\rangle = {}^3D_2$ with two laser pulses. The first pulse coherently excites $|\,i\rangle$ to the meta-stable, intermediate states $|e\rangle, |e'\rangle = {}^3P_1$. After a delay τ allowing the intermediate state coherence to evolve, a second laser

pulse populates the final state $|f\rangle$ (Fig. la). There are several paths leading from $|i\rangle$ to $|f\rangle$. In analogy to Young's classical double slit experiment, the final state population of particular isotopes is either enhanced or suppressed depending on the phase differences between the paths. Subsequently, isotope selective photoionization may be performed. The phase factor between the paths is determined by the angle between the polarization vectors of the laser beams and by the quantity $\omega_{ee'}\tau$. Generally, isotopes with an even number of nucleons have no nuclear spin and thereby no hyperfine structure. The two laser beams are linearly polarized with the direction of the electrical field component perpendicular to the magnetic field. In summary, a modulation in the two-step excitation probability depends upon:

- the angle between the polarization vectors of the two laser beams
- the Zeeman splitting of the magnetic sub-levels
- the h.f.s. splitting

Starting point is the quantum beat expression:

$$P(t) \propto \sum \left\langle F_e\, m_e \left| \mathbf{e}_1^{(1)} \cdot \mathbf{T}^{(1)} \right| F_i\, m_i \right\rangle \left\langle F_i\, m_i \left| \left(\mathbf{e}_1^{(1)} \cdot \mathbf{T}^{(1)} \right)^{\dagger} \right| F_{e'}\, m_{e'} \right\rangle$$
$$\left\langle F_{e'}\, m_{e'} \left| \mathbf{e}_2^{(1)} \cdot \mathbf{T}^{(1)} \right| F_f\, m_f \right\rangle \left\langle F_f\, m_f \left| \left(\mathbf{e}_2^{(1)} \cdot \mathbf{T}^{(1)} \right)^{\dagger} \right| F_e\, m_e \right\rangle \exp\left[-(i\omega_{ee'} + \Gamma_e)t\right] \tag{8.16}$$

Here, subsequent use of equations (3.16), (3.39) and (3.51a) now yields e.g.:

$$\left\langle (J_e I) F_e m_e \right| \mathbf{e}^{(1)} \cdot \mathbf{T}^{(1)} \left| (J_i I) F_i m_i \right\rangle = \sum_{q_1} (-1)^{q_1}\, e^{(1)}_{-q_1}\, (-1)^{F_e - m_e} \begin{pmatrix} F_e & 1 & F_i \\ -m_e & q_1 & m_i \end{pmatrix}$$
$$(-1)^{J_e + I + F_i + 1} \left[F_e, F_i\right]^{\frac{1}{2}} \begin{Bmatrix} F_e & 1 & F_i \\ J_i & I & J_e \end{Bmatrix} \left\langle J_e \parallel T^{(1)} \parallel J_i \right\rangle \tag{8.17}$$

With all the magnetic quantum numbers $m_i, m_e, m_{e'}$ and m_f summed over, using equation (3.6) for the Hermitian conjugates, this yields the final expression:

$$P(t) \propto (-1)^{J_i - J_f} \left| \left\langle J_i \parallel \mathbf{T}^{(1)} \parallel J_e \right\rangle \right|^2 \left| \left\langle J_e \parallel \mathbf{T}^{(1)} \parallel J_f \right\rangle \right|^2$$
$$\cdot \sum_k \begin{Bmatrix} J_e & J_e & k \\ 1 & 1 & J_i \end{Bmatrix} \begin{Bmatrix} J_e & J_e & k \\ 1 & 1 & J_f \end{Bmatrix} \cdot \sum_q (-1)^q \left(E_q^{(k)}(1) \right)' \, E_{-q}^{(k)}(2)$$
$$\cdot \sum_{F_e, F_{e'}} \left[F_e, F_{e'}\right] \begin{Bmatrix} J_e & J_e & k \\ F_e & F_{e'} & I \end{Bmatrix}^2 \cdot \exp\left[-(i\omega_{ee'} + \Gamma_e)t\right] \tag{8.18}$$

Linear polarized light is used, but at right angles to the $\vec{B}$–field: $\rightarrow \sigma^{\pm}$ yields a coherent superposition of ${}^3P_1, (m = -1, 1)$, where the phase factors are interrelated by synchronous creation. The energy difference is caused by the Zeeman effect. The phase difference between $\Psi(m = -1)$ and $\Psi(m = 1)$ is determined by the magnitude of the $\vec{B}$–field, and is reflected in the transition to the excited Cd (Z=48) state $4d^{10}5s5d(m = 0)$: sometimes a maximal, sometimes a minimal population.

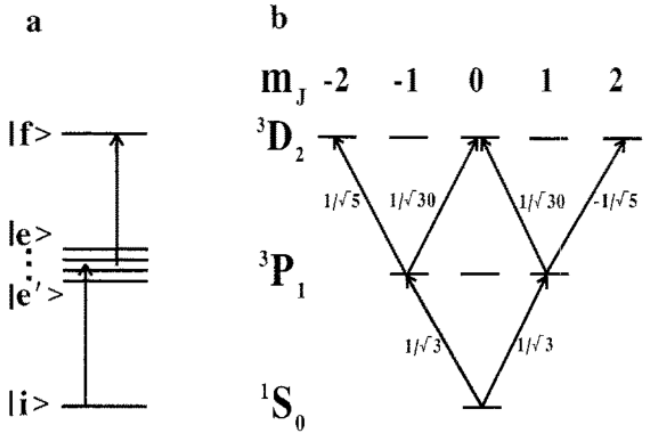


Fig. 1. a The excitation path from the ground state $|i\rangle$, via the excited states $|e\rangle, \ldots, |e'\rangle$ to the final state $|f\rangle$ is given schematically. **b** In this excitation scheme the two paths to the $m=0$ final state can interfere. To the $m=2$ states only one path is possible

Intermezzo:
Gauge transformations can be used to bring potentials into various convenient forms. One particularly important form, referred to as the transverse or Coulomb gauge, is defined by the condition:

$$\nabla \cdot \mathbf{A}_{\pm}(\mathbf{r},\omega) = 0 \tag{8.19}$$

It follows from the Lorentz condition that, in the transverse gauge, the scalar potential vanishes:

$$\phi_{\pm}(\mathbf{r},\omega) = 0 \tag{8.20}$$

In the transverse gauge, the electric and magnetic fields are given by:

$$\begin{aligned} \mathbf{E}_{\pm}(\mathbf{r},\omega) &= \pm i\omega \mathbf{A}_{\pm}(\mathbf{r},\omega) \\ \mathbf{B}_{\pm}(\mathbf{r},\omega) &= \nabla \times \mathbf{A}_{\pm}(\mathbf{r},\omega) \end{aligned} \tag{8.21}$$

For plane-wave solutions to the source-free Maxwell equations propagating in the direction $\mathbf{k}$, the transverse-gauge vector potential is:

$$\mathbf{A}_{\pm}(\mathbf{r},\omega) = \mathbf{e}\, \exp\left(\pm i\, \mathbf{k}\cdot\mathbf{r}\right) \tag{8.22}$$

With each laser, a polarization tensor, actually the tensor product (equation (3.7)) of the corresponding spherical unit vectors, is associated:

$$E_Q^{(k)} = \left(\mathbf{e}^{(1)}\mathbf{e}^{(1)}\right)_Q^{(k)} = \sum_{qq'} (1q\ 1q'|kQ)\, e_q^{(1)} e_{q'}^{(1)} = \sum_{qq'} (-1)^Q\, [k]^{\frac{1}{2}} \begin{pmatrix} 1 & 1 & k \\ q & q' & -Q \end{pmatrix} \cdot e_q^{(1)}\, e_{q'}^{(1)} \tag{8.23}$$

where the $e_q^{(1)}$ (see equations (3.10) refer to the spherical components of the polarization tensor, i.e. the unit vector directed along the electric field component of the laser light. From the 3j-symbol it follows that only the tensor ranks $k = 0, 1, 2$ (so-called scalar, vector and alignment terms) are allowed, yielding a total number of 9

components. Here, one deals with a linear polarization in the $XY-$plane described by the spherical unit vectors:

$$e_1^{(1)} = \frac{1}{\sqrt{2}} \quad \text{and} \quad e_{-1}^{(1)} = -\frac{1}{\sqrt{2}}$$

This is equivalent to the statement that linearly polarized light consists of an equal amount of left and right hand circularly polarized light. As the sum in equation (8.23) is now restricted to the corresponding 'circular' components $q = 1, -1$,
it can be shown by straightforward calculation that there are only four non-zero components of $E_q^{(k)}$ left:

$$E_0^{(0)} = -\frac{1}{\sqrt{3}}, \qquad E_0^{(2)} = -\frac{1}{\sqrt{6}}, \quad \text{and} \quad E_{-2}^{(2)} = E_2^{(2)} = \frac{1}{2}.$$

As is to be expected, the vector $(k = 1)$ part of the polarization tensor does not appear at all. In order to define the polarization of the first laser beam in the same coordinate system as the second, one has to rotate the associated polarization tensor:

$$\left(E_q^{(k)}\right)' = \sum_{q'} D^k_{q'q} \cdot E_q^{(k)}$$

where the prime denotes the action of the rotation matrix $D^k_{q'q}$. In the present situation, we have only a rotation over an angle Φ, the angle between the polarizations of the two laser beams) of the $XY-$plane:

$$\left(E_q^{(k)}\right)' = \sum_{q'} D^k_{q'q}(0,0,\Phi) \cdot E_q^{(k)} = \sum_{q'} \delta(q,q') \, \exp\left(-iq\Phi\right) \cdot E_q^{(k)}.$$

With these results, one obtains:

$$\begin{aligned} \sum_q (-1)^q \left(E_q^{(k)}(1)\right)' \; E_{-q}^{(k)}(2) &= \tfrac{1}{3} && (k = 0) \\ &= \cos^2\Phi - \tfrac{1}{3} && (k = 2) \end{aligned} \tag{8.24}$$

If $B = 0$, the easiest description of the experiment is with the linear polarizations in the z-direction (π light), which yields the common result:

$$\sum_q (-1)^q \left(E_q^{(k)}(1)\right)' \; E_{-q}^{(k)}(2) = [k] \begin{pmatrix} 1 & 1 & k \\ 0 & 0 & 0 \end{pmatrix}^2 P_k(\cos\Phi) \tag{8.25}$$

Recall that: $P_0(\cos\Phi) = 1$ and $P_2(\cos\Phi) = \frac{3}{2}\cos^2\Phi - \frac{1}{2}$. As is to be expected, equations (8.24) and (8.25) give identical results in the limit $B \to 0$.
Abbreviating the k-dependent terms by:

$$X_k = (-1)^{J_i - J_f} \begin{Bmatrix} J_e & J_e & k \\ 1 & 1 & J_i \end{Bmatrix} \begin{Bmatrix} J_e & J_e & k \\ 1 & 1 & J_f \end{Bmatrix} [F_e, F_{e'}] \begin{Bmatrix} J_e & J_e & k \\ F_e & F_{e'} & I \end{Bmatrix}^2$$

the basic quantum beat equation finally becomes:

$$P(t) \propto \sum_{F_e, F_{e'}} \left(\tfrac{1}{3}X_0 + (\cos^2\Phi - \tfrac{1}{3})X_2\right) \cdot \left|\left\langle J_i \parallel \mathbf{T}^{(1)} \parallel J_e \right\rangle\right|^2 \left|\left\langle J_e \parallel \mathbf{T}^{(1)} \parallel J_f \right\rangle\right|^2 \exp\left[-(i\omega_{ee'} + \Gamma_e)t\right] \tag{8.26}$$

where the first term may be simplified to: $X_0 = \delta(F_e, F_{e'})\,[I]/(3\,[J_e])$. It is readily seen that complete extinction of the signal is only possible if $-2 \leq X_0/X_2 \leq 1$. Due to the nuclear spin dependence, if the photoionization yield is reduced to zero for $I = 0$, there still remains an appreciable signal for $I \neq 0$ (I = 1/2 for Cd). The method discussed in this section thus proves very effective in discriminating between odd and even isotopes. If only one odd isotope is present, it can be separated completely if the angular momentum of the ground state J_i is zero or one. The two-step excitation probability is modulated with the hfs-splitting frequency, which is isotope dependent and zero for $I = 0$. The hyperfine splitting is generally large when unpaired s-electrons are present. The bandwidth and the duration of a pulse are connected by the equation $\Delta\omega \cdot \Delta t \approx 2\pi \rightarrow \tau = 2\pi/\omega_{ee'}$, obtained by the Fourier transformation of a square pulse shape.

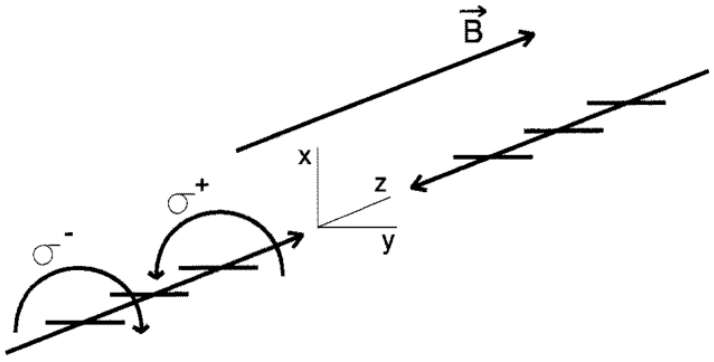


Fig. 2. Geometric arrangement of the laser beams and the magnetic field. Note that linearly polarized light can be considered as a superposition of right (σ^+) and left hand (σ^-) circularly polarized light

Chapter 9

Parity violation

Up until 1957, physicists thought that the four fundamental forces were invariant under mirror inversion. The parity operator P maps $\boldsymbol{r} \to -\boldsymbol{r}$, i.e. it transforms $\phi \to \phi + \pi$ and $\theta \to \pi - \theta$ in spherical coordinates. Parity transformation is therefore described by:

$$P\,Y_{lm}(\theta,\phi) = Y_{lm}(\pi-\theta,\phi+\pi) = (-1)^l \cdot Y_{lm}(\theta,\phi) \tag{9.1}$$

Spherical spinors are thereby eigenfunctions of P with eigenvalues $(-1)^l$.

However, [Lee and Yang, 1956] were awarded the Nobel price in 1957 for their theoretical work from 1956, in which they demonstrated that 'parity' is not conserved in weak interactions. [Wu et al., 1957] indisputably verified this in her famous 'Wu Co-60' experiment, thereby starting a parity crisis. She aligned the nuclear spins of the ^{60}Co nuclei in a magnetic field (alignment of axial vectors) and subsequently observed the emitted electrons after decay: ${}^{60}_{27}\mathrm{Co} \to {}^{60}_{28}\mathrm{Ni} + \mathrm{e}^- + \bar{\nu}_e$. The electrons turn out to possess a preferential direction, a polar vector! As a result, this experiment defines a specific chirality and is therefore not mirror-symmetric! Pauli sighed learning the news: 'I don't believe in a left-handed God!'.

In parity non-conserving effects, a neutral vector boson Z^0 is exchanged between the atomic nucleus and the $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ electrons, causing the atomic state as a whole not to have a well-defined parity. It is therefore possible to test the electroweak interaction in atomic physics experiments. The exchange particles, the so-called 'weak' bosons $W^\pm$ (plus Z^0), thus change the 'mirror-identity' or 'handedness' of the participating particles. The $W^\pm$ gauge bosons mediate the weak interaction in β decay. With the theoretical unification of the weak and electromagnetic interactions, an important prediction was the existence of a new gauge boson, called Z^0, mediating weak neutral current interactions. The Z^0 boson carries no electric charge, so it couples to the fundamental particles such as electrons and quarks like a heavy photon. In 1971, the Weinberg-Salam model (1961-1967) uniting the electromagnetic and the weak interaction turned out to be renormalizable (Gerard 't Hooft), and thus mathematically manageable. In 1979, Glashow, Salam and Weinberg received the Nobel price for their theory, that unifies the weak and the electromagnetic interaction. In their theory, the slightly heavier neutral vector (gauge) boson Z^0 makes its appearance, mediating a new kind of weak interaction. As a neutral particle,

Z_0 interacts like a heavy photon; as a pseudovector particle, it exhibits chiral, parity violating behavior. The electroweak interaction between electrons and nucleons destroys The electroweak interaction between electrons and nucleons thereby destroys the mirror symmetry of an atom. The size of the effect depends on the weak interaction constants as well as on the atomic structure.

$$\begin{matrix} Z^0 \sim \\ W^{\pm} \end{matrix} \quad \begin{matrix} 1.6256 \times 10^{-25}\,\mathrm{kg} \\ \end{matrix} \quad \begin{matrix} \sim 91.1867\ \mathrm{GeV} \\ \sim 80.4\ \mathrm{GeV} \end{matrix} \quad \text{with: } \cos\theta_W = \frac{M_W}{M_Z} = 0.882$$

The range, represented by the Compton wavelength, is mass-determined:

$$\frac{\hbar}{M_{Z_0} c} \sim 2 \times 10^{-18}\ \mathrm{m}$$

and therefore so short that a chiral electron-nucleon interaction may only take place inside the nucleus. The Fermi coupling constant G_F is, next to WS angle θ_W the second free parameter in the WS-theory:

$$\begin{aligned} G_F = (m_e c^2) \times \left(\frac{\hbar}{m_e c}\right)^3 \times 3 \times 10^{-12} &\sim 1.4 \times 10^{-62}\ \mathrm{J\ m^3} \\ &\sim 89.6\ \mathrm{eV\ fm^3} \\ &\sim 2.22 \times 10^{-14}\ \text{in a.u.: } \mathrm{Ry} \cdot a_0^3 \end{aligned}$$

9.1 Helicity: the intrinsic photon angular momentum

The photon, a zero mass, spin 1 particle ih exchanged by the 'long range' electromagnetic interaction. This in contrast to the weak interaction where so-called vector bosons $W^{\pm}, Z^0$ are exchanged, likewise with spin 1 but, as a result of the short range, with a mass $\neq 0$ ($\sim 1.5 \times 10^{-25} kg$). Both interactions are coupled or 'unified' via the Weinberg-Salam model.

According to the Heisenberg relation: $\Delta m \cdot \Delta r \geq \hbar/c$; the range is thus equal to the reduced Compton wavelength $\hbar/mc$.

The photon spin is not half-integral because:

- The classical limit of QED is found for $n \to \infty$, which is not reconcilable with the Pauli principle.
- 'Many photons' constitute a macroscopic ensemble that can be described by the Maxwell equations for $\vec{A}$ that may be regarded as the Schrödinger equation of the photon. However, a spin $\frac{1}{2}$ can not be interpreted within the Maxwell theory: there may be infinitely many photons with the same quantum properties ω and polarization.

The concept 'spin' cannot be used unambiguously.
According to the common interpretation:
spin represents the angular momentum left when the particle is at rest, in contrast to the orbital angular momentum.
However, a photon is never at rest! From an answer to Ehrenfest in 1926, it turns

out that Einstein did not know what to do with that (what is the definition of a rest frame?), and even proposed to possibly give up the concept of conservation of angular momentum at all!
There are three spatial projections that 'go' with a spin-1 particle: $m = -1, 0, 1$; under rotation, they can make a transition from one to the other (spherical symmetry!) However, a photon has a cylindrical symmetry by virtue of its inherent velocity, and therefore cannot possess spin=0 (which reflects perfect spherical symmetry, as with s–electrons).
In accordance with 'Maxwell', the photon has only two projections $h = -1, 1$ on the propagation direction (z-axis) corresponding to the two possible circular polarizations:

- $h = -1 \rightarrow \Delta m = 1 : \sigma^-,$ left – handed
- $h = \ 1 \rightarrow \Delta m = -1 : \sigma^+,$ right – handed

If m is associated with the lower energy state and m' with the higher one, then according to the Wigner-Eckart theorem:

$$< \Phi_i \mid D_h^{(1)} \mid \Phi_f >= (-1)^{j-m} \begin{pmatrix} j & 1 & j' \\ -m & h & m' \end{pmatrix} < \Phi_i \parallel D^{(1)} \parallel \Phi_f >$$

$$\text{so: } \begin{cases} h = 1 \rightarrow \Delta m = m' - m = -1 \\ h = -1 \rightarrow \Delta m = m' - m = 1 \end{cases}$$

These are called the two *helicity states* of the photon (with reference to the word helix as in DNA).
Linear polarization is a mixture of these $h = 1$ en $h = -1$ states. There are of course two independent polarization directions in the (transverse) plane perpendicular to the direction of light propagation. By contrast, the electron helicity h_e is defined as the scalar product of the spin of the electron by its linear momentum: $h_e = \boldsymbol{\sigma}_e \cdot \boldsymbol{p_e}/p_e$. Like the circular polarization of the photon, the helicity h_e is odd under space reflection.

9.2 Parity Non-Conservative (PNC) interaction

The electron-quark interaction mediated by Z_0 is proportional to the pseudoscalar electron helicity $h_e = \boldsymbol{\sigma}_e \cdot \boldsymbol{p_e}/p_e$, which is odd under space reflection. Frequently, a scalar angular momentum 'helicity' or 'handedness' operator $K = \vec{\sigma} \cdot \vec{p}$ (for the spin component along the direction of motion) is introduced in relativistic calculations. Alternatively, one may introduce the electron helicity h_e, defined as the scalar product of the spin of the electron and its velocity: $h_e = \boldsymbol{\sigma}_e \cdot \boldsymbol{p_e}/p_e$. Like the circular polarization of the photon, the helicity h_e is odd under space reflection; the PNC interaction is thereby proportional to $h_e\, Q_W\, G_F$, see equation (9.2). A reasonable try is a Hamiltonian of the form:

$$V_{PNC} = \frac{G_F\, Q_W}{2\sqrt{2}\, m_e c} \left(\vec{s} \cdot \vec{p}\ \delta(\vec{r}) + \delta(\vec{r})\ \vec{s} \cdot \vec{p} \right) = -\frac{G_F}{2\sqrt{2}}\, \gamma_5\, Q_W \rho(r) \tag{9.2}$$

where the 'weak charge' Q_W represents the sensitivity (susceptibility) of the nucleus to the weak interaction and γ_5 is the Dirac matrix associated with pseudoscalars, see further explanation in chapter 19. Chirality can be defined in terms of the two chiral projection operators, P_L and P_R that project out the left-handed and right-handed chiral components of a spinor ψ (and the reverse for anti-particles):

$$P_L = \tfrac{1}{2}(1-\gamma_5) \rightarrow P_L\,\psi = \psi_L \tag{9.3a}$$

$$P_R = \tfrac{1}{2}(1+\gamma_5) \rightarrow P_R\,\psi = \psi_R \tag{9.3b}$$

The quantity $\rho(r)$ is a nuclear density function, which is approximately the neutron density. The inner product of a pseudo- or axial vector ($\vec{s}$) and a polar vector ($\vec{p}$) changes sign under reflection (parity inversion) and is thus the desired pseudoscalar.

quarks	Q_W	e.m. charge
up	$\left(1-\frac{8}{3}\sin^2\theta_W\right)$	$\frac{2}{3}e$
down	$\left(-1+\frac{4}{3}\sin^2\theta_W\right)$	$-\frac{1}{3}e$

with: $\sin^2\theta_W = 0.22290(30)$

it follows directly that the weak charge of a nucleus consisting of Z protons and N neutrons is given by:

$$Q_W = Z(1-4\sin^2\theta_W) - N$$

if $\sin^2\theta_W$ were = 0.25, this would yield $Q_W = -N$.

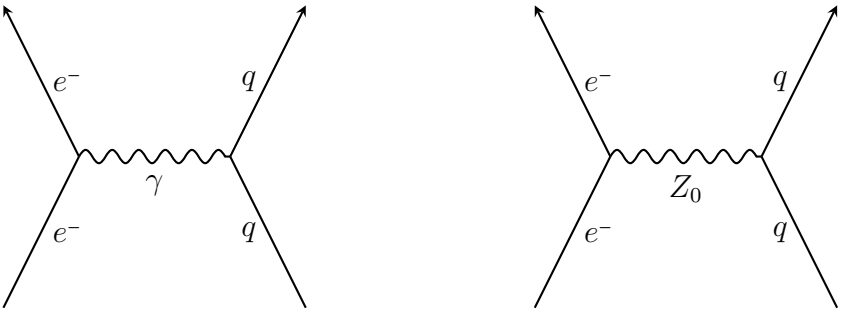


Figure 9.1: Feynman diagrams of the electromagnetic and weak electron-quark interactions.

V_{PNC} violates parity and may therefore mix s- and p-electrons. Thus, the uneven hydrogenic matrix element $\langle 2s_{1/2}|V_{PNC}|2p_{1/2}\rangle$ does not vanish. This gives the $2p$-electron a right-handed screw w.r.t. its spin axis: the left-handed situation does *not* occur in nature. The interference of a magnetic dipole transition with a transition of electric dipole character between the same states, allowed only through the parity non-conserving weak interaction, would make even such an apparently symmetric object as an atom optically active. The Z^0 exchange consequently violates Laporte's rule [Laporte, 1924], i.e. radiative (E_1) transitions may only take place between states of opposite parity.

The cesium atom still represents the best compromise between high Z and simple atomic structure allowing for precise atomic structure calculations.
Irradiating linearly polarized light on ^{133}Cs (Z=55: the magnitude of the observable effect progresses roughly as Z^3, with a theoretical value $Q_W = -72$), yields a right-handed rotation of the polarization direction of 10^{-5} degree, corresponding to the width of a needle observed from a distance of 7.5 km!

In one of the current experiments, one irradiates unpolarized Cs gas with a 5395 Å laser, alternately with left- and right circularly polarized light. Left and right handed photons are absorbed and emitted slightly differently, i.e., the atoms (the intensity of the transmitted light) show optical activity, so-called circular dichroism. Parity is no longer conserved, and the left-right asymmetry A_{LR} of the pertinent cross sections for absorption is given by:

$$A_{LR} = \frac{\sigma_D - \sigma_L}{\sigma_D + \sigma_L} \propto \left\langle 6s_{1/2}|\tilde{E}_1|7s_{1/2}\right\rangle \propto \left\langle 6s_{1/2}|V_{PNC}|\text{ e.g. } 6p_{1/2}\right\rangle$$

where:

$$\left\langle 6s_{1/2}|\tilde{E}_1|7s_{1/2}\right\rangle = \sum\!\!\!\!\!\!\int_n \frac{\left\langle 6s_{1/2}|E_1|np_{1/2}\right\rangle \left\langle np_{1/2}|V_{PNC}|7s_{1/2}\right\rangle}{E_{7s_{1/2}} - E_{np_{1/2}}} + \frac{\left\langle 6s_{1/2}|V_{PNC}|np_{1/2}\right\rangle \left\langle np_{1/2}|E_1|7s_{1/2}\right\rangle}{E_{6s_{1/2}} - E_{np_{1/2}}}$$

An order of magnitude estimate of A_{LR} was first given by [Zel'dovich, 1959]:

$$A_{LR} \propto \left(\alpha \frac{m_e}{M_Z}\right)^2 \approx 10^{-15} \tag{9.4}$$

Fortunately, the [Bouchiat and Bouchiat, 1974] found the below Z^3 law, thus increasing the effect to observable magnitudes in heavy atoms.
Apart from some serious relativistic corrections, $\left\langle 6s_{1/2}|V_{PNC}|6p_{1/2}\right\rangle$ can be calculated with angular momentum algebra to yield:

$$\left\langle ns_{1/2}|V_{PNC}|mp_{1/2}\right\rangle = \frac{3i\hbar}{16\pi m_e c} \frac{G_F Q_W}{\sqrt{2}} R_{ns}(0) \frac{\mathrm{d}}{\mathrm{d}r} R_{mp}(0)$$

Remember that $\vec{p} \to -i\hbar\nabla$ is both imaginary and differentiates.

Approximations for $\mathrm{R}_n s(0)$ and $\mathrm{dR}_{mp}(0)/\mathrm{d}r$ for alkali atoms may be found using quantum defects $n^* = n - \delta(l)$ and an outer charge $Z_0 = Z - (N-1)$.
[Bouchiat et al., 1984] gives:

$$\begin{aligned} |\,\psi(0)\,|^2 &= \left(\text{ Hydrogen: } \frac{Z^3}{\pi n^3 a_0^3}\right) = \frac{Z_i Z_0^2}{\pi n^{*3} a_0^3} \\ R_{ns}(0) &= 2\pi\psi(0) = \frac{2 Z_i^{1/2} Z_0}{n_s^{*3/2} a_0^{3/2}} \end{aligned}$$

Similarly, one finds:

$$\frac{\mathrm{d}}{\mathrm{d}r} R_{mp}(0) = \left(\text{ Hydrogen: } \frac{2}{3}\frac{Z^{5/2}}{n^{3/2} a_0^{5/2}}\right) = \frac{2}{3}\frac{Z_i^{3/2} Z_0}{n_p^{*3/2} a_0^{5/2}}$$

So, for Z_0=1:

$$\left\langle ns_{1/2}|V_{PNC}|mp_{1/2}\right\rangle = \frac{i\hbar}{4\pi m_e c} \frac{G_F Q_W}{\sqrt{2}} \frac{Z_i^2}{n_s^* n_p^{*3/2} a_0^4}$$

Because Q_W ~ Z, one concludes:

$\langle ns_{1/2}|V_{PNC}|mp_{1/2}\rangle \sim Z^3$

PNC is one of the more likely candidates to explain the observed homochirality in nature, and may thus be linked to the origins of life.

Part II

Orthogonal operators

Chapter 10

Hartree-Fock

The inter-electronic Hartree-Fock potential U_{HF} is defined by the equation:

$$(H_{BN} + U_{HF})\,|a\rangle = \varepsilon_a\,|a\rangle \tag{10.1}$$

with the bare nucleus part given by:

$$H_{BN} = \left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}\right)$$

The Restricted Hartee-Fock (RHF) equation, with the 'self-interaction' terms $Y_k(aa,r)\,|a\rangle$ written explicitly, is given by:

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}\right)|a\rangle + \frac{(q_a-1)}{r}\left(Y_0(aa,r) - \sum_{k>0}\frac{\langle l_a \parallel C^{(k)} \parallel l_a\rangle^2}{(2l_a+1)(4l_a+1)}Y_k(aa,r)\right)|a\rangle$$
$$+\sum_{b\neq a}\frac{q_b}{r}\left(Y_0(bb,r) - \frac{1}{2}\sum_k\frac{\langle l_a \parallel C^{(k)} \parallel l_b\rangle^2}{(2l_a+1)(2l_b+1)}Y_k(ab,r)\,|b\rangle\right) + \sum_{b\neq a}\delta(l_a,l_b)q_b\lambda_{ab}\,|b\rangle = \varepsilon_a\,|a\rangle \tag{10.2}$$

The Hartree $Y_k(ab,r) = Y_k(ba,r)$ function is defined as:

$$\begin{aligned}\frac{1}{r}Y_k(ab,r) &= \int_0^\infty \frac{r_<^k}{r_>^{k+1}}P_a(s)P_b(s)\,\mathrm{d}s \\ &= \frac{1}{r^{k+1}}\int_0^r s^k P_a(s)P_b(s)\,\mathrm{d}s + r^k\int_r^\infty \frac{1}{s^{k+1}}P_a(s)P_b(s)\,\mathrm{d}s \\ &= \left\langle a(s)\left|\frac{s^k}{r^{k+1}}\varepsilon(r-s) + \frac{r^k}{s^{k+1}}\varepsilon(s-r)\right|b(s)\right\rangle \end{aligned} \tag{10.3a}$$

The $Y_k(ab,r)$ integral may, according to equation (6.4), also be defined implicitly:

$$R^k(ab,cd) = \int_0^\infty P_a(r)P_c(r)\,\frac{1}{r}\,Y_k(bd,r)\,\mathrm{d}r \tag{10.3b}$$

All this implies the asymptotic behaviour:

$$\lim_{r\to\infty} Y_k(ab,r) = \frac{\langle a(s)|s^k|b(s)\rangle}{r^k} = \delta(k,0)\delta(a,b) \tag{10.4}$$

Neglecting long-range exchange effects that are physically not meaningful, the asymptotic form of U_{HF} becomes:

$$\lim_{r\to\infty} U_{HF}(r) = \frac{q_a-1}{r} + \sum_{b\neq a}\frac{q_b}{r} = \frac{N-1}{r} \tag{10.5}$$

10.1 Average energies in the potential

The interaction energy of a pair of equivalent electrons is given by:

$$C(aa) = \sum_k \left\langle F^k \right\rangle^{(N)} = \binom{N}{2} \frac{\langle l \parallel C^{(k)} \parallel l \rangle^2}{(2l+1)(4l+1)} \left((4l+2)\cdot\delta(k,0) - 1\right) F^k(ll) \tag{10.6}$$

Similarly for the interaction energy of a pair of nonequivalent electrons:

$$\begin{aligned} C(ab) &= N_1 N_2 \left(F^0(ll') - \sum_k \left\langle G^k \right\rangle \right) \\ &= N_1 N_2 \left(F^0(ll') - \tfrac{1}{2}[l,l']^{-1} \left\langle l \parallel C^{(k)} \parallel l' \right\rangle^2 G^k(ll') \right) \end{aligned} \tag{10.7}$$

For a Brillouin excitation $a \to v$ with $l_a = l_v$, generalized pair energies for equivalent and non-equivalent electrons are given by:

$$C(va;aa) = R^0(va;aa) - \sum_{k>0} \frac{\langle l_a \parallel C^{(k)} \parallel l_a \rangle^2}{(2l_a+1)(4l_a+1)} R^k(va;aa) \tag{10.8a}$$

$$C(vb;ab) = R^0(vb;ab) - \frac{1}{2}\sum_k \frac{\langle l_a \parallel C^{(k)} \parallel l_b \rangle^2}{(2l_a+1)(2l_b+1)} R^k(vb;ba) \tag{10.8b}$$

If one incorrectly replaces b by a in equation (10.8b), subscripted 'non-eq', one obtains only part of the correct result (10.8a), subscripted 'eq':

$$C(va;aa)_{\text{non-eq}} = \delta(l_a,l_v)\,\frac{4l_a+1}{4l_a+2}\,C(va;aa)_{\text{eq}} \tag{10.9}$$

Equation (10.9) in fact provides the key to the existence of non-diagonal Lagrange multipliers (NDLM).

Defining $I(a,b) = \langle a|H_{BN}|b\rangle$, one uses expressions (10.8a) and (10.8b) to express the matrix element of the HF potential:

$$\begin{aligned} \langle a|H_{HF}|v\rangle &= \delta(l_a,l_v)\ \left(I(a,v) + \langle a|U_{HF}|v\rangle\right) \\ &= \delta(l_a,l_v)\ \left(I(a,v) + (q_a-1)C(va;aa) + \sum_{b\neq a} q_b\, C(vb;ab) \right) \end{aligned} \tag{10.10}$$

10.2 Koopmans' theorem

By definition, the single electron energy is given by:

$$\varepsilon_a = I(a,a) + \langle a|U_{HF}|a\rangle \tag{10.11}$$

Furthermore, it is straightforward to derive for the total energy of an occupied configuration A:

$$\begin{aligned} E_A &= \sum_a q_a \left(I(a,a) + \tfrac{1}{2}(q_a-1)\,C(aa;aa) + \sum_{b\neq a} \tfrac{1}{2}\, q_b\, C(ab;ab) \right) \\ &= \sum_a q_a\ \left(I(a,a) + \tfrac{1}{2}\,\langle a|U_{HF}|a\rangle \right) \end{aligned} \tag{10.12}$$

Assume configuration B originates from configuration A by substituting a virtual electron v for an occupied electron o ($o \rightarrow v$). The energy E_B is found from equation (10.12) by the replacement $q_o \rightarrow q_o - 1$ and the addition of the $q_v = 1$ terms. Note that both in U^{N-1} and U^{N-2}, one has to solve for the virtual orbitals only; the occupied orbitals remain frozen in going from A to B.
For U^{N-1}, one retrieves Koopmans' theorem in its classic form:

$$E_A - E_B = \varepsilon_o - \varepsilon_v \tag{10.13a}$$

However, a similar derivation for the U^{N-2} case $o_1 o_2 \rightarrow v_1 v_2$ reveals a non-trivial generalization of the energy denominator:

$$E_A - E_B = \varepsilon_{o_1} + \varepsilon_{o_2} - \varepsilon_{v_1} - \varepsilon_{v_2} + C(v_1 v_2; v_1 v_2) - C(o_1 o_2; o_1 o_2) \tag{10.13b}$$

Equation (10.13b) is also valid if $o_1 = o_2$.

10.3 Brillouin's theorem

For a single excitation from an occupied to a virtual shell $o \rightarrow v$, one obtains multiplying equation (10.2) with $\langle v|$ from the right:

$$\langle v|H_{HF}|o\rangle = \delta(l_o, l_v)\left(I(v,o) + (q_o - 1)C(oo;ov)_{\text{eq}} + \sum_{a\neq o,v} q_a\, C(ao;av)\right) = 0 \tag{10.14a}$$

Subsequently, one calculates $|v\rangle$ in U^{N-1}, with the replacement $q_o \rightarrow q_o - 1$. This gives:

$$\langle o|H_{HF}|v\rangle = \delta(l_o, l_v)\left(I(o,v) + (q_o - 1)C(oo;ov)_{\text{non-eq}} + \sum_{a\neq o,v} q_a\, C(ao;av) + (q_o - 1)\lambda_{ov}\right) = 0 \tag{10.14b}$$

Apparently, with the uses of equation (10.9), one has:

$$\lambda_{ov} = \delta(l_o, l_v)\,\frac{C(oo;ov)_{\text{eq}}}{4l_0 + 2} \qquad (q_o > 1) \tag{10.15}$$

Equation (10.14a), one of the forms of Brillouin's theorem, can be used in perturbation theory to eliminate effects from the interaction that are included in the Hartree-Fock potential already. Given the approximation of a frozen core, one can simplify Brillouin type interactions in Rydberg series interactions like $l^n l' \leftrightarrow l^n l''$ ($l' = l''$), where the interaction integrals can be treated exactly as the single configuration Slater integrals when removing average energy contributions. Closed shells effects and $R^0(ll';ll'')$ are canceled and the exchange terms of equation (10.8b) are subtracted from the corresponding coefficients of the exchange integrals $R^k(ll';l''l)$.
Consequently, Brillouin type interactions may be rewritten in terms of outer shells only [Froese Fischer, 1978, Froese Fischer, 1977].

10.4 NDLM involving passive and virtual orbitals

Assuming orbital a to be a spectator of an excitation $o \to v$ (U^{N-1} case, but here $l_0 \neq l_v$ is allowed as well), one obtains directly:

$$q_a \lambda_{av} = \delta(l_a, l_v) \left[\left(\frac{q_a}{4l_a + 2} - 1 \right) C(aa; av) + C(oa; ov) \right] \tag{10.16}$$

For the excitation $1s^2 2p\underline{3d} \to 1s^2 2p\underline{2s}$ in beryllium, this leads to:

$$\lambda_{1s,2s} = \tfrac{1}{2} C(3d\,1s; 3d\,2s)$$

In the B-spline approach to basis set calculations, equation (10.16) cannot be used directly if the occupied orbital (3d in the example) is an orbital to be determined: a double or triple occurrence of such orbitals makes the eigenvalue problem non-linear (Landtman *et al* 1993). In that case, however, $C(oa; ov)$ can simply be eliminated from equation (10.14a).
The NDLM in the above example then becomes:

$$\lambda_{1s,2s} = -\tfrac{1}{2} \left(I(1s, 2s) + C(1s^2; 1s\,2s) + C(2p\,1s; 2p\,2s) \right)$$

For NDLM between occupied orbitals, one of the two shells being a closed shell c, one obtains:

$$\lambda_{co} = \delta(l_c, l_o) \, \frac{C(oo; oc)}{4l_o + 2} \tag{10.17}$$

Again, if orbital o has to be determined in a B-spline approach, the triple occurrence in the above equation prevents it from being used in this form. However, the Brillouin condition $\langle c|H_{HF}|o\rangle = 0$ can again be used to eliminate the problem. For the Li $1s^2 2s$ case, this yields:

$$\lambda_{1s,2s} = \tfrac{1}{2} C(2s^2; 2s\,1s) = -\tfrac{1}{2} \left(I(1s, 2s) + C(1s^2; 1s\,2s) \right)$$

10.5 Silverstone-Huzinaga potential

In a perturbation calculation, one first calculates the model space states e.g. with a fully relaxed Hartree-Fock calculation, and subsequently the virtual states as excitations from this model space, i.e. in the original potential with one or two electrons removed. In this way, both the occupied and the virtual orbitals feel the asymptotically correct potential. However, as the U^{N-1} and U^{N-2} potentials for virtual states do not coincide with the full U_{HF}, it is not immediately obvious that all virtual states are orthogonal to all occupied states. For this reason, Silverstone and Huzinaga independently developed an operator projection method to define a new potential U_{SH} in which both occupied and virtual orbitals could be determined simultaneously. Below, it is shown that a natural choice for the potential extension will exactly yield the U^{N-1} and U^{N-2} potentials for the virtual orbitals. The above requirement may be fulfilled if one subtracts from U_{HF} a potential part Ω that only operates on virtual states:

$$U_{SH} = U_{HF} - Q^\dagger \, \Omega \, Q \tag{10.18}$$

where

$$Q = 1 - P = 1 - \sum_{a \neq v} |a\rangle \langle a| \tag{10.19}$$

is the projection operator on the space of virtual states, i.e. $Q|a\rangle = 0$ and $Q|v\rangle = |v\rangle$, and the potential Ω is as yet undefined.
From the above definition of Q, it is a simple matter to work out that for all occupied orbitals a:

$$\langle a|U_{SH}|a\rangle = \langle a|U_{HF}|a\rangle \tag{10.20}$$

On the other hand, from the action of U_{SH} on the virtual orbitals:

$$U_{SH}\,|v\rangle = (U_{HF} - \Omega + P\,\Omega)\,|v\rangle$$

one finds directly:

$$\langle v|U_{SH}|v\rangle = \langle v|U_{HF} - \Omega|v\rangle \tag{10.21}$$

10.5.1 Choice Ω in the single particle case

To achieve a correct asymptotical behaviour for the case $o \to c$, one defines $\Omega\,|v\rangle$ in accordance with $U_{HF}\,|v\rangle$, the only non-zero occupation being $+1$ for shell o:

$$\Omega\,|v\rangle = \frac{1}{r}\left(Y_0(oo,r)\,|v\rangle - \frac{1}{2}\sum_k \frac{\langle l_v \parallel C^{(k)} \parallel l_o\rangle^2}{(2l_v+1)(2l_o+1)} Y_k(vo,r)\,|o\rangle\right) + \delta(l_v,l_o)\lambda_{vo}\,|o\rangle \tag{10.22}$$

This gives:

$$U_{SH}\;|v\rangle = U^{N-1}\;|v\rangle + P\,\Omega\;|v\rangle \tag{10.23}$$

the remaining difference between U_{SH} and U^{N-1} being:

$$\begin{aligned} P\,\Omega\;|v\rangle = \sum_{a \neq v} |a\rangle\langle a|\Omega|v\rangle &= \sum_{a \neq o,v} \delta(l_a,l_v)\,C(ao;vo)\;|a\rangle \\ &+\delta(l_o,l_v)\left(\frac{4l_o+1}{4l_o+2}\,C(oo;ov) + \lambda_{vo}\right)|o\rangle \end{aligned} \tag{10.24}$$

This residue takes the form of NDLM!
With the above specified potential, the quantities λ_{vo} and λ_{va} are given by:

$$\lambda_{va} = \delta(l_a,l_v)\left(\frac{1}{4l_a+2} - \frac{1}{q_a}\right) C(aa;av) \tag{10.25}$$

which is valid whether the orbital a remains passive or equals the excited orbital o.
Combining equations (10.24) and (10.25) to give the total NDLM for the U_{SH} case, they turn out to coincide exactly with the NDLM of the U^{N-1} potential.
Use of U^{N-1} (with correctly defined NDLM) is indeed equivalent to using a U_{SH}. As a result, the orthogonality of virtual orbitals calculated with U^{N-1} is assured.

10.5.2 Choice Ω in the two-particle case

One may generalize the above method to the two-particle case $o_1 o_2 \to v_2 v_2$ to define $\Omega\,|v_1\rangle$ in analogy to $U_{HF}\,|v_1\rangle$. Here, the non-zero occupation numbers are +1 for o_1 and o_2 and -1 for v_2. Obviously, $\Omega\,|v_2\rangle$ is defined in a similar way. The analogue of equation (10.24) then becomes:

$$\begin{aligned} P\,\Omega\,|v_1\rangle = \sum_{a\neq o1,o2} & \delta(l_a, l_{v1})\,(C(ao_1; v_1 o_1) + C(ao_2; v_1 o_2) - C(av_1; v_1 v_2))\;|a\rangle \\ & + \delta(l_{o1}, l_{v1})\left(\frac{4l_{o1}+1}{4l_{o1}+2}\,C(o_1 o_1; v_1 o_1) + C(o_1 o_2; v_1 o_2)\right. \\ & \left. - C(o_1 v_2; v_1 v_2) + \lambda_{o_1 v_1}\right)|o_1\rangle \\ & + \delta(l_{o2}, l_{v1})\left(\frac{4l_{o2}+1}{4l_{o2}+2}\,C(o_2 o_2; v_1 o_2) + C(o_2 o_1; v_1 o_1)\right. \\ & \left. - C(o_2 v_2; v_1 v_2) + \lambda_{o_2 v_1}\right)|o_2\rangle \end{aligned} \tag{10.26}$$

The NDLM appearing here are the same as in the one-particle case:

$$\lambda_{v1\,a} = \delta(l_a, l_{v1})\left(\frac{1}{4l_a+2} - \frac{1}{q_a}\right)C(aa; av_1) \tag{10.27}$$

which is valid whether the orbital a refers to a spectator electron or to an excited electron. A similar formula applies to the NDLM involving v_2.
Again, the total NDLM for the U_{SH} potential exactly yield the NDLM U^{N-2} potential. Like U^{N-1}, U^{N-2} turns out to be equivalent to the corresponding U_{SH} potential, and the orthogonality of its virtual orbitals is guaranteed.

Chapter 11

B-splines

To solve the Schrödinger equation including valence and core-valence correlation for atoms and ions, finite basis sets may be constructed from piecewise polynomials known as B-splines. The radial Schrödinger equation may be written as

$$0 = \mathcal{L}F := \left[\frac{1}{2}\frac{d^2}{dr^2} + E - V(r)\right]F(r) \tag{11.1}$$

$\mathcal{L}$ is seen as a quantummechanical operator. The solution of the differential equation can be approximated by a finite linear superposition of *a priori* known basis functions. This approach is associated with the names of Rayleigh, Ritz and Galerkin. With the use of these basis functions, we can write the solution to the differential equation as:

$$\tilde{F} = \sum_{\nu} C_\nu F_\nu(r) \tag{11.2}$$

in which $\tilde{F}$ is the approximation to the exact solution of the differential equation, C_ν are the unknowns to be determined by a calculation and $F_\nu(r)$ are the basis functions. In the Galerkin scheme, we require that the projections of $\mathcal{L}\tilde{F}$ on the basis functions F_μ are zero for each μ

$$0 = \langle F_\mu | \mathcal{L}\tilde{F} \rangle \tag{11.3}$$

yielding the matrix equation:

$$0 = \sum_{\nu} C_\nu \langle F_\mu | \mathcal{L} F_\nu \rangle \tag{11.4}$$

to be solved by straightforward by matrix diagonalization. This diagonalization provides the eigenvectors that determine the solution with respect to the (*a priori*) known basis functions. The desired solution of the radial Schrödinger equation (equation (11.1)) is then constructed as a linear combination of these basis functions with the eigenvector components as coefficients (equation (11.2)). This method can also be used to construct the solutions to our RHF equation, which is after all just another differential equation like the radial Schrödinger equation.
For a given angular momentum channel, it usually suffices to work with 40 basis functions. Radial grid points can be chosen freely: to accurately describe continuum

states, a set of points can be evenly placed at large distances from the atom, and if the finite size of the nucleus is important, extra points can be placed at very small distances. Integrals can be evaluated to machine accuracy with Gaussian integration.
The atom or ion under consideration is confined in a spherical cavity of radius R, next the interval $[0, R]$ is divided in segments. In the non-relativistic case, this leads to the boundary conditions that the wavefunction vanish at $r = 0$ and $r = R$.
Choosing $R \approx 40/Z_{\text{ion}}$ au, where Z_{ion} is the ionic charge, is accurate enough to calculate low-lying excited states. For Rydberg states a larger radius is chosen, say twice the average radius of the outmost state.
The endpoints of the segments are given by the knot sequence $\{t_i\}, i = 1, 2, ..., n + k$. The B-splines of order $k, B_{i,k}(r)$, on this knot sequence are defined recursively by the relations:

$$B_{i,1}(r) = \begin{cases} 1, & t_i \le r < t_{i+1} \\ 0, & \text{otherwise} \end{cases} \tag{11.5}$$

and

$$B_{i,k}(r) = \frac{r - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(r) + \frac{t_{i+k} - r}{t_{i+k-1} - t_{i+1}} B_{i+1,k-1}(r) \tag{11.6}$$

The knots $t_k, t_{k+1}, ..., t_n$ are distributed on an exponential scale between 0 and the cavity radius R.
The spline basis is an expansion of $P_l(r)$ in terms of B-splines of order k:

$$P_l(r) = \sum_{i=2}^{n-1} p_i \, B_i(r) \leftrightarrow |a\rangle = \sum_i p_i \, |B_i\rangle \quad \text{First and last splines are discarded.} \tag{11.7}$$

Application of the variational principle leads to an $(n-2)\times(n-2)$ eigenvalue equation:

$$H \, \mathbf{v} = \varepsilon \, S \, \mathbf{v} \tag{11.8}$$

with $\mathbf{v}$ the vector of expansion coefficients $\mathbf{v}^T = (p_2, p_3, ..., p_{n-1})^T$.
For single-electron atoms, the matrices H and S are given by:

$$H_{ij} = \langle B_i | H_{BN} | B_j \rangle = \left\langle B_i \left| -\frac{1}{2} \frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right| B_j \right\rangle \tag{11.9a}$$

$$S_{ij} = \langle B_i | B_j \rangle = \int_0^R B_i(r) \, B_j(r) \, \mathrm{d}r \tag{11.9b}$$

The notation $\langle B_i | O | B_j \rangle$ implies the integration $\int_0^R (B_i \, O \, B_j) \, \mathrm{d}r$.
The matrices H and S are sparse, diagonally dominant banded matrices; the definition directly implies: $\langle B_i | B_j \rangle = 0$ for $|i - j| \ge k$.
After solution, one obtains $(n-2)$ real eigenvalues ε^λ and $(n-2)$ eigenvectors v^λ. The eigenvectors satisfy the orthogonality relations:

$$\sum_{i,j} v_i^\lambda \, S_{ij} \, v_j^\mu = \delta_{\lambda\mu} \tag{11.10}$$

With $H = H_{BN} + U$, one may derive equation (11.8):

$$H \left| \sum_i p_i B_i \right\rangle = E \left| \sum_i p_i B_i \right\rangle \rightarrow \sum_i \langle B_j|H|p_i B_i\rangle = \sum_i E_i \delta_{ij} p_i \langle B_j|B_i\rangle$$

In Hartree-Fock calculations, the matrix elements H_{ij} are extended with the U_{HF} contribution. Below, equation (10.2) is used with $q_a = 1$; note that the remaining core remains frozen for applications in perturbation theory, and the sum runs over occupied states b.

$$\begin{aligned} H_{ij} &= \langle B_i|H_{BN} + U_{HF}|B_j\rangle = \langle B_i|H_{BN}|B_j\rangle \\ &+ \sum_b q_b \left\langle B_i \left| \frac{1}{r} Y_0(bb,r) \right| B_j \right\rangle - \frac{1}{2} \sum_k \frac{\langle l_a \parallel C^{(k)} \parallel l_b \rangle^2}{(2l_a+1)(2l_b+1)} \langle B_i|Y_k(bB_j,r)|b\rangle + \sum_b \delta(l_a,l_b) q_b \lambda_{ab}|b> \end{aligned} \tag{11.11}$$

11.1 Projection operators [Bentley, 1994]

The orthogonality-constrained one-body eigenvalue problem is formulated for complete, finite-dimensional spaces in terms of projection operators that partition the space into two orthogonal subspaces, one containing the constraints and one containing the desired solutions. We derive a Hermitian operator, associated with the Hamiltonian, having eigenvectors that are correspondingly partitioned, each subset of the eigenvectors providing a basis for one of the subspaces. This Hermitian operator advantageously replaces a non-Hermitian operator that was proposed in recent work of this group. The non-zero spectrum of the two operators is demonstrably the same, and the occurrence of null eigenvalues is clarified through characterization of the associated eigenvectors. The deviation from zero of these eigenvalues (apart from numerical inaccuracies) is related directly to the normalization of the constraint vectors. The formalism is extended to the case of non-orthonormal primitive basis sets, and a numerical application is carried out using B-spline functions.

Analogous to the projection operator $Q = 1 - P$ defined earlier in equation (10.19), a Hermitian virtual space projector Q is found that satisfies both

$$\begin{aligned} Q|v> &= |v> \text{ and} \\ QH|v> &= \varepsilon|v> \end{aligned} \tag{11.12}$$

whereas $P|a> = |a>$ and $P|v> = 0$.

Any eigensolution of QH corresponding to $\varepsilon \neq 0$ lies entirely in Q-space and is therefore orthogonal to $|a>$. In principle, QH may be non-Hermitian, but the Hermitian operator QHQ (by definition with real eigenvalues and orthogonal eigenvectors) shares the same spectrum:

$$\begin{aligned} QHQ|v> &= \varepsilon|v> \\ QHQ|a> &= 0 \cdot |a> \end{aligned} \tag{11.13}$$

More general: expand an arbitrary model state $|a>=\sum_i u_i|\phi_i>$ in an orthonormal basis, with the coefficient vector $\mathbf{u}^T=(u_1,u_2,\cdots,u_N)^T$. Then:

$$P=\mathbf{u}\mathbf{u}^T \qquad Q=1-\mathbf{u}\mathbf{u}^T \tag{11.14}$$

the constrained eigenvalue problem for the v_i then becomes:

$$(1-\mathbf{u}\mathbf{u}^T)\,H\,(1-\mathbf{u}\mathbf{u}^T)\,\mathbf{v}=\varepsilon\,\mathbf{v} \tag{11.15}$$

with the Hamiltonian matrix H defined as $H_{ij}=<\phi_i|H|\phi_j>$.
If there are M independent vectors of constraint, QHQ will have $N-M$ eigenvectors lying in Q-space and M zero eigenvalues corresponding to eigenvectors lying in P-space spanned by M eigenvectors.

11.2 Extension to non-orthonormal basis sets

The matrix relation (11.15) must be modified upon representation of the states in terms of a non-orthonormal basis, as for example the increasingly popular B-spline functions (which are neither normalized, in the usual sense, nor orthogonal) or the long-established Gaussian functions.
Let the states $|a>$ and $|v>$ be represented by $|a>=\sum_{i=1}^{N}\,p_i\,|B_i>$ and $|v>=\sum_{i=1}^{N}\,q_i\,|B_i>$.
The coefficient vectors are $\mathbf{p}^T=(p_1,p_2,\cdots,p_N)^T$ and $\mathbf{q}^T=(q_1,q_2,\cdots,q_N)^T$.
The non-diagonal overlap matrix S is by equation (11.9b) defined as $S_{ij}=\langle B_i|B_j\rangle$.
Now, normalization and orthogonality are expressed by:

$$<a|a>=\mathbf{p}^T\,S\,\mathbf{p}=1 \qquad \text{and} \tag{11.16a}$$

$$<a|v>=\mathbf{p}^T\,S\,\mathbf{q}=0 \tag{11.16b}$$

The eigenvalue equation (see equation (11.8)) becomes:

$$H\,\mathbf{q}=\varepsilon\,S\,\mathbf{q} \tag{11.17}$$

In the non-orthonormal B-spline basis set, the matrices P and Q remain Hermitian but do not remain projectors.
Introducing the constraint matrix $C=\mathbf{p}\mathbf{p}^T$, one obtains for P:

$$P=\sum_{m,n}p_m p_n\,|B_m><B_n| \;\rightarrow P_{ij}=\sum_{m,n}p_m p_n\,S_{im}S_{nj}$$
$$P=S\mathbf{p}\mathbf{p}^TS=SCS\rightarrow Q=S-SCS \tag{11.18}$$

Upon defining, for notational convenience:

$$U=CS\rightarrow P=SU \text{ and } W=1-U\rightarrow Q=SW \tag{11.19}$$

From this, it is straightforward to show: $WW=W \quad UU=U \quad UW=WU=0$.
So, though non-Hermitian, U and W are orthogonal projectors.

$$U\mathbf{p}=\mathbf{p}\mathbf{p}^TS\mathbf{p}=\mathbf{p} \quad \text{and} \quad W\mathbf{q}=\mathbf{q} \tag{11.20}$$

demonstrates that states $|a>$ lie in $U-$space and $|v>$ in $W-$space.
As a result, solutions $|v>$ will automatically be orthogonal to all $|a>$:

$$\langle a|v\rangle = \mathbf{p}^T S\mathbf{q} = \mathbf{p}^T SW\mathbf{q} = \mathbf{p}^T(S - SCS)\mathbf{q} = \mathbf{p}^T S\mathbf{q} - \mathbf{p}^T S\mathbf{p}\mathbf{p}^T S\mathbf{q} = \mathbf{p}^T S\mathbf{q} - \mathbf{p}^T S\mathbf{q} = 0.$$

The analogon of equation (11.13) thus becomes:

$$W^T\, H\, W\, \mathbf{q} = \varepsilon\, S\, \mathbf{q} \tag{11.21}$$

Written out more explicitly, the final expression to be compared with equation (11.15) becomes:

$$(1 - S\mathbf{p}\mathbf{p}^T)H(1 - \mathbf{p}\mathbf{p}^T S)\, \mathbf{q} = \varepsilon\, S\, \mathbf{q} \tag{11.22}$$

As the contraint orbitals $|a>$ and their coefficient vectors $\mathbf{p}$ are supposed to be known in advance, it is straightforward to construct the required operator W.

Chapter 12

Least Squares Fitting

In the least squares fitting process (LSF), one seeks to obtain an optimal agreement between measured data and corresponding quantities calculated from a theoretical model (i.e. an assumed functional form of the data). The model is based on a restricted number of parameters. These parameters are adjusted, or 'fitted', so as to minimize the LSF sum R^2. If we denote the experimental values as E_i and the associated model values T_i, then:

$$R^2 = \sum_i w_i (E_i - T_i)^2 = \sum_i \varepsilon_{ii}^2 \tag{12.1}$$

In the above, the index i ($i = 1, ..., N$) is assumed to run over the known experimental values E_i. The factor w_i represents the weight assigned to the ith value. Taking the derivative of R^2 with respect to a particular parameter P_l ($l = 1, ..., M$ where M equals the number of parameters) and requiring it to be zero, one obtains:

$$\sum_i w_i (E_i - T_i) \frac{\partial T_i}{\partial P_l} = 0 \qquad (\forall l = 1, ..., M) \tag{12.2}$$

If (12.2) is not satisfied by the actual parameters P_l, the latter will be improved by increments ΔP_l following from the requirement that (12.2) is now satisfied by $P^* = P_k + \Delta P_l$. This leads to the well known set of equations to be solved iteratively in the LSF:

$$\sum_{m=1,..,M} A_{lm} \cdot \Delta P_m = \sum_{m=1,..,M} \left(\sum_i w_i \frac{\partial T_i}{\partial P_l} \frac{\partial T_i}{\partial P_m} \right) \Delta P_m$$

$$= \sum_i w_i \frac{\partial T_i}{\partial P_l} (E_i - T_i) \qquad (\forall l = 1, ..., M) \tag{12.3}$$

In the present case, we want to assign to each energy level a weight proportional to its number of degenerate magnetic sublevels $(2J+1)$. In order to retain a meaningful definition of the mean errors and compatibility with previous LSF (w_i(old)= 1 for each level). the weighting factors have to be normalized in the sense:

$$\sum_i w_i(\text{new}) = \sum_i w_i(\text{old}) \tag{12.4a}$$

or

$$\sum_i w_i(\text{new}) = N \tag{12.4b}$$

Equation (12.4) implies that:

$$w_i(\text{new}) = \frac{(2J_i+1)}{(2J+1)_{\text{av}}} = (2J_i+1)\left(\sum_k \frac{(2J_k+1)}{N}\right)^{-1}. \tag{12.5}$$

N denotes the number of known experimental levels.
Using (12.5), one can verify equation (12.4b), again provided that the indices i and k in (12.4) and (12.5) only run over known experimental levels.

Racah's average deviation σ between experimental and calculated levels is still defined as:

$$\sigma = \left(\frac{R^2}{N-M}\right)^{\frac{1}{2}} = \left(\frac{\sum_i w_i(E_i-T_i)^2}{N-M}\right)^{\frac{1}{2}} = \left(\frac{\sum_i \varepsilon_{ii}^2}{N-M}\right)^{\frac{1}{2}} \tag{12.6}$$

but of course now the w_i(new) have to be inserted. The same is true for the mean errors RMS_l on the parameters P_l:

$$\text{RMS}_l = \sigma \left(A_{ll}^{-1}\right)^{-\frac{1}{2}} \tag{12.7a}$$

where A_{ll}^{-1} is a diagonal matrix element of the inverted matrix A_{lm} occurring on the LHS of (12.3):

$$\left(\sum_i w_i \frac{\partial T_i}{\partial P_l}\frac{\partial T_i}{\partial P_m}\right) \tag{12.7b}$$

On the whole process of the above weighted fitting, a general remark is in order. In other fields, LSF are often used to 'smooth away' irregularities in the experimental data due to measuring errors. In the parametric theory of atoms, however, the experimental accuracy is mostly as least a factor of ten better than the theoretical one, even after the parameters have been fitted. So in this case it is rather the deficient model that causes the remaining differences between calculation and measurement. Reduction of these differences can only be achieved by an improvement (i.e. an extension) of the model, not by improving the experimental accuracy. Therefore, the introduction of the weighting factor is not based on the experimental grounds of reliability of *measurements*, but on the idea of making the *model* as consistent as possible. It takes into account the number of physical levels that, although degenerate, actually do exist for a particular J-value; the same applies to the inner products of operators.
In the same spirit, it has been suggested by [Judd et al., 1989] to minimize the alternative expression $\sum_{ij} \varepsilon_{ij}\,\varepsilon_{ji}$ instead of the conventional $\sum_i \varepsilon_{ii}^2$. However, this would complicate the above introduction of a new weighting factor.

12.1 Orthogonality

Consider the solution to a system of non-homogeneous equations described by a matrix equation $A\mathbf{x} = \mathbf{b}$ where $\mathbf{x}$ is a vector of parameters (to be determined) and the vector $\mathbf{b}$ corresponds to the observed energy level values in our case while the

matrix A contains the (diagonal) matrix elements of the operators associated with the parameters. The number of parameters is assumed to be smaller or equal to the number of energy levels. In our case due to errors of measurement the system most likely will not have an exact solution. In linear algebra it is shown that in this case the best solution in the least-squares sense is given by

$$\mathbf{x} = \left(A^T A\right)^{-1} A^T \mathbf{b} \tag{12.8a}$$

where A^T is the transpose of A. Thus a solution involves inverting the product matrix $A^T A$. In general this will make the value of each x_i dependent on all others. However, if the matrix A is orthogonal, so that each row (column) is orthonormal to any other row (column) we have $A^T = A^{-1}$ and the equation simplifies to:

$$\mathbf{x} = A^T \mathbf{b} \tag{12.8b}$$

if we write the above in terms of components we have

$$x_i = \sum_j a_{ij} b_j \tag{12.8c}$$

In this equation the summation is over the experimental energy levels (the **b** vector) multiplied by the matrix elements of the i'th operator (the a_{ij}). Thus the value of the parameters x_i associated with the i'th operator is determined independently of any other parameter which is the situation we want. If the rows (columns) of the matrix A are orthogonal to each other but not normalized to 1, the inverse of the $A^T A$ matrix is still a diagonal matrix, but not the unit matrix, which only changes the sizes of the parameters but not their dependence.
As the model matrix A may be rectangular and thus has no inverse, the system is not exactly soluble.
One multiplies both sides of the expression $A\mathbf{x} \approx \mathbf{b}$ from the left with the transposed matrix A^T, resulting in $A^T A\mathbf{x} = A^T\mathbf{b}$.
As the matrix $A^T A$ is known to be invertable, one may multiply both sides with $(A^T A)^{-1}$, ending up with $\mathbf{x} = (A^T A)^{-1} A^T \mathbf{b}$.

Steps:

1. Calculate A^T from A.
2. Next, calculate $(A^T A)^{-1}$
3. The RHS of the equation $\mathbf{x} = (A^T A)^{-1} A^T \mathbf{b}$ is now completely known.

Chapter 13

Group theory, a bird's-eye view

1931,1932 [Weyl, 1931, Wigner, 1931, van der Waerden, 1932] introduce groups among other things in angular momentum theory. Groups account for symmetries in physical structure. [Noether, 1918]: to every symmetry, there belongs a conserved quantity i.e. a 'constant of motion'.

1935 [Condon and Shortley, 1935]: one can do without!

1942 [Racah, 1942a, Racah, 1942b] introduces the tensor operator $T_q^{(k)}$ with the same transformation
properties as the angular momentum state $|J, M_J>$ with $J = k$ and $M_J = q$.
For scalars (like energy operators): $k = 0$, the operator cannot change the J-value between bra and ket.
For vectors (like the electric dipole operator): $k = 1, \Delta J = 1$ at maximum.

Transformation under the *generators* A_x, A_y and A_z of a continuous Lie group.
For example, an electron i is rotated by $A_z = \ell_z = -i\frac{\partial}{\partial\phi}$:
$\rightarrow$ the operator $\exp(i\Delta\phi A_z)$ converts $f(\theta, \phi)$ into $f(\theta, \phi + \Delta\phi)$.
Terminology: $\vec{A}$ generates the group R_3 or SO(3).

$\vec{A} = \vec{\ell}$ rotates each electron individually

$\vec{A} = \vec{L}$ rotates all electrons as a whole: $SO_L(3)$

$\vec{A} = \vec{S}$ rotates total electron spin: $SO_S(3)$

The Wigner-Eckart theorem can be applied: this separates the geometric features of a problem (like M_L, q, M_S) from intrinsically physical aspects. This simplification allows for the calculation of many matrix elements!

1949, 1951 [Racah, 1949] introduced in the f^n configuration space a scheme of basis states belonging to unitary irreducible representations of a chain of semi-simple continuous groups, each of which is a subgroup of the preceding group in the chain. Racah established the chain from groups of unitary transformations in the space spanned by the $2l + 1$ single-electron wave functions ψ_{nlm_l}. As the largest group he chose the unitary group $U(2l+1)$. It has as subgroups the orthogonal group $O(2l + 1)$ which leaves invariant the symmetric S state $|l^2 L = 0\rangle$ of two electrons, and the group $O(3)$ of three dimensional rotations.

For $l \geq 2$, the corresponding group chain is $\mathrm{U}(2l+1) \supset \mathrm{O}(2l+1) \supset \mathrm{O}(3)$, or even a longer chain. The reduction chain $\mathrm{SO}(7) \supset \mathrm{G}_2 \supset \mathrm{SO}(3)$ is historically among the first examples of the so-called internal labeling problem. The irreducible representations of $\mathrm{U}(2l+1)$ are characterized by their permutational symmetry and the corresponding quantum number is S. The irreducible representations of $\mathrm{O}(2l+1)$ are characterized by the seniority quantum number ν, and the irreducible representations of $\mathrm{O}(3)$ are characterized by L. Thus group theory leads one to the seniority scheme with basis states $|l^n \nu L M_L S M_S\rangle$, which for the configurations d^n overcomes the term multiplicity problem without additional quantum numbers α. For f^n, additional quantum numbers are still required. Racah found that for $l = 3$, there is a unitary group G_2 [one of the five special groups in Cartan's classification in his 1894 thesis], which is a subgroup of $\mathrm{O}(7)$ and contains $O(3)$. He adopted a scheme corresponding to irreducible representations of the group chain $U(7) \supset O(7) \supset G_2 \supset O(3)$ with basis states $|f^n \alpha W U L M_L S M_S\rangle$, where W is a three-component vector characterizing the irreducible representations of $\mathrm{O}(7)$ similarly to the seniority, U is a two-dimensional vector characterizing the irreducible representations of G_2, and α denotes additional quantum numbers when required. In the f shell, there are four Slater parameters F^0, F^2, F^4 and F^6, and three generalized Trees [Trees, 1963] parameters α, β and γ. The effects of distant configurations involving single-electron excitations involve six additional parameters T^i, which are associated with three-electron scalar operators [Judd, 1966]. The principal difference of this analysis from that of the d shell lies in the more extensive use of the theory of groups. Instead of the F^k, it is more convenient to use the four linear combinations E^0, E^1, E^2 and E^3 introduced by [Racah, 1949]. The associated operators e_0, e_1, e_2 and e_3 are each labeled by an irreducible representation W of $\mathrm{SO}(7)$ and U of G_2. The same is true of the operators t_i, associated with the T^i. The use of groups simplifies the calculation of matrix elements and helps distinguish spectroscopic terms possessing the same values of the quantum numbers S and L, the total spin and total orbital angular momentum.

Group theory helps in other ways. One of the more remarkable developments is the construction of orthogonal operators. Consider the two operators H_1 and H_2 that belong to the two non-adjoint irreducible representations Γ_1 and Γ_2 of a group $\mathcal{G}$. If the collection of states $|\psi_n\rangle$ forms a basis for a representation (not necessarily irreducible) of the group $\mathcal{G}$, then the equation

$$\sum_{n,m} \langle \psi_n | H_1 | \psi_m \rangle \langle \psi_m | H_2 | \psi_n \rangle = 0 \tag{13.1}$$

follows from the fact that $H_1 H_2$ does not contain the identity representation Γ_0 of $\mathcal{G}$ [Judd, 1984]. Any two operators of differing symmetries Γ_1 and Γ_2 (i.e., for which $\Gamma_1 \Gamma_2$ does not contain the identity representation) are automatically orthogonal. The fact that the operators of a set are all mutually orthogonal in their parent configuration, and that among them is to be found the total scalar E_{av}, guarantees orthogonality in all configurations with larger N [Judd, 1984].

The construction of the orthogonal operators for configurations of equivalent

electrons is greatly facilitated by the use of Lie groups such as $U(4l+2)$, $Sp(4l+2)$ (the symplectic group in $4l+2$ dimensions), $SO(2l+1)$ and G_2.
Operators that are characterized by different sets of irreducible representations are necessarily orthogonal provided that the collection of terms ψ (or ψ') over which the sums are made form a basis for a representation (not necessarily irreducible) of the group being used [Judd, 1984]. However, it does not always turn out that operators constructed with well defined group theoretical properties are the most appropriate. The operator e_2, mentioned earlier, corresponds to a single set of irreducible representations of the groups $U(14)$, $Sp(14)$, $SO(7)$ and G_2: but e_3 does not. We can resolve e_3 into two parts, each having a single set of group labels, by writing $e_3 = (e_3 + \Omega) - \Omega$, where Ω is related to Casimir's operator for G_2 [Racah, 1949], but the separate parts $e_3 + \Omega$ and Ω incorporate not only the Coulomb interaction between the f electrons but also effective operators of the Trees type. It would clearly be better to use a different pair of orthogonal operators, one of which is e_3. A detailed calculation reveals that the other has to be $e_3 + 5\Omega$ [Judd and Crosswhite, 1984]. The $SO(7)$ and G_2 labels remain good, but the symplectic representations become mixed. This disadvantage is offset by having two operators (e_3 and $e_3 + 5\Omega$) whose strengths are represented by a large parameter (for e_3) and a small one (for the generalized Trees operator $e_3 + 5\Omega$). The corresponding parameters for $e_3 + \Omega$ and Ω would both be large and the effects of configuration interaction would be masked by the larger first-order Coulomb interaction.
Racah also introduces *non-invariance* or *non-symmetry* groups:
the generators of these groups do *not* commute with the Hamiltonian, i.e. they are not conserved quantities or constants of motion. Therefore, they do *not* yield 'good' quantum numbers to label states in nature.
A typical example is given by the two ^{2}D states in d^3: $^2_1$D corresponds to a different SO(5) label then $^2_3$D; the 'real' ^{2}D's are linear combinations of them. Non-symmetry groups provide a convenient basis to construct energy matrices from. In this respect, SO(3) is an exception as L is a physical label.

1965,1967 [Racah, 1949, Judd, 1967]: The $4l+2$ components of the creation operator $\mathbf{a}^\dagger$ form a basis for the irreducible representation of the special unitary group $SU(4l+2)$; this representation remains irreducible with respect to the below chain of groups:

$$SU(4l+2) \supset Sp(4l+2) \supset SO_S(3) \times SO(2l+1) \supset SO_S(3) \times SO_L(3)$$

For the d^N configuration, this results in the following:

$$SU(10) \rightarrow Sp(10) \rightarrow SO_S(3) \times [SO(5) \rightarrow SO_L(3)]$$

The symplectic group Sp(10) leaves bilinear, anti-symmetric forms (like Slater determinants) invariant in the ten-dimensional space spanned by the two m_s and the five m_l components of the d-electron.
The rotation group in five dimensions SO(5) leaves the angle between the five-dimensional vectors of the orbital space of the d-electron invariant.

1982 [Judd et al., 1982] introduce the concept of orthogonality. For a more thorough understanding of the orthogonalized Trees operator [Trees, 1963] T_1,

group theory comes into play. The groups of interest are O(5), the orthogonal (rotation) group in the space of the five orbitals of the d electron, Sp(10), the symplectic group spanning the 10 spin orbitals, and O(20), the orthogonal group whose generators include operators that create and annihilate pairs of electrons. The sequence

$$\mathrm{O}(20) \supset \mathrm{O}_Q(3) \times \mathrm{Sp}(10) \supset \mathrm{O}_Q(3) \times \mathrm{O}(5) \supset \mathrm{O}_Q(3) \times \mathrm{O}_L(3)$$

indicate a succession of groups and subgroups. The groups $\mathrm{O}_Q(3)$ and $\mathrm{O}_L(3)$ have $\mathbf{Q}$ and $\mathbf{L}$ as their respective generators.

1967,1985 [Hansen and Judd, 1985]: introduce 5 two-electron magnetic operators, the largest two of which have the same SO(5) label (11) as the well-known spin-orbit operator. Operators labeled by different irreducible representations (irreps) are automatically orthogonal.

1997 [Hansen et al., 1997]: a physical higher order symmetry is found! From the 16 possible three-electron magnetic operators, only the four operators labeled by the SO(5) label (11) seem relevant for this interaction: a symmetry of nature!

Search for a model!

To restrict third order effects to the (11) symmetry already found in the spin-orbit operator ζ, the remaining two interactions should be SO(5) scalars:

$$(00) \otimes (00) \otimes (11) = (11)$$

The principle example of a SO(5) scalar is the delta-function interaction:

$$\sum_{i<j} \delta(\vec{r}_i - \vec{r}_j)$$

Surprisingly, this is not too bad an approximation for the Coulomb interaction itself! Below projections of the third-order operators:

$$o_2 \otimes o_2 \otimes \zeta_d \quad \text{and} \quad \delta \otimes \delta \otimes \zeta_d$$

yield the following results:....

A restriction to the pure irreps $\langle 00000 \rangle$ and $\langle 22000 \rangle$ of Sp(10), yielding two operators e_1 and e_2, does even better:

$$e_1 \otimes e_1 \otimes \zeta_d \quad \text{and} \quad e_2 \otimes e_2 \otimes \zeta_d$$

Table 13.2: Theoretical and experimental ratios $p(y_i)/p(y_6)$ between the $y(11)$ parameters. The three theoretical cases A, B and C refer to third order calculations described in [Hansen et al., 1997]; the number of decimals in the experimental ratios reflects the accuracy of the fitted values.

	$p(y_1)$	$p(y_3)$	$p(y_6)$	$p(y_7)$
A	-1.50	2.75	1	- 0.54
B	1.20	0.55	1	- 0.54
C	0.59	0.55	1	- 0.54
Cr IV	0.2	0.5	1	- 0.46
Ni IV	0.2	0.2	1	- 1.0
Fe V	0.4	0.5	1	- 0.1
Ni V	0.1	0.4	1	- 0.45

Table 13.1: ΔE values (in cm^{-1}) for the $3d^3$ and $3d^7$ configurations of triply-ionized iron group elements, with and without a three-particle magnetic contribution from the $y(11)$ set. The seniorities of the two ^{2}D terms are given as a subscripted prefix to the L value. In the least squares fitting, the levels are weighted with their degeneracy $2J+1$.

		Cr IV ($3d^3$)		Ni IV ($3d^7$)	
		without	with	with	without
$J = 1/2$	^{2}P	1.51	1.08	1.27	2.47
	^{4}P	-0.32	-0.83	-1.53	-2.77
$J = 3/2$	$^2_1$D	-0.23	0.00	0.06	0.49
	$^2_3$D	1.38	0.16	-0.12	1.21
	^{2}P	-1.76	-0.66	-0.67	-1.67
	^{4}P	-0.02	-0.05	0.12	-0.26
	^{4}F	1.42	0.10	0.12	-2.97
$J = 5/2$	$^2_1$D	0.16	0.16	-0.01	-0.34
	^{2}F	-0.68	-0.61	0.25	1.13
	$^2_3$D	-0.21	-0.53	-0.03	-0.73
	^{4}P	0.14	0.69	0.54	1.07
	^{4}F	0.83	-0.11	-0.26	-2.04
$J = 7/2$	^{2}F	0.51	0.20	-0.24	-0.85
	^{2}G	-1.31	0.15	-0.04	1.82
	^{4}F	0.22	0.03	0.52	0.58
$J = 9/2$	^{2}H	-0.92	0.13	-0.08	2.23
	^{2}G	1.06	0.50	0.19	-1.55
	^{4}F	-1.24	-0.23	-0.37	1.95
$J = 11/2$	^{2}H	0.72	-0.27	0.02	-1.66

Chapter 14

Inner products and orthogonality

By definition, the inner product of two operators u and v is defined as:

$$u : v = \sum_{\Psi,\Psi'} \langle \Psi \mid u \mid \Psi' \rangle \langle \Psi' \mid v \mid \Psi \rangle \tag{14.1a}$$

where the summation runs over all states Ψ, Ψ' of the system. The inner product is commutative by definition.
Taking magnetic degeneracy into account, this can be reduced to:

$$u : v = \sum_{\Psi_J,\Psi'_J} [J] \langle \Psi_J \mid u \mid \Psi'_J \rangle \langle \Psi'_J \mid v \mid \Psi_J \rangle \tag{14.1b}$$

or, in the case of electrostatic operators:

$$u : v = \sum_{\Psi_{SL},\Psi'_{SL}} [S, L] \langle \Psi_{SL} \mid u \mid \Psi'_{SL} \rangle \langle \Psi'_{SL} \mid v \mid \Psi_{SL} \rangle \tag{14.1c}$$

Mutual orthogonality of two matrices $\boldsymbol{u}$ and $\boldsymbol{v}$ is defined as: Tr $(\boldsymbol{u}\,\boldsymbol{v}^\dagger) = 0$.
For a Hermitian matrix basis $\boldsymbol{u}_\mu$, this reduces to:

$$\text{Tr } (\boldsymbol{u}_\mu\,\boldsymbol{v}_\nu) = \delta_{\mu\nu} \tag{14.2}$$

If $\boldsymbol{u}_\mu$ is such an orthogonal matrix basis, so is $\boldsymbol{T}^\dagger\,\boldsymbol{u}_\mu\,\boldsymbol{T}$, where $\boldsymbol{T}$ is a unitary transformation like a change of coupling matrix.
Therefore, orthogonality implies $u : v = 0$ whereas $u : u$ is the square of the norm of u. Below, we assume the operators to be in their spherical tensor form, with ranks t and t':

$$u : v = \sum_{\Psi,\Psi'} \left\langle \Psi J M_J \mid u^{(t)}_Q \mid \Psi' J' M'_J \right\rangle \left\langle \Psi' J' M'_J \mid v^{(t')\dagger}_{Q'} \mid \Psi J M_J \right\rangle \tag{14.3}$$

Using the Wigner Eckart theorem, and the fact that, according to equation (3.6):

$$v^{(t')\dagger}_{Q'} = (-1)^{Q'} v^{(t')}_{-Q'}$$

we arrive at:

$$u : v = \sum_{\Psi,\Psi'} (-1)^{J-M_J} (-1)^{J'-M'_J} \begin{pmatrix} J & t & J' \\ -M_J & Q & M'_J \end{pmatrix} \begin{pmatrix} J' & t' & J' \\ -M'_J & -Q' & M_J \end{pmatrix} (-1)^{Q'} \left\langle \Psi_J \parallel u^{(t)} \parallel \Psi'_{J'} \right\rangle \left\langle \Psi'_{J'} \parallel v^{(t')} \parallel \Psi_J \right\rangle \tag{14.4}$$

Rearranging:

$$\begin{aligned} u:v &= \sum_{M_J,M'_J} (-1)^{J-J'}(-1)^{J+t+J'}(-1)^{J+t'+J'} \begin{pmatrix} J & J' & t \\ -M_J & M'_J & Q \end{pmatrix} \begin{pmatrix} J & J' & t' \\ -M_J & M'_J & Q \end{pmatrix} \\ &\times \left\langle \Psi_J \parallel u^{(t)} \parallel \Psi'_{J'} \right\rangle \left\langle \Psi'_{J'} \parallel v^{(t')} \parallel \Psi_J \right\rangle \\ &= \sum_{\Psi,\Psi'} (-1)^{J-J'}\, \delta(t,t')\, [t]^{-1} \left\langle \Psi_J \parallel u^{(t)} \parallel \Psi'_{J'} \right\rangle \left\langle \Psi'_{J'} \parallel v^{(t)} \parallel \Psi_J \right\rangle \end{aligned} \tag{14.5}$$

Each energy operator, being a scalar with respect to the total electronic angular momentum J, can be expanded in double tensors $T^{(kk)0}$ where the rank k assumes the values 0, 1 and 2 in the spin and orbital space.
Again, recoupling and summation over J and J' by equation (2.19) can be used to write inner products between double tensors in a J-independent form.
Starting from equation (14.5) with use of equation (3.42):

$$\begin{aligned} u:v &= \sum_{J,J'} (-1)^{J-J'}\, \delta(t,t')\, [J,J'] \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & t \end{Bmatrix} \begin{Bmatrix} S' & S & \kappa' \\ L' & L & k' \\ J' & J & t' \end{Bmatrix} \\ &\cdot \left\langle \Psi\, SL \parallel u^{(\kappa k)} \parallel \Psi'\, S'L' \right\rangle \cdot \left\langle \Psi'\, S'L' \parallel v^{(\kappa' k')} \parallel \Psi\, SL \right\rangle \\ &= \sum_{J,J'} (-1)^{J-J'}\, \delta(t,t')\, [J,J'] \begin{Bmatrix} S & L & J \\ S' & L' & J' \\ \kappa & k & t \end{Bmatrix} \begin{Bmatrix} S & L & J \\ S' & L' & J' \\ \kappa' & k' & t \end{Bmatrix} \\ &\cdot (-1)^{(S+L)+(S'+L')+(\kappa'+k')+(J+J'+t)} \cdot (-1)^{-(2S'+2L'+2J')} \\ &\cdot \left\langle \Psi\, SL \parallel u^{(\kappa k)} \parallel \Psi'\, S'L' \right\rangle \cdot \left\langle \Psi'\, S'L' \parallel v^{(\kappa' k')} \parallel \Psi\, SL \right\rangle \\ = \sum_{\Psi,\Psi'} &\delta(\kappa,\kappa')\, \delta(k,k')\, \delta(t,t')\, (-1)^{\kappa+k+t} \cdot [\kappa,k]^{-1} \cdot (-1)^{(S+L)-(S'+L')} \\ &\cdot \left\langle \Psi\, SL \parallel u^{(\kappa k)} \parallel \Psi'\, S'L' \right\rangle \cdot \left\langle \Psi'\, S'L' \parallel v^{(\kappa k)} \parallel \Psi\, SL \right\rangle \end{aligned} \tag{14.6}$$

14.1 Projections

In parametric theory, the operator space is spanned by a set of orthogonal operators $H_i = p_i P_i$, where the angular operators $p_i : p_j = 0\ (i \neq j)$ form an orthogonal set $\{p_i\}$ and the radial factors P_i are treated as parameters.
In principle, projections of Hamiltonian operators onto this basis can now be calculated exactly. Any physical operator $U = vV$, written as a product of an angular operator v and a radial factor V, can be expressed in terms of a complete basis set of orthogonal operators by elementary linear algebra. Firstly, the angular part is given by:

$$v = \sum_i \alpha_i \cdot p_i = \sum_i \frac{[v:p_i]}{[p_i:p_i]} \cdot p_i \tag{14.7}$$

Consequently, the operator U is expanded as:

$$U = \sum_i p_i \cdot \Delta P_i = v \cdot V = \left(\sum_i \alpha_i \cdot p_i \right) \cdot V$$

The individual contributions ΔP_i now follow immediately:

$$\Delta P_i = \alpha_i \cdot V = \frac{[v : p_i]}{[p_i : p_i]} \cdot V \rightarrow P_i = \sum_U \frac{[v : p_i]}{[p_i : p_i]} \cdot V \tag{14.8}$$

The projection of the operator $U = vV$ on a finite (and possibly incomplete) basis $\{p_i\}$ is complete if and only if the magnitude of the operator equals the sum of the magnitudes of its projections:

$$[v : v] = \sum_i \frac{[v : p_i]^2}{[p_i : p_i]} \tag{14.9}$$

Equation (14.9) can be used to find the percentages by which a given operator is represented in subsets of a particular type like first, second or third order, or of a particular n-particle character.
Alternatively, any 'new' operator t describing effects that are not yet completely covered by the original orthogonal operator set, will naturally not be completely represented by $\{p_i\}$. It may however be orthogonalized straightforwardly:

$$t_\perp = t - \sum_i \alpha_i \cdot p_i = t - \sum_i \frac{[t : p_i]}{[p_i : p_i]} \cdot p_i \tag{14.10}$$

14.2 N-dependence and n-particle character

Denoting the zero-particle unit operator as $\mathbb{1}$, the trace Tr (H) of an operator H will be $[H : \mathbb{1}]$ in this notation. In particular, $[\mathbb{1} : \mathbb{1}] = \binom{4l+2}{N}$ is the number of states in the l^N configuration, the general case being given by $[\mathbb{1} : \mathbb{1}] = \prod_{\text{shell } l} \binom{4l+2}{N}$.
Therefore:

$$[H_1 : H_2]^{(N)} = [H_1 H_2 : \mathbb{1}]^{(N)} = \text{Tr } (H_1 H_2)^{(N)} \tag{14.11}$$

Let H_n be an $n-$particle operator in the l^N shell. Its average energy equals the trace divided by the number of states in the shell. From the useful identity:

$$\binom{4l+2-n}{N-n}\binom{4l+2}{N}^{-1} = \binom{N}{n}\binom{4l+2}{n}^{-1} \tag{14.12}$$

it follows:

$$\text{Tr } H_n^{(N)} = \binom{4l+2-n}{N-n} \text{Tr } H_n^{(n)} \tag{14.13}$$

Given that $[\mathbb{1} : \mathbb{1}] = \binom{4l+2}{N}$, one may conclude that the unit matrix $e_{\text{av}} = \mathbb{1}$, i.e. the angular part of E_{av}, is a zero-particle operator. The trace of an arbitrary operator yields its average energy contribution. From the above, it follows directly that the condition for 'no shift' of any Coulombic operator H means Tr $H = 0$.

This leads to relations like:

$$\begin{aligned} E_{\mathrm{av}}(d^n p) &= E(d^n p) + \frac{2}{3} n(10-n)\alpha_{dd} \\ &+ \frac{1}{18} n(n-1)\beta + \frac{35}{36} n(9-n)(10-n)T + 2\alpha_{dp} \end{aligned} \tag{14.14}$$

The Coulomb interaction, unlike the spin-orbit interaction, shifts the center of gravity while splitting a configuration into terms.
[Slater, 1960] defined his operators f^2 and f^4 as early as 1960 to be traceless by extracting the average energy contributions $-2/63 \cdot (f^2 + f^4)$ and thus orthogonalized them to the average energy operator *avant la lettre*; however, they still remain non-orthogonal to one another, application of equation (14.10) gives:

$$f_\perp^4 = f^4 + \frac{10}{53} f^2 \tag{14.15}$$

Inner products are properties of the operators, not just of their matrix elements in a particular configuration. Therefore, the inner product of two operators in any configuration is closely related to the inner product in their parent configuration, i.e. in the configuration where they both first, as a function of N, appear.
The N-dependence of the inner product is given by:

$$[H_1 : H_2]^{(N)} = \alpha \ \mathrm{Tr}\ H_1^{(n)} \cdot \mathrm{Tr}\ H_2^{(n)} + \beta\ [H_1 : H_2]^{(n)} \tag{14.16}$$

The coefficients α and β only depend on N, the number of electrons the shell, and on n_1 and n_2, the n–particle characters of the two operators: α and β are independent of the operators in question.

Below, two operators H_1 and H_2 are considered, with n–particle characters in the l^N shell of n_1 and n_2, respectively. It is assumed that $n_2 \geq n_1$; for the operator product $H_1 H_2$ to exist in the l^N shell, it follows: $n_2 \leq N \leq 4l+2-n_1$. The n–particle character of $H_1 H_2$ now ranges from n_2 to $n_1 + n_2$.

$$\mathrm{Tr}\ (H_1 H_2)^{(N)} = \binom{4l+2-n}{N-n} \mathrm{Tr}\ (H_1 H_2)^{(n)} \leftrightarrow \mathrm{Tr}\ O_n^{(N)} = \binom{4l+2-n}{N-n} \mathrm{Tr}\ O_n^{(n)} \tag{14.17}$$

$$\begin{aligned} [H_1 : H_2]^{(N)} &= \mathrm{Tr}\ (H_1 H_2)^{(N)} \\ &= \prod_{\text{shell } l} \sum_{n=n_2}^{n_1+n_2} (-1)^{n-n_2} \binom{n_1}{n-n_2} \binom{4l+2-n}{N-n} [H_1 : H_2]^{(n_2)} \\ &= \prod_{\text{shell } l} \binom{4l+2-n_1-n_2}{N-n_2} [H_1 : H_2]^{(n_2)} \end{aligned} \tag{14.18}$$

where n_1 and n_2 are the n–particle characters of the operators H_1 and H_2 in the shell characterized by orbital angular momentum l. Thereby, the expression for the coefficient β introduced in the above turns out be:

$$\beta(n_1, n_2, N) = \binom{4l+2-n_1-n_2}{N-n_2} \tag{14.19}$$

The coefficient α is less interesting when dealing with orthogonal operators, as all of them are traceless except the e_{av} operator. The expression is given below for completeness:

$$\alpha(n_1, n_2, N) = \binom{4l+2}{n_2}^{-1} \left[\binom{N}{n_1} \binom{n_2}{n_1}^{-1} \binom{4l+2-n_2}{N-n_2} - \binom{4l+2-n_1-n_2}{N-n_2} \right] \tag{14.20}$$

The N-dependence of the magnitude $[H:H]$ of an operator H obviously constitutes an important special case of the $\beta(n,n,N)$–coefficient:

$$[H:H]^{(N)} \;=\; \mathrm{Tr}\,\left(H^2\right)^{(N)} = \prod_{\text{shell } l} \binom{4l+2-2n}{N-n} [H:H]^{(n)} \tag{14.21}$$

Equation (14.21) is also given by [Judd and Leavitt, 1986], derived from group-theoretical arguments. One can verify that β is invariant under conjugation, as it should:

$$\beta(n,n,N) = \beta(n,n,4l+2-N) \tag{14.22}$$

The derivation relies on the below mathematical formula, to be proved with the Zeilberger algorithm after a transformation to hypergeometric functions:

$$\sum_{k=0}^{n} (-1)^k \binom{n}{k}\binom{a-k}{b-k} = \binom{a-n}{b} \tag{14.23}$$

With the identifications $a \to 4l+2-n_2$, $b \to N-n_2$, $n \to n_1$ and $k \to n-n_2$, equation (14.18) is retrieved from equation (14.23).
Exactly this relation (14.23), valid for $a \geq n \geq 0$ and $a \geq b \geq 0$, is also given by [Edmonds, 1957] (equations A1.1 and A1.2), leading to:

$$\sum_{k=0}^{n} (-1)^k \frac{(a-k)!}{k!(n-k)!(b-k)!} = \frac{(a-b)!(a-n)!}{n!\,b!\,(a-b-n)!} \tag{14.24}$$

Any operator with a particular n–particle character can be expressed in terms of second quantization, so it basically suffices to calculate inner products of second quantized operators. As an example, the below operator product contains both a two-particle and a one-particle part:

$$\begin{aligned} \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(kk)0} : \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(kk)0} &= [k]^{-1} \sum_{SL} [S,L] \left\langle \Psi_{SL} \left| \left\{ \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(kk)} \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(kk)} \right\}^{(00)} \right| \Psi_{SL} \right\rangle \\ &= \binom{4l+2-2}{N-2} [(4l+2)\delta(k,0)-1] + \binom{4l+2-1}{N-1} \cdot 1 \end{aligned} \tag{14.25}$$

The progression of the N-dependence may be calculated straightforward. For a single shell l^N, the contribution of an arbitrary n–electron operator $U = vV$ to an orthogonal m–electron parameter P_i $(m \leq n)$ is given by:

$$\Delta P_i = \binom{N}{n}\binom{n}{m}\binom{N}{m}^{-1} \frac{[v:p_i]}{[p_i:p_i]}\, V \tag{14.26}$$

Therefore, the dependence on the number of electrons is given by the normalized ratio of weighting factors

$$Q = \binom{N}{n}\binom{n}{m}\binom{N}{m}^{-1}$$

where the inner products are calculated in l^n.
Obviously, $Q = 1$ for $n = m$ or $N = n$; as expected, equation (14.26) is identical to equation (14.8) in these cases.

In the case of direct proportionality: $v = \alpha p_i$, equation (14.26) reduces to $\Delta P_i = \alpha V$.

An operator may have different n–particle ranks in different shells (like $T_{\rm dds}$ has rank 2 in the d shell and rank 1 in the s shell), in which case the total Q is simply found as the product of the Q of each individual shell.
As a result:

$$\Delta E_i^{(N)} = \frac{\binom{N}{n_2}\binom{n_2}{n_1}}{\binom{N}{n_1}}\,\Delta E_i^{(n_2)} \text{ with:} \tag{14.27}$$

$$\Delta E_i^{(n_2)} = \frac{[g:e_i]^{(n_2)}}{[e_i:e_i]^{(n_2)}}\,G \tag{14.28}$$

Given the N–dependence of the inner products, the full matrix of inner products for any particular configuration can be predicted in advance and thus serves as a rather strict check on the parameter calculation.

14.3 Contributions to the spin-orbit interaction

Since the days of [Blume and Watson, 1962], called BW hereafter, it has been realized that the mutual spin-orbit interaction MSO contributes appreciably to the value of the spin-orbit parameter ζ. Even so, the ζ-contribution of the electrostatic spin-orbit interaction EL-SO (see 15.5) turns out to be quite dominant for lower ionization stages.
Before the use of inner products [Uylings and Smid, 1987], only the simpler case of *direct proportionality* has been considered by BW and other *ab initio* calculations. The idea behind our theory is to use equation (14.26) to the projections on zeta of *all* operators of magnetic origin (like MSO and EL-SO operators), not just the proportional ones. Taking the N–dependence of the inner product into account, we obtain in a configuration $l^N l'^M$ the following contribution of U =MSO to ζ:

$$\begin{aligned}[\mathrm{MSO}:z(l)] &= \tfrac{1}{2}\left((k+1)/(k+2)\right)(2l+k+2)(2l-k) \\ &\times \left\langle l \parallel C^{(k)} \parallel l\right\rangle^2 [3-\delta(k,0)(4l+2)]\end{aligned} \tag{14.29a}$$

$$[z(l):z(l)] = \binom{4l'+2}{M}\binom{4l}{N-1} l(l+1)(2l+1)/2 \tag{14.29b}$$

$$[z(l'):z(l')] = \binom{4l+2}{N}\binom{4l'}{M-1} l'(l'+1)(2l'+1)/2 \tag{14.29c}$$

$$[z(l):z(l')] = 0 \tag{14.29d}$$

$$Q = \binom{N}{2}\binom{1}{1}\binom{N}{1}^{-1} = (N-1). \tag{14.29e}$$

The contribution to ζ thus becomes:

$$\Delta\zeta = (N-1)\sum_k \alpha(k,l)\; N^k(aa;aa) \tag{14.30}$$

with

$$\alpha(k,l) = (N-1)\left(-\delta(k,0)[2-(2l)^{-1}] + \sum_{k>0} \frac{3(k+1)(2l+k+2)(2l-k)}{4(k+2)l^2(l+1)(2l+1)} \left\langle l \parallel C^{(k)} \parallel l \right\rangle^2\right) \tag{14.31}$$

The coefficients $\alpha(k,l)$ are given in table 3.1 for p, d and f electrons.
We will work out the contributions to $\zeta(a)$ from direct MSO matrix elements in $l^N l'^M$ in more detail. The $n-$particle ranks of the MSO operator in the shells l^N and l'^M are $n(l) = 1, n(l') = 1$ and, for the spin-orbit operator $z(l)$, $m(l) = 1, m(l') = 0$ respectively; the inner products should be taken in ll'.

$$[\mathrm{MSO_{DIR}} : z(l)] = -(4l'+2)l(l+1)(2l+1)\; N^0(ab;ab) \tag{14.32a}$$

$$[z(l) : z(l)] = (4l'+2)l(l+1)(2l+1)/2 \tag{14.32b}$$

$$Q = \left[\binom{N}{1}\binom{1}{1}\binom{N}{1}^{-1}\right]\left[\binom{M}{1}\binom{1}{0}\binom{M}{0}^{-1}\right] = M \tag{14.32c}$$

The final result can thus be written:

$$\Delta\zeta(a) = -\sum_b \left(\frac{M}{4l'+2}\right)\cdot 4(2l'+1)\; N^0(ab;ab) \tag{14.33}$$

Table 14.1: The coefficients $\alpha(k,l)$ appearing in equation (14.31) for the intra-shell MSO contributions to ζ.

	$k=$	0	2	4
p shell		-3/2	—	—
d shell		-7/4	3/14	—
f shell		-11/6	1/6	5/66

14.4 Choice of orthogonal operator sets

A useful way to extract information from an observed set of atomic energy levels is to fit them to the eigenvalues of an energy matrix in which the strengths of the various interactions among the particles making up the atom in question are determined by a collection of parameters. The rows and columns of the matrix are labeled by a finite set of electronic states (usually one or more complete configurations), and the influence of the omitted states is reproduced by effective operators acting solely within the finite set. These effective operators may themselves be parameterized,

and if one proceeds to a sufficiently high order of perturbation theory one can expect to introduce as many parameters as there are independent non-vanishing elements in the matrix. The fitting of atomic energy levels by orthogonal operators has a number of advantages: the addition of a new operator entails minimal adjustments to the strengths of those already brought into play, and the mean errors are smaller than they otherwise would be. An advantage of the method lies in the fact that we can replace an infinite number of physical interactions from arbitrary orders of perturbation by a set of finite well defined contributions. What we lose, however, is specific information about the physical importance of the operators. In particular, we do not know the order of perturbation at which the operators first arise. Apparently one must explicitly consider the perturbative processes to retrieve this information.
One problem with the new set of operators, which has been mentioned before [Judd and Leavitt, 1986], is the fact that most operators have contributions from low- and high-order effects at the same time. The result is that nearly all operators are significant. This is a problem when, as in the present case, some operators are difficult to determine in particular configurations. It would be advantageous to have particular operators determined by higher-order effects and others by low-order effects so that the operators could be introduced, and perhaps neglected, in batches. There is no unique choice of an orthogonal set (each 'rotation' will yield another one) and we use this freedom to satisfy the following criteria for $l^N l'$ configurations:

1. Due to the fact that the related operators belong to mutually orthogonal subspaces, $l-l$ and $l-l'$ interactions can be covered by different parameters. The l^N core of an $l^N l'$ configuration is thus described by the same parameter set as the corresponding l^N configuration.

2. For the $l-l$ electrostatic interaction, the principal (first-order) and the secondary (higher-order) effects are described by separate operators. A method to work out such a separation is illustrated for pd and fp configurations by [Klinkenberg and Uylings, 1986]. It enhances the 'descriptive power' of the parameter set, as the secondary operators can be neglected to a first approximation in a partially incomplete spectrum.

3. All operators are normalized in batches, i.e. at their first appearance the inner product of an operator with itself is made equal to that for the main operator of a group:

   - two-electron electrostatic operators have the same normalization as the unit operator e_{av};
   - three-electron electrostatic operators in f^3 have the same normalization as the two-electron $f-f$ operators. In the d–shell, however, the three-electron operators share the normalization of the orthogonalized Trees operator $T_1 = o_3''$ in d^3 and as e_{av} in d^2s;
   - magnetic operators have the same normalization as the spin-orbit operators z_l and $z_{l'}$ in l^2 and ll', respectively.

In this way, a complete set of operators is subdivided into groups and subgroups in a tree-like fashion. At the first level, there is a branching into three orthogonal subspaces for the electrostatic, the spin-orbit and the spin-spin effects. At the second level, the operators are sorted according to the number n of electrons they act upon (in most practical cases, $n = 2, 3, 4$ for the electrostatic, $n = 1, 2$ (and possibly 3) for the spin-orbit and $n = 2$ for the spin-spin space). A third branching yields a distinction into the order of perturbation theory. When the operators are written in second quantized form, one can see that in general n-body operators occur in the $(n-1)$ order of perturbation theory for the first time. It is useful to make the same distinction according to first and higher order effects within the group of two-particle operators as well [Klinkenberg and Uylings, 1986, Hansen et al., 1988b, Uylings et al., 1989]. With the above construction, one has a measure of the physical content as well as of the relative importance of the parameters.

With respect to the traditional Slater-Condon approach of parametric fitting, only the average energies E_{av}, the spin-orbit parameters ζ_l and the configuration interaction parameters $R^k()$ are retained. The matrix elements of the other operators, defined on group theoretical or algebraical grounds, need only be given in their parent configuration, i.e. the configuration where they first appear like two-particle operators in l^2 or ll'. The matrix elements of these operators in configurations with more electrons are then found by the expansion formulae given below in section 14.6. The operator set for equivalent electrons in the $p-$, $d-$ and $f-$shell is described in the below subsections. The parent matrix elements (or reduced parent matrix elements for spin-orbit and spin-spin type operators) will either be given directly in tables or by referring to the relevant literature.

14.4.1 The $p-$shell

In addition to the zero-particle unit operator e_{av}, there are two electrostatic two-particle operators in p^2. Unlike [Dothe et al., 1985], the operator o_2 was chosen to cover the complete first order Coulomb interaction, in line with the approach followed by [Klinkenberg and Uylings, 1986]. It is not difficult to see that o_2 is proportional to the traceless Slater operator $f^2(p,p)$; what remains is a Trees-like two-particle operator e_α that is easily orthogonalized. All electrostatic matrix elements are given in table 14.2. Normalization of o_2 and e_α to the length $\sqrt{15}$ of e_{av} is assured by dividing the entries by the constant η given below the column.

Table 14.2: Matrix elements of the electrostatic operators in p^2

SL	e_{av}	o_2	e_α
^3P	1	-1	1
^1S	1	4	6
^1D	1	1	-3
η	1	$\sqrt{2}$	$\sqrt{6}$

In addition to the usual spin-orbit operator z_p for ζ_p, there are two two-particle operators z_c and z_3 of tensorial character $t^{(11)0}$. They are defined in a similar fashion

as the corresponding double-vector operators in d^2 [Hansen and Judd, 1985]. Their reduced matrix elements are given in table 14.3.

Table 14.3: Reduced matrix elements of the double-vector operators in p^2

Ψ	Ψ'	z_p	z_c	z_3
^3P	^3P	$-3\sqrt{3}$	$-3\sqrt{3/2}$	$-3\sqrt{15/2}$
^1S	^3P	$-3\sqrt{2}$	6	0
^3P	^1D	$3\sqrt{5/2}$	$3/2\sqrt{5}$	$-9/2$

The spin-spin operator z_1 has only one non-zero reduced matrix element $\langle {}^3P \parallel z_1 \parallel {}^3P \rangle = 10\sqrt{3}$. The length of all magnetic operators in p^2 equals $\sqrt{12}$. The physical content of these operators is given in equations (14.67), (14.68) and (14.69). Unlike the case of the $d-$ and the $f-$shell, no additional three-particle electrostatic operator appears in p^3.

14.4.2 The $d-$shell

The electrostatic two-particle operators o_2 and o_2' currently used in d^N configurations, were first defined by [Klinkenberg and Uylings, 1986]; the conversion of the associated parameters to Slater integrals is given in equation (14.60). They are supplemented by two Trees-like operators e'_α and e'_β, apart from the normalization introduced by [Judd et al., 1982]. The matrix elements are given in table 14.4; again, normalization to the common length $\sqrt{45}$ requires that all entries are divided by the constant η at the bottom of the relevant column.

Table 14.4: Matrix elements of the electrostatic operators in d^2

SL	e_{av}	o_2	o_2'	e'_α	e'_β
^1S	1	56	0	0	12
^3P	1	-7	21	-14	1
^1D	1	11	-9	-54	-3
^3F	1	-7	-9	6	1
^1G	1	11	5	30	-3
η	1	$\sqrt{140}$	$\sqrt{140}$	$\sqrt{560}$	$\sqrt{20/3}$

The orthogonal two-particle fine-structure operators for the $d-$shell were given in two tables by [Hansen and Judd, 1985]: in table 1 the 5 spin-orbit type operators z_c, z_3, z_4, z_5 and z_6 and in table 2 the 3 spin-spin type operators z_1, z_2 and z_0. In the present tapes, these magnetic operators are all normalized to the length $\sqrt{120}$ of the spin-orbit parameter ζ_d in d^2. The MSO and EL-SO contributions to the corresponding A_i parameters are found in equation (14.64).

In d^3 to d^7, 4 electrostatic three-particle operators $t_1 \cdots t_4$ make their appearance. The first two o_3'' and o_3''' were introduced by [Judd et al., 1982]; $o_3'' = t_1$ is actually the orthogonalized version of the original Trees operator with parameter T.
The newly introduced second three-particle operator o_3''' differs from the later t_2 by a

factor $\sqrt{110}/3$ such that $\sqrt{110}/3\,\langle\psi|o_3'''|\psi'\rangle = \langle\psi|t_2|\psi'\rangle$ for reasons of normalization to the length $\sqrt{162750}$ of t_1 in d^3. As a result, the reverse is true for the corresponding radial parameters: the current T_2 is a factor $\sqrt{110}/3$ smaller than the values originally published before [Hansen et al., 1988a]. The mean error reduction of t_1 and t_2 turned out to be that significant [Uylings et al., 1984, Hansen and Judd, 1985] that they became the only orthogonal operators introduced later by Cowan in his program suite [Cowan, 1981]. [Hansen and Judd, 1985] added two more three-particle operators t_3 and t_4 to include higher order effects; the associated parameters T_3 and T_4 are an order of magnitude smaller.
Using their orthogonality and equation (14.8), the contributions to the two T parameters can be found for all relevant single particle excitations $\bar{l} \rightarrow d$ and $d \rightarrow l'$ to second order. Except for the $s \rightarrow d$ contribution, which is a direct consequence of the definition, the angular coefficients have not yet been found in another way.
The overlap between the $3d$ and the g and i continuum orbitals is most favorable for high angular momenta states with energy large enough to penetrate the centrifugal potential barrier. In Fe VI, the $3s \rightarrow 3d$ contribution is dominant, as the $n = 3$ orbitals have become 'near degenerate'.

Table 14.5: Second-order contributions $\Delta T_1 \propto R^k R^{k'}/\Delta E$ to the 3-particle Trees parameter in Fe VI ($3d^3$)

.

Exc.(kk')	22	24	44
$s \rightarrow 3d$	-12.067	-	-
$3d \rightarrow s$	0.209	-	-
$3d \rightarrow d'$	-0.198	0.405	-0.129
$3d \rightarrow g$	2.391	0.710	-1.107
$3d \rightarrow i$	-	-	0.037
Total calc.		-9.727	
Fitted value		-8.452	

A set of 12 four-particle operators $f_1 \cdots f_{12}$ appearing in d^4, d^5 and d^6 was defined by [Judd and Leavitt, 1986]. They are normalized to unity in d^4. Just like the operators z_0, t_3 and t_4 introduced in the above, these operators only describe third and higher order effects and have no contributions from the first and second order perturbation theory. Still, the impact is not negligible: the mean error σ in Co VI e.g. is reduced from 21 to 4 cm^{-1} by their introduction. Moreover, most parameter values are well determined and show regular trends in the iron group.
A batch of 16 possible three-particle magnetic operators of spin-orbit type may still be added, but [Hansen et al., 1997] showed that only the four operators labeled by the irreducible representation (11) of SO5 are significant. As demonstrated in table 13.1, the accuracy of the description is then comparable with the errors of the experimental levels. A meaningful determination of these higher order effects, however, usually requires a complete set of experimental energies and configurations that are not too much distorted by strong configuration interaction. [Uylings and Raassen, 1996] gives an impression of the use of the d–shell operators in the iron group.

14.4.3 The f–shell

[Racah, 1949] replaced the scalar products $(C_1^{(k)}C_2^{(k)})^{(0)}$ appearing in equation (6.3) by the linear combinations e_0, e_1, e_2 and e_3 to which well defined group-theoretical labels can be attached. In the current set of orthogonal operators, the traceless version e'_1 is used [Judd and Crosswhite, 1984] instead of e_1. The three operators e'_α, e'_β and e'_γ were introduced earlier by [Judd et al., 1982] to orthogonalize the generalized Trees operators. Finally, all two-particle operators are normalized in f^2 to the 'length' $\sqrt{91}$ of the unit operator $\mathbb{1} = e_{av} = e_0$. In this form, they are given in table 3 of [Judd and Crosswhite, 1984] or table B.III of [Klinkenberg and Uylings, 1986], and repeated in table 14.6 for completeness. For normalization each entry has to be divided by the constant η found on the bottom line of the same column.

Table 14.6: Matrix elements of the electrostatic operators in f^2

SL	e_{av}	e'_1	e_2	e_3	e'_α	e'_β	e'_γ
^1S	1	108	0	0	0	0	-18
^3P	1	-9	0	33	-11	-1	-1
^1D	1	17	286	-11	-33	0	3
^3F	1	-9	0	0	0	2	-1
^1G	1	17	-260	-4	-12	0	3
^3H	1	-9	0	-9	3	-1	-1
^1I	1	17	70	7	21	0	3
η	1	$\sqrt{270}$	$\sqrt{11880}$	$\sqrt{1980/13}$	$\sqrt{1980/13}$	$\sqrt{18/3}$	$\sqrt{90/13}$

Most of the orthogonal two-particle magnetic operators happen to be defined already in the sixties by [Judd and Wadzinski, 1967] for the spin-spin interaction and [Judd et al., 1968] for the MSO/EL-SO operators.
After normalization to the length $\sqrt{504}$ of the spin-orbit operator z_f in f^2, the spin-spin operators $z_1 \cdots z_4$ may directly be incorporated into the orthogonal operator set; their reduced matrix elements are given in [Judd and Wadzinski, 1967].
The reduced matrix elements of the 8 spin-orbit type operators $z_5 \cdots z_{12}$ are found in [Judd et al., 1968]. Only z_{12} had to be orthogonalized:

$$z'_{12} = z_{12} - 4/5 \cdot z_{14} \tag{14.34}$$

which seems more straightforward than the definition of the combined operator z_c by [Crosswhite et al., 1968]. In fact, the corresponding parameter A'_{12} turns out to be relatively important and quite stable in the fit. These 8 operators are again normalized to a length $\sqrt{504}$.
The orthogonal three-electron operators needed to describe single electron excitations from and to the f–shell were already defined on group theoretical grounds by [Judd, 1966]. From the six operators t_2, t_3, t_4, t_6, t_7 and t_8, only t_2 needs to be adjusted to remain orthogonal to e_3, see equation (6) of [Judd and Crosswhite, 1984]:

$$t'_2 = t_2 - \frac{N-2}{70\sqrt{2}} \cdot e_3 \tag{14.35}$$

Table 14.7: Parameter values of the $4f^n$ orthogonal operators in Pr III, Pr IV, Nd IV and Nd V.

	Pr III(f^3)	B-spl	Pr IV(f^2)	B-spl	Nd IV(f^3)	B-spl	Nd V(f^2)	B-spl
E_{av}	19709.2		10202.8		24892.1		12248.6	
E'_1	4924.8		60446.9		6393.5		7101.1	
E_2	2191.5		2526.1		2671.0		2915.5	
E_3	4942.9		5899.7		6197.9		6835.0	
E'_α	301.7		236.7		224.5		225.6	
E'_β	0		6.0		7.6		8.0*	
E'_γ	448.1		290.0		261.0		250*	
T'_2	122.7				64.4			
T_3	14.7				14.8			
T_4	24.5				16.0			
T_6	-49.5				-54.7			
T_7	60.3				60.2			
T_8	51.7				53.0			
ζ_f	660.7	711.4	764.6	813.4	892.4	944.0	998.4	1047.7
A_5	-2.7	-2.7	-2.4	-2.0	-3.8	-2.6	-3.7	-2.2
A_6	4.5	4.5	4.2	3.6	4.4	4.5	4.4	4.1
A_7	-2.3	-2.3	-2.8	-2.4	-0.8	-2.8	0	-3.0
A_8	4.6	4.6	5.7	5.0	5.1	5.8	5.7	6.3
A_9	1.3	1.3	5.4	5.1	4.3	4.8	5.9	7.8
A_{10}	-3.8	-3.8	-2.6	-2.2	-2.8	-3.0	-2.3	-2.0
A_{11}	-5.1	-5.1	-4.2	-3.5	-3.8	-4.6	-3.5	-3.7
A'_{12}	-10.5	-9.0	-6.0	-4.8	-8.2	-7.0	-6.7	-4.1
A_1	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.3
A_2	-0.6	-0.6	-0.8	-0.7	-0.8	-0.8	-1.0	-0.9
A_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
A_4	-1.2	-1.2	-1.7	-1.5	-1.7	-1.7	-2.2	-2.0
σ	14.2		6.9		7.6		3.8	

14.5 Orthogonalization of inequivalent electrons

Associating the orbital angular momenta l and l' with electrons from shell a and b, one finds from equation (5.39):

$$\left\langle ll'(SL) \parallel \{(\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)}\,(\mathbf{b}^\dagger\mathbf{b})^{(\kappa' k')}\}^{(tt)} \parallel ll'(S'L') \right\rangle$$
$$= [t]\,[S,L,S',L']^{1/2}\,[\kappa,k,\kappa',k']^{1/2} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ \frac{1}{2} & \frac{1}{2} & \kappa' \\ S & S' & t \end{Bmatrix} \begin{Bmatrix} l & l & k \\ l' & l' & k' \\ L & L' & t \end{Bmatrix} \qquad (14.36)$$

In the above, the tensor rank t equals 0, 1 and 2 for electrostatic, spin-orbit and spin-spin effects, respectively. For reasons of Hermiticity, the permutation phase $P = \kappa + k + \kappa' + k'$ must be even. Given the values of l and l', each allowed combination of $\{\kappa, k, \kappa', k'\}$ then yields another orthogonal operator.
The orthogonal set of operators found from equation (14.36) is used as a basis to

start the construction of a final set of orthogonal operators in which a distinction is made between stronger and less important operators, occurring in first and higher order of perturbation. In the iron group, the standard deviation for orthogonal operator fits of $3d^n4p$ configurations is frequently reduced to well below $\sigma = 10$ cm^{-1}.

14.5.1 The electrostatic case

Orthogonal parameters for the two-electron electrostatic interaction in ll' are found as a special case of equation (14.36) for $t = 0$. The subject has also been discussed by [Dothe et al., 1985]. They introduce the orthogonal operators $e_{\kappa k}$ for the configuration pd but remark in conclusion that it may well be advantageous to separate the $p-d$ interaction as a first order effect from the higher order electrostatic effects attributable to the interaction with many far-lying configurations. We want to investigate this point more thoroughly. If $\mathbf{a}^\dagger$ and $\mathbf{b}^\dagger$ are the creation (or mutatis mutandis annihilation) operators corresponding to l and l' respectively, the operators $e_{\kappa k}$, via their matrix elements, are defined by:

$$\begin{aligned}\langle ll'(SL)|e_{\kappa k}|ll'(SL)\rangle &= 2\,[l,l']^{\frac{1}{2}}\left\langle ll'(SL)\left|\left\{\left(\mathbf{a}^\dagger\mathbf{a}\right)^{\kappa k}\left(\mathbf{b}^\dagger\mathbf{b}\right)^{\kappa k}\right\}^{(00)0}\right|ll'(SL)\right\rangle \\ &= 2\,[l,l',\kappa,k]^{\frac{1}{2}}\,(-1)^{S+L+\kappa+k}(-1)^{l+l'+1} \\ &\times \begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ \frac{1}{2} & \frac{1}{2} & \kappa\end{Bmatrix}\begin{Bmatrix}l & l' & L\\ l' & l & k\end{Bmatrix} \qquad (14.37)\end{aligned}$$

where κ and k are ranks in the spin and orbital spaces respectively. Here, the factor $2[l,l']^{1/2}$ ensures that the 'length' of the operators, defined as the inner product $[e_{\kappa k} : e_{\kappa k}]^{1/2}$, be equal to that of the average energy operator $E_{\rm av} = e_{00}$. The allowed values for κ and k are: $\kappa = 0, 1$ and $0 \le k \le 2l_<$, with $l_<$ the smallest value of l or l'. In order to avoid square roots in the entries, the common normalization factors $\eta_{\kappa k}$ are given below each column: $e'_{\kappa k} = \eta_{\kappa k} \cdot e_{\kappa k}$.

Table 14.8: Matrix elements of operators $e'_{\kappa k}$ for dp

	e'_{00}	e'_{10}	e'_{01}	e'_{11}	e'_{02}	e'_{12}
^1P	1	3	3	9	7	21
^1D	1	3	1	3	-7	-21
^1F	1	3	-2	-6	2	6
^3P	1	-1	3	-3	7	-7
^3D	1	-1	1	-1	-7	7
^3F	1	-1	-2	2	2	-2
$\eta_{\kappa k}$	1	$\sqrt{3}$	2	$2\sqrt{3}$	$2\sqrt{7}$	$2\sqrt{21}$

Mutually orthogonal linear combinations of the $e'_{\kappa k}$ are now to be found such that one batch of operators covers the first order ll' interaction (given in terms of the classical Slater operators f^k and g^k) while the remaining second batch (so-called effective operators) account for the higher order interactions.
We label them c ("Coulomb") and s ("Sack") respectively.

In fact, f^k turns out to be directly proportional to e'_{0k}.
As for all operators, $(e'_{1k} : e'_{1k}) = 3 \cdot (e'_{0k} : e'_{0k})$, it follows that
$(e'_{0k} - e'_{1k}) : (e'_{0k} - e'_{1k}) = 4 \cdot (e'_{0k} : e'_{0k})$ and $(e'_{0k} - e'_{1k}) : (3 \cdot e'_{0k} + e'_{1k}) = 0$.
Three out of six operators may therefore directly be assigned:
$E_{av} = e'_{00}, c_1 = e'_{02}$ and $s_1 = (3 \cdot e'_{01} + e'_{11})$.
Furthermore, all exchange g^k angular matrices can be written as a linear combination of the operator pairs $(e'_{0k} - e'_{1k})$:

$$g^k = \sum_{\tilde{k}=0}^{2l_<} \alpha_{k\tilde{k}} \cdot \left(e'_{0\tilde{k}} - e'_{1\tilde{k}}\right) \tag{14.38}$$

For the case $ll' = pp'$:

$$\begin{aligned} g^0(pp') &= -1/6(e'_{00} - e'_{10}) + 1/24(e'_{01} - e'_{11}) - 1/72(e'_{02} - e'_{12}) \\ g^2(pp') &= -1/15(e'_{00} - e'_{10}) - 1/120(e'_{01} - e'_{11}) - 1/1800(e'_{02} - e'_{12}) \end{aligned} \tag{14.39}$$

As e'_{00} and e'_{02} are already assigned, the remaining operators to consider are:
e'_{10}, e'_{12} and $(e'_{01} - e'_{11})$.
Elimination of the factor $(e'_{01} - e'_{11})$ from g^0 and g^2 (by considering $g^0 + 5g^2$) then yields the required ratio $30 : 1$ of e'_{10} and e'_{12} to be used in c_2. We find $c_2 = (30e'_{10} + e'_{12})$ with the orthogonal counterpart $(24e'_{10} - e'_{12})$. Hence, the second Sack-operator s_2 must be composed of $(e'_{01} - e'_{11})$ and $(24e'_{10} - e'_{12})$, and obey the condition $s_2 : g^0 = 0$ (or equivalently $s_2 : g^2 = 0$). It thus follows that $(e'_{01} - e'_{11})$ is not orthogonal to s_2 and in order to obtain a correct c_3 one has to add a term with $(24e'_{10} - e'_{12})$.
Finally, we end up with, except for normalization:
$c_1 = e'_{02}$ $\quad$ $c_2 = 30e'_{10} + e'_{12}$ $\quad$ $c_3 = 9(e'_{01} - e'_{11}) - (24e'_{10} - e'_{12})$
[first order Coulomb interaction]
$s_1 = 3e'_{01} + e'_{11}$ $\quad$ $s_2 = (e'_{01} - e'_{11}) + 4/9(24e'_{10} - e'_{12})$
[additional higher order operators]
The 'building blocks' are indeed mutually orthogonal: $(e'_{01} - e'_{11}) : (3e'_{01} + e'_{11}) = 0$ and $(30e'_{10} + e'_{12}) : (24e'_{10} - e'_{12}) = 0$.

For the case $ll' = dp$:

$$\begin{aligned} g^1(dp) &= -1/15(e'_{00} - e'_{10}) + 1/20(e'_{01} - e'_{11}) - 1/60(e'_{02} - e'_{12}) \\ g^3(dp) &= -3/70(e'_{00} - e'_{10}) - 3/140(e'_{01} - e'_{11}) - 3/980(e'_{02} - e'_{12}) \end{aligned} \tag{14.40}$$

Elimination of the factor $(e'_{01} - e'_{11})$ from g^1 and g^3 (by considering $3g^1 + 7g^3$) then yields the required ratio $7 : 1$ of e'_{10} and e'_{12} to be used in c_2. We find $c_2 = (7e'_{10} + e'_{12})$ with the orthogonal counterpart $(4e'_{10} - e'_{12})$. Hence, the second Sack-operator s_2 must be composed of $(e'_{01} - e'_{11})$ and $(4e'_{10} - e'_{12})$, and obey the condition $s_2 : g^1 = 0$ (or equivalently $s_2 : g^3 = 0$). It thus follows that $(e'_{01} - e'_{11})$ is not orthogonal to s_2 and in order to obtain a correct c_3 one has to add a term with $(4e'_{10} - e'_{12})$.
Finally, we end up with, except for normalization:
$c_1 = e'_{02}$ $\quad$ $c_2 = 7e'_{10} + e'_{12}$ $\quad$ $c_3 = 11(e'_{01} - e'_{11}) - (4e'_{10} - e'_{12})$
[first order Coulomb interaction]

$s_1 = 3e'_{01} + e'_{11}$ $\quad s_2 = \frac{3}{2}(e'_{01} - e'_{11}) + 2(4e'_{10} - e'_{12})$
[additional higher order operators]
The 'building blocks' are indeed mutually orthogonal: $(e'_{01} - e'_{11}) : (3e'_{01} + e'_{11}) = 0$ and $(7e'_{10} + e'_{12}) : (4e'_{10} - e'_{12}) = 0$.

Table 14.9: Matrix elements of the c_i and s_i operators for dp

	e_{av}	c_1	c_2	c_3	s_1	s_2
^1P	1	7	42	-57	9	-27
^1D	1	-7	0	-55	3	63
^1F	1	2	27	38	-6	18
^3P	1	7	-14	63	3	15
^3D	1	-7	0	33	1	-19
^3F	1	2	-9	-42	-2	-10
η_i	1	$2\sqrt{7}$	$\sqrt{231}$	$2\sqrt{517}$	$2\sqrt{3}$	$2\sqrt{141}$

Table 14.10: Matrix elements of operators $e'_{\kappa k}$ for df

	e'_{00}	e'_{10}	e'_{01}	e'_{11}	e'_{02}	e'_{12}	e'_{03}	e'_{13}	e'_{04}	e'_{14}
^1P	1	3	8	24	24	72	6	18	66	198
^1D	1	3	6	18	6	18	-3	-9	-99	-297
^1F	1	3	3	9	-11	-33	-4	-12	66	198
^1G	1	3	-1	-3	-15	-45	4	12	-22	-66
^1H	1	3	-6	-18	10	30	-1	-3	3	9
^3P	1	-1	8	-8	24	-24	6	-6	66	-66
^3D	1	-1	6	-6	6	-6	-3	3	-99	99
^3F	1	-1	3	-3	-11	11	-4	4	66	-66
^3G	1	-1	-1	1	-15	15	4	-4	-22	22
^3H	1	-1	-6	6	10	-10	-1	1	3	-3
$\eta_{\kappa k}$	1	$\sqrt{3}$	$2\sqrt{6}$	$6\sqrt{2}$	$2\sqrt{42}$	$6\sqrt{14}$	$2\sqrt{3}$	6	$6\sqrt{77}$	$6\sqrt{231}$

Five out of ten operators may therefore directly be assigned:
$E_{av} = e'_{00}, c_1 = e'_{02}, c_2 = e'_{04}, s_3 = (3 \cdot e'_{01} + e'_{11})$ and $s_4 = (3 \cdot e'_{03} + e'_{13})$.
The actual values of the $\alpha_{k\tilde{k}}$ coefficients may always be established by projecting the g^k operators one by one onto the orthogonal $e_{\kappa k}$ basis, e.g. with the program PARCALC based on equation (14.8).
Next, the g^k may be added to eliminate $(e'_{01} - e'_{11})$ and $(e'_{03} - e'_{13})$. The orthogonal counterpart $(\gamma e'_{10} - e'_{12})$ of the remaining contribution $(ae'_{10} + be'_{12})$ to the $\sum_k g^k$ is subsequently used as a new building block for s_1.
Taking $c_1 = e'_{02}$ we try $(e'_{01} - e'_{11})$ as the second Coulomb operator, which requires $s_1 = (3e'_{01} + e'_{11})$ as its orthogonal counterpart. Elimination of the factor $(e'_{01} - e'_{11})$ from g^k (by considering $\alpha g^2 + \beta g^4$) then yields the required ratio of e'_{10} and e'_{12} in c_2. We find $c_2 = (15e'_{10} + e'_{12})$ with the orthogonal counterpart $(8e'_{10} - e'_{12})$. Hence the second Sack-operator s_2 must be composed of $(e'_{01} - e'_{11})$ and $(8e'_{10} - e'_{12})$, and obey the condition $s_2 : g^2 = 0$ and $s_2 : g^4 = 0$. It thus follows that $(e'_{01} - e'_{11})$ is not orthogonal to s_2 and in order to obtain a correct c_3 one has to add a term with

Table 14.11: Matrix elements of operators $e'_{\kappa k}$ for dh

	e'_{00}	e'_{10}	e'_{01}	e'_{11}	e'_{02}	e'_{12}	e'_{03}	e'_{13}	e'_{04}	e'_{14}
^1F	1	3	12	36	52	156	91	273	39	117
^1G	1	3	8	24	0	0	-91	-273	-91	-273
^1H	1	3	3	9	-35	-105	-56	-168	84	252
^1I	1	3	-3	-9	-33	-99	96	288	-36	-108
^1K	1	3	-10	-30	30	90	-30	-90	6	18
^3F	1	-1	12	-12	52	-52	91	-91	39	-39
^3G	1	-1	8	-8	0	0	-91	91	-91	91
^3H	1	-1	3	-3	-35	35	-56	56	84	-84
^3I	1	-1	-3	3	-33	33	96	-96	-36	36
^3K	1	-1	-10	10	30	-30	-30	30	6	-6
$\eta_{\kappa k}$	1	$\sqrt{3}$	$2\sqrt{15}$	$6\sqrt{5}$	$2\sqrt{273}$	$6\sqrt{91}$	$2\sqrt{1365}$	$6\sqrt{455}$	$6\sqrt{91}$	$6\sqrt{273}$

$(8e'_{10} - e'_{12})$.
The normalization, by which $c_i : c_i = s_j : s_j = 4[l, l']$, greatly facilitates comparison of the magnitudes of the associated parameters.
The results of this procedure for *dp*-electrons is given in the above table (14.9).

For $M = 1$ when l' is highly excited and thus $l^N l'$ close to the ionization limit, the only ll' operator with an appreciable contribution to the structure will be $c_1 = e'_{02}$. Even this parameter will usually be much less important than ζ_l, which indicates that the intermediate jK-coupling scheme may be used to attain more 'unambiguous' level assignments.
To transform SL-matrices to jK-coupling, one may first recouple from SL to LK-coupling with equation (2.41) and multiply with the recoupling coefficient (2.40) from LK to jK-coupling; alternatively, one may directly employ the recoupling identity (2.49) to arrive at:

$$\left\langle S_1 L_1(J_1), l' [K] \; \tfrac{1}{2}; J \mid (S_1, \tfrac{1}{2}) S \, (L_1, l') L; J \right\rangle =$$
$$[J_1, K, S, L]^{\frac{1}{2}} \cdot (-1)^{L_1 + l' - L} \cdot \begin{Bmatrix} S_1 & L_1 & J_1 \\ l' & K & L \end{Bmatrix} \cdot (-1)^{\frac{1}{2} + S - S_1} \cdot \begin{Bmatrix} S_1 & \frac{1}{2} & S \\ J & L & K \end{Bmatrix} \qquad (14.41)$$

14.5.2 The magnetic case

Using equation (14.36) with $t = 1$ to find spin-orbit type *dp*-operators, 12 independent orthogonal combinations z_i can be classified [Uylings and Raassen, 1996].
The first two $(\kappa, k, \kappa', k') = (1, 1, 0, 0)$ and $(0, 0, 1, 1)$ are directly proportional to the matrix elements of ζ_d and ζ_p, respectively. To retain an understanding of the physical content, the EL-SO operators are projected onto the remaining 10 operators. EL-SO is a perturbative effect arising from Brillouin-type substitutions $p \to p'$ and $d \to d'$. The ranks of the Slater integrals involved being 2 (direct), 1 or 3 (exchange), there are 6 independent EL-SO operators in second order (see section 15.5 for more details). These operators are projected on the basis operators z_i and subsequently orthogonalized. The resulting operators are named $Z^k_{ll'}$; $Z^1_{pp'}$ turns out to be the largest in most cases.

With the multiplication numbers η_i of table 14.12 included, one obtains e.g.:

$$\begin{aligned} \zeta_d &= \eta_1 \cdot z_1 \\ \zeta_p &= \eta_2 \cdot z_2 \\ S_d \cdot L_p &= \eta_3 \cdot z_3 \\ S_p \cdot L_d &= \eta_4 \cdot z_4 \\ Z^2_{pp'} &= \eta_6 \cdot z_6 \end{aligned}$$

For pp' configurations, the operators z_9 and z_{10} do not appear and one is left with a set of 10 independent orthogonal operators to fully describe the spin-orbit effects.

Table 14.12: $z_i(dp)$ tensor ranks. The numbers η_i multiply all entries z_i to avoid square roots.

z_i	κ	k	κ'	k'	η_i
z_1	1	1	0	0	$-3\sqrt{10}$
z_2	0	0	1	1	$-\sqrt{30}$
z_3	1	0	0	1	$7\sqrt{30}$
z_4	0	1	1	0	$7\sqrt{10}$
z_5	1	2	0	1	$14\sqrt{210}$
z_6	0	2	1	1	$14\sqrt{210}$
z_7	1	1	0	2	$70\sqrt{2}$
z_8	0	1	1	2	$70\sqrt{2}$
z_9	1	3	0	2	$70\sqrt{7}$
z_{10}	0	3	1	2	$70\sqrt{7}$
z_{11}	1	2	1	2	$90/7\sqrt{35}$
z_{12}	1	1	1	1	$14\sqrt{15}$

Spin-spin operators are directly defined by equation (14.36), with $(\kappa, \kappa', t) = (1, 1, 2)$. The operators are labeled $S_{kk'}$; the most important cases $(k, k') = (0, 2), (2, 0)$ and $(4, 2)$ are included and cover all the direct spin-spin dp–interactions associated with $N^0(pd; pd), N^0(dp; dp)$ and $N^2(dp; dp)$, respectively.

14.5.3 Three-electron operators

The account for perturbing configurations to second or higher order is to introduce such schematic operators as $(\mathbf{p}^\dagger\mathbf{p}^\dagger\mathbf{d}^\dagger\ \mathbf{ppd})^{(00)}$, $(\mathbf{d}^\dagger\mathbf{d}^\dagger\mathbf{p}^\dagger\ \mathbf{ddp})^{(00)}$ or $(\mathbf{d}^\dagger\mathbf{d}^\dagger\mathbf{s}^\dagger\ \mathbf{dds})^{(00)}$. From ds and d^2, we find six electrostatic operators for d^2s: e_{av}, c_{ds} and four operators that describe the d^2 structure. As there are seven terms in d^2s, we expect one new three-electron operator, labeled t_{dds}.

To see how such an operator t_{dds} arises, consider the Coulomb excitation of an s electron of d^2s into an unoccupied d or g state. This can be accomplished by an operator of the type $(\mathbf{d}^\dagger\mathbf{g}^\dagger\ \mathbf{ds})^{(00)}$. Returning with the adjoint operator in second-order perturbation theory, one obtains the product $(\mathbf{s}^\dagger\mathbf{d}^\dagger\ \mathbf{gd})^{(00)} \cdot (\mathbf{d}^\dagger\mathbf{g}^\dagger\ \mathbf{ds})^{(00)}$. Using equation (5.14) for the interchange of the virtual g electrons, one is left with a residue of the form $(\mathbf{s}^\dagger\mathbf{d}^\dagger\ \mathbf{dd}^\dagger\ \mathbf{ds})^{(00)}$. The $\mathbf{dd}^\dagger$ tensors can be rearranged to yield

the two-electron operator $(\mathbf{s}^\dagger\mathbf{d}^\dagger\ \mathbf{ds})^{(00)}$ together with the anticipated three-electron operator $(\mathbf{s}^\dagger\mathbf{d}^\dagger\mathbf{d}^\dagger\ \mathbf{dds})^{(00)}$. A more detailed study is presented in section 15.3.

The three-electron electrostatic p^2d operators t_i introduced by [Dothe et al., 1985], turn out to be orthogonal to all two-electron pd operators but not to the two-electron p^2 operators. The corrected orthogonalization procedure reduces all entries of t_1 and t_2 to zero, so these operators are removed from the operator set as their effects will already be absorbed by the existing p^2 operators. All current t'_i operators are normalized to a length of $\sqrt{240}$; the required multiplication factors w.r.t. to [Dothe et al., 1985, Hansen et al., 1987] are found in table 14.13.

Table 14.13: Multiplication factors for the parameters values of the three-electron operators t'_i and the four-electron operators f'_i w.r.t. [Dothe et al., 1985].

t'_i	Value	f'_i	Value
t'_3	$\sqrt{60}$	f'_1	$\sqrt{105/2}$
t'_4	$\sqrt{24}$	f'_2	$\sqrt{245/2}$
t'_5	$\sqrt{120}$	f'_3	$\sqrt{15/4}$
t'_6	$\sqrt{56}$	f'_4	$\sqrt{245/2}$
t'_7	$\sqrt{1176}$	f'_5	$\sqrt{45/4}$
t'_8	$\sqrt{28}$	f'_6	$\sqrt{15}$
t'_9	$\sqrt{35/6}$		
t'_{10}	$\sqrt{35/2}$		
t'_{11}	$\sqrt{735/2}$		

In addition, the four-body operator f'_8 introduced by [Hansen et al., 1987], is not orthogonal to three (out of five) of the dp operators. The operators f'_7, f'_8 and f'_9 are removed from the operator set, also for reasons explained in that article. The current f'_i operators are normalized to $\sqrt{480}$, with the parameter multiplication factors given in table 14.13.

14.6 Towards higher N

Matrix elements of orthogonal operators are, unlike the matrix elements of the traditional Slater-Condon operators, usually not given by closed angular momentum formulae. Instead, they are defined in their parent configuration, i.e. the most elementary configuration where they first occur. To find the required matrix elements in more general configurations, expansion formulae are needed to express them in terms of the matrix elements of configurations with lower occupation numbers.
Depending on the complexity of the cases at hand, this can either be done directly or recursively. Both types of expansion formulae are given below.
Occasionally, conjugation properties may be used as well, but care should be taken if the operators correspond to a mixture of odd and even quasispin ranks as mentioned in section 5.10.

Expansion of matrix elements of $n-$particle operators in l^N can be done by uncoupling one of the electrons from the l^N shell:

$$\begin{aligned}\left\langle l^N\psi|H_n|l^N\psi'\right\rangle &= \binom{N}{n}\binom{N-1}{n}^{-1}\sum_{\phi\phi'}(\psi\{|\phi)\left\langle l^{N-1}\phi|H_n|l^{N-1}\phi'\right\rangle(\phi'|\}\psi') \\ &= \frac{N}{N-n}\sum_{\phi\phi'}(\psi\{|\phi)\left\langle l^{N-1}\phi|H_n|l^{N-1}\phi'\right\rangle(\phi'|\}\psi') \end{aligned} \tag{14.42}$$

Similarly for magnetic operators with $k \neq 0$, using equation (3.51a):

$$\begin{aligned}\left\langle l^N SL \parallel H_n \parallel l^N S'L'\right\rangle = \frac{N}{N-n}\sum_{S_1L_1S_1'L_1'}&\left(l^N SL\{|l^{N-1}S_1L_1\right)\left(l^{N-1}S_1'L_1'|\}l^N S'L'\right) \\ (-1)^{S_1+\frac{1}{2}+S'}\cdot(-1)^{L_1+l+L'}\cdot[S,L,S',L']^{\frac{1}{2}}&\cdot\begin{Bmatrix}S & k & S'\\ S_1' & \frac{1}{2} & S_1\end{Bmatrix}\cdot\begin{Bmatrix}L & k & L'\\ L_1' & l & L_1\end{Bmatrix} \\ &\cdot\left\langle l^{N-1}S_1L_1 \parallel H_n \parallel l^{N-1}S_1'L_1'\right\rangle\end{aligned} \tag{14.43}$$

For the special case of the zero-particle unit operator $e_{\text{av}} = \mathbb{1}$, equation (14.42) reduces to $\delta(\psi,\psi') = \sum_{\phi\phi'}(\psi\{|\phi)(\phi'|\}\psi')\cdot\delta(\phi,\phi')$, which is just the completeness cfp sum rule (5.145).

The progression as a function of N of the $l^N l'$ operators, now originally defined in their parent configuration ll', is carried through by a chain calculation analogous to equation (14.42):

$$\left\langle l^N l'\,\psi|\,G\,|l^N l'\,\psi'\right\rangle = \frac{N}{N-1}\sum_{\phi\phi'}(\psi\{|\phi)\left\langle l^{N-1}l'\,\phi|\,G\,|l^{N-1}l'\,\phi'\right\rangle(\phi'|\}\psi') \tag{14.44}$$

where the coefficients of fractional parentage for inequivalent electrons are introduced, as defined earlier in equation (5.169).

For a general operator T with rank n in the l^N shell and rank 1 in the l' shell, the more detailed chain formula becomes thereby:

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'SL\,|\,T\,|\,l^N(S_1'L_1')\,l'SL\right\rangle = \frac{N}{N-n}\cdot\sum_{S_2L_2,S_2'L_2',S_pL_p}&[S_p,L_p]\cdot(-1)^{S_1-S_1'+L_1-L_1'} \\ \cdot[S_1,S_1',L_1,L_1']^{\frac{1}{2}}\cdot\begin{Bmatrix}S_1 & S & \frac{1}{2}\\ S_p & S_2 & \frac{1}{2}\end{Bmatrix}&\cdot\begin{Bmatrix}L_1 & L & l'\\ L_p & L_2 & l\end{Bmatrix}\cdot\begin{Bmatrix}S_1' & S & \frac{1}{2}\\ S_p & S_2' & \frac{1}{2}\end{Bmatrix}\cdot\begin{Bmatrix}L_1' & L & l'\\ L_p & L_2' & l\end{Bmatrix} \\ \left(l^N\,S_1L_1\{|l^{N-1}S_2L_2\right)&\left(l^N\,S_1'L_1'\{|l^{N-1}S_2'L_2'\right)\cdot\left\langle l^{N-1}(S_2L_2)\,l'S_pL_p\,|\,T\,|\,l^{N-1}(S_2'L_2')l'S_pL_p\right\rangle\end{aligned} \tag{14.45}$$

This is readily generalized to $l^N l'^M$ configurations:

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'^M(S_2L_2)SL\,|\,T\,|\,l^N(S_1'L_1')\,l'^M(S_2'L_2')SL\right\rangle = \frac{N}{N-n}\cdot\sum_{S_3L_3,S_3'L_3',S_pL_p}&[S_p,L_p] \\ \cdot(-1)^{S_1-S_1'+S_2-S_2'}\cdot(-1)^{L_1-L_1'+L_2-L_2'}\cdot[S_1,S_1',L_1,L_1']^{\frac{1}{2}}\cdot\begin{Bmatrix}S_3 & \frac{1}{2} & S_1\\ S & S_2 & S_p\end{Bmatrix}&\cdot\begin{Bmatrix}L_3 & l & L_1\\ L & L_2 & L_p\end{Bmatrix} \\ \left(l^N\,S_1L_1\{|l^{N-1}S_3L_3\right)&\left(l^N\,S_1'L_1'\{|l^{N-1}S_3'L_3'\right)\cdot\begin{Bmatrix}S_3' & \frac{1}{2} & S_1'\\ S & S_2' & S_p\end{Bmatrix}\cdot\begin{Bmatrix}L_3' & l & L_1'\\ L & L_2' & L_p\end{Bmatrix} \\ \cdot\left\langle l^{N-1}(S_3L_3)\,l'^M(S_2L_2)S_pL_p\,|\,T\,|\,l^{N-1}(S_3'L_3')l'^M(S_2'L_2')S_pL_p\right\rangle&\end{aligned} \tag{14.46}$$

The comparable expression for magnetic $k \neq 0$ operators:

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'SL \parallel G_{ll'} \parallel l^N(S_1'L_1')\,l'S'L'\right\rangle &= \frac{N}{N-1}\cdot\sum_{S_p,L_p,S_p',L_p'}[S,L,S',L']^{\frac12}\cdot[S_p,L_p,S_p',L_p']^{\frac12}\\ &\cdot(-1)^{S_1+L_1+S+L+\frac12+l}\cdot(-1)^{S_1'+L_1'+S'+L'+\frac12+l}\cdot[S_1,S_1',L_1,L_1']^{\frac12}\cdot(-1)^{\frac12+S_p'+S+k}\cdot(-1)^{l+L_p'+L+k}\\ &\cdot\begin{Bmatrix}S_1 & S & \frac12\\ S_p & S_2 & \frac12\end{Bmatrix}\cdot\begin{Bmatrix}L_1 & L & l'\\ L_p & L_2 & l\end{Bmatrix}\cdot\begin{Bmatrix}S_1' & S' & \frac12\\ S_p' & S_2' & \frac12\end{Bmatrix}\cdot\begin{Bmatrix}L_1' & L' & l'\\ L_p' & L_2' & l\end{Bmatrix}\cdot\begin{Bmatrix}S & k & S'\\ S_p' & \frac12 & S_p\end{Bmatrix}\cdot\begin{Bmatrix}L & k & L'\\ L_p' & l & L_p\end{Bmatrix}\\ &\cdot\left(l^N\,S_1L_1\{|l^{N-1}S_2L_2\right)\left(l^N\,S_1'L_1'\{|l^{N-1}S_2'L_2'\right)\cdot\left\langle l^{N-1}(S_2L_2)\,l'S_pL_p \parallel G_{ll'} \parallel l^{N-1}(S_2'L_2')l'S_p'L_p'\right\rangle\end{aligned} \tag{14.47}$$

Again, generalization to $l^Nl'^M$ configurations is straightforward:

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'^M(S_2L_2)SL \parallel G_{ll'} \parallel l^N(S_1'L_1')\,l'^M(S_2'L_2')S'L'\right\rangle &= \frac{N}{N-1}\cdot\sum_{S_p,L_p,S_p',L_p'}[S,L,S',L']^{\frac12}\\ &\cdot[S_p,L_p,S_p',L_p']^{\frac12}\cdot(-1)^{S_1+L_1+S+L+S_2+L_2}\cdot(-1)^{S_1'+L_1'+S'+L'+S_2'+L_2'}\cdot[S_1,S_1',L_1,L_1']^{\frac12}\\ &\cdot(-1)^{\frac12+S_p'+S+k}\cdot(-1)^{l+L_p'+L+k}\cdot\left(l^N\,S_1L_1\{|l^{N-1}S_3L_3\right)\left(l^N\,S_1'L_1'\{|l^{N-1}S_3'L_3'\right)\\ &\cdot\begin{Bmatrix}S_1 & S & S_2\\ S_p & S_3 & \frac12\end{Bmatrix}\cdot\begin{Bmatrix}L_1 & L & L_2\\ L_p & L_3 & l\end{Bmatrix}\cdot\begin{Bmatrix}S_1' & S' & S_2'\\ S_p' & S_3' & \frac12\end{Bmatrix}\cdot\begin{Bmatrix}L_1' & L' & L_2'\\ L_p' & L_3' & l\end{Bmatrix}\cdot\begin{Bmatrix}S & k & S'\\ S_p' & \frac12 & S_p\end{Bmatrix}\cdot\begin{Bmatrix}L & k & L'\\ L_p' & l & L_p\end{Bmatrix}\\ &\cdot\left\langle l^{N-1}(S_3L_3)\,l'^M(S_2L_2)S_pL_p \parallel G_{ll'} \parallel l^{N-1}(S_2'L_2')l'^M(S_2'L_2')S_p'L_p'\right\rangle\end{aligned} \tag{14.48}$$

Another, compared to a chain calculation possibly more direct way to proceed is to un- and recouple the ll' matrix elements from the l^Nl' configuration, after a fourfold (spin- and orbit, bra and ket) application of equation (2.40). In this alternative for a direct calculation, one calculates (two-particle) reduced matrix elements for higher N from the matrix elements in its original two-particle configuration:

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'(SL)\,|\,G_{ll'}\,|\,l^N(S_1'L_1')\,l'(SL)\right\rangle &= N\cdot\sum_{\overline{S_1}\,\overline{L_1}}[S_1,S_1',L_1,L_1']^{\frac12}\\ &\cdot\sum_{S_p,L_p}\begin{Bmatrix}\overline{S_1} & \frac12 & S_1\\ \frac12 & S & S_p\end{Bmatrix}\cdot\begin{Bmatrix}\overline{S_1} & \frac12 & S_1'\\ \frac12 & S & S_p\end{Bmatrix}\cdot\begin{Bmatrix}\overline{L_1} & l & L_1\\ l' & L & L_p\end{Bmatrix}\cdot\begin{Bmatrix}\overline{L_1} & l & L_1'\\ l' & L & L_p\end{Bmatrix}\\ &\left(l^N\,S_1L_1\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right)\left(l^N\,S_1'L_1'\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right)\cdot[S_p,L_p]\cdot\langle ll'\,S_pL_p\,|\,G_{ll'}\,|\,ll'\,S_pL_p\,\rangle\end{aligned} \tag{14.49}$$

The corresponding formula for magnetic operators with $k \neq 0$ is slightly more complex due to the additional uncoupling equation (3.51b):

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'(SL) \parallel G_{ll'} \parallel l^N(S_1'L_1')\,l'(S'L')\right\rangle &= N\sum_{\overline{S_1}\,\overline{L_1}}[S_1,L_1,S_1',L_1',S_p,L_p,S_p',L_p']^{\frac12}\\ &\cdot\sum_{S_pL_p,S_p'L_p'}(-1)^{\overline{S_1}+S_p'+S'}\cdot\begin{Bmatrix}\overline{S_1} & \frac12 & S_1\\ \frac12 & S & S_p\end{Bmatrix}\cdot\begin{Bmatrix}\overline{S_1} & \frac12 & S_1'\\ \frac12 & S' & S_p'\end{Bmatrix}\cdot\begin{Bmatrix}S & k & S'\\ S_p' & \overline{S_1} & S_p\end{Bmatrix}\\ &\cdot[S,L,S',L']^{\frac12}\cdot(-1)^{\overline{L_1}+L_p'+L'}\cdot\begin{Bmatrix}\overline{L_1} & l & L_1\\ l' & L & L_p\end{Bmatrix}\cdot\begin{Bmatrix}\overline{L_1} & l & L_1'\\ l' & L' & L_p'\end{Bmatrix}\cdot\begin{Bmatrix}L & k & L'\\ L_p' & \overline{L_1} & L_p\end{Bmatrix}\\ &\cdot\left(l^N\,S_1L_1\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right)\left(l^N\,S_1'L_1'\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right)\cdot\left\langle ll'\,S_pL_p \parallel G_{ll'} \parallel ll'\,S_p'L_p'\right\rangle\end{aligned} \tag{14.50}$$

The generalization of the above towards $l^N l'^M$ configurations is straightforward:

$$\begin{aligned}\left\langle l^N(S_1L_1)\, l'^M(S_2L_2)SL \,|\, G_{ll'} \,|\, l^N(S'_1L'_1)\, l'^M(S'_2L'_2)SL \right\rangle &= N\cdot M \sum_{\overline{S_1}\,\overline{L_1}} \sum_{\overline{S_2}\,\overline{L_2}} \\ \cdot \left(l^N\, S_1L_1\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right) \left(l^N\, S'_1L'_1\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right) &\cdot \left(l'^M\, S_2L_2\{|l'^{M-1}\overline{S_2}\,\overline{L_2}\right) \left(l'^M\, S'_2L'_2\{|l'^{M-1}\overline{S_2}\,\overline{L_2}\right) \\ \cdot \sum_{S_pL_p} \quad (-1)^{S'_1-S_1} \begin{bmatrix} \frac{1}{2} & S_1 & \frac{1}{2} & S'_1 \\ \overline{S_2} & S_p & S & \overline{S_1} \\ S_2 & S'_2 & \frac{1}{2} & \frac{1}{2} \end{bmatrix} &\cdot (-1)^{L'_1-L_1} \begin{bmatrix} l' & L_1 & l' & L'_1 \\ \overline{L_2} & L_p & L & \overline{L_1} \\ L_2 & L'_2 & l & l \end{bmatrix} \\ \cdot [S_1,L_1,S_2,L_2,S'_1,L'_1,S'_2,L'_2]^{\frac{1}{2}} &\cdot [S_p,L_p] \cdot \langle ll'\; S_pL_p \,|\, G_{ll'} \,|\, ll'\; S_pL_p\rangle \end{aligned} \tag{14.51}$$

Again, a small extension is found for $k \neq 0$ magnetic operators:

$$\begin{aligned}\left\langle l^N(S_1L_1)\, l'^M(S_2L_2)SL \parallel G_{ll'} \parallel l^N(S'_1L'_1)\, l'^M(S'_2L'_2)S'L' \right\rangle &= N\cdot M \sum_{\overline{S_1}\,\overline{L_1}} \sum_{\overline{S_2}\,\overline{L_2}} \\ \cdot \left(l^N\, S_1L_1\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right) \left(l^N\, S'_1L'_1\{|l^{N-1}\overline{S_1}\,\overline{L_1}\right) &\cdot \left(l'^M\, S_2L_2\{|l'^{M-1}\overline{S_2}\,\overline{L_2}\right) \left(l'^M\, S'_2L'_2\{|l'^{M-1}\overline{S_2}\,\overline{L_2}\right) \\ \cdot \sum_{S_{13}L_{13}} [S_{13},L_{13}] \cdot \begin{Bmatrix} \overline{S_1} & \overline{S_2} & S_{13} \\ \frac{1}{2} & \frac{1}{2} & S_p \\ S_1 & S_2 & S \end{Bmatrix} \begin{Bmatrix} \overline{S_1} & \overline{S_2} & S_{13} \\ \frac{1}{2} & \frac{1}{2} & S'_p \\ S'_1 & S'_2 & S' \end{Bmatrix} &\begin{Bmatrix} \overline{L_1} & \overline{L_2} & L_{13} \\ l & l' & L_p \\ L_1 & L_2 & L \end{Bmatrix} \begin{Bmatrix} \overline{L_1} & \overline{L_2} & L_{13} \\ l & l' & L'_p \\ L'_1 & L'_2 & L' \end{Bmatrix} \\ \cdot (-1)^{S_{13}+S'_p+S} \cdot (-1)^{L_{13}+L'_p+L} \cdot [S,S',L,L']^{\frac{1}{2}} &\begin{Bmatrix} S & k & S' \\ S'_p & S_{13} & S_p \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ L'_p & L_{13} & L_p \end{Bmatrix} \\ \cdot [S_1,L_1,S_2,L_2,S'_1,L'_1,S'_2,L'_2]^{\frac{1}{2}} \cdot \sum_{S_pL_p,S'_pL'_p} [S_p,L_p,S'_p,L'_p]^{\frac{1}{2}} &\left\langle ll'\; S_pL_p \parallel G_{ll'} \parallel ll'\; S'_pL'_p \right\rangle \end{aligned} \tag{14.52}$$

Leading to 15j-symbols of the third kind, not much is gained by carrying out the summation over (S_{13}, L_{13}) analytically.
The case $M = 1$ has already been treated in equation (14.50).

With the magnitude in the parent configuration ll' given by $4[l,l']$, equation (14.21) yields the below result for the operator magnitudes in every $l^N l'^M$ configuration:

$$[G:G]^{l^N l'^M} = \binom{4l}{N-1} \cdot \binom{4l'}{M-1} \cdot 4[l,l'] \tag{14.53}$$

Similar to the two-electron case, the $l^2 l'$ electrons can be uncoupled from the bra and ket $l^N l'^M$ configurations to retrieve the expressions for the three-electron $T_{l^2 l'}$

operators in higher N and/or M configurations:

$$\begin{aligned}\left\langle l^N(S_1L_1)\,l'^M(S_2L_2)SL\,|T_{l^2l'}|\,l^N(S'_1L'_1)\,l'^M(S'_2L'_2)SL\right\rangle &= \tfrac{1}{2}N(N-1)\cdot M\sum_{\overline{S}\,\overline{L}}\sum_{\overline{S_2}\,\overline{L_2}}\sum_{\overline{S'}\,\overline{L'}}\\ \cdot\left(l^N\,S_1L_1\{|l^{N-1}\overline{S}\,\overline{L}\right)\cdot\left(l^{N-1}\,\overline{S}\,\overline{L}\{|l^{N-2}\overline{S_1}\,\overline{L_1}\right)\cdot\left(l'^M\,S_2L_2\{|l'^{M-1}\overline{S_2}\,\overline{L_2}\right)&\\ \cdot\left(l^N\,S'_1L'_1\{|l^{N-1}\overline{S'}\,\overline{L'}\right)\cdot\left(l^{N-1}\,\overline{S'}\,\overline{L'}\{|l^{N-2}\overline{S_1}\,\overline{L_1}\right)\cdot\left(l'^M\,S'_2L'_2\{|l'^{M-1}\overline{S_2}\,\overline{L_2}\right)&\\ \cdot\sum_{S_{13}L_{13}}[S_{13},L_{13}]\cdot\begin{Bmatrix}\overline{S_1}&\tilde{S}&S_1\\ \overline{S_2}&\frac{1}{2}&S_2\\ S_{13}&S_p&S\end{Bmatrix}\begin{Bmatrix}\overline{S_1}&\tilde{S'}&S'_1\\ \overline{S_2}&\frac{1}{2}&S'_2\\ S_{13}&S_p&S\end{Bmatrix}\begin{Bmatrix}\overline{L_1}&\tilde{L}&L_1\\ \overline{L_2}&l'&L_2\\ L_{13}&L_p&L\end{Bmatrix}\begin{Bmatrix}\overline{L_1}&\tilde{L'}&L'_1\\ \overline{L_2}&l'&L'_2\\ L_{13}&L_p&L\end{Bmatrix}&\\ (-1)^{S_1-S'_1}\cdot(-1)^{L_1-L'_1}\cdot\left[\overline{S},\overline{L},S_1,L_1,S_2,L_2\right]^{\frac{1}{2}}\cdot\left[\overline{S'},\overline{L'},S'_1,L'_1,S'_2,L'_2\right]^{\frac{1}{2}}\cdot\left[\tilde{S},\tilde{L},\tilde{S'},\tilde{L'}\right]^{\frac{1}{2}}&\\ \begin{Bmatrix}\overline{S_1}&\frac{1}{2}&\overline{S}\\ \frac{1}{2}&S_1&\tilde{S}\end{Bmatrix}\begin{Bmatrix}\overline{L_1}&l&\overline{L}\\ l&L_1&\tilde{L}\end{Bmatrix}\begin{Bmatrix}\overline{S_1}&\frac{1}{2}&\overline{S'}\\ \frac{1}{2}&S'_1&\tilde{S'}\end{Bmatrix}\begin{Bmatrix}\overline{L_1}&l&\overline{L'}\\ l&L'_1&\tilde{L'}\end{Bmatrix}&\\ \cdot\sum_{S_pL_p}[S_p,L_p]\left\langle l^2(\tilde{S}\tilde{L})\;l'\;S_pL_p\,|T_{l^2l'}|\,l^2(\tilde{S'}\tilde{L'})\;l'\;S_pL_p\right\rangle&\end{aligned} \tag{14.54}$$

Given the magnitude in the parent configuration l^2l', equation (14.21) provides the operator magnitudes in $l^Nl'^M$ configurations:

$$[T:T]^{l^Nl'^M} = \binom{4l-2}{N-2}\cdot\binom{4l'}{M-1}\cdot[T:T]^{l^2l'} \tag{14.55}$$

14.7 Conversion of operator sets

Given the equation (14.8) or, more generally, (14.26), it is straightforward to translate conventional or *ab initio* calculated parameters into their orthogonal counterparts. By contrast, the reverse generally requires a full matrix inversion.
Let the matrix $\mathbf{A} = A_{ij}$ comprise the elements with row index i of a set of operators with column index j, then the translation matrix $\mathbf{T}$ for two parameter sets, 1 and 2, is given by $\mathbf{T} = \mathbf{A}(1)\mathbf{A}^{-1}(2)$, or in index notation:

$$T_{ik} = A_{ij}(1)A^{-1}_{jk}(2). \tag{14.56}$$

The required relations between parameters $F_k(2)$ and $F_i(1)$ then become:

$$F_i(1) = T_{ik}F_k(2). \tag{14.57}$$

As an example, we give the matrix elements of the conventional operators for d^2 in condensed notation:

$$A_{ij} = \begin{pmatrix} 1 & 126 & 126 & -12 & 5\\ 1 & 63 & -84 & -10 & 0\\ 1 & -27 & 36 & -6 & 0\\ 1 & -72 & -9 & 0 & 0\\ 1 & 36 & 1 & 8 & 0\\ (1) & (441) & (441) & (1) & (1)\end{pmatrix} \tag{14.58}$$

$$A^{-1}_{jk} = \begin{pmatrix} 0 & 24 & 88 & 36 & 108 \\ 0 & 210 & 350 & -910 & 630 \\ 0 & -504 & 1512 & -756 & 252 \\ 0 & -5 & -15 & 5 & 15 \\ 1 & 0 & -160 & 100 & -36 \\ (5) & (200) & (280) & (200) & (280) \end{pmatrix} \tag{14.59}$$

Relations between Cowan's most relevant parameters [Cowan, 1981] and their orthogonal counterparts are given below:

$$O_2 = \frac{50}{63}\frac{1}{\sqrt{140}}\left(F^2(dd) + F^4(dd)\right) \tag{14.60a}$$

$$O_2' = \frac{10}{7}\frac{1}{\sqrt{140}}\left(F^2(dd) - \frac{5}{9}F^4(dd)\right) \tag{14.60b}$$

$$O_2 + O_2' = \frac{20}{9}\frac{1}{\sqrt{140}} \cdot F^2(dd) \tag{14.60c}$$

[Racah, 1952] and Trees introduced the concept of effective operators, in l^N defined as:

$$\begin{aligned} \left\langle l^N SL\,|\hat{\alpha}|\,l^N SL\right\rangle &= L(L+1)\cdot\alpha \\ \left\langle l^N SL\,|Q|\,l^N SL\right\rangle &= \frac{1}{4}(N-\nu)(4l+4-N-\nu)\cdot\beta \;\rightarrow [N=2,\nu=0,2]: \\ &= (2l+1)\cdot\delta(L,0)\cdot\beta \end{aligned} \tag{14.61}$$

These operators became a standard extension of the Slater-Condon theory in the d-shell with matrix elements $\langle d^2\,SL|\hat{\alpha},Q|d^2\,SL\rangle = (0,5)(2,0)(6,0)(12,0)(20,0)$.
In the f-shell, [Rajnak and Wybourne, 1963] introduced similar operators:

$$\left\langle f^N\psi|H_{\text{eff}}|f^N\psi'\right\rangle = \delta(\psi,\psi')\left[L(L+1)\cdot\alpha + G(G_2)\cdot\beta + G(R_7)\cdot\gamma\right] \tag{14.62}$$

Here, $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operator for the groups G_2 and R_7, used by [Racah, 1949] to classify f-shell states unambiguously with labels $U = (u_1u_2)$ and $W = (w_1w_2w_3)$ respectively, see chapter 13.
In terms of these labels, the eigenvalues are given by:

$$\langle u_1u_2|\,G(G_2)\,|u_1u_2\rangle = \frac{1}{12}\left[u_1^2 + u_1u_2 + u_2^2 + 5u_1 + 4u_2\right] \tag{14.63a}$$

$$\langle w_1w_2w_3|\,G(R_7)\,|w_1w_2w_3\rangle = \frac{1}{10}\left[w_1(w_1+5) + w_2(w_2+3) + w_3(w_3+1)\right] \tag{14.63b}$$

Table 14.14: Matrix elements of the conventional effective electrostatic operators α, β and γ in f^2

SL	$U\ W$	$\hat{\alpha}$	$12G(G_2)$	$10G(R_7)$
^1S	(00)(000)	0	0	0
^3P	(11)(110)	2	12	10
^1D	(20)(200)	6	14	14
^3F	(10)(110)	12	6	10
^1G	(20)(200)	20	14	14
^3H	(11)(110)	30	12	10
^1I	(20)(200)	42	14	14

The two-body magnetic dd parameters have both MSO and EL-SO contributions:

$$\begin{aligned}
A_c(dd) &= -\frac{11}{12}M^0(dd) - \frac{1}{42}M^2(dd) + \frac{5}{56}\left(P^2(d\to d') + \frac{2}{9}P^4(d\to d')\right)\\
A_3(dd) &= \frac{3}{7}\sqrt{\frac{7}{6}}\left(M^0(dd) - \frac{3}{7}M^2(dd)\right) + \frac{3}{98}\sqrt{\frac{7}{6}}\left(P^2(d\to d') - \frac{5}{9}P^4(d\to d')\right)\\
A_4(dd) &= \frac{4}{21}\sqrt{\frac{7}{4}}\left(M^0(dd) + \frac{37}{7}M^2(dd)\right) + \frac{2}{49}\sqrt{\frac{7}{4}}\left(P^2(d\to d') - \frac{5}{9}P^4(d\to d')\right)\\
A_5(dd) &= \frac{1}{3}\sqrt{\frac{7}{2}}\left(M^0(dd) + \frac{37}{7}M^2(dd)\right) + \frac{1}{98}\sqrt{\frac{7}{2}}\left(P^2(d\to d') - \frac{5}{9}P^4(d\to d')\right)\\
A_6(dd) &= -\frac{1}{21}\sqrt{\frac{7}{2}}\left(\frac{107}{2}M^0(dd) - \frac{23}{7}M^2(dd)\right) + \frac{5}{196}\sqrt{\frac{7}{2}}\left(P^2(d\to d') + \frac{2}{9}P^4(d\to d')\right)\\
A_1(dd) &= 6\sqrt{\frac{7}{6}}\left(\frac{1}{7}M^0(dd) - \frac{8}{49}M^2(dd)\right)\\
A_2(dd) &= -\frac{60}{49}\sqrt{\frac{7}{3}}M^2(dd)
\end{aligned} \tag{14.64}$$

Here (see section 15.5): $P^k(d\to d') = \sum\!\!\!\!\!\!\int_{d\to d'} \frac{2\zeta(dd')R^k(dd;dd')}{E_{dd'}}$

$$C_{ls} = \frac{1}{4l+2}\sqrt{3}\cdot G^l(ls) \to C_{ds} = \frac{1}{10}\sqrt{3}\cdot G^2(ds) \tag{14.65}$$

$$C_1(dp) = \frac{1}{\sqrt{28}}\left(\frac{4}{5}F^2(dp) - \frac{7}{15}G^1(dp) - \frac{3}{35}G^3(dp)\right) \tag{14.66a}$$

$$C_2(dp) = \frac{1}{\sqrt{231}}\left(\frac{14}{5}G^1(dp) + \frac{81}{70}G^3(dp)\right) \tag{14.66b}$$

$$C_3(dp) = \frac{1}{\sqrt{2068}}\left(\frac{47}{5}G^1(dp) - \frac{141}{35}G^3(dp)\right) \tag{14.66c}$$

For p^N configurations, the first order parameter O_2 and the effective parameter E_α are used. The contribution of $F^2(pp)$ is given by:

$$O_2 = \frac{3}{25}\sqrt{2}\cdot F^2(pp) \tag{14.67}$$

For the two-particle magnetic operators A_c and A_3, one obtains the below first and second order contributions:

$$\begin{aligned}
A_c &= \frac{1}{4}\sqrt{2}\left(-5M^0(pp) + \frac{3}{10}P^2(p\to p')\right)\\
A_3 &= \frac{1}{4}\sqrt{\frac{2}{5}}\left(-37M^0(pp) + \frac{3}{10}P^2(p\to p')\right)
\end{aligned} \tag{14.68}$$

where the EL-SO contribution (section 15.5) $P^2(p \to p')$ is given by:

$$P^2(p \to p') = \sum\!\!\!\!\!\!\int_{p \to p'} \frac{2\zeta(pp')R^2(pp;pp')}{E_{pp'}}$$

$$A_1 = -\frac{2}{5}\sqrt{15} \cdot M^0(pp) \tag{14.69}$$

In $p^N s$ configurations, two-electron ps interactions make their appearance as well:

$$C_{ls} = \frac{1}{4l+2}\sqrt{3} \cdot G^l(ls) \to C_{ps} = \frac{1}{6}\sqrt{3} \cdot G^1(ps) \tag{14.70}$$

Contributions to the mutual spin-orbit parameter A_{mso} in ls configurations, are frequently dominated by the second order effect called EL-SO, discussed more fully in section 15.5. From equation (5.108), one finds:

$$A_{\text{mso}} = -\frac{6}{2l+1}W^{l-1}(ls;sl) + 4N^0(ls;ls) - \frac{1}{4l+2}P^l(l \to l') \tag{14.71}$$

where again $P^l(l \to l')$ is defined as:

$$P^l(l \to l') = \delta(l,l') \sum\!\!\!\!\!\!\int_{l \to l'} \frac{2\zeta(ll')R^l(ls;sl')}{E_{ll'}}$$

More specifically, for ps configurations, one obtains:

$$A_{\text{mso}}(ps) = -2 \cdot W^0(ps;sp) + 4N^0(ps;ps) - \frac{1}{6}P^1(p \to p') \tag{14.72}$$

A numerical example for ds configurations is worked out later in the text in equation (15.56) and the below table.

$$A_{ss} = 2\sqrt{\frac{6}{(2l-1)(2l+3)}} \cdot N^0(ls;ls) \tag{14.73}$$

Of course, the parameters also receive contributions from higher-order effects, so the above equations should be regarded as providing first, possibly second, order contributions rather than their entire values.

14.8 Parametric fitting

As in many branches of atomic physics, the challenge of the calculation lies in finding an efficient way to include correlations and, secondary, relativity. The power of a particular approach varies considerably with the type of system at hand. Roughly, we may distinguish two cases:
(i) The element is 'light' ($Z < 20$) or contains less than three electrons outside closed shells. This results in energy spectra with a few, relatively well separated levels. Here, correlation determines the eigenvector composition of the levels to a considerable degree. As electrostatic effects dominate the description of the system. the

mixing is limited to terms with the same $SL-$value. Nevertheless, massive configuration interaction (CI) calculations are necessary to include the right amount of correlation.
(ii) The energy structure is 'complex', i.e. there are several $d-$ or $f-$electrons outside closed shells. The configurations contain quite a number of levels of the same J-value in a relatively small energy interval. Here, the eigenvector composition of the levels is mainly determined by the (non-diagonal) magnetic interactions and the spacing between the levels. In the orthogonal operator approach, the focus lies on the second case. To calculate energy spacings in complex systems as accurately as possible, an effectively complete set of orthogonal operators has been introduced [Hansen et al., 1988b, van het Hof et al., 1991a]. Explicit configuration interaction can be included in this approach by full diagonalization of a more-configuration space [Uylings et al., 1993]. Purely *ab initio* approaches are seldom sufficient to describe complex spectra, i.e. spectra from atoms with more than two electrons or holes outside closed shells. Often a large number of close-lying levels is involved in these systems. The correct LS-coupling fractions therefore critically depend on an accurate determination of the energy spacings. An alternative is to use experimental data in the description as well. In the classic *semi-empirical* approach used e.g. by Racah, one proceeds as follows:
(i) the usual Hamiltonian including all important interactions is set up,
(ii) the radial parts of the energy operators are, after an initial estimate, treated as free parameters,
(iii) the eigenvalues of the Hamiltonian are fitted to the experimental energy levels by adjusting these radial parameters iteratively,
(iv) the final eigenvectors, yielding the level composition in terms of the applied coupling scheme (like LS-coupling), are used to calculate transition probabilities if required.
A weak point of the above procedure is the interdependence of the parameters. Addition of a new parameter (associated with a different physical effect) may change earlier parameter values as the new operator may in part have the same angular structure as some of the older ones. This instability and the associated errors on the parameters are reduced in the orthogonal operator approach [Judd et al., 1982]. "In this approach, the introduced orthogonalization of the conventional Slater-Condon operators increases the accuracy of the parameter values obtained in the fit and improves the stability of the fitting procedure. The stability of the fit offers the possibility to fit parameters one after another and extend the operator set to include a number of small effects, such as two-body magnetic and three-body electrostatic interactions. This method has been successfully applied to the 3d-, 4d- and 5d-spectra and has resulted in reduction of the mean deviations of the fits by an order of magnitude or more compared to the parametric descriptions based on the conventional Slater-Condon approach. The accuracy of the fits permitted experimental determination of the mentioned small effects. These effects have been systematically studied in the 3d- and 4d-spectra. In the 5d-spectra, three isoelectronic sequences have been studied systematically with the orthogonal operators." [Azarov, 2018]
Replacing step (i), a basis set of independent operators each with its own angular structure is constructed (the various allowed angular symmetries may e.g. be determined by group theory). In this way, no unintended effects will be mixed into

the parameter values. This facilitates *ab initio* calculations of the parameters and allows the determination of less important effects as well. One may think of the orthogonal operator method as defining a linear space of operators whereupon physical effects are projected by means of a fit; the coefficient on each orthogonal axis, i.e. its parameter value, yields the strength of the effect.

14.9 Completeness

Each complete set of operators is shown to yield a unique joint solution to level energies and level compositions. Consequently, an operator set which consists of more operators than the number of levels in the configuration is not overcomplete. In principle there is, in addition to the level energies. sufficient physical information dependent on the level compositions (g factors, line strengths) to determine all parameter unambiguously. If, in practice, the experimental information is incomplete, theoretical or empirical knowledge of the parameters can readily be used to reduce the number of parameters to be varied.
Complex bound systems like free atoms and ions can accurately be described if the strengths of the model energy operators are adjusted so as to obtain an optimal agreement between the measured energies and the eigenvalues of the Hamiltonian. Orthogonal operators are introduced in this fitting procedure both to minimize the correlation and, thereby, the mean error of the parameters [Judd et al., 1982, Hansen et al., 1988b], and to facilitate comparison with *ab initio* calculations [Uylings and Smid, 1987, Hansen et al., 1987].
A set of orthogonal operators consists of suited linear combinations of conventional, for instance Slater-type, operators, completed with effective higher order operators like three- and four-electron operators.
The principal, though not fully independent, questions to be answered are the following:

- What is the meaning of a least-squares fit (LSF) involving more parameters than level values?
- Which of the numerous 'perfect energy fits' is physically acceptable and by what criteria does one select the correct solution?
- What information is hidden in the 'superfluous' parameters?

14.9.1 (Over)completeness

Consider the Hamiltonian of a configuration (or possibly more configurations of the same parity), with matrix elements explicitly written in terms of an arbitrary 'pure' coupling scheme such as SL coupling. Because good quantum numbers, and the corresponding symmetry restrictions on the system, only exist as an approximation (except, in the absence of strong external fields, the total angular momentum J) , every mixing between basis states is allowed, i.e. each off-diagonal matrix element may be non-zero. By definition, a set of operators is said to be 'complete' if the number of operators equals the number of independent matrix elements, including

off-diagonals, so quite generally $M > N$ in our context. When only the N energies are used as experimental input, there is an infinite number of sets of M parameter values which describe them perfectly.
To be specific, let the Hamiltonian be defined by:

$$\langle b\,|H|\,k\rangle = \sum_{i=1}^{M} \langle b\,|O_i|\,k\rangle\, P_i \tag{14.74}$$

In the above, O_i is an angular (orthogonal) operator and P_i is the associated radial operator strength, which is treated as a parameter. In the parametric approach, only the angular matrix elements depend explicitly on the basis states. Each unitary transformation UHU^{-1} of H rotates the basis states $|k\rangle$ towards a new coupling scheme, and leaves the values of P_i unchanged. If, on the other hand, the strength P_i of one or more operators is changed, we will after diagonalization end up with different compositions of eigenvectors in terms of the same basis states $|k\rangle$. Such a different 'intermediate coupling' therefore describes a different physical situation: a different set of parameter values may possibly yield the same energies, but never the same set of eigenvectors. Returning to the questions posed in the introduction, we can conclude that the answer to all three of them lies in the physical significance of the level composition. Even for $M > N$, there exists only one 'correct' solution since the level compositions can, at least in principle, be determined from other observables than the energies. The so-called 'overcompleteness' or 'overparametrization' is a consequence of the fact that the experimental information is limited to energy values alone.
Each complete set of operators can be shown to yield a unique joint solution to level energies and level compositions. Consequently, an operator set which consists of more operators than the number of levels in the configuration is not overcomplete. In principle there is, in addition to the level energies, sufficient physical information dependent on the level compositions (g-factors, line strengths) to determine all parameters unambiguously. If, in practice, the experimental information is incomplete, theoretical or empirical knowledge of the parameters can readily be used to reduce the number of parameters to be varied. The noble-gas configurations p^5s have been used to illustrate these points [van het Hof et al., 1991b].

14.9.2 The use of the parameter set

Although mathematically sound, the use of complete sets may still raise points to be clarified.
(i) If the condition of full knowledge of the system (energies and compositions) is satisfied, which hardly ever is the case in practice, one may wonder what purpose is served describing such a system semi-empirically.
(ii) If this condition is not met, one may wonder if application of a complete set is not impracticable and whether the predictive power of such a set, if part of the spectrum is experimentally unknown, is not inferior with respect to a conventional set with considerably fewer parameters.
In reply to (i), if all experimental data of a system are present, the goal to understand the system in the sense of performing *ab initio* calculations that conform to the experiment with sufficient accuracy, still remains. A parametric calculation is

a means of translating the experimental data into quantities that are traceable to theory. It is possible to calculate each parameter independently as the sum of the projections of 'theoretical' operators derived for instance from perturbation theory, onto the basis of orthogonal operators. For every particular *ab initio* calculation, one can therefore select the parameters of interest.
Secondly, parameters (unlike experimental data) provide the possibility to compare systems like d^N configurations isoionically as a function of N, such as the seemingly different configurations d^3 and d^4 [Hansen et al., 1988b].
Thirdly, it is likewise easier to inter- or extrapolate the parameters than the experimental data themselves from one atomic system to analogous (isoionic, isoelectronic) spectra that are not yet completely known.
In reply to (ii), if the experimental data are incomplete, it is obvious that one cannot vary all the parameters; however, there are several ways to proceed.
(a) Direct truncation of the parameter set, i.e. fixing several less important parameters to zero. In this way, one can always obtain an equivalent (same number of parameters, same scope of description) of the older, conventional parameter set, with the additional advantage of having an orthogonal, and thus more independent and stable parameter set.
(b) A more sophisticated approach is to fix the less important parameters to their *ab initio* values. Although these values may sometimes be hard to calculate (contributions from higher order perturbation theory), they are usually more plausible than zero. Especially magnetic effects can fruitfully be added to the Hamiltonian in this way.
(c) Another possibility is to fix parameters at inter- or extrapolated values from analogous spectra. An example of the superiority of orthogonal operators in this respect is the prediction made for the $3d^5$ configuration in Cu VII [van het Hof et al., 1990].
In some cases, experience with other spectra can be combined with *ab initio* calculations, by extrapolating the ratios between fitted and calculated values as scaling factors.
Finally it should be mentioned that, on occasion, other stratagems characteristic to the system under study, like varying parameters in a fixed relation to others, can be used.

14.9.3 Truncation of the basis

In principle, a bound-state eigenvector is composed of all possible model states of the same parity belonging to a particular atom or ion. In practice, the eigenvector space is partitioned into a model space P consisting of a relatively small number of configurations (frequently one) and an orthogonal space Q of far-lying configurations. Effects of the far-away configurations on P can be accounted for by so-called 'effective' operators, that formally act only within P. Therefore, the strength of these operators (i.e. the associated parameter value) is zero to first order. As in our construction the number of real intra-P operators is relatively small, a complete set is mainly characterized by the presence of 'all' effective operators. In this approach, the energies can always be satisfactorily described, but the eigenvectors are inherently approximated by the truncation of Q states. This procedure is therefore justified only if the distance between the configurations $A \in P$ and the configurations $B \in Q$ is 'large' compared with the energy spread of A, in which case only the repul-

sion has to be described and eigenvector mixing between A and B can be neglected in an energy description (in principle, one should use effective dipole operators for transitions). Comparison between experimental and elementary theoretical results, as well as purely theoretical arguments can be used to mark the departure from the single configuration model.
(i) The number of spectral lines is larger, and their intensities deviate from what would be expected on theoretical grounds.
(ii) Fitted parameters deviate markedly from extrapolated results or theoretical predictions: the parameters apparently adapt to effects they were not meant to describe. This situation is analogous to that discussed in subsection (14.9.1): it is true that the energies are described satisfactorily, but the eigenvectors, and thereby the predictions of other observables, are deficient.
(iii) Sum rules for g factors fail.
(iv) Hartree-Fock calculations predict either the proximity (energy overlap) of another configuration B, or large interaction integrals between A and B (orbital overlap), or both. This leads to a transfer of B from Q to P. Especially in several times ionized systems, this situation is often encountered in the set of configurations with equal principal quantum numbers, called the Layzer complex. As suggested by Brillouin's theorem, interactions are often larger if A and B differ by a two-particle substitution than by a one-particle substitution.
If B is transferred to P, the effective operators of A only describe the effects of the remaining configurations in Q. The contribution of B to these effective operators (actually to all operators of A) will thereby be subtracted from the corresponding parameter values. If V_{AB} is the interaction operator between the configurations A and B, this contribution is found from the projection of the perturbation operator

$$U = \frac{V_{AB}V_{BA}}{E_A - E_B} + \frac{V_{AB}\left[V_{BB}, V_{BA}\right]}{\left(E_A - E_B\right)^2} + \cdots \tag{14.75}$$

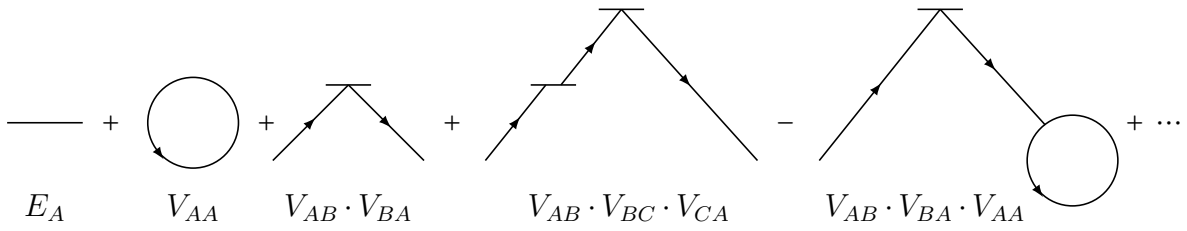
14.9.4 Conclusions

It is argued that for a Hamiltonian consisting of angular operators and associated radial parameters to yield correct energies and level compositions, a complete operator set should be used in the construction, even though the number of operators may exceed the number of fitted energy levels. With complete experimental information lacking in most cases, this is a more philosophical than practical point, but it shows that there is nothing principally wrong in dealing with complete sets. In practice, one can always neglect the smaller effects, or add them as non-variable quantities derived from empirical or theoretical knowledge.

Chapter 15

Perturbation theory

The omission of interaction between configurations is the chief defect of the model based on a central-field potential. The residual Coulomb interaction not only splits up each configuration into terms, but it also connects like terms in different configurations. If the levels of two or more configurations overlap or interact strongly, the only appropriate technique may be to diagonalise their combined matrix. A notation of the type $(3d + 4s)^8$ implies that eight electrons are assigned to the six orbitals provided by the five $3d$ states and the single $4s$ state. We are thus left with a superconfiguration $3d^8 + 3d^7 4s + 3d^6 4s^2$.
In perturbation theory, the eigenvector space is divided into a model space P containing the configuration A (or a small number of strongly interacting configurations) under study and an orthogonal space Q of far-lying configurations B.
A symbolic graphical picture of perturbation theory, with the number of arrows indicating the $0, 1, 2, 3...$ order, is given below:



To be able to deal with a group of levels simultaneously, the Rayleigh-Schrödinger formulation is used.
Following equation (10.19):

$$Q = 1 - P = 1 - \sum_{a \neq v} |a\rangle \langle a| \quad \text{with } Q|a\rangle = 0 \text{ and } Q|v\rangle = |v\rangle \tag{15.1}$$

the corresponding projection operators are given by:

$$P = \sum_{\alpha \in P} |\alpha\rangle \langle \alpha| \tag{15.2a}$$

$$Q = \sum_{\beta \notin P} |\beta\rangle \langle \beta| \qquad \text{with its resolvent: } R = \sum_{\beta \notin P} \frac{|\beta\rangle \langle \beta|}{E_A - E_B} \tag{15.2b}$$

The second-order energy and transition corrections, with $A \in P$ and $B \in Q$, are then respectively:

$$\begin{aligned}\langle A\alpha|H'|A\alpha'\rangle &= \sum_{B\notin P}(E_A-E_B)^{-1}\sum_{\beta}\langle A\alpha|V_{AB}|B\beta\rangle\langle B\beta|V_{BA}|A\alpha'\rangle \\ \langle A\alpha|\mathbf{r}'|C\gamma\rangle &= \sum_{B\notin P}(E_A-E_B)^{-1}\sum_{\beta}\langle A\alpha|V_{AB}|B\beta\rangle\langle B\beta|\mathbf{r}_{BC}|C\gamma\rangle\end{aligned}$$

When formulated in second quantization, the operators automatically select the relevant states $|B\beta\rangle$ from the Q-space, and yield zero otherwise. Therefore, one can extend the summation over β to a summation over all states, the additional ones yielding only additional zeros. This enables the use of the closure relation:

$$\begin{aligned}\langle A\alpha|H'|A\alpha'\rangle &= \sum_{B\notin P}(E_A-E_B)^{-1}\langle A\alpha|V_{AB}V_{BA}|A\alpha'\rangle \\ \langle A\alpha|\mathbf{r}'|C\gamma\rangle &= \sum_{B\notin P}(E_A-E_B)^{-1}\langle A\alpha|V_{AB}\,\mathbf{r}_{BC}|C\gamma\rangle\end{aligned} \tag{15.3}$$

The principle perturbation terms are: $V_{AB} = (C_{AB} - U_{AB}) + Z_{AB}$ where C represents the Coulomb interaction, Z the spin-orbit interaction and U the potential used to generate the zeroth-order wavefunctions. U_{AB} only comes into play with single electron (Brillouin) excitations $nl \to n'l$, when $(C-U)$ or $(Z-U)$ rather than C or Z are to be used. This will introduce cross terms in the perturbation expansion such as:

$$-2\sum_{\beta}\frac{\langle A\alpha|U_{AB}|B\beta\rangle\langle B\beta|C_{BA}|A\alpha'\rangle}{E_A-E_B}$$

The second quantized form for U_{AB} is given by:

$$U_{AB} = -\delta(l,l')\,[\tfrac{1}{2},l]^{\frac{1}{2}}\,(\mathbf{a}^{\dagger}\mathbf{b})^{(00)0}\,\langle a|U|b\rangle \tag{15.4a}$$

In the Hartree-Fock average of configuration approach, a natural choice for perturbation theory, with $A = l^N l'^M$ and $B = l^{N-1}l'^{M+1}$, the off-diagonal potential matrix element becomes:

$$\begin{aligned}\langle a|U|b\rangle = \langle b|U|a\rangle &= \delta(l,l')\left[(N-1)\langle C_{aa;ab}\rangle + M\,\langle C_{ab;bb}\rangle + \sum_c N_c\langle C_{ac;bc}\rangle\right] \\ &= \delta(l,l')\Bigg[(N-1)\left(R^0(aa,ab) - \sum_{k>0}\frac{\langle l\parallel C^{(k)}\parallel l\rangle^2}{(2l+1)(4l+1)}R^k(aa,ab)\right) \\ &\qquad + M\left(R^0(ab,bb) - \sum_{k>0}\frac{\langle l\parallel C^{(k)}\parallel l\rangle^2}{(2l+1)(4l+1)}R^k(ab,bb)\right) \\ &\qquad + \sum_c N_c\left(R^0(ab,ac) - \tfrac{1}{2}\sum_{k'}\frac{\langle l\parallel C^{(k')}\parallel l'\rangle^2}{(2l+1)(2l'+1)}R^k(ab,ca)\right)\Bigg]\end{aligned} \tag{15.4b}$$

as defined earlier in equations (10.8a) and (10.8b), $\langle C_{ab;cd}\rangle$ is the average Coulomb interaction between the electron pairs (ab) and (cd):

$$\langle C_{ab;cd}\rangle = \frac{\sum_{SL}[S,L]\langle l_1 l_2(SL)|C|l_3 l_4(SL)\rangle}{\sum_{SL}[S,L]} \tag{15.5}$$

The notation H_k^n is used to indicate an n-particle operator of the kth-order Hamiltonian in the below. Terms like $(E_A - E_B)^{-1} C_{AB} C_{BA}$ give rise to two- and three-particle electrostatic operators in second order, written further below as H_2^2 and H_2^3.
As for both the angular and the radial parts, by far the most dominant contributions to the two-particle parameters in l^N configurations come from terms with a radial factor $R^0(ll; ll')R^k(ll; ll')(E_A - E_B)^{-1}$. Here, the angular coefficients all turn out to be proportional to the coefficients $f^k(l, l)$ of the Slater parameter F^k. This can be calculated from the corresponding general formulae (e.g. [Uylings, 1985]), but it can be understood more easily by considering the individual cases, graphically represented by their Feynman diagrams in figure 15.1 (the circled cross denoting the potential interaction). Here, lines with a double arrow represent valence electrons, lines a single upward arrow represent virtual electrons and with a single downward arrow closed shells electrons. The topologically equivalent angular momentum diagrams are given in figure 15.2.

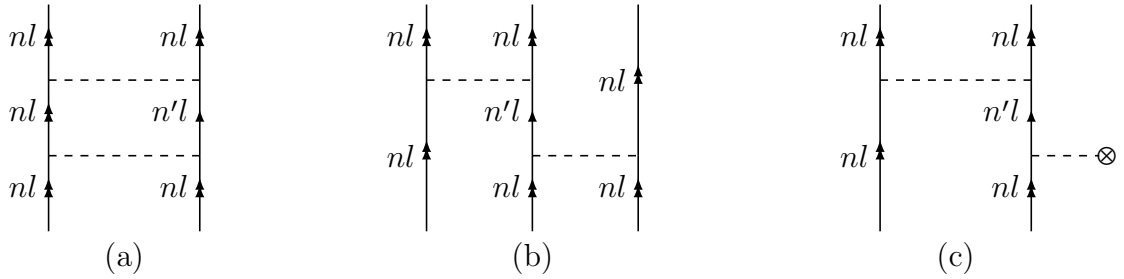


Figure 15.1: Feynman graphs for the two-particle (a), the three-particle (b) and potential (c) operators that appear in the second-order Hamiltonian for an $nl \to n'l$ excitation.

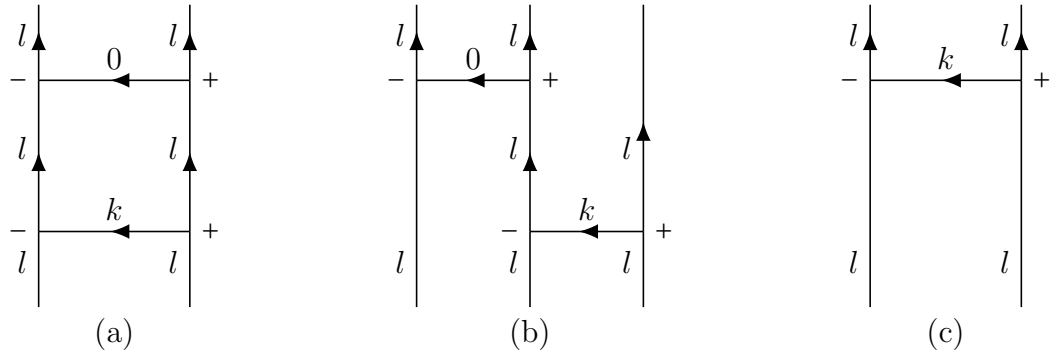


Figure 15.2: Angular momentum graphs corresponding to the cases (a), (b) and (c) of the topologically equivalent diagrams of figure 15.1

After the removal of the zero branches (the factor $[l]^{-1}$ is canceled by $\langle l \parallel C^{(0)} \parallel l \rangle^2$) figures 15.2(a,b) reduce to the form indicated in figure 15.2(c) , which is precisely the graphical representation of $f^k(l, l)$. Realizing that unlike $\langle l^2|C|l^2\rangle$ the matrix elements $\langle l^2|C|ll'\rangle$ and $\langle l^2|U|ll'\rangle$ carry a weighting factor $\sqrt{2}$ and that in addition there are two possible choices for the zero line, we see that the first two terms have angular coefficients $4f^k(l, l)$; the potential term has the coefficient $-4f^k(l, l)$ as a

result of the factor of −2 that occurs in the second-order energy expression. From equation (14.26) it can be seen that the N-dependence of the three-particle contribution is given by $Q = \binom{N}{3}\binom{3}{2}/\binom{N}{2} = (N-2)$; the R^0 term in $\langle nl|U|n'l\rangle$ according to equation (15.4b) is prefaced by $(N-1)$; recall that closed shells can be neglected in this equation. In summary, the contributions of the three terms to the two-particle parameters are:

$$\sum_k 4f^k(l,l)R^0(ll;ll')R^k(ll;ll')\left[1+(N-2)-(N-1)\right](E_A-E_B)^{-1}=0 \tag{15.6}$$

The three dominating contributions therefore cancel for all values of N and only smaller ones are left, e.g. $\langle d|U|d'\rangle$ simply becomes $-2/63\cdot(N-1)[R^2(d^2;dd')+R^4(d^2;dd')]$. Similar cancellations of unphysically large contributions connected with the occurrence of R^0 in the radial factor also occur in the third-order calculation. This result indicates the danger involved in arbitrarily selecting some large contributions of a particular radial class without calculating them all.

15.1 Two perturbed levels

Given that two levels with initial energies E_1 and E_2 (assuming $E_1 > E_2$) are perturbed by an interaction F, the equation to solve becomes:

$$\begin{vmatrix} E_1-\lambda & F \\ F & E_2-\lambda \end{vmatrix} = 0 \tag{15.7}$$

with the solution:

$$\lambda_{1,2} = \frac{E_1+E_2}{2} \pm \sqrt{\left(\frac{E_1-E_2}{2}\right)^2 + F^2} \tag{15.8}$$

The perturbed eigenvalues λ_1 and λ_2 retain the center of gravity: $\frac{1}{2}(E_1+E_2) = \frac{1}{2}(\lambda_1+\lambda_2)$. Both are repelled by an amount Δ w.r.t. their original energy value: $\lambda_1 - E_1 = E_2 - \lambda_2 = \Delta$. Or:

$$\tfrac{1}{2}(E_1-E_2) = \tfrac{1}{2}(\lambda_1-\lambda_2) - \Delta \tag{15.9}$$

It follows: $F^2 = \Delta(E_1-E_2)+\Delta^2$ or $F^2 = \Delta(\lambda_1-\lambda_2)-\Delta^2$.
The eigenvectors are determined by:

$$\begin{pmatrix} E_1-\lambda & F \\ F & E_2-\lambda \end{pmatrix}\begin{pmatrix} C \\ C' \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \text{ with } C^2+C'^2=1 \tag{15.10}$$

yielding:

$$\begin{aligned} C^2 &= \frac{F^2}{F^2+\Delta^2} \text{ and } C'^2 = \frac{\Delta^2}{F^2+\Delta^2} \\ F^2 &= \frac{C^2\cdot\Delta^2}{1-C^2} \end{aligned} \tag{15.11}$$

Therefore, finally:

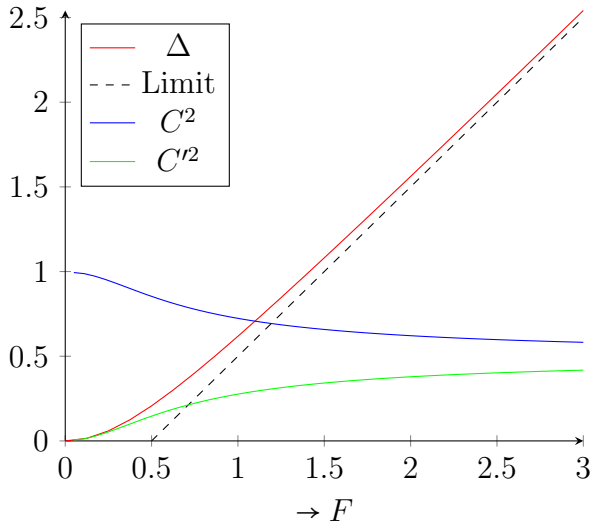
$$\begin{aligned} \Delta &= (\lambda_1-\lambda_2)\cdot(1-C^2) \\ F^2 &= (\lambda_1-\lambda_2)^2\cdot C^2\cdot(1-C^2) \end{aligned} \tag{15.12}$$

Without loss of generality, one may take $E_1 = 1, E_2 = 0$ and express the energies Δ and F in terms of the unperturbed energy distance $E_1 - E_2$. Put differently, the quantities displayed below are actually $\Delta/(E_1 - E_2)$ and $F/(E_1 - E_2)$.
Both Δ and C^2 are a function of F^2:

$$\begin{aligned} \Delta &= \tfrac{1}{2}\left(\sqrt{1+4F^2} - 1\right) \\ C^2 &= \frac{2F^2}{1+4F^2-\sqrt{1+4F^2}} \end{aligned} \tag{15.13}$$

It follows:

$$\begin{aligned} &\lim_{F\to 0}\Delta = 0 \qquad \lim_{F\to 0} C^2 = 1 \qquad \lim_{F\to 0} C'^2 = 0 \\ &\lim_{F\to \infty}\Delta = F - \tfrac{1}{2} \qquad \lim_{F\to \infty} C^2 = \tfrac{1}{2} \qquad \lim_{F\to \infty} C'^2 = \tfrac{1}{2} \end{aligned} \tag{15.14}$$



15.2 l^N configuration

The following definition from [Rajnak and Wybourne, 1963] (RW) and [Racah and Stein, 1967] (RS) is adopted:

$$\begin{aligned} P(kk', l_1l_2, l_3l_4) &= \Delta E^{-1} R^k(l_1l_2, l_3l_4)\, R^{k'}(l_1l_2, l_3l_4) \\ &\times \left\langle l_1 \parallel C^k \parallel l_3\right\rangle \left\langle l_2 \parallel C^k \parallel l_4\right\rangle \left\langle l_1 \parallel C^{k'} \parallel l_3\right\rangle \left\langle l_2 \parallel C^{k'} \parallel l_4\right\rangle \end{aligned} \tag{15.15}$$

As an example:

$$P(22, 22, 20) = -\frac{10}{7}\,\frac{\left(R^2(sd, dd)\right)^2}{E_A - E_B}.$$

The Trees operator [Trees, 1963] T is associated with an inner shell excitation $l' \to l$ from
$A = l'^{4l'+2}l^N$ to $B = l'^{4l'+1}l^{N+1}$. Now, according to the basic perturbation equation (15.3), the quantity to be calculated is: $V_{AB}V_{BA}(E_A - E_B)^{-1}$.
Using equation (5.77) for the Coulomb interaction, one finds:

$$V_{AB} = 2 \cdot \sum_k (-1)^k [k]^{-\frac{1}{2}} R^k(aa; ac') \left\langle l \parallel C^{(k)} \parallel l\right\rangle \left\langle l \parallel C^{(k)} \parallel l'\right\rangle \left\{(\mathbf{c}^\dagger\mathbf{a})^{(0k)}(\mathbf{a}^\dagger\mathbf{a})^{(0k)}\right\}^{(00)}$$

and

$$V_{BA} = 2\cdot\sum_{k'}(-1)^{k'}[k']^{-\frac{1}{2}}R^{k'}(aa;ac)\left\langle l \parallel C^{(k')} \parallel l\right\rangle\left\langle l \parallel C^{(k')} \parallel l'\right\rangle\left\{(\mathbf{a}^\dagger\mathbf{a})^{(0k')}(\mathbf{a}^\dagger\mathbf{c})^{(0k')}\right\}^{(00)}$$

Next, the operator product is reduced by means of equation (5.12):

$$\left[\left\{(\mathbf{c}^\dagger\mathbf{a})^{(0k)}(\mathbf{a}^\dagger\mathbf{a})^{(0k)}\right\}^{(00)}\left\{(\mathbf{a}^\dagger\mathbf{a})^{(0k')}(\mathbf{a}^\dagger\mathbf{c})^{(0k')}\right\}^{(00)}\right] \rightarrow \left[\left\{\mathbf{a}^\dagger(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{SL}\right\}^{S_3L_3}\left\{(\mathbf{aa})^{S'L'}\mathbf{a}\right\}^{S_3L_3}\right]^{(00)}$$

Using equations (5.16) and (5.17), one obtains for the pure three-, two- and one-particle matrix elements:

$$\begin{aligned}&\left\langle l^3(S_3L_3\nu_3)|H_2^3|l^3(S_3L_3\nu_3')\right\rangle = -3(E_A-E_B)^{-1}\\ &\times\sum_{SL,S'L'}[S,L,S',L']^{\frac{1}{2}}\left\langle l'l(SL)|C|l^2(SL)\right\rangle\left\langle l'l(S'L')|C|l^2(S'L')\right\rangle\\ &\times\begin{Bmatrix}\frac{1}{2} & S & S_3\\ \frac{1}{2} & S' & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}l & L & L_3\\ l & L' & l'\end{Bmatrix}\left(l^3(S_3L_3\nu_3)\{|l^2(SL)\right)\left(l^2(S'L')|\}l^3(S_3L_3\nu_3')\right)\end{aligned} \tag{15.16a}$$

$$\begin{aligned}\left\langle l^2(S_2L_2)|H_2^2|l^2(S_2L_2)\right\rangle = -2\sum_{kk'}P(kk',ll,ll')\Bigg(&2(-1)^{L_2}\delta(kk')[k]^{-1}\begin{Bmatrix}k & l & l\\ L_2 & l & l\end{Bmatrix}\\ &-(-1)^{L_2}\begin{Bmatrix}k' & l & l\\ k & l' & l\end{Bmatrix}\left(\begin{Bmatrix}k & l & l\\ L_2 & l & l\end{Bmatrix}+\begin{Bmatrix}k' & l & l\\ L_2 & l & l\end{Bmatrix}\right)-\begin{Bmatrix}k' & l' & l\\ l & l & L_2\\ l & k & l\end{Bmatrix}\Bigg)\end{aligned} \tag{15.16b}$$

$$\left\langle l\,|H_2^1|\,l\right\rangle = -[l]^{-1}\sum_{kk'}P(kk',ll,ll')\left(2\delta(kk')\,[k]^{-1}-\begin{Bmatrix}k' & l & l\\ k & l' & l\end{Bmatrix}\right). \tag{15.16c}$$

For the Trees operator, $l'=0$ and $l=2$. In fact, as $\Delta E^{-1} = -(E_A-E_B)^{-1}$:

$$T = \frac{(R^2(sd,dd))^2}{35^2(E_A-E_B)} = -\frac{P(22,22,20)}{1750}.$$

Here, $(SL)=(S'L')=(02)$ and $\langle sd(^1D)|C|d^2(^1_2D)\rangle = -2/\sqrt{35}\cdot R^2(sd,dd)$. For the angular n-electron matrices O_3, O_2 and O_1 of the Trees operator, one obtains:

$$\begin{aligned}\left\langle d^3(S_3L_3\nu_3)|O_3|d^3(S_3L_3\nu_3')\right\rangle &= 210\cdot\delta(S_3,\tfrac{1}{2})(-1)^{L_3}\\ &\times\left(d^3(S_3L_3\nu_3)\{|^1_2D\right)\left(^1_2D|\}d^3(S_3L_3\nu_3')\right)\end{aligned} \tag{15.17a}$$

$$\left\langle d^2(S_2L_2)|O_2|d^2(S_2L_2)\right\rangle = -700\begin{Bmatrix}L_2 & 2 & 2\\ 2 & 2 & 2\end{Bmatrix} \tag{15.17b}$$

$$\langle d\,|O_1|\,d\rangle = 70. \tag{15.17c}$$

Below, the contributions to the $A = l^N$ configuration deriving from all accessible configurations B are explored to second order.

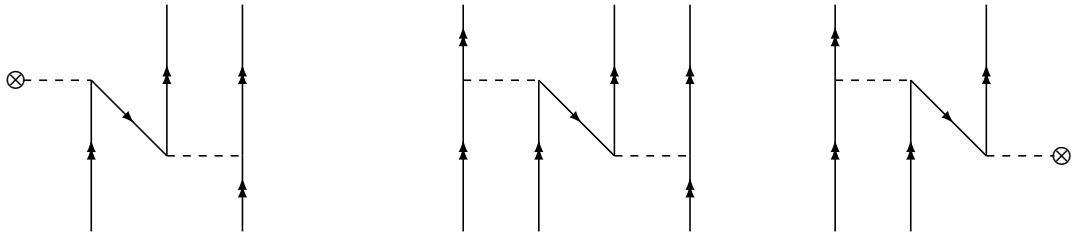
Here, every electrostatic operator in which an l^2 pair is participating in the Coulomb interaction, will be seen to satisfy the joint formula:

$$H_2^2 = (E_A-E_B)^{-1}\sum_{SL}\left\langle l^2(SL)|C|l'l''(SL)\right\rangle^2\ H_{SL} \tag{15.18}$$

where there is no restriction on l' and l''.

15.2.1 $B = l'^{4l'+1} l^{N+1}$

The one-, two- and three-particle parts of the Coulomb interaction $C_{l'l;ll}$ have already been considered in the above equations (15.16).
Some relevant Feynman diagrams are given below. Downward lines refer to closed shells electrons.

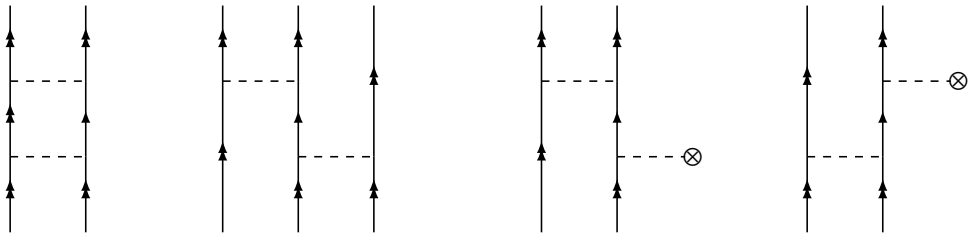


Therefore, only the two-particle contributions of the Coulomb interaction $C_{l'l';ll}$ and the potential are considered below.

$$\left\langle l^2(SL)|H_2^2|l^2(SL)\right\rangle = -4\delta(ll')\left(E_A - E_B\right)^{-1}$$
$$\times\left([l]^{-1}\sum_k \left\langle l \parallel C^{(k)} \parallel l\right\rangle^2 \left(2[l]^{-1}\delta(k,0)-1\right) R^k(l'l;l'l') - \langle n'l'|U|nl\rangle\right)$$
$$\times\sum_{k'}\left\langle l \parallel C^{(k')} \parallel l\right\rangle^2 R^{k'}(l'l;ll)\,(-1)^L \begin{Bmatrix} k' & l & l \\ L & l & l \end{Bmatrix}. \qquad (15.19)$$

15.2.2 $B = l^{N-1} l'$

In this case, there is a potential contribution present if $l' = l$; as illustrated by equation (15.6), closed shells are removed from U by cancellation. The Feynman diagrams were given earlier in figure 15.1:

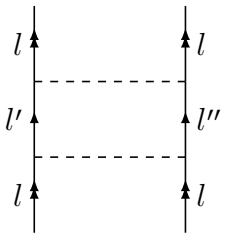


$$\left\langle l^2(SL)|H_2^2|l^2(SL)\right\rangle = -2\sum_{kk'} P(kk',ll,ll') \begin{Bmatrix} k & l & l' \\ L & l & l \end{Bmatrix} \begin{Bmatrix} k' & l & l' \\ L & l & l \end{Bmatrix}$$
$$-4\delta(ll')\left(E_A - E_B\right)^{-1}\sum_k \left\langle l \parallel C^{(k)} \parallel l\right\rangle^2 (-1)^L \begin{Bmatrix} k & l & l \\ L & l & l \end{Bmatrix} \langle nl|U|n'l'\rangle\, R^k(ll,ll') \quad (15.20a)$$

$$\left\langle l^3(S_3L_3\nu_3)|H_2^3|l^3(S_3L_3\nu_3')\right\rangle = 3(E_A-E_B)^{-1}$$
$$\times \sum_{SL,S'L'}[S,L,S',L']^{\frac{1}{2}}\ \left\langle l^2(SL)|C|ll'(SL)\right\rangle\left\langle ll'(S'L')|C|l^2(S'L')\right\rangle$$
$$\times \begin{Bmatrix} \frac{1}{2} & S & S_3 \\ \frac{1}{2} & S' & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} l & L & L_3 \\ l & L' & l'\end{Bmatrix}\ \left(l^3(S_3L_3\nu_3)\{|l^2(SL)\right)\left(l^2(S'L')|\}l^3(S_3L_3\nu_3')\right) \tag{15.20b}$$

Notice the similarity between the equations (15.16a) and (15.20b).

15.2.3 $B = l^{N-2}l'l''$

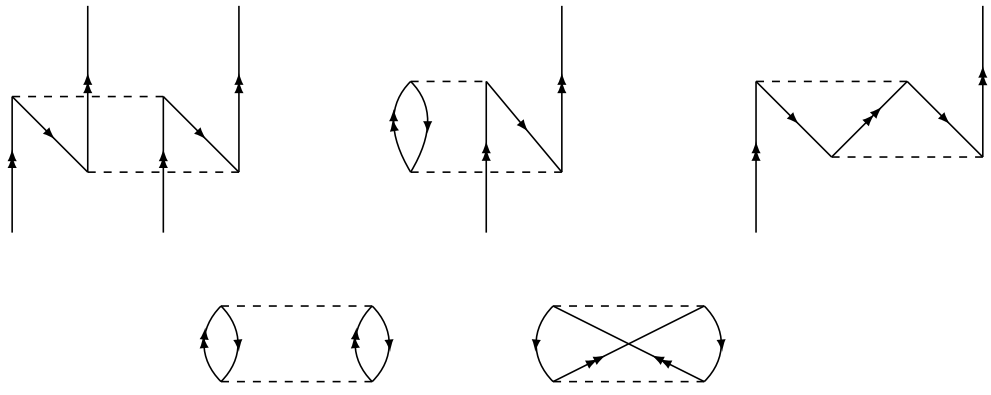


$$\left\langle l^2(SL)|H_2^2|l^2(SL)\right\rangle = -2\sum_{kk'}P(kk',ll,l'l'')\begin{Bmatrix} k & l & l'' \\ L & l' & l\end{Bmatrix}\begin{Bmatrix} k' & l & l'' \\ L & l' & l\end{Bmatrix} \tag{15.21}$$

15.2.4 $B = l^{N-2}l'^2$

$$\left\langle l^2(SL)|H_2^2|l^2(SL)\right\rangle = -\sum_{kk'}P(kk',ll,l'l')\begin{Bmatrix} k & l & l' \\ L & l' & l\end{Bmatrix}\begin{Bmatrix} k' & l & l' \\ L & l' & l\end{Bmatrix} \tag{15.22}$$

15.2.5 $B = l'^{4l'+1}l''^{4l''+1}l^{N+2}$



$$\left\langle l^2(SL)|H_2^2|l^2(SL)\right\rangle = -2\sum_{kk'}P(kk',l'l'',ll)\begin{Bmatrix} k & l'' & l \\ L & l & l'\end{Bmatrix}\begin{Bmatrix} k' & l'' & l \\ L & l & l'\end{Bmatrix} \tag{15.23a}$$

$$\left\langle l|H_2^1|l\right\rangle = \frac{-2(2l+1-N)}{(2l+1)}\sum_{kk'}P(kk',l'l'',ll)\left(2\delta(kk')\,[k]^{-1}-\begin{Bmatrix} l & l'' & k' \\ l & l' & k\end{Bmatrix}\right) \qquad (15.23b)$$

.

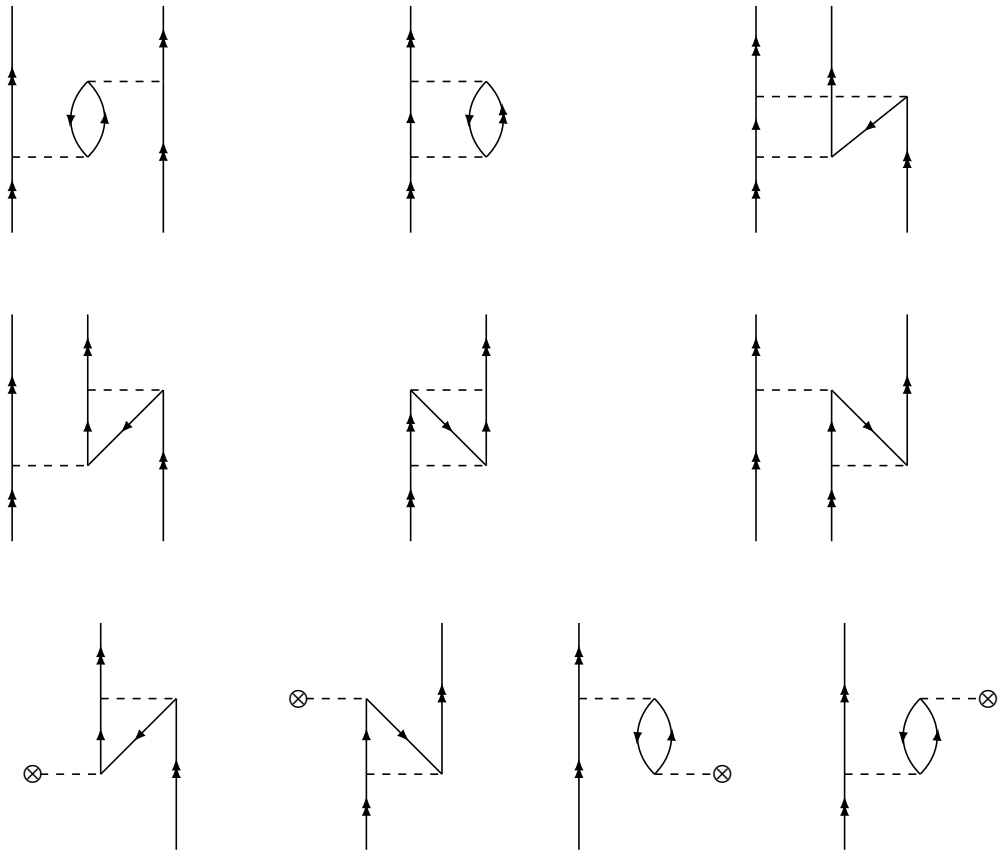
15.2.6 $B = l'^{4l'}l^{N+2}$

$$\left\langle l^2(SL)|H_2^2|l^2(SL)\right\rangle = -\sum_{kk'}P(kk',l'l',ll)\begin{Bmatrix} k & l' & l \\ L & l & l'\end{Bmatrix}\begin{Bmatrix} k' & l' & l \\ L & l & l'\end{Bmatrix} \qquad (15.24a)$$

$$\left\langle l|H_2^1|l\right\rangle = \frac{-(2l+1-N)}{(2l+1)}\sum_{kk'}P(kk',l'l',ll)\left(2\delta(kk')\,[k]^{-1}-\begin{Bmatrix} l & l' & k' \\ l & l' & k\end{Bmatrix}\right) \qquad (15.24b)$$

.

15.2.7 $B = l'^{4l'+1}l^N l''$



In this case, the Coulomb matrix element $\langle l'l(SL)\,|C|\,ll''(SL)\rangle$ contains both direct and exchange terms. As a result, the product CC includes three radial factors: $P(kk',l'l,ll'')$, $P(kk',l'l,l''l)$ and a cross term $M(kk')$, defines by RW and RS:

$$\begin{aligned} M(kk') &= \Delta E^{-1}\,R^k(l'l,ll'')\,R^k(l'l,l''l) \\ &\times \left\langle l' \parallel C^{(k)} \parallel l\right\rangle\left\langle l \parallel C^{(k)} \parallel l''\right\rangle\left\langle l' \parallel C^{(k')} \parallel l''\right\rangle\left\langle l \parallel C^{(k')} \parallel l\right\rangle \end{aligned} \qquad (15.25)$$

$$\begin{aligned}\left\langle l^2(SL)|H_2^2|l^2(SL)\right\rangle = &-4\sum_{kk'}P(kk',l'l,l''l)\;\delta(kk')\;[k]^{-1}(-1)^L\begin{Bmatrix}k & l & l\\ L & l & l\end{Bmatrix}\\ &+4\sum_{kk'}(-1)^k M(kk')(-1)^L\begin{Bmatrix}k' & l & l\\ L & l & l\end{Bmatrix}\begin{Bmatrix}l & l'' & k\\ l' & l & k'\end{Bmatrix}\\ &+2\sum_{kk'}P(kk',l'l,ll'')(-1)^L\begin{Bmatrix}L & l & l\\ l & k' & l''\\ l & l' & k\end{Bmatrix}. \qquad (15.26a)\end{aligned}$$

$$\begin{aligned}\left\langle l|H_2^1|l\right\rangle = &-2\sum_{kk'}P(kk',l'l,l''l)\;\delta(kk')\;[k]^{-1}[l]^{-1}\\ &+2\sum_{kk'}(-1)^k M(kk')\begin{Bmatrix}k' & l & l\\ k & l' & l''\end{Bmatrix}[l]^{-1}\\ &-2\sum_{kk'}P(kk',l'l,ll'')\;\delta(kk')\;[k]^{-1}[l]^{-1}\\ &-2\;\delta(l'l'')\;(E_A-E_B)^{-1}[l]^{-1}\left\langle n'l'\,|U|\,n''l''\right\rangle\\ &\times\left(2[l,l']\,R^0(ll'',ll')-\sum_k\left\langle l\parallel C^{(k)}\parallel l'\right\rangle^2 R^k(ll'',l'l)\right) \qquad (15.26b)\end{aligned}$$

Again, note the similarity with equations (15.16).

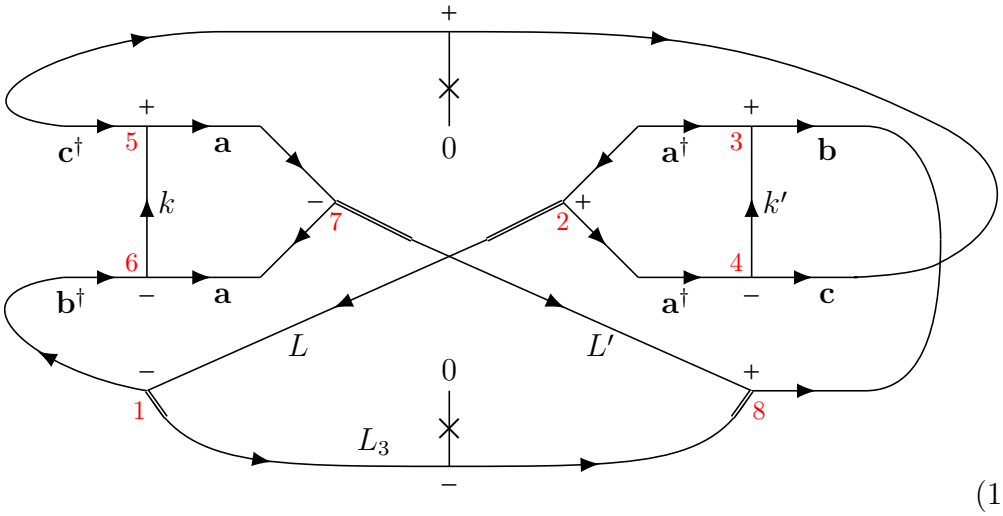
15.3 Three-electron operators in l^2l'.

Below, we will associate the radial orbitals a, b, c and v with the orbital angular momenta $l, l', \bar{l}, l''$, the first two referring to open shells and the last two to closed and virtual shells, respectively. We consider the two-particle excitation $cb \to a^2$ in detail as a running example of the general method, and give the formulae for the other excitations in appendix A. Numerical applications are given in 17.3. Actually, it is an exception that a two-electron excitation yields a three-electron operator, but this is readily understood from the schematic form of $V_{AB}V_{BA}$:
$(\mathbf{c}^\dagger\mathbf{a}\mathbf{b}^\dagger\mathbf{a})(\mathbf{a}^\dagger\mathbf{b}\mathbf{a}^\dagger\mathbf{c})$. The combination $(\mathbf{c}^\dagger\mathbf{c})$ is coupled to zero ranks and removed while the remainder is rearranged towards $(\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{b}^\dagger)(\mathbf{aab})$, with a phase $(-1)^P = 1$ because of the even number of permutations P. We multiply V_{AB} and V_{BA} by joining their graphical expressions given in the below figure 15.27, while extracting the numerical factor from the two Coulomb graphs as in 5.84:

$$\sum_{k,k'}4(-1)^{k+k'}\left\langle\bar{l}\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k')}\parallel\bar{l}\right\rangle\left\langle l'\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k')}\parallel l'\right\rangle\frac{R^k(cb;aa)R^{k'}(aa;bc)}{E_A-E_B}.$$

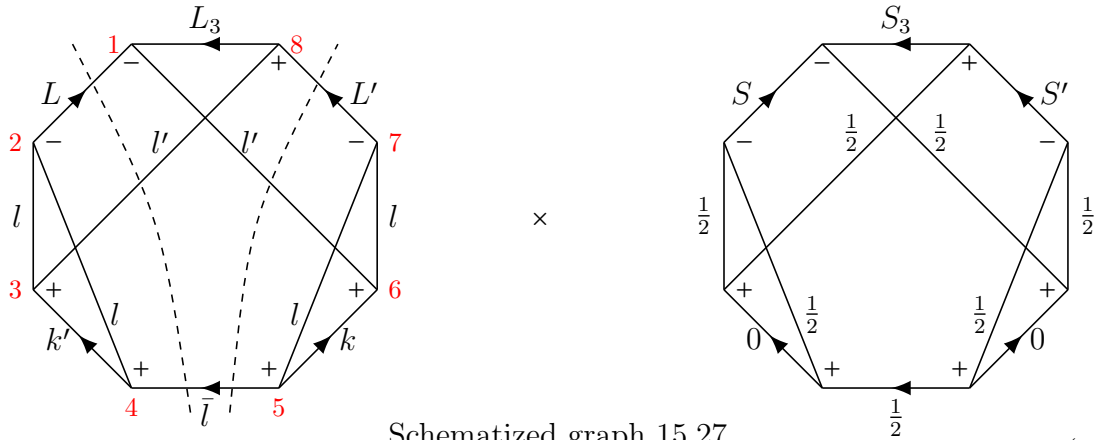
As prescribed, $\mathbf{c}^\dagger$ and $\mathbf{c}$ are coupled to zero. Both the creation and the annihilation operators are coupled to the angular momenta S_3L_3 of the terms of l^2l', anticipating the standard three-particle matrix element from equation (5.18).

The resulting graph 15.27 is reduced by standard graphical algebra [Lindgren and Morrison, 1982].



(15.27)

Using a 'Hamiltonian' line (that passes through every vertex once) along the route of the consecutive red node numbers, we obtain the graph of figure 15.28 with all the nodes now on the periphery. Figure 15.28 can be cut over the two dashed lines to yield three $6j$-symbols.



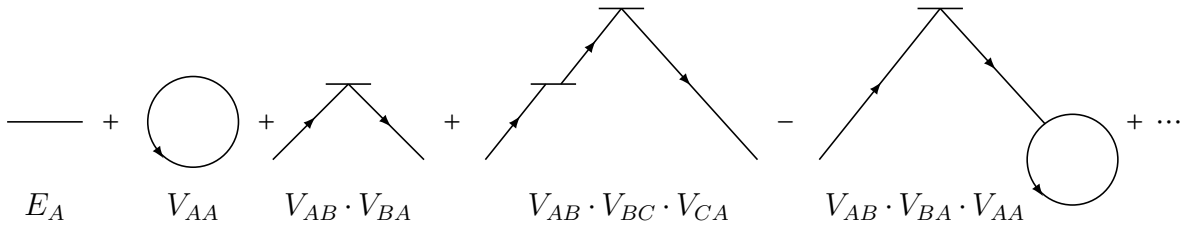
Schematized graph 15.27. (15.28)

Multiplying the result with the corresponding spin-expression for which $k = k' = 0$, we obtain the final equation:

$$\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3)\left|T(cb\to a^2)\right|l^2(S'L')l'(S_3L_3)\right\rangle \\
&= \sum_{k,k'} 2\left\langle \bar{l}\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k')}\parallel \bar{l}\right\rangle\left\langle l'\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k')}\parallel l'\right\rangle \\
&\times [S,L,S',L']^{\frac{1}{2}}\,(-1)^{S+S'+1}\begin{Bmatrix} S & \frac{1}{2} & \frac{1}{2} \\ S' & S_3 & \frac{1}{2}\end{Bmatrix} \\
&\times \begin{Bmatrix} L & \bar{l} & l' \\ k' & l & l\end{Bmatrix}\begin{Bmatrix} L' & \bar{l} & l' \\ k & l & l\end{Bmatrix}\begin{Bmatrix} L & \bar{l} & l' \\ L' & L_3 & l'\end{Bmatrix}\frac{R^k(cb;aa)R^{k'}(aa;bc)}{E_A-E_B}
\end{aligned} \tag{15.29}$$

15.4 Third order

The symbolic graphical picture of perturbation theory is repeated below:



In third order, one finds therefore:

$$\begin{aligned}\langle A\alpha|H_3|A\alpha'\rangle &= \sum_{B,C\notin P} (E_A - E_B)^{-1} (E_A - E_C)^{-1} \sum_{\beta,\gamma} \langle A\alpha|V_{AB}|B\beta\rangle \langle B\beta|V_{BC}|C\gamma\rangle \langle C\gamma|V_{CA}|A\alpha'\rangle \\ &- \sum_{B\notin P} (E_A - E_B)^{-2} \sum_{\beta,\alpha''} \langle A\alpha|V_{AB}|B\beta\rangle \langle B\beta|V_{BA}|A\alpha''\rangle \langle A\alpha''|V_{AA}|A\alpha'\rangle\end{aligned}$$

After closure, this gives for the leading 'diagonal' third-order correction:

$$\langle A\alpha|H_3|A\alpha'\rangle = \sum_{B\notin P} (E_A - E_B)^{-2} \left(\langle A\alpha|V_{AB}V_{BB}V_{BA}|A\alpha'\rangle - \langle A\alpha|V_{AB}V_{BA}V_{AA}|A\alpha'\rangle\right) \tag{15.30}$$

Except for some terms in the $l' = 0$ case, the interactions for the configurations A and B are the same: $V_{BB} = V_{AA}$. Thus, one can reformulate equation (15.30) as follows:

$$H_3 = \frac{V_{AB}\,[V_{BB}, V_{BA}]}{(E_A - E_B)^2} \tag{15.31}$$

As a result, passive closed shells will not appear in the above.
Five terms $(\alpha)...(\varepsilon)$ remain in V_{AA}:

$$\begin{aligned}V_{AA} = &-\tfrac{1}{2}\sum_{SL}[S,L]^{\frac{1}{2}} \left\langle l'^2(SL)|C|l'^2(SL)\right\rangle \left\{(\mathbf{b}^\dagger\mathbf{b}^\dagger)^{SL}(\mathbf{bb})^{SL}\right\}^{(00)} && (\alpha)\\ &+ [\tfrac{1}{2},l']^{\frac{1}{2}} \langle n'l'|U|n'l'\rangle \left(\mathbf{b}^\dagger\mathbf{b}\right)^{(00)} && (\beta)\\ &- \sum_{S'L'}[S',L']^{\frac{1}{2}} \langle l'l(S'L')|C|l'l(S'L')\rangle \left\{(\mathbf{b}^\dagger\mathbf{a}^\dagger)^{S'L'}(\mathbf{ba})^{S'L'}\right\}^{(00)} && (\gamma)\\ &-\tfrac{1}{2}\sum_{S''L''}[S'',L'']^{\frac{1}{2}} \left\langle l^2(S''L'')|C|l^2(S''L'')\right\rangle \left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{S''L''}(\mathbf{aa})^{S''L''}\right\}^{(00)} && (\delta)\\ &+ [\tfrac{1}{2},l]^{\frac{1}{2}} \langle nl|U|nl\rangle \left(\mathbf{a}^\dagger\mathbf{a}\right)^{(00)} && (\varepsilon)\end{aligned} \tag{15.32}$$

15.5 EL-SO: Electrostatic spin-orbit effects

In second order, the most important spin-dependent operators are given by:

$$\begin{aligned}(E_A - E_B)^{-1}V_{AB}V_{BA} &= (E_A - E_B)^{-1}\left(C_{AB}Z_{BA} + Z_{AB}C_{BA} - U_{AB}Z_{BA} - Z_{AB}U_{BA}\right)\\ &:= H_2(ZC) - H_2(ZU)\end{aligned} \tag{15.33}$$

These perturbative mixed electrostatic-magnetic contributions are called EL-SO effects. The off-diagonal potential matrix elements are given equation (15.4b).

In many cases, especially with lower ionization, EL-SO proves to be dominant over the MSO effects discussed in chapter 14. As a consequence of the properties of the spin-orbit interaction, EL-SO only connects members A and B of the same channel or Rydberg series (including the continuum), so B differs from A by a single electron substitution $(n/\varepsilon)\,l \to (n'/\varepsilon')\,l'$, where the orbital angular momentum is conserved: $l = l'$, B is a Brillouin excited configuration.
Assuming $\delta(l,l')$, only excitations $a \to b$ between configurations
$A = l^N l'^M (N \neq 0)$ and $B = l^{N-1} l'^{M+1} (M \neq 4l'+2)$ with a magnetic connection $\zeta(a,b)$ will be considered. Closed shells $c(N = 4l+2)$ and virtual shells $v(M = 0)$ will appear as special cases. For practical purposes, effects involving a third shell will only be considered for those cases.
EL-SO is schematically illustrated in figure (15.3):

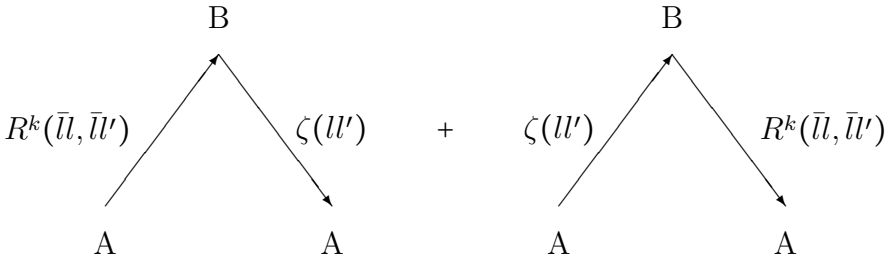


Figure 15.3: Graphical representation of EL-SO.

Using equations (3.51b) and (5.89), off-diagonal spin-orbit matrix elements are calculated straightforwardly, e.g.:

$$\left\langle l^N(SL) \parallel z(a,b) \parallel l^{N-1}(S_1L_1), l'(S'L') \right\rangle = \delta(l,l') \cdot \boldsymbol{\zeta}(\mathbf{a},\mathbf{b}) \cdot -3\sqrt{N} \cdot \left(l^N SL\{|l^{N-1} S_1 L_1 \right)$$
$$\cdot (-1)^{S_1+\frac{1}{2}+S+L_1+l+L} \cdot [S,L,S',L']^{\frac{1}{2}} \cdot \begin{Bmatrix} S & 1 & S' \\ \frac{1}{2} & S_1 & \frac{1}{2} \end{Bmatrix} \cdot \begin{Bmatrix} L & 1 & L' \\ l & L_1 & l \end{Bmatrix} \cdot (l(l+1)(2l+1)/2)^{\frac{1}{2}} \tag{15.34}$$

Yielding an additional minus sign in the angular factor because of the positive denominator, the radial factors have the form $P^k = \oint_B 2\zeta(a,b) R^k/(E_B - E_A)$ and $T = \oint_B 2\zeta(a,b)\,\langle b|U|a\rangle\,/(E_B - E_A)$. Candidates for the Slater integral are: $R^k(aa;ab)$, $R^k(ab;bb)$ and finally $R^k(ac;bc)$ plus $R^k(ac;cb)$; these three cases will be labeled in the operators $H_2(ZC)$, $H_2(ZU)$ and the radial integrals P^k, as (a), (b) and (c), respectively.
To exemplify the general course of the calculation, we put one of the above terms, i.e. $C_{AB}Z_{BA}$, into second quantized form for $A = l^N$ and $B = l^{N-1}l'$ (associating v with l'):

$$C_{AB}Z_{BA} = \sum_k 2 \cdot [k]^{-\frac{1}{2}} \left\langle l \parallel C^{(k)} \parallel l \right\rangle^2 \left\{ (\mathbf{a}^\dagger \mathbf{a})^{(0k)} (\mathbf{a}^\dagger \mathbf{v})^{(0k)} \right\}^{(00)} R^k(aa,av)$$
$$\cdot (l(l+1)(2l+1)/2)^{\frac{1}{2}} \cdot (\mathbf{v}^\dagger \mathbf{a})^{(11)} \cdot \zeta(a,v) \tag{15.35}$$

Following the prescription given directly above section 5.1, this operator may be converted to an operator acting within configuration A only.
Interchanging $\mathbf{v}$ and $\mathbf{v}^\dagger$, the operator part is recoupled after application of equation (5.14) to a two-particle operator:

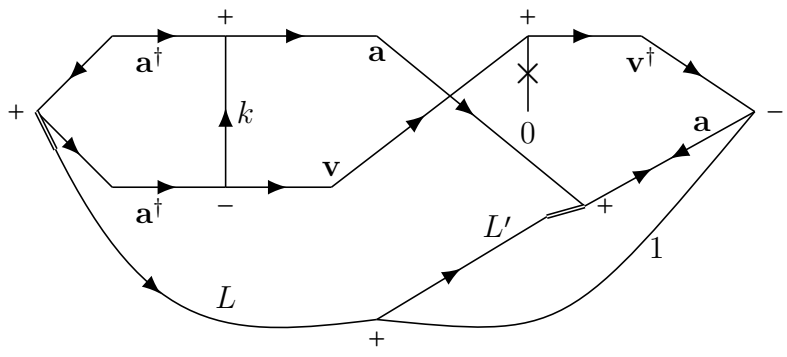
$$C_{AB}Z_{BA} = \sum_k 2\cdot\left[k,\tfrac{1}{2}\right]^{-\frac{1}{2}}\cdot\left\langle l \parallel C^{(k)} \parallel l\right\rangle^2\cdot\left(l(l+1)(2l+1)/2\right)^{\frac{1}{2}}\cdot R^k(aa,av)\cdot\zeta(a,v)$$
$$\cdot\sum_{K\neq k}[K]^{\frac{1}{2}}\cdot\begin{Bmatrix}k & 1 & K\\ l & l & l\end{Bmatrix}\cdot\left\{(\mathbf{a}^\dagger\mathbf{a})^{(0k)}(\mathbf{a}^\dagger\mathbf{a})^{(1K)}\right\}^{(11)} \qquad (15.36)$$

As an example, the matrix elements of $C_{AB}Z_{BA}+Z_{AB}C_{BA}$ in l^2 are, after application of equation (5.39) and summing over K using equation (2.18):

$$\left\langle l^2(SL) \parallel H_2(ZC) \parallel l^2(S'L')\right\rangle$$
$$= -3\left((l(l+1)(2l+1)/2)^{\frac{1}{2}}[S,L,S',L']^{\frac{1}{2}}\begin{Bmatrix}L & L' & 1\\ l & l & l\end{Bmatrix}\begin{Bmatrix}S & S' & 1\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\right.$$
$$\left.\times\sum_k\left\langle l \parallel C^{(k)} \parallel l\right\rangle^2 P^k(a)\left((-1)^L\begin{Bmatrix}L & l & l\\ k & l & l\end{Bmatrix}+(-1)^{L'}\begin{Bmatrix}L' & l & l\\ k & l & l\end{Bmatrix}\right)\right\rightarrow$$

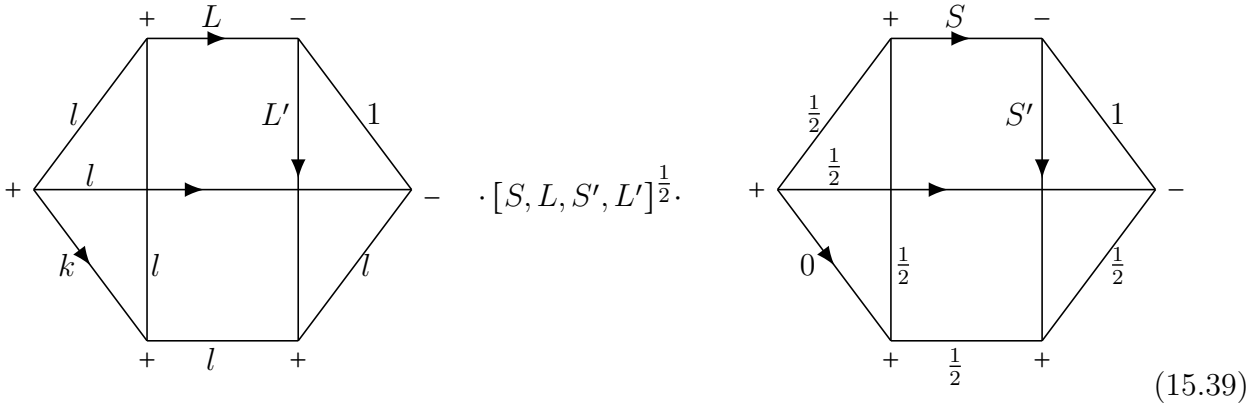
$$\left\langle l^2(SL) \parallel H_2(ZC) \parallel l^2(S'L')\right\rangle = -\left\langle l^2(SL) \parallel z(l) \parallel l^2(S'L')\right\rangle$$
$$\cdot\tfrac{1}{2}\left[\sum_k\left\langle l^2(SL)|c_k|l^2(SL)\right\rangle+\left\langle l^2(S'L')|c_k|l^2(S'L')\right\rangle\right]\cdot\oint_{l\rightarrow l'}\frac{2\zeta(ll')R^k(aa,av)}{\Delta E} \qquad (15.37)$$

Alternatively, equation (15.37) may also be derived directly by graphical second quantization. In anticipation of equation (5.37), $(\mathbf{a}^\dagger\mathbf{a}^\dagger)$ is coupled to (SL), $(\mathbf{aa})$ to $(S'L')$ while $(\mathbf{v}\mathbf{v}^\dagger)$ is coupled to zero for use of equation (5.14).
The numerical factors from (5.84) and (5.89) are $2\sum_k\left\langle l \parallel C^{(k)} \parallel l\right\rangle^2 R^k(aa,av)$ and $(l(l+1)(2l+1)/2)^{\frac{1}{2}}\zeta(va)$, respectively; in addition, the reduced matrix element (5.37) yields a factor −6 and the conversion of $R^k()\cdot\zeta()$ to $P^k(a)$ a factor −2.



(15.38)

Placing the nodes on the periphery and multiplying with the associated spin symbol for which $k = 0$, this yields:



(15.39)

The graphs are reduced by JLV3 to:

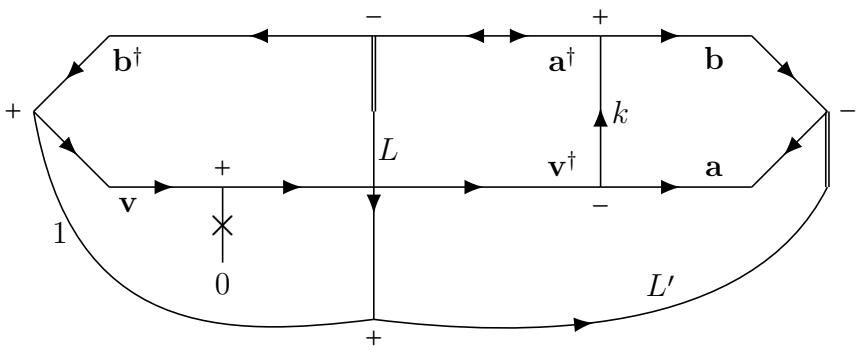
$$(-1)^{S+1} \cdot [\tfrac{1}{2}]^{-1} \cdot \begin{Bmatrix} L & l & l \\ k & l & l \end{Bmatrix} \cdot \begin{Bmatrix} L & L' & 1 \\ l & l & l \end{Bmatrix} \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot [S, L, S', L']^{\frac{1}{2}}$$

The final result after taking the numerical factors into account, becomes:

$$\begin{aligned} &\left\langle l^2(SL) \parallel -C_{AB}Z_{BA}/\Delta E \parallel l^2(S'L') \right\rangle \\ &= -3\left((l(l+1)(2l+1)/2\right)^{\frac{1}{2}} [S, L, S', L']^{\frac{1}{2}} \begin{Bmatrix} L & L' & 1 \\ l & l & l \end{Bmatrix} \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \\ &\times \sum_k \left\langle l \parallel C^{(k)} \parallel l \right\rangle^2 P^k(a) \left((-1)^L \begin{Bmatrix} L & l & l \\ k & l & l \end{Bmatrix} \right) \end{aligned} \tag{15.40}$$

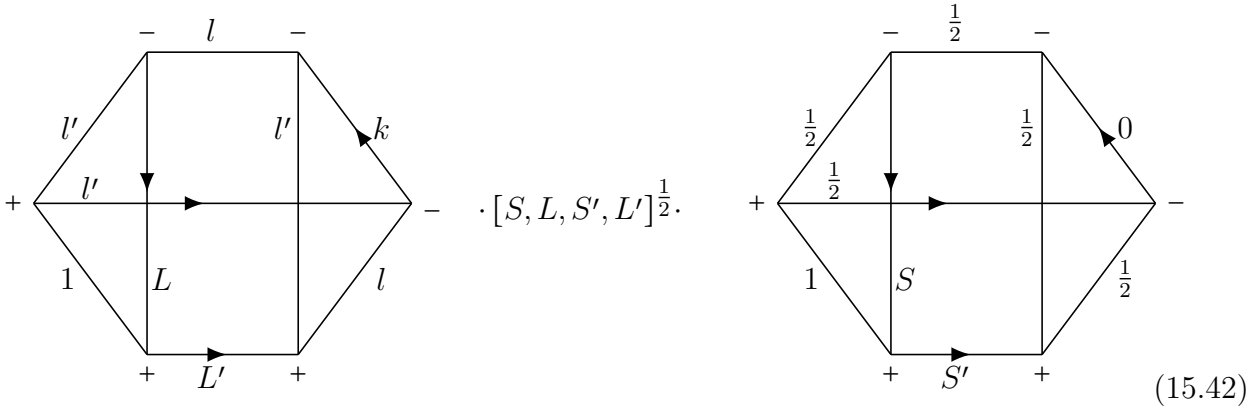
This corresponds exactly to the first term of equation (15.37); the second term is derived in much the same way.

The exchange term $Z_{AB}C_{BA}$ for ll' configurations is selected as a second example of graphical second quantization of EL-SO operators:



(15.41)

Similar to the preceding example, this reduces to:



(15.42)

Combined with the associated numerical factors from equations (5.36), (5.86) and (5.89) plus reordering of the ket state, this yields:

$$\begin{aligned}\langle ll'(SL) \parallel Z_{AB}C_{BA} \parallel ll'(S'L')\rangle = -3 \cdot (-1)^{l+l'} \cdot (-1)^{S+L+S'} \cdot [S,L,S',L']^{\frac{1}{2}} \\ \cdot (l'(l'+1)(2l'+1)/2)^{\frac{1}{2}} \cdot \zeta(bv) \cdot \begin{Bmatrix} L & L' & 1 \\ l' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \\ \cdot \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l' \right\rangle^2 \cdot \begin{Bmatrix} L' & l & l' \\ k' & l & l' \end{Bmatrix} \cdot R^{k'}(av,ba) \end{aligned} \tag{15.43}$$

The expressions for $\langle ll'(SL) \parallel z_{l'} \parallel ll'(S'L')\rangle$ (6.25) and $\left\langle ll'(S'L')|g^{k'}|ll'(S'L')\right\rangle$ (6.14a) are readily recognized in the above.
Combined with $C_{AB}Z_{BA}$, one arrives at a general expression for EL-SO operators:

$$\begin{aligned}\langle ll'(SL) \parallel H_2(ZC) \parallel ll'(S'L')\rangle = -\langle ll'(SL) \parallel z_{l'} \parallel ll'(S'L')\rangle \\ \cdot \tfrac{1}{2}\left[\sum_k \langle ll'(SL)|c_k|ll'(SL)\rangle + \langle ll'(S'L')|c_k|ll'(S'L')\rangle\right] \cdot \oint_{b\to v} \frac{2\zeta(bv)R^k()}{\Delta E} \end{aligned} \tag{15.44}$$

For the dp two-particle magnetic EL-SO operators, the contributions originate from $p \to p'$ and $d \to d'$ excitations. An example of the first:

$$\begin{aligned}\langle dp(SL) \parallel H_2(ZC) \parallel dp(S'L')\rangle \ &= -\langle dp(SL) \parallel z_p \parallel dp(S'L')\rangle \\ \cdot \tfrac{1}{2}\left[\sum_k \langle dp(SL)|c_k|dp(SL)\rangle + \langle dp(S'L')|c_k|dp(S'L')\rangle\right] &\cdot \oint_{p\to p'} \frac{2\zeta(pp')R^k()}{\Delta E} \end{aligned} \tag{15.45}$$

For dp EL-SO, the operator tensor rank k equals 2 for the direct part, and 1 or 3 for the exchange. These operators may be projected onto the spin-orbit orthogonal basis operators defined in section 14.5.2.
EL-SO effects are expected to be particularly large in systems with an inner shell hole, if parity($\bar{l}$) ≠ parity(l) notably for excitations $\bar{l} \to l'$:

$$\begin{aligned}\left\langle \bar{l}^{4\bar{l}+1} l^N (S_1 L_1) SL \parallel z(\bar{l}l') \parallel \bar{l}^{4\bar{l}} (S_2 L_2) l^N (S_1 L_1) S_3 L_3,\ l'\ S'L' \right\rangle &= -3 \cdot \delta(\bar{l}l') \left(\bar{l}(\bar{l}+1)(2\bar{l}+1)\right)^{\frac{1}{2}} \\ \cdot(-1)^N \cdot (-1)^{1+S_1+L_1+S_3+L_3} \cdot [S_2, L_2, S_3, L_3]^{\frac{1}{2}} &\begin{Bmatrix} \frac{1}{2} & S & S_1 \\ S_3 & S_2 & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} \bar{l} & L & L_1 \\ L_3 & L_2 & \bar{l} \end{Bmatrix} \\ \cdot(-1)^{S_3+\frac{1}{2}+S} \cdot (-1)^{L_3+l'+L} \cdot [S, S', L, L']^{\frac{1}{2}} \cdot &\begin{Bmatrix} S & 1 & S' \\ \frac{1}{2} & S_3 & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & 1 & L' \\ l' & L_3 & \bar{l} \end{Bmatrix}\end{aligned} \tag{15.46}$$

Given the above expressions, the contributions of $H_2(ZU)$ and $H_2(ZC)$ can subsequently be calculated from equation (14.26) as projections to ζ. Adding the results, we see that the unrealistically large contribution from $P^0(a)$ to ζ is canceled, which is characteristic for a central-field perturbation theory:

$$\Delta\zeta(a) = (N-1)\left(1 - \frac{M}{4l+2}\right) \sum_{k>0} \beta(k,l)\, P^k(a) \tag{15.47}$$

and

$$\Delta\zeta(b) = \frac{N(4l+1)}{4l+2}) \left(1 - \frac{M}{4l+1}\right) \sum_{k>0} \beta(k,l)\, P^k(b) \tag{15.48}$$

where

$$\beta(k,l) = \frac{\langle l \parallel C^{(k)} \parallel l \rangle^2}{2l(2l+1)(4l+1)} \left((2l+1) - \frac{(4l+1)k(k+1)}{4l(l+1)}\right) \tag{15.49}$$

The coefficients $\beta(k,l)$ are listed in table (15.1) for p, d and f electrons.

Table 15.1: The coefficients $\beta(k,l)$ appearing in equation (15.47) and (15.48) for the EL-SO contributions to $\zeta(a)$ and $\zeta(b)$.

$k =$	2	4	6
p shell	-3/100	—	—
d shell	11/504	-5/252	—
f shell	43/2340	19/5148	-875/66924

For the ζ contributions involving interactions with a third shell c not directly involved in the excitation $a \to b$, only two special cases: $M = 0$ and $N = 4l+2$ are investigated. They yield similar results, with only contributions to $\zeta(c)$:

$$M = 0:$$
$$\Delta\zeta(c) = \frac{N}{4l+2} \sum_k \gamma(k,l,l_c)\, P^k(c,\text{exch}) \tag{15.50a}$$

$$N = 4l+2:$$
$$\Delta\zeta(c) = \left(1 - \frac{M}{4l+2}\right) \sum_k \gamma(k,l,l_c)\, P^k(c,\text{exch}) \tag{15.50b}$$

where the "exch" in P^k means that only the Slater integral $R^k(ac;cb)$ contributes and γ is given by:

$$\gamma(k,l,l_c) = \frac{l(l+1)+l_c(l_c+1)-k(k+1)}{2l_c(l_c+1)(2l_c+1)} \left\langle l \parallel C^{(k)} \parallel l_c \right\rangle^2 \tag{15.51}$$

Combined MSO and EL-SO effects can be compared to experimental orthogonal parameters, see table 15.2:

Table 15.2: Values of one- and two-body magnetic operators in Fe VI $3d^3$

	Fit(1)	DF	DF+Breit	B-splines	Fit(2)
ζ_d	578.63	636.97	579.56	598.09	594.52
A_c	0	4.43	2.95	3.16	2.84
A_3	0	0.18	2.07	1.97	2.41
A_4	0	4.39	4.37	4.31	3.86
A_5	0	1.64	7.18	7.05	6.86
A_6	0	2.33	-9.22	-9.08	-9.85
A_1	0	-0.12	0.41	0.88	0.90
A_2	0	0.12	-2.31	-2.73	-2.90
σ	28.3	73.4	14.2	5.8	1.9

Table 15.3: Values of one- and two-body magnetic operators in Os VI $5d^3$

	DF	DF & B	B-splines	Fit
ζ_d	4387	4280	4619	4546
A_c	29.8	30.9	0.00	21.6
A_3	5.4	6.3	0.00	2.4
A_4	8.3	8.1	0.00	4.2
A_5	6.4	9.6	0.00	4.3
A_6	13.2	13.5	0.00	11.7

It has been known for some time that the inverted fine structure of the ^{2}D states of Na-like ions is due to the spin polarization of the core by an electrostatic exchange effect [Lindgren and Mårtensson, 1982, Lindgren and Morrison, 1982].
This spin polarization effect is in our framework given by a second order contribution to the fine structure parameter ζ_{nd} with $a = 2p, b = p'$ and $c = nd$, equation (15.50):

$$\Delta\zeta_{nd} = \tfrac{1}{5} \sum\!\!\!\!\!\!\int_{2p\to p'} \frac{2\zeta(2p,p')R^1(2p,nd;nd,p')}{\varepsilon_{p'}-\varepsilon_{2p}} - \tfrac{3}{35} \sum\!\!\!\!\!\!\int_{2p\to p'} \frac{2\zeta(2p,p')R^3(2p,nd;nd,p')}{\varepsilon_{p'}-\varepsilon_{2p}} \tag{15.52}$$

As opposed to the first-order fine splitting, this effect is larger and negative, hence the inversion. The same effect is responsible for the inverted fine structure of the 3s3d(^{3}D) term in Mg-like systems; in this case, the interpretation is complicated by additional 3s3d two-particle magnetic effects such as mutual spin-orbit and spin-spin interaction. Some details of the calculation and a comparison with the experiment

are given in table (15.4).
A similar effect in the $3s^23d(^2D)$ term in neutral Al is vastly overshadowed by a magnetic correlation in the $3s3p^2(^2D)$ perturber [Uylings and Buurman, 1990].
It should be noted that the sign of the second-order contributions is not always negative: EL-SO corrections in the $3s3p(^3P)$ term of Al^+ raise the fine-structure splitting ($^3P_2$–$^3P_1$) -and thereby ζ_{3p} in the absence of a two-body sp-parameter $A_{\rm mso}$- from the first-order value 101.6 cm^{-1} to 124.1 cm^{-1}, to be compared with an experimental value of 123.9 cm^{-1}. Other approaches give 125 cm^{-1} [Konovalova and Kozlov, 2015] (CI+AO) and 122.4 cm^{-1} [Cheng et al., 2010] (RCI).

Table 15.4: Second order contributions to the 3d fine structure splitting in Al^+ and Al^{2+}, compared with experiment. Two-particle mutual spin-orbit (MSO) and magnetic correlation effects (due to 3d→ d′ excitations) are included in the first case; here, the splitting is taken between the $J = 1$ and $J = 3$ levels.

	Al^+ $3s3d(^3D)$	Al^{2+} $3d(^2D)$
First order HF	1.284	3.461
$2p \rightarrow p'$	-2.556	-6.032
MSO	0.670	-
$3d \rightarrow d'$	-1.182	-
Total calc.	-1.784	-2.57
Experiment	-2.02	-2.29
Relativistic[a]	-2.17	-3.41
Other theory[b]	-	-2.96

[a] MCDHF

[b] [Lindgren and Mårtensson, 1982]

Another important example of EL-SO effects is found with:
$\Delta\zeta(p) = \zeta(p, MSO) + \zeta(p, \text{EL-SO})$. Here:

$$\begin{aligned}\zeta(p,\text{EL-SO}) = &-\frac{3}{25}\sum\!\!\!\!\!\!\int_{p\rightarrow p'}\frac{2\zeta(p,p')R^2(pp;pp')}{\varepsilon_{p'}-\varepsilon_p}\\ &+\sum\!\!\!\!\!\!\int_{\bar{d}\rightarrow d'}\frac{2\zeta(\bar{d},d')R^1(\bar{d}p;pd')}{\varepsilon_{d'}-\varepsilon_{\bar{d}}}-\frac{3}{7}\sum\!\!\!\!\!\!\int_{\bar{d}\rightarrow d'}\frac{2\zeta(\bar{d},d')R^3(\bar{d}p;pd')}{\varepsilon_{d'}-\varepsilon_{\bar{d}}}\\ &+\sum\!\!\!\!\!\!\int_{\bar{p}\rightarrow p'}\frac{2\zeta(\bar{p},p')R^0(\bar{p}p;pp')}{\varepsilon_{p'}-\varepsilon_{\bar{p}}}-\frac{1}{5}\sum\!\!\!\!\!\!\int_{\bar{p}\rightarrow p'}\frac{2\zeta(\bar{p},p')R^2(\bar{p}p;pp')}{\varepsilon_{p'}-\varepsilon_{\bar{p}}}\end{aligned} \tag{15.53}$$

The second most important magnetic effect in $d^{n-1}s$ configurations is given by the two-body parameter $A_{\rm mso}$ [Uylings et al., 1989].
Recall that, to compare parameter values T (of operators t) with the results of *ab initio* perturbation theory, one can project the perturbation operators onto the orthogonal model operators by means of inner products, assumed to be taken in their parent configurations by means of equation (14.26):

$$T = \sum_p \left(\frac{t:p}{p:p}\right) P \tag{15.54}$$

This results in the below second order expressions for $A_{\rm mso}$ and $A_{\rm ss}$:

$$A_{\rm mso} = -\frac{6}{5}W^1(ds;sd) + 4N^0(ds;ds) - \frac{1}{10}\sum\!\!\!\!\!\!\int_{d\to d'} \frac{2\zeta(dd')R^2(ds;sd')}{E_{dd'}} \tag{15.55}$$

$$A_{\rm ss} = \frac{4}{\sqrt{14}}N^0(ds;ds) \tag{15.56}$$

The W^k- and N^k integrals are defined in equation (5.97).
Numerical values for Fe VI and Ga V are given in table 15.5:

Table 15.5: First and second order contributions to the $A_{\rm mso}$ parameter in Fe VI and Ga V, compared with experiment.

	Fe VI ($3d^2 4s$)	Ga V ($3d^8 4s$)
$-6/5 \cdot W^1$	-0.18	-0.26
$4 \cdot N^0$	1.78	2.24
$3d \to d'$	1.60	4.06
Total calc.	3.20	6.04
Experiment	2.98	6.59

The parameters of the 2-particle magnetic interaction (spin-orbit type) of the ds-type ($A_{\rm mso}$) in the $5d^{N-1}6s$ and of the dp-type ($Z^k_{ll'}$) in the $5d^{N-1}6p$ configuration, as well as the parameter of the 3-particle electrostatic interaction ($T_{\rm dds}$) in the $5d^{N-1}6s$ configuration, are usually well defined with small uncertainty. The high order parameters $A_{\rm mso}$ and $T_{\rm dds}$ are very important for theoretical description of the $5d^{N-1}6s$ configurations as they improve the fit to the experimental levels considerably. The obtained values of the two parameters are in reasonable agreement with those obtained in the neighboring ions.

15.6 EL-HFS: CP-C effects in hyperfine structure

As mentioned in section 3.8.2 already, a single parameter $\langle r^{-3}\rangle$ does not suffice to adequately describe the effects of configuration interaction and relativity on the hyperfine structure. Relativity will be discussed later in section 22.1.
In addition to an extended model space and similar to the approach of EL-SO, second order perturbation theory may be used to describe the remaining EL-HFS effects of core polarization and correlation (CP-C):

$$(E_A - E_B)^{-1}V_{AB}V_{BA} = (E_A - E_B)^{-1}\left(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA} - U_{AB}T^{(t)}_{BA} - T^{(t)}_{AB}U_{BA}\right) \tag{15.57}$$

Here, $T^{(t)} = \sum_{\kappa k} F^{(\kappa k)t}$ with according to equation (5.53):
$F^{(\kappa k)t} = -[\kappa,k]^{-\frac{1}{2}}\,\langle a \parallel F^{(\kappa k)} \parallel b\rangle\,(\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)t}$. $T^{(t)}$ is the electronic part of either the magnetic dipole operator $T^{(1)}$: $(\kappa k) = (10),(12)$ or (10) or the electric quadrupole operator $T^{(2)}$: $(\kappa k) = (02),(11)$ or (13). The second order perturbation terms will therefore involve the off-diagonal reduced matrix elements:

$$\left\langle a \parallel F^{(\kappa k)} \parallel b\right\rangle = -[\kappa,k]^{\frac{1}{2}} \cdot a^{\kappa k}_{nl}(b^{\kappa k}_{nl}) \cdot f^{\kappa k} \tag{15.58}$$

In equation (15.58), $a_{nl}^{\kappa k}(b_{nl}^{\kappa k})$ are the well known hfs interaction parameters defined by equations (3.87) and (3.102), obviously now in off-diagonal form. The coefficients $f^{\kappa k}$ are found in equations (5.66) and (5.59).

Further on, the $S_{nl}^{\kappa k}$–integrals defined by $S_{nl}^{\kappa k} = [\kappa, k]^{-\frac{1}{2}} \langle a \parallel F^{(\kappa k)} \parallel b \rangle$ are specified relativistically in equation (22.17) .

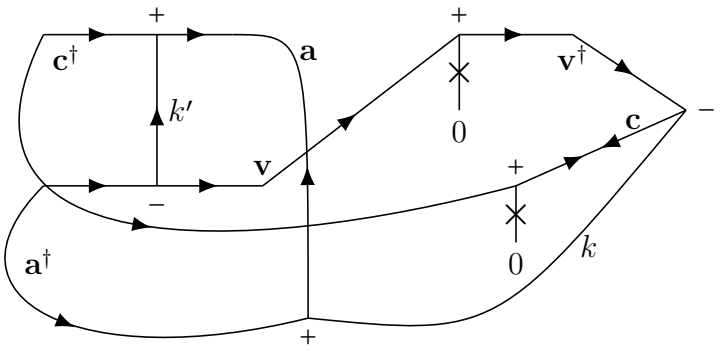
The complete expression for the first order hyperfine interaction in terms of second quantization is given in equation (5.67). In second order, two- and even three-particle hfs operators make their appearance, in which case the usual $(1 + \Delta)$ corrections do not suffice and one has to throw equation (14.26) into battle to find the required contributions to the first order parameters. To this end, only the reduced matrix elements of the second order operators in their parent configurations are needed: they will be given explicitly in the following subsections.

As $T^{(t)}$ is a one-particle operator, the excited configurations B are related to configuration A by a single electron excitation only.

The four pertinent excitation classes are [Bauche-Arnoult, 1971, Bauche-Arnoult, 1973]: core → virtual, core → valence, valence → virtual and valence to → valence.

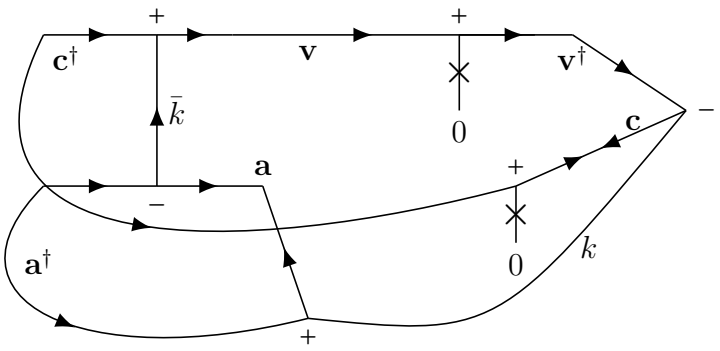
15.6.1 Core → virtual

In graphical second quantization, the first class $C_{AB}T_{BA}^{(t)}$ for $c(\frac{1}{2}\bar{l}) \rightarrow v(\frac{1}{2}l')$ -where C_{AB} contains both direct and exchange terms- is depicted by:



(15.59a)

and:



(15.59b)

With the numerical factors taken from equations (5.79) with (5.84) and $S_{cv}^{\kappa k} = [\kappa, k]^{-\frac{1}{2}} \langle c \parallel F^{(\kappa k)} \parallel v \rangle$, followed by application of equation (5.12) and (5.14) to reduce the first graph to a $6j$–symbol and using JLV2 for the second, the final second

order perturbation contribution becomes:

$$-\frac{C_{AB}T^{(t)}_{BA}+T^{(t)}_{AB}C_{BA}}{\Delta E} = 2\cdot\sum_{k'}(-1)^{k+k'+1}\cdot\begin{Bmatrix} l & l & k\\ l' & \bar{l} & k'\end{Bmatrix}\cdot\left\langle\bar{l}\parallel C^{(k')}\parallel l\right\rangle\cdot\left\langle l\parallel C^{(k')}\parallel l'\right\rangle \cdot \sum\!\!\!\!\!\!\int_{c\to v}\frac{R^{k'}(ca,av)\cdot S^{\kappa k}_{cv}}{\Delta E}\cdot\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)t} + \frac{4\cdot\delta(\kappa,0)}{(2k+1)}\cdot\left\langle\bar{l}\parallel C^{(k)}\parallel l'\right\rangle\cdot\left\langle l\parallel C^{(k)}\parallel l\right\rangle\cdot\sum\!\!\!\!\!\!\int_{c\to v}\frac{R^{k}(ca,va)\cdot S^{\kappa k}_{cv}}{\Delta E}\cdot\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)t} \tag{15.60}$$

Being directly proportional to the first order term $-S^{\kappa k}_{nl}\cdot\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)t}$, this gives the second order correction:

$$S^{\kappa k}_{nl}\to S^{\kappa k}_{nl}-2\cdot\sum_{k'}(-1)^{k+k'+1}\cdot\begin{Bmatrix} l & l & k\\ l' & \bar{l} & k'\end{Bmatrix}\cdot\left\langle\bar{l}\parallel C^{(k')}\parallel l\right\rangle\cdot\left\langle l\parallel C^{(k')}\parallel l'\right\rangle\cdot\sum\!\!\!\!\!\!\int_{c\to v}\frac{R^{k'}(ca,av)\cdot S^{\kappa k}_{cv}}{\Delta E} -\frac{4\cdot\delta(\kappa,0)}{(2k+1)}\cdot\left\langle\bar{l}\parallel C^{(k)}\parallel l'\right\rangle\cdot\left\langle l\parallel C^{(k)}\parallel l\right\rangle\cdot\sum\!\!\!\!\!\!\int_{c\to v}\frac{R^{k}(ca,va)\cdot S^{\kappa k}_{cv}}{\Delta E} \tag{15.61}$$

Dividing both sides by $S^{\kappa k}_{nl}$ and using $S(a,b)=[\kappa,k]^{-\frac{1}{2}}\cdot\langle a\parallel F^{(\kappa k)}\parallel b\rangle$, this matches exactly the expression given by [Judd, 1963] for $S^{\kappa k}_{nl}\to(1+\Delta)S^{\kappa k}_{nl}$:

$$\Delta=-2\sum\!\!\!\!\!\!\int_{c\to v}\frac{\langle c\parallel F^{(\kappa k)}\parallel v\rangle}{\langle a\parallel F^{(\kappa k)}\parallel a\rangle}\cdot\left[\sum_{k'}(-1)^{k+k'+1}\cdot\begin{Bmatrix} l & l & k\\ l' & \bar{l} & k'\end{Bmatrix}\cdot\left\langle\bar{l}\parallel C^{(k')}\parallel l\right\rangle\cdot\left\langle l\parallel C^{(k')}\parallel l'\right\rangle\cdot\frac{R^{k'}(ca,av)}{\Delta E} +\frac{2\cdot\delta(\kappa,0)}{(2k+1)}\cdot\left\langle\bar{l}\parallel C^{(k)}\parallel l'\right\rangle\cdot\left\langle l\parallel C^{(k)}\parallel l\right\rangle\cdot\frac{R^{k}(ca,va)}{\Delta E}\right] \tag{15.62}$$

Derived along the lines of Many-Body Perturbation Theory, [Lindgren and Morrison, 1982] give an equivalent expression (p 351). Equation (15.62) is the dominant CI correction to the hyperfine structure: it covers both the spin polarization for $(\kappa k)=(10)$ and the Sternheimer effect (orbital polarization) [Sternheimer, 1986] for $(\kappa k)=(02)$. When $\bar{l}=l'=0$ and $t=1$, equation (15.60) specializes to the well-known expression for the hyperfine spin polarization of the core by the inter-configuration Fermi contact term with $S^{(1)}=\sum_i s^{(1)}_i$:

$$\begin{aligned}-\frac{C_{AB}T^{(t)}_{BA}+T^{(t)}_{AB}C_{BA}}{\Delta E} &= -[l]^{-\frac{1}{2}}\cdot\sum\!\!\!\!\!\!\int_{\bar{n}s\to n's}\frac{2R^{l}(\bar{n}s\,nl,nl\,n's)\cdot S^{10}_{\bar{n}s\,n's}}{\Delta E}\cdot\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(10)1}\\ &= \alpha^2\cdot\frac{8\pi}{3}\sum\!\!\!\!\!\!\int_{\bar{n}s\to n's}\frac{2R^{l}(\bar{n}s\,nl,nl\,n's)\cdot\langle\bar{n}s\,|\delta(\boldsymbol{r})|\,n's\rangle}{(2l+1)\cdot\Delta E}\cdot S^{(1)}\end{aligned} \tag{15.63}$$

where in the last line, equation (5.66c) and $S(a,b)=(8\pi\alpha^2)/(3\sqrt{2})\cdot\langle a\,|\delta(\boldsymbol{r})|\,b\rangle$ are used. Given that non-relativistically $\langle\bar{n}s\,|\delta(\boldsymbol{r})|\,n's\rangle=\Psi_{\bar{n}s}(0)\cdot\Psi_{n's}(0)$, the corresponding contribution to the Hamiltonian becomes thereby:

$$H^D_{\rm hfs}=\frac{\alpha^2}{2}\cdot\left(\frac{m_e}{m_p}\right)\cdot\frac{\mu_I}{I}\cdot\frac{8\pi}{3}\sum\!\!\!\!\!\!\int_{\bar{n}s\to n's}\frac{2R^{l}(\bar{n}s\,nl,nl\,n's)\cdot\Psi_{\bar{n}s}(0)\cdot\Psi_{n's}(0)}{(2l+1)\cdot\Delta E}\cdot\left(S^{(1)}\cdot I^{(1)}\right) \tag{15.64}$$

Derived by more conventional tensor operator techniques, this expression was given earlier by [Bauche and Judd, 1964]; using second quantization in the uncoupled form, the same result was derived by [Judd, 1967]. Comparison with equation (3.86) immediately gives the important spin polarization correction:

$$\delta\, a_{nl}^{10} = \frac{\alpha^2}{2}\cdot\left(\frac{m_e}{m_p}\right)\cdot\frac{\mu_I}{I}\cdot\frac{2}{3}\sum\!\!\!\!\!\!\int_{\bar{n}s\to n's}\frac{2R^l(\bar{n}s\,nl, nl\,n's)\cdot\langle\bar{n}s\,|\delta(r)/r^2|\,n's\rangle}{(2l+1)\cdot\Delta E} \tag{15.65}$$

For $l \neq 0$, the first order contribution to a_{nl}^{10} is purely relativistic and the above spin polarization term is expected to dominate in most cases. In fully relativistic calculations, $8\pi/3\cdot\Psi_{\bar{n}s}(0)\cdot\Psi_{n's}(0) = \frac{2}{3}\langle\bar{n}s\,|\delta(r)/r^2|\,n's\rangle$ is to be replaced by $-4/3\alpha\cdot\int_0^\infty\left(F_{\bar{n}s}G_{n's}+F_{n's}G_{\bar{n}s}\right)/r^2\,\mathrm{d}r$; the correspondence between the first expression as the non-relativistic limit of the second is worked out in some detail in equation (22.24).

15.6.2 Core → valence

A core → valence excitation $c \to a$ is written schematically in second quantization as: $\{(\mathbf{c}^\dagger\mathbf{a})(\mathbf{a}^\dagger\mathbf{a})\}(\mathbf{a}^\dagger\mathbf{c}) + (\mathbf{c}^\dagger\mathbf{a})\{(\mathbf{a}^\dagger\mathbf{a})(\mathbf{a}^\dagger\mathbf{c})\}$. Application of equations (5.11) and (5.12) then yields both a one- and a two-particle operator. How to use graphical second quantization in such cases is exemplified in the next subsection.
The two-particle reduced matrix element in l^2 becomes:

$$\begin{aligned}&\left\langle l^2(SL)\parallel -(C_{AB}T_{BA}^{(t)}+T_{AB}^{(t)}C_{BA})/\Delta E\parallel l^2(S'L')\right\rangle = \\ &-2\sum\!\!\!\!\!\!\int_{c\to a}\left\langle c\parallel F^{(\kappa k)}\parallel a\right\rangle\cdot[S,L,S',L']^{\frac{1}{2}}\cdot\begin{Bmatrix}S & \kappa & S'\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\cdot(-1)^{\kappa+k}\cdot\sum_{k'}\left\langle l_c\parallel C^{(k')}\parallel l\right\rangle\left\langle l\parallel C^{(k')}\parallel l\right\rangle \\ &\cdot R^{k'}(aa,ac)\cdot\Delta E^{-1}\left[(-1)^{S'}\cdot\begin{Bmatrix}L' & l_c & l\\ k' & l & l\end{Bmatrix}\cdot\begin{Bmatrix}L' & k & L\\ l & l & l_c\end{Bmatrix}+(-1)^{S}\cdot\begin{Bmatrix}L & l_c & l\\ k' & l & l\end{Bmatrix}\cdot\begin{Bmatrix}L & k & L'\\ l & l & l_c\end{Bmatrix}\right]\end{aligned} \tag{15.66}$$

Application of equation (5.11) yields an additional one-particle term after an identical recoupling as depicted in graph 15.59a, with a instead of v. Obviously, the operator expression is quite similar:

$$\begin{aligned}-\frac{C_{AB}T_{BA}^{(t)}+T_{AB}^{(t)}C_{BA}}{\Delta E} &= 2\cdot\sum\!\!\!\!\!\!\int_{c\to a}[\kappa,k]^{-\frac{1}{2}}\cdot\left\langle c\parallel F^{(\kappa k)}\parallel a\right\rangle\cdot\Delta E^{-1} \\ \sum_{k'}(-1)^{k+1}\cdot\begin{Bmatrix}l & l & k\\ l & l_c & k'\end{Bmatrix}&\cdot\left\langle l_c\parallel C^{(k')}\parallel l\right\rangle\cdot\left\langle l\parallel C^{(k')}\parallel l\right\rangle\cdot R^{k'}(ca,aa)\cdot\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)t}\end{aligned} \tag{15.67}$$

Dividing the above by the first order operator $-[\kappa,k]^{-\frac{1}{2}}\cdot\langle a\parallel F^{(\kappa k)}\parallel a\rangle\,(\mathbf{a}^\dagger\mathbf{a})^{(\kappa k)t}$ gives immediately:

$$\Delta = -2\sum\!\!\!\!\!\!\int_{c\to a}\frac{\langle c\parallel F^{(\kappa k)}\parallel a\rangle}{\langle a\parallel F^{(\kappa k)}\parallel a\rangle}\cdot\sum_{k'}(-1)^{k+1}\cdot\begin{Bmatrix}l & l & k\\ l & l_c & k'\end{Bmatrix}\cdot\left\langle l_c\parallel C^{(k')}\parallel l\right\rangle\cdot\left\langle l\parallel C^{(k')}\parallel l\right\rangle\cdot\frac{R^{k'}(ca,aa)}{\Delta E} \tag{15.68}$$

For the Brillouin excitation $c \to a$ with $l_c = l$, the configurations A and B are connected by the potential matrix element (15.4b) as well. The pertinent single particle operator is:

$$\left[\left\{(\mathbf{c}^\dagger\mathbf{a})^{(00)}(\mathbf{a}^\dagger\mathbf{c})^{(\kappa k)}\right\}^{(\kappa k)} + \left\{(\mathbf{c}^\dagger\mathbf{a})^{(\kappa k)}(\mathbf{a}^\dagger\mathbf{c})^{(00)}\right\}^{(\kappa k)}\right] = 2\cdot[\tfrac{1}{2},l]^{-\frac{1}{2}}\cdot\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)} \tag{15.69}$$

The corresponding potential term becomes:

$$\left(U_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}U_{BA}\right)/\Delta E = 2\sum\!\!\!\!\!\!\int_{c\to a}[\kappa,k]^{-\frac{1}{2}}\cdot\langle a|U|c\rangle\cdot\left\langle c \parallel F^{(\kappa k)} \parallel a\right\rangle\cdot\Delta E^{-1}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)t} \tag{15.70}$$

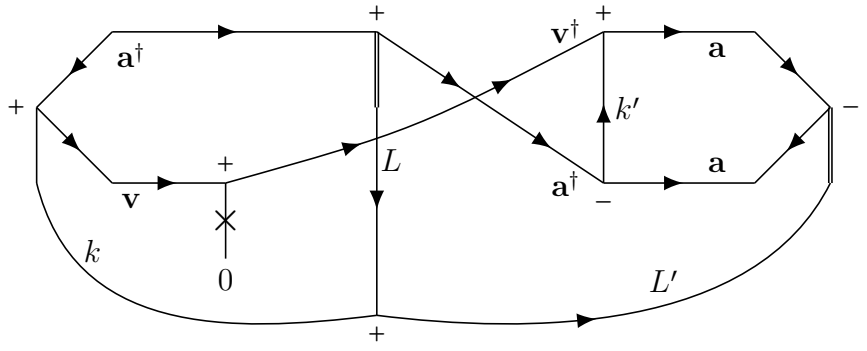
With equation (5.30) and the potential matrix element given by equation (15.4b), the reduced matrix element of 15.70 becomes:

$$\begin{aligned}&\left\langle l^2(SL) \parallel \left(U_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}U_{BA}\right)/\Delta E \parallel l^2(S'L')\right\rangle = \\ &4\sum\!\!\!\!\!\!\int_{c\to a}\left\langle c \parallel F^{(\kappa k)} \parallel a\right\rangle\cdot\Delta E^{-1}\cdot[S,L,S',L']^{\frac{1}{2}}\cdot(-1)^{\kappa+k}\cdot\begin{Bmatrix}S & \kappa & S'\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}L & k & L'\\ l & l & l\end{Bmatrix} \\ &\cdot\left[R^0(ca,aa) - \sum_{k'>0}\frac{\left\langle l \parallel C^{(k')} \parallel l\right\rangle^2}{(2l+1)(4l+1)}R^{k'}(ca,aa)\right]\end{aligned} \tag{15.71}$$

Use of the correct potential in this a priori spherical model therefore automatically cancels the dominant spherical deviation $R^0(ca,aa)$ in equation (15.66), in addition to some corrections for the higher ranks k'.
Unfortunately, this effect has frequently been overlooked in the literature [Bauche-Arnoult, 1971, Bauche-Arnoult, 1973, Dembczyński et al., 1985].

15.6.3 Valence → virtual

As usual in perturbation theory, the spin-angular matrix elements of single electron core → valence excitations are, except for a minus sign, identical to valence → virtual excitations. The latter is schematically displayed as $\{(\mathbf{a}^\dagger\mathbf{a})(\mathbf{a}^\dagger\mathbf{v})\}(\mathbf{v}^\dagger\mathbf{a}) + (\mathbf{a}^\dagger\mathbf{v})\{(\mathbf{v}^\dagger\mathbf{a})(\mathbf{a}^\dagger\mathbf{a})\}$. To demonstrate the course of the calculation, the class $T^{(t)}_{AB}C_{BA}$ for a valence to virtual excitation $a \to v$ is considered below:



(15.72)

A pure two-particle operator in normal form $\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}(\mathbf{aa})^{(S'L')}\right\}^{(\kappa k)}$ is found.
Parallel for the orbital and spin quantum numbers, the graph is reduced to a product

of two 6j-symbols, with the result:

$$[\tfrac{1}{2}]^{-1}\cdot[S,L,S',L']^{\frac{1}{2}}\cdot(-1)^{\kappa+k+S'}\cdot\begin{Bmatrix}S&\kappa&S'\\ \frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{Bmatrix}\cdot\begin{Bmatrix}L'&l_v&l\\ k'&l&l\end{Bmatrix}\cdot\begin{Bmatrix}L'&k&L\\ l&l&l_v\end{Bmatrix}$$

The final second order reduced matrix element in l^2 thus becomes:

$$\Big\langle l^2(SL)\parallel -(C_{AB}T^{(t)}_{BA}+T^{(t)}_{AB}C_{BA})/\Delta E\parallel l^2(S'L')\Big\rangle =$$
$$2\sum\!\!\!\!\!\!\int_{a\to v}\big\langle a\parallel F^{(\kappa k)}\parallel v\big\rangle\cdot[S,L,S',L']^{\frac{1}{2}}\cdot\begin{Bmatrix}S&\kappa&S'\\ \frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{Bmatrix}\cdot(-1)^{\kappa+k}\cdot\sum_{k'}\big\langle l_v\parallel C^{(k')}\parallel l\big\rangle\big\langle l\parallel C^{(k')}\parallel l\big\rangle$$
$$\cdot R^{k'}(aa,av)\cdot\Delta E^{-1}\left[(-1)^S\cdot\begin{Bmatrix}L&l_v&l\\ k'&l&l\end{Bmatrix}\cdot\begin{Bmatrix}L&k&L'\\ l&l&l_v\end{Bmatrix}+(-1)^{S'}\cdot\begin{Bmatrix}L'&l_v&l\\ k'&l&l\end{Bmatrix}\cdot\begin{Bmatrix}L'&k&L\\ l&l&l_v\end{Bmatrix}\right] \tag{15.73}$$

As expected, equation (15.73) bears a close resemblance to equation (15.66), except for a minus sign and an interchange of the two RHS terms.
As is usual in perturbation theory, Brillouin excitations $nl\to n_vl_v$ with $l_v=l$ entail a potential correction, represented by the single particle operator:

$$\Big[\big\{(\mathbf{a}^\dagger\mathbf{v})^{(00)}(\mathbf{v}^\dagger\mathbf{a})^{(\kappa k)}\big\}^{(\kappa k)}+\big\{(\mathbf{a}^\dagger\mathbf{v})^{(\kappa k)}(\mathbf{v}^\dagger\mathbf{a})^{(00)}\big\}^{(\kappa k)}\Big]=-2\cdot[\tfrac{1}{2},l]^{-\frac{1}{2}}\cdot\big(\mathbf{a}^\dagger\mathbf{a}\big)^{(\kappa k)} \tag{15.74}$$

The corresponding potential term becomes:

$$\Big(U_{AB}T^{(t)}_{BA}+T^{(t)}_{AB}U_{BA}\Big)/\Delta E=-2\sum\!\!\!\!\!\!\int_{a\to v}[\kappa,k]^{-\frac{1}{2}}\cdot\langle a|U|v\rangle\cdot\big\langle a\parallel F^{(\kappa k)}\parallel v\big\rangle\cdot\Delta E^{-1}\big(\mathbf{a}^\dagger\mathbf{a}\big)^{(\kappa k)t} \tag{15.75}$$

Using equation (15.4b) for the potential, this yields the required reduced matrix element:

$$\Big\langle l^2(SL)\parallel\Big(U_{AB}T^{(t)}_{BA}+T^{(t)}_{AB}U_{BA}\Big)/\Delta E\parallel l^2(S'L')\Big\rangle =$$
$$-4\sum\!\!\!\!\!\!\int_{a\to v}\big\langle a\parallel F^{(\kappa k)}\parallel v\big\rangle\cdot\Delta E^{-1}\cdot[S,L,S',L']^{\frac{1}{2}}\cdot(-1)^{\kappa+k}\cdot\begin{Bmatrix}S&\kappa&S'\\ \frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{Bmatrix}\begin{Bmatrix}L&k&L'\\ l&l&l\end{Bmatrix}$$
$$\cdot\left[R^0(aa,av)-\sum_{k'>0}\frac{\big\langle l\parallel C^{(k')}\parallel l\big\rangle^2}{(2l+1)(4l+1)}R^{k'}(aa,av)\right] \tag{15.76}$$

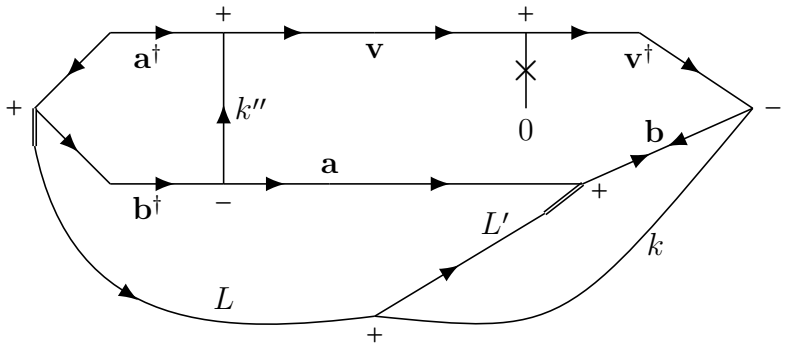
As expected, the potential cancels the large term containing $R^0(aa,av)$ in equation (15.73) exactly and corrects the remaining terms.

The final resulting two-particle operator is neither orthogonal nor proportional to the single particle first order term: the projection formula (14.26) has to be used to find the contribution with the $N-$dependence $Q=\binom{N}{2}\binom{1}{1}\binom{N}{1}^{-1}=(N-1)$.
According to equations (5.31) and (5.53), or alternatively equation (14.43), the corresponding first order reduced matrix element in l^2 is given by:

$$\big\langle l^2(SL)\parallel F^{(\kappa k)}\parallel l^2(S'L')\big\rangle=-2\big\langle a\parallel F^{(\kappa k)}\parallel a\big\rangle[S,L,S',L']^{\frac{1}{2}}(-1)^{\kappa+k}\begin{Bmatrix}S&\kappa&S'\\ \frac{1}{2}&\frac{1}{2}&\frac{1}{2}\end{Bmatrix}\begin{Bmatrix}L&k&L'\\ l&l&l\end{Bmatrix} \tag{15.77}$$

According to equation (15.58), $\langle a \parallel F^{(\kappa k)} \parallel a\rangle = -[\kappa,k]^{\frac{1}{2}} \cdot a_{nl}^{\kappa k} \cdot f^{\kappa k}$ for the magnetic dipole interaction or $-[\kappa,k]^{\frac{1}{2}} \cdot b_{nl}^{\kappa k} \cdot f^{\kappa k}$ for the electric quadrupole interaction.

For configurations $l^N l'$ with two open shells occupied with electrons a and b, $a \to v$ or $b \to v$ excitations bring both direct and exchange Coulomb interactions into play with associated Slater integrals $R^{k'}(ab,vb)$, $R^{k''}(ab,bv)$, $R^{k'}(ab,av)$ and $R^{k''}(ab,va)$; these four cases are labeled below a_D, a_E, b_D and b_E. They all give rise to two-particle operators of the normal form $\left\{(\mathbf{a}^\dagger\mathbf{b}^\dagger)^{(SL)}(\mathbf{ab})^{(S'L')}\right\}^{(\kappa k)}$. As an example, the exchange term of $-C_{AB}T_{BA}^{(t)}/\Delta E$ for $b \to v$ excitations is explored in some detail:



(15.78)

After reducing the graph, one obtains the result:

$$\left[\left\{(\mathbf{a}^\dagger\mathbf{v})^{(0k'')}(\mathbf{b}^\dagger\mathbf{a})^{(0k'')}\right\}^{(00)}(\mathbf{v}^\dagger\mathbf{b})^{(\kappa k)}\right]^{(\kappa k)} = (-1)^{L+k''+1+\kappa+k}\cdot[k'']^{\frac{1}{2}}\cdot[S,L,S'L']^{\frac{1}{2}}$$
$$\cdot\left[\tfrac{1}{2}\right]^{-1}\cdot\begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\cdot\begin{Bmatrix} L & k & L' \\ l' & l & l_v\end{Bmatrix}\cdot\begin{Bmatrix} L & l_v & l \\ k'' & l' & l\end{Bmatrix}\cdot\left\{(\mathbf{a}^\dagger\mathbf{b}^\dagger)^{(SL)}(\mathbf{ab})^{(S'L')}\right\}^{(\kappa k)}$$

The reduced matrix elements of the above four cases are given below:

$$\left\langle ll'(SL) \parallel -(C_{AB}T_{BA}^{(t)} + T_{AB}^{(t)}C_{BA})^{a_D}/\Delta E \parallel ll'(S'L')\right\rangle =$$
$$\oint\!\!\!\!\!\!\int_{a\to v}\left\langle a \parallel F^{(\kappa k)} \parallel v\right\rangle\cdot[S,L,S',L']^{\frac{1}{2}}\cdot\begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\cdot(-1)^{\kappa+k+S'}\cdot\sum_{k'}\left\langle l \parallel C^{(k')} \parallel l_v\right\rangle\left\langle l' \parallel C^{(k')} \parallel l'\right\rangle$$
$$\cdot R^{k'}(ab,vb)\cdot\Delta E^{-1}\left[(-1)^{L+L'}\cdot\begin{Bmatrix} L & l_v & l' \\ k' & l' & l\end{Bmatrix}\cdot\begin{Bmatrix} L & k & L' \\ l & l' & l_v\end{Bmatrix} + \begin{Bmatrix} L' & l_v & l' \\ k' & l' & l\end{Bmatrix}\cdot\begin{Bmatrix} L' & k & L \\ l & l' & l_v\end{Bmatrix}\right] \tag{15.79a}$$

$$\left\langle ll'(SL) \parallel -(C_{AB}T_{BA}^{(t)} + T_{AB}^{(t)}C_{BA})^{a_E}/\Delta E \parallel ll'(S'L')\right\rangle =$$
$$\oint\!\!\!\!\!\!\int_{a\to v}\left\langle a \parallel F^{(\kappa k)} \parallel v\right\rangle\cdot[S,L,S',L']^{\frac{1}{2}}\cdot\begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\cdot(-1)^{\kappa+k+L'}\cdot\sum_{k''}\left\langle l \parallel C^{(k'')} \parallel l'\right\rangle\left\langle l' \parallel C^{(k'')} \parallel l_v\right\rangle$$
$$\cdot R^{k''}(ab,bv)\cdot\Delta E^{-1}\left[(-1)^{S+S'}\cdot\begin{Bmatrix} L & l_v & l' \\ k'' & l & l'\end{Bmatrix}\cdot\begin{Bmatrix} L & k & L' \\ l & l' & l_v\end{Bmatrix} + \begin{Bmatrix} L' & l_v & l' \\ k'' & l & l'\end{Bmatrix}\cdot\begin{Bmatrix} L' & k & L \\ l & l' & l_v\end{Bmatrix}\right] \tag{15.79b}$$

$$\left\langle ll'(SL) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{b_D}/\Delta E \parallel ll'(S'L') \right\rangle =$$
$$\sum\!\!\!\!\!\!\int_{b\to v} \left\langle b \parallel F^{(\kappa k)} \parallel v \right\rangle \cdot [S,L,S',L']^{\frac{1}{2}} \cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot (-1)^{\kappa+k+S} \cdot \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l \right\rangle \left\langle l' \parallel C^{(k')} \parallel l_v \right\rangle$$
$$\cdot R^{k'}(ab,av) \cdot \Delta E^{-1} \left[\begin{Bmatrix} L & l_v & l' \\ k' & l & l \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l' & l & l_v \end{Bmatrix} + (-1)^{L+L'} \cdot \begin{Bmatrix} L' & l_v & l' \\ k' & l & l \end{Bmatrix} \cdot \begin{Bmatrix} L' & k & L \\ l' & l & l_v \end{Bmatrix} \right] \tag{15.79c}$$

$$\left\langle ll'(SL) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{b_E}/\Delta E \parallel ll'(S'L') \right\rangle =$$
$$\sum\!\!\!\!\!\!\int_{b\to v} \left\langle b \parallel F^{(\kappa k)} \parallel v \right\rangle \cdot [S,L,S',L']^{\frac{1}{2}} \cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot (-1)^{\kappa+k+L} \cdot \sum_{k''} (-1)^{k''} \left\langle l \parallel C^{(k'')} \parallel l_v \right\rangle \left\langle l' \parallel C^{(k'')} \parallel l \right\rangle$$
$$\cdot R^{k''}(ab,va) \cdot \Delta E^{-1} \left[\begin{Bmatrix} L & l_v & l \\ k'' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l' & l & l_v \end{Bmatrix} + (-1)^{S+S'} \cdot \begin{Bmatrix} L' & l_v & l \\ k'' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L' & k & L \\ l' & l & l_v \end{Bmatrix} \right] \tag{15.79d}$$

It is gratifying to verify that Hermiticity as prescribed by equation (3.46) is satisfied in all cases.
Brillouin excitations necessitate the implementation of potential terms (15.75). Using equations (5.32), the pertinent reduced matrix elements become:

$$\left\langle ll'(SL) \parallel \left(U_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}U_{BA} \right)^a /\Delta E \parallel ll'(S'L') \right\rangle =$$
$$-2 \sum\!\!\!\!\!\!\int_{a\to v} \left\langle a \parallel F^{(\kappa k)} \parallel v \right\rangle \cdot \Delta E^{-1} \cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{l+l'+S'+L'+\kappa+k} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & l' & l \end{Bmatrix}$$
$$\cdot \left[R^0(ab,vb) - \tfrac{1}{2} \sum_{k''} [l,l']^{-1} \left\langle l \parallel C^{(k'')} \parallel l' \right\rangle^2 R^{k''}(ab,bv) \right] \tag{15.80a}$$

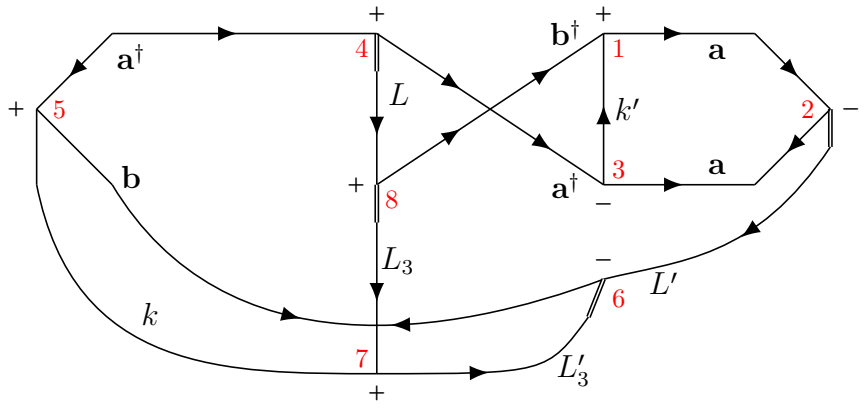
$$\left\langle ll'(SL) \parallel \left(U_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}U_{BA} \right)^b /\Delta E \parallel ll'(S'L') \right\rangle =$$
$$-2 \sum\!\!\!\!\!\!\int_{b\to v} \left\langle b \parallel F^{(\kappa k)} \parallel v \right\rangle \cdot \Delta E^{-1} \cdot [S,L,S',L']^{\frac{1}{2}} (-1)^{l+l'+S+L+\kappa+k} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l' & l & l' \end{Bmatrix}$$
$$\cdot \left[R^0(ab,av) - \tfrac{1}{2} \sum_{k''} [l,l']^{-1} \left\langle l \parallel C^{(k'')} \parallel l' \right\rangle^2 R^{k''}(ab,va) \right] \tag{15.80b}$$

As always, the $R^0(ab,vb)$ and the $R^0(ab,av)$ terms cancel exactly in addition to some corrections in the exchange terms.
The above contributions may again be compared with the corresponding first order expression:

$$\left\langle ll'(SL) \parallel F^{(\kappa k)} \parallel ll'(S'L') \right\rangle = -[S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{l+l'+\kappa+k} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix}$$
$$\cdot \left[(-1)^{S'+L'} \begin{Bmatrix} L & k & L' \\ l & l' & l \end{Bmatrix} \left\langle a \parallel F^{(\kappa k)} \parallel a \right\rangle + (-1)^{S+L} \begin{Bmatrix} L & k & L' \\ l' & l & l' \end{Bmatrix} \left\langle b \parallel F^{(\kappa k)} \parallel b \right\rangle \right] \tag{15.81}$$

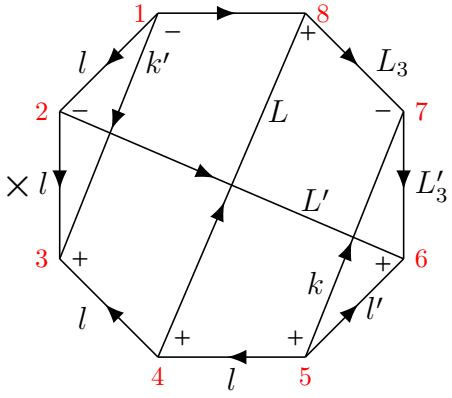
15.6.4 Valence → valence

Valence→valence excitations concern single electron excitations $a \to b$ and $b \to a$ between open shells. With $A = l^N l'^M$, this corresponds to $B = l^{N-1} l'^{M+1}$ and $B = l^{N+1} l'^{M-1}$, respectively. The EL-HFS operators are represented schematically by expressions like: $\{(\mathbf{a}^\dagger\mathbf{a})(\mathbf{a}^\dagger\mathbf{b})\}(\mathbf{b}^\dagger\mathbf{a}) + (\mathbf{a}^\dagger\mathbf{b})\{(\mathbf{b}^\dagger\mathbf{a})(\mathbf{a}^\dagger\mathbf{a})\}$. Reduction to normal form now gives rise to both three- and two-particle operators. Below, graphical second quantization applied to the second term shows the recoupling to a pure three-particle operator $[\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}\mathbf{b}^\dagger\}^{(S_3L_3)}\{(\mathbf{aa})^{(S'L')}\mathbf{b}\}^{(S'_3L'_3)}]^{(\kappa k)}$, anticipating equation (5.42):



(15.82)

$$= -[S, L, S', L', S_3, L_3, S'_3, L'_3]^{\frac{1}{2}}$$



$$= \tfrac{1}{2} \cdot [S, L, S', L', S_3, L_3, S'_3, L'_3]^{\frac{1}{2}}$$
$$\cdot (-1)^{l-\frac{1}{2}+S'+S_3+L_3+\kappa+k} \begin{Bmatrix} l & l & L' \\ l' & l & k' \end{Bmatrix} \begin{Bmatrix} l & l' & L' \\ L_3 & l & L \end{Bmatrix}$$
$$\cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S' \\ S_3 & \frac{1}{2} & S \end{Bmatrix} \begin{Bmatrix} l & L_3 & L' \\ L'_3 & l' & k \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & S_3 & S' \\ S'_3 & \frac{1}{2} & \kappa \end{Bmatrix}$$

(15.83)

After multiplication with the factors from equation (5.42), (5.79) and (5.84), the corresponding reduced matrix elements combined with the first term become:

$$\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{a^2b}/\Delta E_{a\to b} \parallel l^2(S'L')l'(S'_3L'_3)\right\rangle = \\
&2\left\langle a \parallel F^{(\kappa k)} \parallel b\right\rangle \cdot [S,L,S',L',S_3,L_3,S'_3,L'_3]^{\frac{1}{2}} \cdot (-1)^{l-\frac{1}{2}+S_3+L_3+\kappa+k} \\
&\cdot \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l\right\rangle \left\langle l \parallel C^{(k')} \parallel l'\right\rangle \cdot R^{k'}(aa,ab) \cdot \Delta E^{-1} \\
&\cdot \left[(-1)^S \begin{Bmatrix} l & l & L \\ l' & l & k' \end{Bmatrix} \begin{Bmatrix} l & l' & L \\ L'_3 & l & L' \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ S'_3 & \frac{1}{2} & S' \end{Bmatrix} \begin{Bmatrix} l & L'_3 & L \\ L_3 & l' & k \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & S'_3 & S \\ S_3 & \frac{1}{2} & \kappa \end{Bmatrix} \right. \\
&\left. + (-1)^{S'} \begin{Bmatrix} l & l & L' \\ l' & l & k' \end{Bmatrix} \begin{Bmatrix} l & l' & L' \\ L_3 & l & L \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S' \\ S_3 & \frac{1}{2} & S \end{Bmatrix} \begin{Bmatrix} l & L_3 & L' \\ L'_3 & l' & k \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & S_3 & S' \\ S'_3 & \frac{1}{2} & \kappa \end{Bmatrix} \right]
\end{aligned} \tag{15.84}$$

Remember that with an $a \to b$ excitation, equation (10.13a) implies $\Delta E = \varepsilon_b - \varepsilon_a$. A two-particle operator $\left\{(\mathbf{a}^\dagger\mathbf{a}^\dagger)^{(SL)}(\mathbf{aa})^{(S'L')}\right\}^{(\kappa k)}$ arises from the second term of equation (5.11), which is equivalent to considering b as a virtual electron. The reduced matrix element matches therefore exactly equation (15.73):

$$\begin{aligned}
&\left\langle l^2(SL) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{a^2}/\Delta E_{a\to b} \parallel l^2(S'L')\right\rangle = \\
&2\left\langle a \parallel F^{(\kappa k)} \parallel b\right\rangle \cdot [S,L,S',L']^{\frac{1}{2}} \cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot (-1)^{\kappa+k} \cdot \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l'\right\rangle \left\langle l \parallel C^{(k')} \parallel l\right\rangle \\
&\cdot R^{k'}(aa,ab) \cdot \Delta E^{-1} \left[(-1)^S \cdot \begin{Bmatrix} L & l' & l \\ k' & l & l \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l & l & l' \end{Bmatrix} + (-1)^{S'} \cdot \begin{Bmatrix} L' & l' & l \\ k' & l & l \end{Bmatrix} \cdot \begin{Bmatrix} L' & k & L \\ l & l & l' \end{Bmatrix} \right]
\end{aligned} \tag{15.85}$$

Still more operators appear when considering a second schematic expression: $\{(\mathbf{a}^\dagger\mathbf{b})(\mathbf{b}^\dagger\mathbf{b})\}(\mathbf{b}^\dagger\mathbf{a}) + (\mathbf{a}^\dagger\mathbf{b})\{(\mathbf{b}^\dagger\mathbf{b})(\mathbf{b}^\dagger\mathbf{a})\} \to (\mathbf{a}^\dagger\mathbf{b}^\dagger\mathbf{b}^\dagger)(\mathbf{abb}) + (\mathbf{a}^\dagger\mathbf{b}^\dagger)(\mathbf{ab})$.

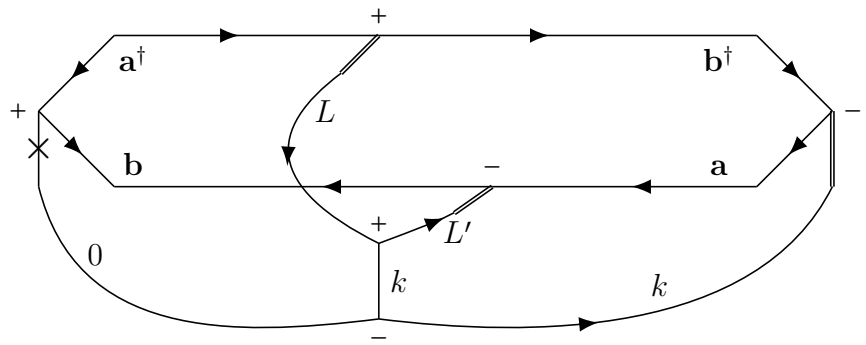
$$\begin{aligned}
&\left\langle l\,l'^2(SL)S_3L_3 \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{ab^2}/\Delta E_{a\to b} \parallel l\,l'^2(S'L')S'_3L'_3\right\rangle = \\
&2\left\langle a \parallel F^{(\kappa k)} \parallel b\right\rangle \cdot [S,L,S',L',S_3,L_3,S'_3,L'_3]^{\frac{1}{2}} \cdot (-1)^{l-\frac{1}{2}+S'_3+L'_3+\kappa+k} \\
&\cdot \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l'\right\rangle \left\langle l' \parallel C^{(k')} \parallel l'\right\rangle \cdot R^{k'}(ab,bb) \cdot \Delta E^{-1} \\
&\cdot \left[(-1)^{S'} \begin{Bmatrix} L' & l & l' \\ k' & l' & l' \end{Bmatrix} \begin{Bmatrix} L' & l' & L_3 \\ L & l & l' \end{Bmatrix} \begin{Bmatrix} S' & \frac{1}{2} & S_3 \\ S & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L'_3 & k & L_3 \\ l' & L' & l \end{Bmatrix} \begin{Bmatrix} S'_3 & \kappa & S_3 \\ \frac{1}{2} & S' & \frac{1}{2} \end{Bmatrix} \right. \\
&\left. + (-1)^S \begin{Bmatrix} L & l & l' \\ k' & l' & l' \end{Bmatrix} \begin{Bmatrix} L & l' & L'_3 \\ L' & l & l' \end{Bmatrix} \begin{Bmatrix} S & \frac{1}{2} & S'_3 \\ S' & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L_3 & k & L'_3 \\ l' & L & l \end{Bmatrix} \begin{Bmatrix} S_3 & \kappa & S'_3 \\ \frac{1}{2} & S & \frac{1}{2} \end{Bmatrix} \right]
\end{aligned} \tag{15.86}$$

In fact, the $(\mathbf{a}^\dagger\mathbf{b}^\dagger)(\mathbf{ab})$ term derives from two different $(\mathbf{bb}^\dagger)$ annihilations that were unnecessarily treated by [Bauche-Arnoult, 1973] as two separate operators d3 and

d4 in their table 4. The reduced matrix element of the combined operator becomes:

$$\Big\langle ll'(SL) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{ab}/\Delta E_{a\to b} \parallel ll'(S'L')\Big\rangle = \big\langle a \parallel F^{(\kappa k)} \parallel b\big\rangle \cdot [S,L,S',L']^{\frac{1}{2}}$$
$$\cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot (-1)^{\kappa+k} \cdot \sum_{k'} \big\langle l \parallel C^{(k')} \parallel l' \big\rangle \big\langle l' \parallel C^{(k')} \parallel l' \big\rangle \cdot R^{k'}(ab,bb) \cdot \Delta E^{-1} \cdot$$
$$\Bigg[(-1)^{S'+L'}(1+(-1)^{S+L})(-1)^{S} \cdot \begin{Bmatrix} L & l' & l' \\ k' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l & l' & l' \end{Bmatrix}$$
$$+ (1+(-1)^{S'+L'})(-1)^{S'} \cdot \begin{Bmatrix} L' & l' & l' \\ k' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L' & k & L \\ l & l' & l' \end{Bmatrix} \Bigg] \tag{15.87}$$

Hermiticity according to equation (3.46) is thereby directly manifest.
For the Brillouin case $l = l'$, potential contributions $\Big(U_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}U_{BA}\Big)$ make their appearance again. The schematic expression $\Big[\{(\mathbf{a}^\dagger\mathbf{b})^{(00)}(\mathbf{b}^\dagger\mathbf{a})^{(\kappa k)}\}^{(\kappa k)} + \{(\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)}(\mathbf{b}^\dagger\mathbf{a})^{(00)}\}^{(\kappa k)}\Big]$ reveals a one- and a two-particle part. The graphical second quantized recoupling of the first two-particle term is given below:



(15.88)

The reduced two-particle potential matrix element thereby becomes:

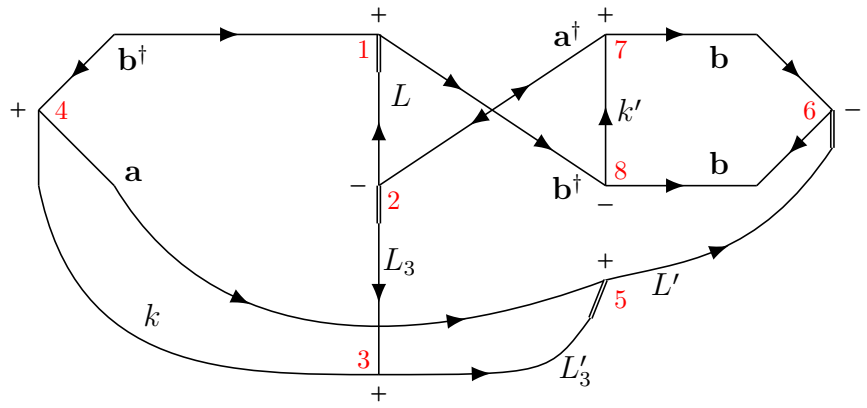
$$\Big\langle ll'(SL) \parallel \Big(U_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}U_{BA}\Big)/\Delta E_{a\to b} \parallel ll'(S'L')\Big\rangle = -\delta(l,l') \cdot \langle a\,|U|\,b\rangle$$
$$\cdot \big[(-1)^{S+L+S'+L'}+1\big] \cdot \big\langle a \parallel F^{(\kappa k)} \parallel b\big\rangle \cdot \Delta E^{-1} \cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{\kappa+k} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & l & l \end{Bmatrix} \tag{15.89a}$$

After one $(\mathbf{b}\mathbf{b}^\dagger)$ annihilation, the reduced one-particle matrix element becomes:

$$\Big\langle ll'(SL) \parallel \Big(U_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}U_{BA}\Big)^{a}/\Delta E_{a\to b} \parallel ll'(S'L')\Big\rangle = -2 \cdot \delta(l,l') \cdot \langle a\,|U|\,b\rangle$$
$$(-1)^{S'+L'} \cdot \big\langle a \parallel F^{(\kappa k)} \parallel b\big\rangle \cdot \Delta E^{-1} \cdot [S,L,S',L']^{\frac{1}{2}} \cdot (-1)^{\kappa+k} \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & l & l \end{Bmatrix} \tag{15.89b}$$

Considering next $b \to a$ excitations from the initial configuration $A = l^N l'^M$, it is clear that all the foregoing $a \to b$ equations can be adopted directly with the obvious substitutions $a \leftrightarrow b, l \leftrightarrow l', N \leftrightarrow M$ and the phase-factor from equation (2.36).

To verify this point, an example of the direct calculation is carried out below:



(15.90)

Comparison immediately reveals that graph 15.90 is topologically equivalent to graph 15.82 and can likewise be reduced to a product of three 6j-symbols each in the spin and orbital space. After multiplication with $-\Delta E^{-1}$ times the factors from equation (5.44), (5.79) and (5.84): $2[\kappa,k]^{\frac{1}{2}} \cdot -[\kappa,k]^{-\frac{1}{2}} \langle b \parallel F^{(\kappa k)} \parallel a \rangle \cdot 2R^{k'}(ab,bb) \langle l \parallel C^{(k')} \parallel l' \rangle \langle l' \parallel C^{(k')} \parallel l' \rangle$, the corresponding reduced matrix elements combined with the first term become:

$$
\begin{aligned}
&\left\langle ll'^2(SL)(S_3L_3) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{ab^2}/\Delta E_{b\to a} \parallel ll'^2(S'L')(S'_3L'_3) \right\rangle = \\
&2 \left\langle a \parallel F^{(\kappa k)} \parallel b \right\rangle \cdot [S,L,S',L',S_3,L_3,S'_3,L'_3]^{\frac{1}{2}} \cdot (-1)^{l'-\frac{1}{2}+S'_3+L'_3+\kappa+k} \\
&\cdot \sum_{k'} \left\langle l' \parallel C^{(k')} \parallel l' \right\rangle \left\langle l' \parallel C^{(k')} \parallel l \right\rangle \cdot R^{k'}(bb,ba) \cdot \Delta E^{-1} \\
&\cdot \left[(-1)^{S} \begin{Bmatrix} l' & l' & L \\ l & l' & k' \end{Bmatrix} \begin{Bmatrix} l' & l & L \\ L'_3 & l' & L' \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ S'_3 & \frac{1}{2} & S' \end{Bmatrix} \begin{Bmatrix} L_3 & k & L'_3 \\ l' & L & l \end{Bmatrix} \begin{Bmatrix} S_3 & \kappa & S'_3 \\ \frac{1}{2} & S & \frac{1}{2} \end{Bmatrix} \right. \\
&\left. + (-1)^{S'} \begin{Bmatrix} l' & l' & L' \\ l & l' & k' \end{Bmatrix} \begin{Bmatrix} l' & l & L' \\ L_3 & l' & L \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S' \\ S_3 & \frac{1}{2} & S \end{Bmatrix} \begin{Bmatrix} L'_3 & k & L_3 \\ l' & L' & l \end{Bmatrix} \begin{Bmatrix} S'_3 & \kappa & S_3 \\ \frac{1}{2} & S' & \frac{1}{2} \end{Bmatrix} \right]
\end{aligned}
$$

(15.91)

As stated above, equation (15.91) may also be retrieved from equation (15.84) with the substitutions $a \leftrightarrow b, l \leftrightarrow l'$ and the phase-factor $(-1)^{(S_3+L_3)-(S'_3+L'_3)}$ from equation (2.36). This procedure can be followed to find all the required $b \to a$ cases from the corresponding $a \to b$ equations.

Chapter 16

Fano-Weiss theory

The long-range interaction between a series of bound and continuum $nl/\varepsilon l$ states and a perturber coupled to this channel, is formulated by [Fano, 1961] for the continuum and [Weiss, 1969] for the discrete region; [Smid and Hansen, 1983] combined their theories with application to the rare gases. Due to Brillouin's theorem, intra-channel interactions are absent if the series members are calculated from a frozen core, see equation (10.14a). Remains a bordered matrix to diagonalize, with no other non-diagonal matrix elements than those between the perturber and each of the series members:

$$\begin{pmatrix} E_p & V_{nl} & V_{(n+1)l} & \cdots \\ V_{nl} & E_{nl} & 0 & \\ V_{(n+1)l} & 0 & E_{(n+1)l} & \\ \vdots & & & \ddots \end{pmatrix} \tag{16.1}$$

where E_p is the diagonal energy of the perturber, $E_{(n+k)l}$ is the diagonal energy for the $(n+k)l$ series member and $V_{(n+k)l}$ is the non-diagonal matrix element connecting the perturber with the $(n+k)l$ term.
Thus, eigenfunctions of the perturbed states are of the form:

$$\phi^E = C_p^E \phi_p + \sum_m C_{ml}^E \, \phi_{ml} + \int C_{\varepsilon l}^E \, \phi_{\varepsilon l} \, \mathrm{d}\varepsilon \tag{16.2}$$

The perturber energy is shifted by a quantity $F(E)$ and the eigenvalues, E, of the matrix (16.1) must fulfill:

$$E - E_p = \sum_m \frac{V_{ml}^2}{E - E_{ml}} + PV \int \frac{V_\varepsilon^2}{E - \varepsilon} \, \mathrm{d}\varepsilon = F(E) \tag{16.3}$$

where the principal value of the integral is taken when necessary.

$$\left(C_p^E\right)^2 \left(1 + \sum_m \frac{V_{ml}^2}{\left(E - E_{ml}\right)^2} + PV \int \frac{V_\varepsilon^2}{(E-\varepsilon)^2} \, \mathrm{d}\varepsilon\right) = \left(C_p^E\right)^2 \left(1 - F'(E)\right) = 1 \tag{16.4}$$

Including the continuum, the perturber percentages in this framework, are given by:

$$\left(C_p^E\right)^2 = \left(1 - F'(E)\right)^{-1} \qquad E < 0 \tag{16.5a}$$

$$\left(C_p^E\right)^2 = \frac{V_E^2}{\left(E - E_p - F(E)\right)^2 + \pi^2 V_E^4} \qquad E > 0 \tag{16.5b}$$

Using B-splines to describe the whole Rydberg channel, the continuum is effectively included in the higher discrete states and as a result, all integral and/or continuum effects are circumvented.
In fact, the equation:

$$E - E_p = \sum_m \frac{V_{ml}^2}{E - E_{ml}} = F(E) \tag{16.6}$$

then reduces to standard perturbation theory cut after the second order because the intra-channel interaction is negligible.
Neglecting off-diagonal spin-orbit interactions, the actual term splitting $\Delta\nu^E$ of bound states is found from the weighted average of the unperturbed splittings $\Delta\nu_p$ (of the perturber) and $\Delta\nu_{ml}$ (of the channel:

$$\Delta\nu^E = \left(C_p^E\right)^2 \left(\Delta\nu_p + \sum_m \frac{V_{ml}^2}{\left(E - E_{ml}\right)^2} \Delta\nu_{ml}\right) \tag{16.7}$$

The absorption probability from a ground state ϕ_0 exhibits a characteristic broad, asymmetrical Fano-Beutler profile.
The contributions of the perturber and the series interfere positively on one side of the resonance $E = E_p + F(E)$ and negatively at the other side:

$$\left\langle \phi^E \mid \vec{r} \mid \phi_0 \right\rangle = a^E \left\langle \phi_p^E \mid \vec{r} \mid \phi_0 \right\rangle + \sum_m b_{ml}^E \left\langle \phi_{ml}^E \mid \vec{r} \mid \phi_0 \right\rangle$$

The energy dependent coefficients a^E and b_{ml}^E have different signs at different sides of the resonance.
In the present discussion, the matrix elements connecting the perturber with the series are all proportional to the Slater integral $R^1(ns\,md; np^2)$.
In the rare gases Cl I, Ar II and K III (group 17 elements), one finds:

$$V_{md} = \left\langle ns\,np^6\ {}^2S \,|C|\, ns^2np^4({}^1D)md\ {}^2S \right\rangle = -\sqrt{2/3}\ R^1(ns\,md; np^2) \tag{16.8a}$$

in the group 13 elements Al I, Ga I and In I, one finds:

$$V_{md} = \left\langle ns\,np^2({}^1D)\ {}^2D \,|C|\, ns^2\,md\ {}^2D \right\rangle = -\sqrt{2/15}\ R^1(ns\,md; np^2) \tag{16.8b}$$

similarly, for the group 12 elements Zn I, Cd I and Hg I, one finds:

$$V_{md} = \left\langle np^2\ {}^1D \,|C|\, ns\,md\ {}^1D \right\rangle = \sqrt{4/15}\ R^1(ns\,md; np^2) \tag{16.8c}$$

16.1 Fano theory for the nsnp² perturber

For the $ns^2\,md$ (^{2}D) series in Al I, Ga I and In I (n = 3, 4 or 5, respectively and $m \geq n$), the interaction with the $ns\,np^2(^2\mathrm{D})$ perturber is given by:
$V_{md} = -\sqrt{2/15}\ R^1(\mathrm{n s m d; n p^2})$ [Uylings and Buurman, 1990]. The second order result from equations (2.40), (3.54b) and subsection 15.2.3 is identical to equation (16.6):

$$\left\langle sp^2(^1\mathrm{D})^2\mathrm{D}|H_2^2|\, sp^2(^1\mathrm{D})^2\mathrm{D} \right\rangle = -\frac{2}{15} \sum\!\!\!\!\!\!\int_{md} \frac{R^1(ns\,md; np^2)^2}{\Delta E} = \frac{2}{15} \sum\!\!\!\!\!\!\int_{md} \frac{R^1(ns\,md; np^2)^2}{E_A - E_B} \tag{16.9}$$

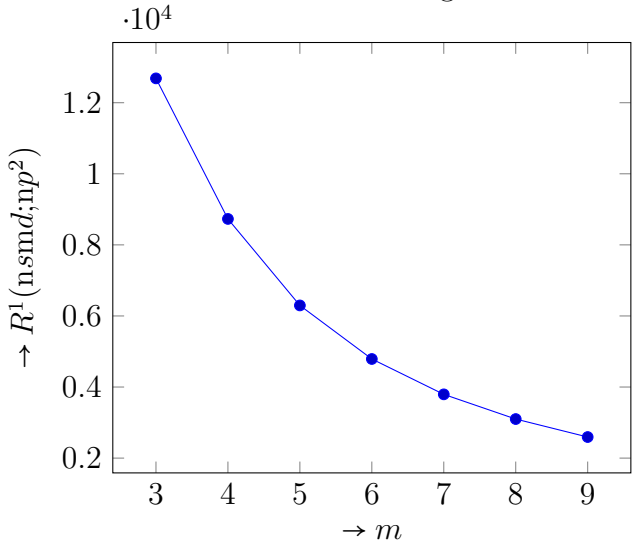
More generally, the Coulomb interaction between ns^2ml (^{2}L) states and a nsnl'^2(^{2}L) perturber equals (viz. subsection A.9 for $N = 2$):

$$\begin{aligned}\left\langle ns^2ml\,SL\,|C|\,ns\,nl'^2(S'L')\,SL)\right\rangle \;&=\; \delta(SL,\tfrac{1}{2}l)\cdot\delta(L',l)\cdot(-1)^{l'}\cdot[l,l']^{-\frac{1}{2}}\cdot\left\langle l'\parallel C^{(l')}\parallel l\right\rangle \\ &\quad\cdot(-1)^{S'+1}\cdot[S']^{\frac{1}{2}}\cdot\mathbf{R^{l'}(sl;l'^2)}\end{aligned} \tag{16.10}$$

Before [Uylings and Buurman, 1990], the fine structure of the ^{2}D series has not been considered theoretically, although the behavior over the series: the lowest member has a smaller splitting than the succeeding one, and notably the magnitude of the effect seriously deviate from what would be expected in a normal Rydberg series (being 'too large' by a factor of 10 in In, 20 in Ga and 250 in Al).
The contributions of the second term in expression (16.7) being at least an order of magnitude smaller than the experimental values, the perturber apparently exhibits a relatively large fine splitting. The source of the perturber fine splitting is found to be the two-body magnetic [MSO+EL-SO] s-p interaction; EL-SO constitutes here 95% to 99% of the effect.

$$\Delta\nu_p = 5W^0(ps;sp) - 10N^0(ps;ps) + \frac{5}{12}\sum\!\!\!\!\!\!\int_{p'}\frac{2\zeta(pp')R^1(ps;sp')}{\varepsilon_{p'}-\varepsilon_p} \tag{16.11}$$

The W^k and the N^k MSO integrals in the above are defined in equation (5.97).



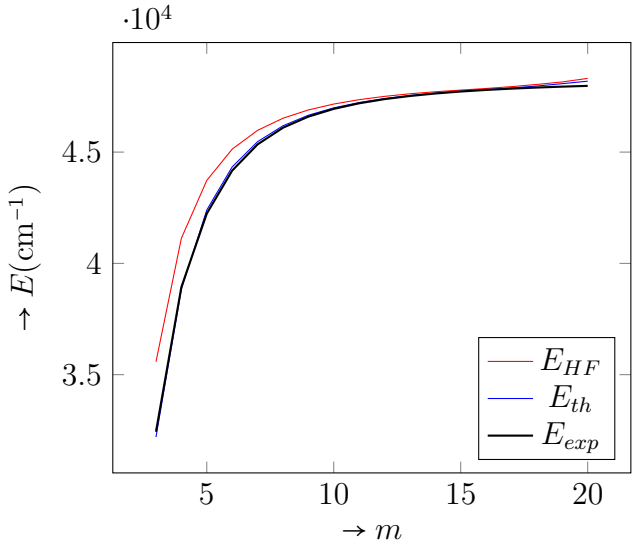


Figure 16.1: Theoretical (HF vs. Fano) and experimental $3s^2md$ energies.

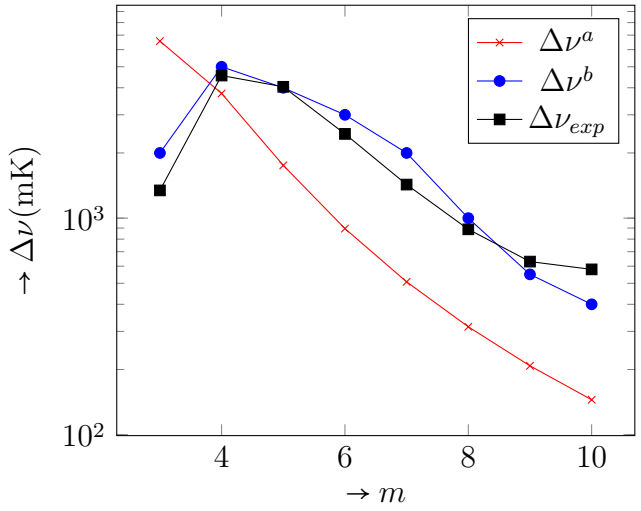


Figure 16.2: Theoretical[a,b] and experimental FS ^{2}D splittings.

[a] This work; [b] [Papoulia et al., 2019].

The calculation will be performed for Al I, core charge Z = 13, effective core charge Z_{eff} = 1; l-value of channel: l = 2. E(limit) = 48278.5 E(perturber) = 44501.3
Electron configuration of the perturber is given by:

shell	1s	2s	2p	3s	3p
occupation	2	2	6	1	2

m	E_{HF}	C_p^2	$\sum_{C_p^2}$	E_{th}	E_{exp}
3	35577.8	0.32049	0.32049	32197.7	32436.3
4	41127.7	0.18365	0.50415	38838.8	38932.1
5	43725.5	0.08551	0.58966	42396.9	42236.2
6	45131.7	0.04364	0.63330	44333.5	44167.9
7	45975.5	0.02480	0.65809	45468.3	45345.0
8	46520.8	0.01535	0.67345	46181.3	46094.0
9	46893.2	0.01015	0.68360	46655.9	46593.7
10	47158.8	0.00706	0.69065	46986.7	46941.3
11	47354.7	0.00511	0.69576	47226.2	47192.4
12	47503.4	0.00382	0.69958	47405.0	47379.7
13	47618.9	0.00293	0.70251	47541.9	47521.1
14	47710.4	0.00230	0.70481	47649.0	47632.6
15	47785.6	0.00185	0.70665	47734.6	47721.3
16	47857.6	0.00168	0.70833	47806.9	47793.0
17	47940.9	0.00190	0.71023	47881.1	47850.9
18	48039.9	0.00223	0.71246	47968.7	47900.1
19	48151.6	0.00269	0.71515	48073.6	47940.7
20	48310.8	0.00289	0.71804	48185.5	47975.1

Additional perturbers like $nsnp(^3\mathrm{P})mp\,^2\mathrm{D}$ (and $nsnp(^1\mathrm{P})mp\,^2\mathrm{D}$) were later emphasized by [Komninos et al., 1995]. Here, with $S_1 = 1, 3$ the spin of the $nsnp(^{1,3}\mathrm{P})$ limit:

$$V_{md} = \frac{1}{\sqrt{15}} \cdot [S_1]^{\frac{1}{2}} \cdot \left[2 \cdot \delta(S_1, 0) R^1(sd; pp') - R^1(sd; p'p)\right] \tag{16.12}$$

16.2 Fano theory for the np^2 perturber in Cd

In the case of Cd, the perturber is $|5p^2\ {}^1_2\mathrm{D}\rangle$ and the series: $|5s\,md\ {}^1\mathrm{D}\rangle$.
that satisfies equation (16.6) for $m = 5, 6, ..$:

$$E - E_p = \sum_{m=5,6,..} \frac{V_{md}^2}{E - E_{md}} = F(E)$$

To calculate the energies of the $5s\,md$ series as perturbed by the $5p^2$ state, intra channel interactions are neglected and the below Hamiltonian is diagonalized:

$$\begin{pmatrix} E_{p^2} & V_{5d} & V_{6d} & \cdots \\ V_{5d} & E_{5d} & 0 & \\ V_{6d} & 0 & E_{6d} & \\ \vdots & & & \ddots \end{pmatrix}$$

In the present case, $V_{md} = \sqrt{4/15}\ R^1(5s\,\mathrm{m}d;5p^2)$.
The second order result from subsection 15.2.3 is again identical to equation (16.6):

$$\left\langle p^2(^1\mathrm{D})|H_2^2|\,p^2(^1\mathrm{D})\right\rangle = -\frac{4}{15} \sum\!\!\!\!\!\!\int_{md} \frac{R^1(ns\,md; np^2)^2}{\Delta E} = \frac{4}{15} \sum\!\!\!\!\!\!\int_{md} \frac{R^1(ns\,md; np^2)^2}{E_A - E_B} \tag{16.13}$$

The program 'Fano' returns the following result:

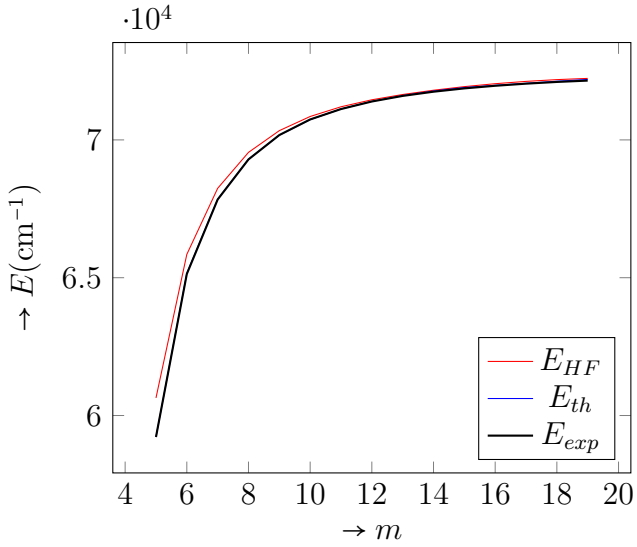


Figure 16.3: Theoretical (HF vs. Fano) and experimental $5smd$ energies.

Channel: 5s md (m=5,6,..,ε) $^1D_2$.
E(limit) = 72538.8 cm^{-1}
E(perturber) = 80813.0 cm^{-1}

Electron configuration of the perturber is given by:

shell	1s	2s	2p	3s	3p	3d	4s	4p	4d	5p
occupation	2	2	6	2	6	10	2	6	10	2

Experimental and calculated energies with their percentages are calculated as:

$5smd$	E_{HF}	C_{p^2}	$\sum_{C_p^2}$	E_{th}	E_{exp}
5	60637.8	0.08306	0.08306	59218.2	59219.8
6	65845.4	0.04765	0.13071	65164.0	65134.9
7	68242.5	0.03103	0.16174	67845.7	67837.1
8	69547.2	0.02054	0.18228	69299.7	69292.5
9	70336.0	0.01402	0.19630	70172.7	70175.9
10	70849.4	0.00988	0.20618	70736.6	70741.9
11	71202.1	0.00713	0.21332	71121.8	71119.5
12	71455.4	0.00520	0.21852	71398.3	71393.6
13	71646.9	0.00394	0.22246	71607.7	71596.3
14	71802.3	0.00377	0.22623	71773.3	71748.9
15	71932.6	0.00602	0.23225	71899.8	71869.2
16	72039.1	0.00723	0.23948	71980.6	71964.1
17	72123.1	0.00181	0.24129	72053.5	72040.7
18	72187.4	0.00034	0.24163	72129.5	72103.2
19	72231.7	0.00010	0.24173	72192.7	72151.7

Chapter 17

CI versus perturbation

An effective parameter set is based on the assumption that the effects of configuration interaction on the configuration under study can be accounted for by perturbation theory. In principle, they allow CI to be included to infinite order in a perturbation expansion. However, it is well known that if the interaction with a configuration of equal parity is very strong, either by proximity or by orbital overlap, it is more realistic to include this interaction explicitly. This is because, if a strong mixing exists, the choice of which of the mixed terms to include in a single-configuration fit becomes arbitrary. However, the explicit inclusion of these interactions means that it is difficult to determine all the effective parameters at the same time with the direct CI integrals and the parameters describing the excited configuration.

The merits and pitfalls of using orthogonal operators in systems with strong configuration interaction are illustrated by a study of a number of $(5d + 6s)^N$ configurations ($N = 8, 9$) ranging from Ir to Pb. Both the perturbational and the full diagonalization approach are applied. Criteria are given to indicate the regions where either operators based on perturbation theory or explicit configuration interactions are dominant. In both regions, orthogonal operators describe the (ground and) excited states well, provided they are extended by interconfiguration operators in the case of lower ionization, where full diagonalization of the three $(5d + 6s)^N$ configurations is required.

Ab initio calculations using second order perturbation theory show satisfactory agreement with the results from fits to experimental energy levels, except again for the lowest ionization stages, where perturbation theory breaks down.

In both the even and odd parity systems, three configurations may be included in the calculations: $(5d^N + 5d^{N-1}6s + 5d^{N-2}6s^2)$ and $(5d^{N-1}6p + 5d^{N-2}6s6p + 5d^{N-3}6s^26p)$. Interaction between the configurations in these cases is added explicitly. The interaction integrals, parameters of yet unknown configurations and some of the parameters of the studied configurations are kept fixed at the predetermined values.

It turns out to be a good approximation to exclude interactions treated by complete diagonalization from the perturbation expressions: both approaches can then be combined to describe excited state interactions.

17.1 Where do orthogonal operators come in?

Parametric fitting with orthogonal operators can be used to extract second- and higher order effects from experimental data of complex atoms [Hansen et al., 1988a]. In contrast to (near) closed shell systems, small but theoretically interesting effects like three- and four-body interactions manifest themselves in the structure of complex spectra, and can be isolated one by one by fitting orthogonal operators with the corresponding angular definition. With orthogonal operators, the reference states are (only) distinguished by their angular behavior, whereas the radial parameters are taken equal for a configuration as a whole. In this respect, the procedure is consistent with the configuration average approach [Froese Fischer, 1977, Cowan, 1981] or the average level formalism [Grant et al., 1976] but, due to the fitting, corrected to all orders of perturbation theory. With large configuration interaction effects, the efficiency is increased by including more configurations into the first order. If the fitting process converges to physically realistic values, one may assume that the eigenvector composition as well as the (experimentally unknown) predicted level values are quite accurate. Like the energies, the transition probabilities are not calculated state-by-state but for a whole configuration at the time. In addition to the fitted eigenvector compositions, one has to rely here on *ab initio* calculated transition integrals. The effect of configurations outside the model space as well as the state dependence of the orbitals are basically neglected in this procedure. Both effects are usually small and can in principle be dealt with by perturbation theory. In summary, the orthogonal operator method is most effective for complex spectra, where the number of relevant configurations and the term dependence of the orbitals are comparatively small. Starting with *ab initio* calculations or extrapolations, perturbation effects up to infinite order are subsequently embodied in the fit.

17.2 Two classes of configuration interaction

Interactions between configurations can somewhat arbitrarily be partitioned into two kinds, usually called strong and weak configuration interactions. With the strong interaction, the interacting configurations are assumed to lie close enough to 'see' each other's energy structure. Such a system has to be diagonalized as a whole, which means that those configurations will be included into the reference or model space where the zero and first order calculations are carried out. Weak configuration interaction, on the other hand, refers to the effects of many far-lying configurations. In this case one may construct operators that accommodate the totals of these interactions within the original model space. These so-called 'effective' operators are usually less important than the pure single configuration operators, although they frequently dominate over two-particle magnetic effects. The physical content is found in the net result of a large number of small interactions with far-away configurations

17.3 Interplay explicit and implicit CI

Below, we derive from equation (14.8) the complete second-order expression of $T_{\rm dds}$, the only three-electron operator in the d^2s configuration. The first two terms were originally omitted [Uylings et al., 1989, van het Hof et al., 1991a]. Summation implies both summation over virtual discrete states and integration over virtual continuum states. The energy denominators ΔE_v are defined as $E_B - E_A$ and, as a result, they are normally positive.

$$T_{\rm dds} = \frac{-\sqrt{7}}{735}\left(18\sum_{d\to d'}\frac{R^2(ds;sd')R^2(d^2;dd')}{\Delta E_{d'}} - 10\sum_{d\to d'}\frac{R^2(ds;sd')R^4(d^2;dd')}{\Delta E_{d'}}\right.$$
$$+18\sum_{s\to d'}\frac{R^2(ds;dd')R^2(ds;d'd)}{\Delta E_{d'}} - 9\sum_{s\to d'}\frac{\left(R^2(ds;d'd)\right)^2}{\Delta E_{d'}}$$
$$\left.-10\sum_{s\to g}\frac{R^4(ds;dg)R^2(ds;gd)}{\Delta E_g} + 9\sum_{s\to g}\frac{\left(R^2(ds;gd)\right)^2}{\Delta E_g}\right) \qquad (17.1)$$

The second line of equation (17.1) describes (to second order) the net effect of the $s \to d$ and the $d \to s$ excitations from the $d^{N-1}s$ configuration, i.e. amongst others the interactions with the configurations d^N and $d^{N-2}s^2$, respectively; their contribution should be omitted if these interactions are included into the first order already by a more-configuration approach. As the four-particle parts of the two interactions cancel each other exactly, only a three-particle part contributes to $T_{\rm dds}$.

Table 17.1: Second order contributions to the $T_{\rm dds}$ parameter in MnV, Fe VI and Ga V, compared with experiment.

	Mn V ($3d^24s$)	Fe VI ($3d^24s$)	Ga V ($3d^84s$)
$3d \to d'$	33.3	27.8	37.0
$4s \to d'$	-111.8	-118.7	-99.0
$4s \to g$	3.0	3.0	2.3
Total calc.	-75.5	-87.9	-59.7
Experiment	-82.0	-91.2	-58.6

Table 17.2: Second order contributions to the $T_{\rm dds}$ parameter in Ir I and Bi VII, with and without the $5d \leftrightarrow 6s$ interaction.

	Ir I ($5d^86s$)	Bi VII ($5d^86s$)
$5d \to d'$	56.98	25.75
$6s \to d'$	-26.30	-69.20
$6s \to g$	-4.74	1.03
Subtotal	25.94	-42.42
$5d \leftrightarrow 6s$	703.00	98.90
Total	729.00	56.50

Although the magnetic $5d^2$ parameters are considerably larger than in corresponding $3d$- and $4d$- systems, they are less important than $T_{\rm dds}$ and $A_{\rm mso}$, and the current

amount of experimental data does not allow to fit them reliably. Therefore, they are frequently fixed to their *ab initio* values in the fits.
Finally, spin-spin effects are neglected throughout; they are expected to be negligible in systems with high Z.
A complication in fitting the three lowest even configurations for neutral to six times ionized systems is that only a limited amount of information about the $5d^{N-2}6s^2$ configuration exists; even in the other two configurations there are several energy levels unknown. Therefore one cannot vary all parameters freely and constraints have to be introduced. Except for the I- and II-spectra, the average energy of the $5d^{N-2}6s^2$ configuration is derived from the Hartree-Fock energy difference with the $5d^{N-1}6s$ configuration whereas the other $5d^{N-2}6s^2$ parameters are linearly extrapolated from corresponding $5d^N$ and $5d^{N-1}6s$ parameters.
For the single configuration approach, the agreement between fitted and *ab initio* values of $T_{\rm dds}$ runs from very satisfactory to poor in the direction of lower ionization, the serious discrepancies starting with the three times ionized systems. Apparently we witness the breakdown of the (second order) perturbation theory in favor of a full diagonalization of explicit configuration interactions.

17.4 Turning point in the validity perturbational approach

Most calculations in complex $(3d+4s)^N$ systems have been carried out within the single configuration approach. Is this approximation justified and, if so, by what criterion? Below, we formulate a criterion for the introduction of more configurations in the model space and investigate this criterion with the $(5d+6s)^N$ systems.
First, one has to identify the candidate configurations for strong interaction with the reference configuration: they have to possess the same parity, lie 'nearby', and differ in no more than two single electron states with a reasonable overlap of their respective wavefunctions. Then, the normalized values of the effective parameters and the interaction integrals are compared to see their relative importance. This may be done in advance of a full study of the system if *ab initio* or extrapolated parameter values are used. To compare an effective parameter $P_{\rm weak}$ acting within configuration A with a strong interaction effect between the configurations A and B described by a Slater-type R^k-integral, the average magnitude of the angular coefficients should be equal.
We introduce the quantity $P_{\rm strong} = (R^k)^2/E_{AB}$ with E_{AB} the energy difference between the centres of gravity of A and B. Then the quantities $N_{\rm weak}P_{\rm weak}$ and $N_{\rm strong}P_{\rm strong}$, with N the angular 'length' of the operator defined by $p_i : p_j = N_i^2\delta_{ij}$, are to be compared.
For the present system, we take $T_{\rm dds}$ and $A_{\rm mso}$ as $P_{\rm weak}$ and use the two integrals $R^2(5d5d;5d6s)$ for the interactions $5d^N \leftrightarrow 5d^{N-1}6s$ and $5d^{N-1}6s \leftrightarrow 5d^{N-2}6s^2$ respectively, to form $P_{\rm strong}$.
The turning point of the normalized $P_{\rm weak}$ and $P_{\rm strong}$ are seen to take place around the III-spectra. For lower ionization, full diagonalization of the three strongly interacting configurations is clearly indispensable, while for higher ionization the 'weak' correlation operators dominate and perturbation theory alone may be sufficient.

Compared to corresponding $5d$-systems, the R^k-integrals in the $3d$-systems are roughly four times as small, whereas the relevant energy distances are about twice as large. As a result, P_{strong} is in the order of 2^5 times smaller in $3d$-systems than in $5d$-systems, while P_{weak} is comparable in magnitude: it therefore seems justified to describe many $3d$-systems with effective correlation parameters in the single configuration approach.
To investigate the validity of the above criterion, we considered the behavior of the mean error σ of the fit as a function of ionization stage in three steps:
(i) the three interaction integrals are set to zero to see the effect of the effective operators alone.
(ii) The effective parameters are set to zero to study the impact of the strong interaction alone.
(iii) Both the interaction integrals as well as the effective operators are used in the fit.
The turning point of steps (i) and (ii) takes place in the vicinity of the III-spectrum for N = 9 and is shifted towards the IV-spectrum for N=8; this shift reflects the fact that the relevant N = 8 configurations have a broader spread in energy which enhances the importance of a more-configuration description.

17.5 Conclusion

We conclude that it is possible to meaningfully combine perturbation theory (using effective parameters) and a diagonalization approach (using interaction integrals) into one description of an atomic system.
Satisfactory agreement between *ab initio* and fitted values of the effective parameters can be obtained if the interactions accounted for explicitly by diagonalization are omitted from the (perturbative) *ab initio* calculation.
Using $(5d + 6s)^N$ $(N = 8, 9)$ systems as an example, the breakdown of the purely perturbative single configuration description can actually be followed (in a direction from high to low ionization) in three different ways:
(i) comparison of the *ab initio* and fitted values of an effective parameter (here T_{dds}) that includes a contribution of the interaction with the nearby configurations;
(ii) comparison of (normalized) parameter values of an effective parameter and a parameter $(R^k)^2/E_{AB}$ associated with a strong configuration interaction;
(iii) comparison of the mean error of a fit using effective parameters only with a fit using explicit interactions only.
All three methods show the breakdown point for the same ionization stage (here the III-spectra). Higher order electrostatic and magnetic effects (described by effective orthogonal operators) can only be determined reliably if the first order model is reasonably accurate. In cases of close-lying configurations of the same parity, this implies a more-configuration model as starting point.

Chapter 18

Core polarization

The electric field of valence electrons induces a dipole moment opposite to the original dipole moment. This core-valence effect reduces the transition probability. A non-penetrating valence electron 'far outside' the core carries an electric dipole moment $\boldsymbol{d} = -e\boldsymbol{r}$, producing an electric field $\boldsymbol{E} = -\boldsymbol{d}/r^3$ at the nucleus. This induces in the 'dielectric' core an electric dipole moment:

$$\alpha_d \boldsymbol{E} = -\frac{\alpha_d \boldsymbol{d}}{r^3} \tag{18.1}$$

This effect yields the above mentioned reduction:

$$\boldsymbol{d} \to \boldsymbol{d}\left(1 - \frac{\alpha_d}{r^3}\right) \tag{18.2}$$

Therefore, one may include core polarization into the transition integral by means of the replacement:

$$r \to r\left(1 - \frac{\alpha_d}{r^3} W_3\left(\frac{r}{r_\alpha}\right)\right) \tag{18.3}$$

where the cut-off function W_3 was introduced by [Laughlin, 1992] in his model potential approach to avoid unphysical infinities at $r = 0$:

$$W_n\left(\frac{r}{r_\alpha}\right) = 1 - \exp\left(\frac{r}{r_\alpha}\right)^n \tag{18.4}$$

Here, the cut-off radius $r_\alpha(nl)$ is equated to the radius for which the partial norm of P_{nl} equals 99%:

$$\int_0^{r_\alpha} P_{nl}^2 \, \mathrm{d}r = 0.99 \tag{18.5}$$

An alternative cut-off procedure is used by Migdalek and coworkers [Migdalek and Baylis, 1978]:

$$r \to r\left(1 - \frac{\alpha_d}{(r^2 + r_0^2)^{\frac{3}{2}}}\right) \tag{18.6}$$

Here, the cut-off radius r_0 corresponds to the mean radius $\langle r \rangle$ of the outermost core orbital.

A similar procedure was introduced by P. Quinet and E. Biémont, e.g. [Quinet et al., 1999]. They employ the replacement:

$$\int_0^\infty P_{nl}\, r\, P_{n'l'}\, \mathrm{d}r \rightarrow$$
$$\int_0^\infty P_{nl}\, r \left(1 - \frac{\alpha_d}{(r^2 + r_c^2)^{\frac{3}{2}}}\right) P_{n'l'}\, \mathrm{d}r - \frac{\alpha_d}{r_c^3} \int_0^{r_c} P_{nl}\, r\, P_{n'l'}\, \mathrm{d}r \tag{18.7}$$

The cut-off radius r_c corresponds here as well to the expectation value of r for the outermost core orbital.
In fact, all of these procedures boil down to scaling the dipole transition integral by 80 to 90%.

The static dipole polarizability α_d of the core is defined as:

$$\alpha_d = -\frac{2}{3} \sum_{c \rightarrow v} \frac{\langle c | \vec{r} | v \rangle \cdot \langle v | \vec{r} | c \rangle}{\varepsilon_c - \varepsilon_v} \tag{18.8}$$

Therefore:

$$\begin{aligned} \alpha_d &= -\frac{2}{3} \sum_{\gamma J} \frac{1}{2J+1} \sum_{\gamma' J'} \frac{|\langle \gamma J \parallel rC^{(1)} \parallel \gamma' J' \rangle|^2}{E(\gamma J) - E(\gamma' J')} \\ &= -\frac{2}{3} \sum_{nl} \frac{q_{nl}}{2l+1} \sum_{l'=l\pm1} \left\langle l \parallel C^{(1)} \parallel l' \right\rangle^2 \not\sum_{l \rightarrow l'} \frac{\left[\int_0^\infty P_{nl}\, r\, P_{n'l'}\, \mathrm{d}r\right]^2}{\varepsilon_{nl} - \varepsilon_{n'l'}} \end{aligned} \tag{18.9}$$

In the case of hydrogen, this simplifies to:

$$\alpha_d = -\frac{2}{3} \not\sum_{1s \rightarrow np} \frac{\langle 1s | r | np \rangle^2}{\varepsilon_{1s} - \varepsilon_{np}} \tag{18.10}$$

More in general, the polarization correction to electric multipole transition integrals is given by:

$$D_k(r) = r^k \cdot C^{(k)}(\Omega) \cdot \left[1 - \frac{\alpha_k}{r^{2k+1}} \cdot W_{2k+1}\left(\frac{r}{r_\alpha}\right)\right] \tag{18.11}$$

Where:

$$\alpha_k = 2 \cdot \not\sum \frac{|\langle \Psi | r^k | \Psi' \rangle|^2}{E_{\Psi'} - E_\Psi} \tag{18.12}$$

For hydrogenic atoms, the polarizabilities α_d and α_q are for $k = 1, 2$ given by:

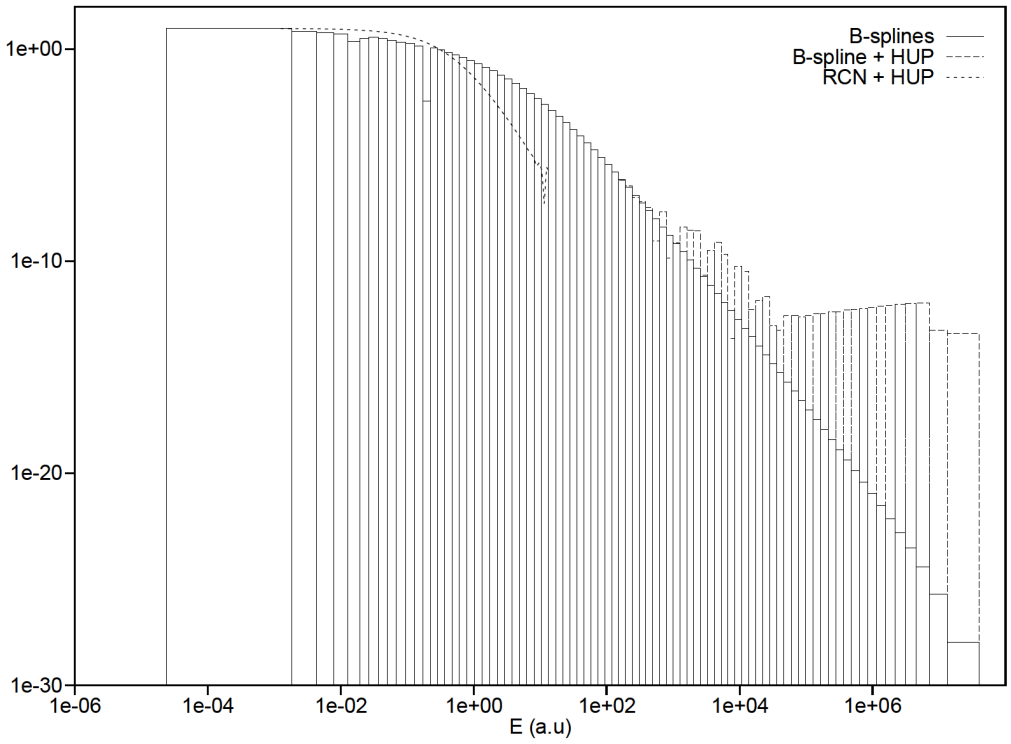
$$\alpha_k = \frac{(2k+2)!(k+2)}{2^{2k+1} \cdot Z^{2k+2} \cdot k(k+1)} \tag{18.13}$$

Bearing in mind that 10^{-24} cm^3 = 6.74833 a_0^3, this yields the exact value $\alpha_d = \frac{9}{2} \cdot \frac{1}{Z^4} = 4.5\ (a_0^3)$ for hydrogen:

Table 18.1: Comparison of various hydrogen dipole polarizability calculations.

	B-splines	HF+B-spl+HUP	RCN+B-spl+HUP	Analytical
Discrete:	3.66424935360687935	3.6635	3.6501	3.663257890309
Continuum:	0.83575064639396738	0.8365	0.8513	0.836742109691
Total:	4.50000000000084673	4.5000	4.5014	4.500000000000

Figure 18.1: Individual contributions from continuum orbitals in the calculation of the hydrogen polarizability.



Likewise, the hydrogenic quadrupole polarizability is found to be $\alpha_q = \frac{15}{Z^6}\ (a_0^5)$.

Various neutral closed-shell atoms are known to support bound states; the electron binds to the closed core to form a one-electron negative ion. The valence electron induces a dipole moment (18.1) in the core and interacts with this induced moment as a kind of self-energy. The binding force is provided by the polarization potential of the core $-\frac{1}{2}\alpha_d/r^4$, this being the classical interaction of a valence electron with the induced dipole field. The effect may be described approximately by adding a phenomenological polarization term $V_{\rm pol} = -\frac{1}{2}\alpha_d/r^4 - \frac{1}{2}(\alpha_q - \beta_1)/r^6$ to the HF potential and solving the modified Schrödinger equation. Here, α_d and α_q are the static dipole and quadrupole core polarizabilities and β_1 is a dynamical correction term. The contribution to the orbital energy ε_{nl} of high angular momentum Rydberg states becomes thereby:

$$\Delta E_{\rm pol} = -\tfrac{1}{2}\alpha_d\, Z_c^4 \left\langle r^{-4}\right\rangle - \tfrac{1}{2}(\alpha_q - 6\beta_1)\, Z_c^6 \left\langle r^{-6}\right\rangle \tag{18.14}$$

where the expectation values are calculated from hydrogenic radial functions. Values for α_d and $(\alpha_q - 6\beta_1)$ may therefore be obtained semi-empirically from the difference between experimental term energies E_{nl} and the eigenvalues ε_{nl}.
In this form, $V_{\rm pol}$ is less valid for penetrating low angular momentum electrons and singular for ns states, and again a cut-off procedure becomes necessary:

$$V_{\rm pol} = -\frac{1}{2}\,\frac{\alpha_d}{r^4}\,W_6\left(\frac{r}{r_\alpha}\right) - \frac{1}{2}\,\frac{\alpha_q - 6\beta_1}{r^6}\,W_8\left(\frac{r}{r_\alpha}\right) \qquad \text{[Laughlin, 1992]} \qquad (18.15a)$$

$$V_{\rm pol} = -\frac{1}{2}\frac{\alpha_d \cdot r^2}{(r^3 + r_0^3)^2} - \frac{1}{2}\frac{(\alpha_q - 6\beta_1)\cdot r^4}{(r^5 + r_0^5)^2} \qquad \text{[Migdalek and Baylis, 1978]} \qquad (18.15b)$$

In reaction to an electric field $\boldsymbol{E}$, a polarizable medium will adjust its potential energy with an amount ΔE given by:

$$\Delta E = -\tfrac{1}{2}\alpha_d \overline{\boldsymbol{E}^2}$$

This so-called Stark effect is found under varied circumstances:

$$\Delta E = -\tfrac{1}{2}\alpha_d \boldsymbol{E}^2 \qquad \text{d.c. Stark effect} \qquad (18.16a)$$

$$\Delta E = -\tfrac{1}{4}\alpha_d \boldsymbol{E}^2 \qquad \text{a.c. Stark effect} \qquad (18.16b)$$

$$\Delta E = -\tfrac{1}{2}\alpha_d \left\langle r^{-4}\right\rangle \qquad \text{internal Stark (core-valence) effect} \qquad (18.16c)$$

Table 18.2: Values of the dipole polarizabilities α_d (and their cut-off radii r_α) in the iron group elements.

	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
II	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
α_d(3p)	3.54(2.5)	2.68(2.4)	2.07(2.2)	1.63(2.1)	1.31(2.1)	1.06(2.0)	0.87(1.9)	0.72(1.7)
α_d(3d)	5.88(4.1)	5.86(3.5)	5.52(3.3)	5.10(3.1)	4.68(3.0)	4.29(2.9)	3.39(2.6)	3.61(2.7)
III	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
α_d(3p)	2.50(2.4)	1.95(2.2)	1.55(2.0)	1.25(1.9)	1.01(1.8)	0.83(1.7)	0.69(1.6)	
α_d(3d)	3.23(3.0)	3.08(2.9)	2.89(2.7)	2.69(2.6)	2.50(2.5)	2.33(2.4)	2.16(2.3)	
IV	V	Cr	Mn	Fe	Co	Ni	Cu	
α_d(3p)	1.82(2.0)	1.46(1.9)	1.18(1.8)	0.96(1.7)	0.80(1.7)	0.66(1.6)	0.56(1.6)	
α_d(3d)	2.16(2.5)	2.00(2.4)	1.86(2.3)	1.72(2.2)	1.60(2.1)	1.49(2.1)	1.35(2.0)	
V	Cr	Mn	Fe	Co	Ni	Cu		
α_d(3p)	1.37(1.9)	1.11(1.8)	0.91(1.7)	0.76(1.7)	0.63(1.6)	0.53(1.6)		
α_d(3d)	1.56(2.1)	1.42(2.0)	1.31(2.0)	1.21(1.9)	1.12(1.8)	1.04(1.8)		
VI	Mn	Fe	Co	Ni	Cu			
α_d(3p)	1.05(1.7)	0.87(1.7)	0.72(1.6)	0.61(1.5)	0.52(1.5)			
α_d(3d)	1.17(2.0)	1.08(1.9)	0.98(1.9)	0.90(1.8)	0.85(1.7)			

Table 18.3: Example of a B-spline calculation of α_d in Fe VI.

	Length form	Velocity form
$3s \rightarrow np$	0.011	0.010
$3p \rightarrow ns$	0.035	0.028
$3p \rightarrow nd$	0.827	0.808
$\alpha_d(3p)$	(0.873)	(0.846)
$3d \rightarrow np$	0.041	0.040
$3d \rightarrow nf$	0.165	0.151
$\alpha_d(3d)$	1.079	1.037

18.1 Core and valence excitations

The calculation of transition probabilities now proceeds in three steps:
(i) Calculation of the eigenvectors (expanded in pure $|SLJ\rangle$ coupled states) of both the even and the odd system.
(ii) *Ab initio* calculation of the transition integrals from fully relativistic Dirac-Hartree-Fock (MCDHF) wavefunctions [Parpia et al., 1996].
(iii) Calculation of the final transition matrix by transforming the pure SLJ transition matrix, including the above transition integral(s), by means of the fitted eigenvectors.
Due to the large amount of possibly unknown levels, the fitting procedure is inherently restricted to a limited number of strongly interacting configurations.
Energy effects from configurations outside the model space can be fitted with 'effective' operators based on perturbation theory. Still, the eigenvectors will be truncated to the components of the model space only. The resulting transition probabilities, very sensitive to correlation, therefore remain somewhat defective.
It is the aim of the present paragraph to include correlation with the large number of configurations outside the reference space with second-order perturbation theory.
Let $|\Psi\rangle$ and $\langle\Psi'|$ refer to the full odd and even states of the system, to be approximated by the model states $|\alpha\rangle$ and $\langle\alpha'|$, respectively:

$$\langle\Psi'|\,\boldsymbol{r}\,|\Psi\rangle = \langle\alpha'|\,\boldsymbol{r}\,|\alpha\rangle + \sum_{\beta} \frac{\langle\alpha'|\,\boldsymbol{r}\,|\beta\rangle\,\langle\beta|V|\alpha\rangle}{E_\alpha - E_\beta} + \sum_{\gamma} \frac{\langle\alpha'|V|\gamma\rangle\,\langle\gamma|\,\boldsymbol{r}\,|\alpha\rangle}{E_{\alpha'} - E_\gamma} \tag{18.17}$$

In principle, the above summation runs over all states $\beta(\gamma)$ with the same parity as $\alpha(\alpha')$ that are not included in the model space.
Perturbation theory seems to be a good approximation to the diagonalization approach, even when the interaction strength would favor the latter over the former method. In summary, application of perturbative corrections in addition to diagonalizing the most relevant configurations seems a promising way towards calculating accurate transition probabilities with orthogonal operators.
A simple example with $\langle\alpha'| = \langle 5d^9|$, $|\alpha\rangle = |5d^8 6p\rangle$ and $|\gamma\rangle = |5d^8 6s\rangle$ would be:

$$\langle\Psi'|\,\mathbf{r}\,|\Psi\rangle \approx \left\langle 5d^9\right|\mathbf{r}\left|5d^8 6p\right\rangle + \frac{\langle 5d^9|V|5d^8 6s\rangle\,\langle 5d^8 6s|\,\mathbf{r}\,|5d^8 6p\rangle}{E_{5d} - E_{6s}} \tag{18.18}$$

The results turn out to be in quite good agreement with the results from the full diagonalization procedure:

$$\langle \Psi' | \mathbf{r} | \Psi \rangle \approx \left\langle 5d^9 + 5d^8 6s | \mathbf{r} | 5d^8 6p \right\rangle \tag{18.19}$$

The iron group elements are complicated by the fact that the $n = 3$ shell is not closed so that core excitations such as $3s \rightarrow 3d$ or $3p^2 \rightarrow 3d^2$ are possible within this shell; the effect of the $3s^2 \rightarrow 3d^2$ excitation is usually much smaller. Due to the good overlap between electrons with the same n value these interactions are very large and significantly influence the energy level structure of, for example, the $3d^N$ configurations.

[Quinet, 1995] pointed out that for the calculation of oscillator strengths, the explicit introduction of core excitations is important when considering transitions out of the open $3d^N$ subshell but it is crucial when considering transitions out of the full $3p^6$ subshell.

The transitions from $\langle \alpha' | = \langle 3p^6 3d | \rightarrow | \alpha \rangle = | 3p^5 3d^2 \rangle$ provide the simplest example of this effect. Here, the even system should be extended by $| \gamma \rangle = | 3s 3p^6 3d^2 \rangle$ and $| \gamma \rangle = | 3s^2 3p^4 3d^3 \rangle$, while $| \beta \rangle = | 3s 3p^5 3d^3 \rangle$ and $| \beta \rangle = | 3s^2 3p^3 3d^4 \rangle$ are included in the odd system. The contributions of the γ configurations are dominant, as they yield allowed dipole transitions with the same $3d \rightarrow 3p$ radial dipole integral.

In summary, it is vital to include $3p^2 \rightarrow 3d^2$ core excitations in the calculation of the $3p^6 3d^N - 3p^5 3d^{N+1}$ transition rates in iron group elements.

Similar considerations underline the importance of the $5p^2 \rightarrow 5d^2$ and $4f^2 \rightarrow 5d^2$ core excitations, in the computed radiative lifetimes of W VIII [Prince and Quinet, 2015] with lifetime changes of about 20%.

Likewise, the $3s \rightarrow 3d$ core excitation plays an important role in $E2$ transitions rates, as it corresponds to an allowed quadrupole transition from $3s^2 3p^6 3d$.

Another striking example of this effect is given by the $\langle \alpha' | = \langle 3p^6 3d^8 | \rightarrow | \alpha \rangle = | 3p^5 3d^9 \rangle$ transitions, where especially $| \gamma \rangle = | 3p^4 3d^{10} \rangle$ should be included in the calculation.

18.2 Use with orthogonal operators

Transition probabilities (gA) are calculated from the final fitted parameter values. Intensities of the spectral lines (Int) are commonly obtained by measuring the plate darkening, converting optical density to spectral intensity and subtracting the spectral background approximated by a spline curve. For isolated, unperturbed and unsaturated lines originating from the same upper level or from close upper levels, agreement between gA and Int is usually quite good. Taking into account the Boltzmann factor describing the decrease of population for levels with increasing energy, agreement between the presented gA and Int is good throughout the entire list. Different exposures may have different T values and thus different Boltzmann factors, $\exp(-E/kT)$.

The conventional (Cowan code [Cowan, 1981]) and orthogonal methods of semi-empirical (LSF) calculations of the energy level structures, level compositions and transition probabilities are compared below. Transition probabilities are calculated using eigenvectors obtained in the LSF. Since the level mixing depends strongly on the separation between levels, it is essential that this separation is described accurately. In complex spectra, the separation is often of the same order as the mean

error of the fit or even smaller. However, one cannot describe the level structure in detail when the spacing between levels is smaller or comparable to the mean error. In that case, the calculated eigenvector composition becomes unreliable.
Transition probabilities, calculated by means of the orthogonal operator approach show much better agreement with experimental intensity numbers than values obtained from the conventional method. This is especially true when close lying levels are considered:
"However, difficulties arise when a much larger number of strongly interacting levels have to be included in the same calculation, either because they do interact strongly, or because they are quite high-lying in energy and all levels with lower energy also need to be included in the calculation. Ions with open d-shells are particularly challenging, and we consider now some calculations which have proven and continue to prove difficult for theorists in their attempts to provide oscillator strengths of sufficient accuracy, and with an accuracy which can be substantiated. In this instance though (the Fe II lines 2507.5 and 2509.1 Å, from the close $3d^6 4p/5p$ levels 90042.884$[^6F_{9/2}]$ and 90067.357$[^4G_{9/2}]$), the upper levels were so close in energy that small modifications to the fine-tuning corrections leads to very different mixings and therefore oscillator strengths. Extrapolation such as a fine-tuning process, needs to be undertaken very carefully, moving from the *ab initio* calculation in small steps." [Hibbert, 2018].
Despite the high accuracy of the experimental as well as the orthogonal operator technique discrepancies between the methods remain. Possible error sources in the compared results are as follows.
(i) Inaccurate values for the *ab initio* calculated transition integrals or other contributions to the transition matrix from neglected valence CI effects. In our approach an average level (AL) approximation is used. This means that the transition integrals are not term dependent to this order, just like the energy parameters. Most fitted (electrostatic and magnetic) interactions differ from the *ab initio* calculated value, resulting in scaling factors. The same might be true for the *ab initio* calculated transition integral. Another approach to model the core polarization, such as a different calculation of the polarizability α_d or another choice for the cut-off radius, will affect the value of the transition integrals, but only in the order of a few per cent. Valence effects are accounted for by applying extended CI, but may also be covered by means of perturbation theory [Uylings and Raassen, 1995]. The latter was not applied here. No deviations may occur from the third power of the wavenumber that appears in the expression for the transition probabilities, since the accurate experimental wavenumbers are used in the theoretical model.
(ii) Inaccurate eigenvector compositions, especially for the small contributions, resulting in deviations for intercombination lines (ΔS = 1). We expect that thanks to the small deviations between the experimental and calculated energy values the eigenvector compositions are optimal within the model space of configurations used.

18.3 Illustrative examples

In [Uylings and Raassen, 1996], using data on the Ni V and Fe III spectra, two examples of comparison of the conventional and orthogonal methods are given. The

mean error can be interpreted as the 'blobsize' used by painters (Seurat and others) of the art-movement 'Pointillism'. They used blobs for their painting and could not paint objects smaller than the blobsize. In the same way we cannot describe level structures in detail when the spacing between levels is smaller or comparable to the mean error.

In the Ni V example, the observed separation (22 cm^{-1}) between two $3d^54p$ levels was five times smaller than the mean error of the conventional fit, resulting in the calculated spacing between the levels 13 times larger than the observed one. The orthogonal method resulted in a mean error of two times smaller than the actual level separation and the calculated spacing between the levels close to observed. For the two methods, the mixing between the levels differed enormously; and so did the calculated probabilities of the transitions from the two considered levels. For these levels, the calculated percentages of the same eigenvector components differed by the factors of 0.57 and 4.0 for the leading and second components, respectively. The calculated probabilities of the transitions differed by a factor of up to 1500. In fact, the conventional method failed to predict three of five strongest lines for the first level and two of five strongest lines for the second level. In the Fe III example, the observed separation (46 cm^{-1}) between two $3d^54p$ levels was about three times smaller than the mean error of the conventional fit and two times larger than that for the orthogonal operators fit. Despite the fact that the calculated splitting for these two levels was about the same (near 28 cm^{-1}), the eigenvectors differed considerably between the two methods. For these levels, the calculated percentages of the same eigenvector components differed by the factors of 0.59 and 4.2 for the leading and second components, respectively. This was due to the better description of the positions and spacing of the neighboring levels in the orthogonal calculations. For eight transitions from the two considered levels, the probabilities differed by a factor from 0.1 to 10 between the two methods.

Table 18.4: Two close lying levels in the J = 4 matrix of the $3d^54p$ configuration of Ni V, calculated by the conventional and by the orthogonal method

Conventional method, mean error full fit σ = 120 cm^{-1}				
Exp.	Calc.	Diff.	Eigenvector composition	
296919.3	296645.1	274.2	68%	$(^4D)^5D + 22\%(^4P)^5D$
296897.0	296925.4	-28.4	91%	$(^4G)^3G$

Orthogonal method, mean error full fit σ = 5.4 cm^{-1}				
Exp.	Calc.	Diff.	Eigenvector composition	
296919.3	296645.1	2.3	45%	$(^4D)^5D + 22\%(^4P)^5D$
296897.0	296925.4	6.1	59%	$(^4G)^3G + 25\%(^4D)^5D$

Table 18.5: Two close lying levels in the $J = 5$ matrix of the $3d^5 4p$ configuration of Fe III, calculated by the conventional and by the orthogonal method

Conventional method, mean error full fit $\sigma = 139$ cm^{-1}				
Exp.	Calc.	Diff.	Eigenvector composition	
139509.2	139407.4	101.8	49%	$(^2H)^3I + 21\%(^4F)^3G$
139463.0	139378.4	84.7	40%	$(^2H)^3I + 32\%(^4F)^3G$

Orthogonal method, mean error full fit $\sigma = 12$ cm^{-1}				
Exp.	Calc.	Diff.	Eigenvector composition	
139509.2	139504.1	5.0	83%	$(^2H)^3I + 6\%(^4F)^3G$
139463.0	139476.0	-13.0	44%	$(^2H)^3I + 29\%(^4F)^3G$

Part III

Relativity

Chapter 19

Dirac-Breit equations

The Hamiltonian for an $N-$electron system is given by:

$$H = \sum_i h_i + \sum_{i<j} h_{ij} \tag{19.1}$$

Electromagnetic interactions are included in minimal coupling by the replacement of the kinetic momentum operator $\boldsymbol{p} \to \boldsymbol{\pi} = \boldsymbol{p} - q\mathbf{A}$, with $q = -e$ the electron charge. As an intermediate step towards full relativity, one may consider the minimally coupled Schrödinger-Pauli equation for an electron moving in an electromagnetic field described by a scalar potential Φ and a vector potential $\mathbf{A}$:

$$\left[\tfrac{1}{2}\left(\boldsymbol{p} - q\mathbf{A}\right)^2 + q\Phi - \boldsymbol{\mu}_s \cdot \mathbf{B}\right]\psi = E\,\psi \tag{19.2}$$

Here, ψ is a two-component spinor and $\boldsymbol{\mu}_s = -\mu_B\,\boldsymbol{\sigma}$. The Schrödinger-Pauli equation is the direct non-relativistic limit of Dirac's equation. It can be derived from the Schrödinger equation by the substitution $\boldsymbol{p}^2 \to (\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2$, see further below.
It demonstrates that the electron spin is, contrary to common belief, basically of a non-relativistic nature.

For full relativity, the one-electron Dirac operator with $c = \alpha^{-1}$ is used for h_i:

$$h_i = c\,\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta_i - \mathbb{1})c^2 + \mathbb{1}\,V_i \text{ with } V_i = -Z/r_i + U_i \tag{19.3}$$

The four Hermitian operators β and $\boldsymbol{\alpha}$ anti-commute and their squares are equal to 1. The three components of the polar vector operator $\boldsymbol{\alpha}$ are given by the Dirac matrices $\boldsymbol{\alpha}_i$. The $\boldsymbol{\alpha}_i$ are related to the usual Pauli spin matrices $\boldsymbol{\sigma}_i$ of the axial vector operator $\boldsymbol{\sigma} = 2\boldsymbol{s}$, with the properties $\boldsymbol{\sigma}\cdot\boldsymbol{\sigma} = 3\cdot\mathbb{1}$, $|\boldsymbol{\sigma}_i| = -1$ and $\mathrm{Tr}(\boldsymbol{\sigma}_i) = 0$, by:

$$\boldsymbol{\alpha}_i = \begin{pmatrix} 0 & \boldsymbol{\sigma}_i \\ \boldsymbol{\sigma}_i & 0 \end{pmatrix} \tag{19.4a}$$

The scalar matrix operator β is given by:

$$\beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \qquad \to (\beta - \mathbb{1}) = \begin{pmatrix} 0 & 0 \\ 0 & -2 \end{pmatrix} \tag{19.4b}$$

For the two-particle relativistic energy operator h_{ij}, the usual Coulomb-Breit interaction [Breit, 1929, Breit, 1932] is used; it is the sum of the Coulomb term and

the zero-frequency limit of the transverse Breit interaction:

$$h_{ij} = \frac{1}{r_{ij}} - \left(\frac{\boldsymbol{\alpha_i} \cdot \boldsymbol{\alpha}_j}{2r_{ij}} + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{2r_{ij}^3} \right) \tag{19.5}$$

The ket state is represented by the column vector $\psi = \begin{pmatrix} \Phi \\ \chi \end{pmatrix}$:

$$|nljm) = \begin{vmatrix} [F_{nj}(r)/r] \; |(sl)jm\rangle \\ [iG_{nj}(r)/r] |(s\bar{l})jm\rangle \end{vmatrix} \text{ with } \bar{l} = l \pm 1 \text{ as } j = l \pm \tfrac{1}{2}, \text{ or: } \bar{l} = 2j - l = j \pm \tfrac{1}{2}. \tag{19.6a}$$

Similarly, the Hermitian conjugate or bra state $\psi^\dagger$ is represented by the row vector:

$$(nljm| = \left(\langle (sl)jm|[F_{nj}(r)/r]; -i\langle (s\bar{l})jm|[G_{nj}(r)/r] \right| \tag{19.6b}$$

F_{nj} and G_{nj} are the large and small radial components, normalized as:

$$\int_0^\infty \left(F_{nj}^2 + G_{nj}^2 \right) \, \mathrm{d}r = 1 \tag{19.7}$$

F_{nj} and G_{nj} are calculated self-consistently as one-electron wavefunctions of the Dirac-Breit Hamiltonian. The projection operators $B_\pm = \frac{1}{2}(\mathbb{1} \pm \beta)$ may be used to select either the large or the small component.

$\mathbb{1}, \mathbf{J}^2, \mathbf{L}^2$ and $\mathbf{S}^2$ all commute with the single electron Hamiltonian (19.3), and so does any operator constructed from them.
As $\boldsymbol{\sigma} \cdot \mathbf{L} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2$, the operator $K = -(\mathbb{1} + \boldsymbol{\sigma} \cdot \mathbf{L}) = -(\mathbb{1} + 2\,\mathbf{S} \cdot \mathbf{L})$ will therefore commute with the Dirac Hamiltonian.
With $K \,|\, jlm) = \kappa \cdot |\, jlm)$, the eigenvalues satisfy $\kappa = -\left(1 + j(j+1) - l(l+1) - \frac{3}{4}\right)$:
$\kappa = (l-j)[j] = l(l+1) - j(j+1) - \frac{1}{4} \rightarrow \kappa_\pm = \mp\left(j + \frac{1}{2}\right)$ as $j = l \pm \frac{1}{2} \rightarrow j = |\kappa| - \frac{1}{2}$:
$\kappa_- = l$ for $j = l - \frac{1}{2}$ and $\kappa_+ = -(l+1)$ for $j = l + \frac{1}{2}$. In each case, $\kappa(\kappa+1) = l(l+1)$.
It should be noted that some authors, e.g. [Armstrong and Feneuille, 1974], define κ with an opposite sign; $\overline{\kappa} = -\kappa$ and $\overline{\overline{\kappa}} = \kappa$ still holds of course.
Except for specifying the total angular momentum, κ therewith also defines the parity $(-1)^l$ of the state: $l = j + \frac{\kappa}{2|\kappa|} = j \mp \frac{1}{2}$. As $(-1)^l = -(-1)^{\bar{l}}$, or equivalently $\kappa = -\bar{\kappa}$, the small component χ has the opposite parity of the large component Φ.
The four operators H, J^2, J_z, K now form a complete set of mutually commuting operators with eigenvalues $E = -\varepsilon_{n\kappa}, j(j+1), m, \kappa$. The Dirac equation conserves total angular momentum, but not its separate spin and orbital parts.

The (2×2) Pauli spin matrices form, up to a factor 2, the Cartesian components of the spin angular momentum $\boldsymbol{s}$, the first row and column corresponding to $m_s = \frac{1}{2}$. Therefore, the resulting identification is $s^{(1)} = \frac{1}{2}\sigma^{(1)}$ or $\boldsymbol{s} = \frac{1}{2}\boldsymbol{\sigma}$:

$$s_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad s_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad s_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{19.8}$$

For any two vector operators $\mathbf{a}$ and $\mathbf{b}$ commuting with $\boldsymbol{\sigma}$, the below identity applies:

$$(\boldsymbol{\sigma} \cdot \mathbf{a})\,(\boldsymbol{\sigma} \cdot \mathbf{b}) = (\mathbf{a} \cdot \mathbf{b})\,\mathbb{1} + i\boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}) \tag{19.9}$$

It follows directly that $(\boldsymbol{\sigma}\cdot\boldsymbol{e}_r)^2 = \mathbb{1}$, $(\boldsymbol{\sigma}\cdot\boldsymbol{p})^2 = \boldsymbol{p^2}\mathbb{1}$ and, using equation (1.3):

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 &= \boldsymbol{\pi^2} - q\,\boldsymbol{\sigma}\cdot[(\nabla\times\mathbf{A}) + (\mathbf{A}\times\nabla)] \\ &= \boldsymbol{\pi^2} - q\,\boldsymbol{\sigma}\cdot\mathbf{B} \end{aligned} \tag{19.10}$$

The substitution: $\boldsymbol{p}^2 \to (\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 = (\boldsymbol{\pi^2} - q\,\boldsymbol{\sigma}\cdot\mathbf{B})$ in the Schrödinger equation yields the Schrödinger-Pauli equation (19.2).
In a constant magnetic field $\mathbf{B}$ with $\mathbf{A} = \frac{1}{2}(\mathbf{B}\times\mathbf{r})$ (see section 22.2), expansion of $\boldsymbol{\pi}^2$ keeping only linear B-terms for weak fields yields:

$$\boldsymbol{\pi}^2 \approx \boldsymbol{p}^2 - q\,\mathbf{L}\cdot\mathbf{B} \to (\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 \approx \boldsymbol{p}^2 - q\,(\mathbf{L}+\boldsymbol{\sigma})\cdot\mathbf{B} \tag{19.11}$$

thus retrieving the atomic magnetic moment $(\mathbf{L}+\boldsymbol{\sigma}) = (\mathbf{L}+2\mathbf{S})$ used in section 3.7.

Equation (19.9) may also be put to use to find the effect of $(\boldsymbol{\sigma}\cdot\boldsymbol{p})$ occurring in equation (19.3):

$$(\boldsymbol{\sigma}\cdot\boldsymbol{p}) = (\boldsymbol{\sigma}\cdot\boldsymbol{e}_r)\,[(\boldsymbol{\sigma}\cdot\boldsymbol{e}_r)(\boldsymbol{\sigma}\cdot\boldsymbol{p})] = -i\,(\boldsymbol{\sigma}\cdot\boldsymbol{e}_r)\left[\boldsymbol{e}_r\cdot\nabla - \frac{\boldsymbol{\sigma}\cdot\mathbf{L}}{r}\right] \tag{19.12}$$

Recall that $\nabla f(r) = (\mathrm{d}f/\mathrm{d}r)\,\boldsymbol{e}_r \to \boldsymbol{e}_r\cdot\nabla = \partial/\partial r$ and $-(\boldsymbol{\sigma}\cdot\mathbf{L}) = (K+\mathbb{1})$, so:

$$(\boldsymbol{\sigma}\cdot\boldsymbol{e}_r)\,|\kappa\,m\rangle = -|\overline{\kappa}\,m\rangle \tag{19.13a}$$

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\boldsymbol{p})\;f(r)|\kappa\,m\rangle &= i\left(\frac{\mathrm{d}f}{\mathrm{d}r} + \frac{\kappa+1}{r}f\right)|\overline{\kappa}\,m\rangle \to \\ (\boldsymbol{\sigma}\cdot\boldsymbol{p})\,F/r\,|\kappa\,m\rangle &= \frac{i}{r}\left(\frac{\mathrm{d}F}{\mathrm{d}r} + \kappa\frac{F}{r}\right)|\overline{\kappa}\,m\rangle \end{aligned} \tag{19.13b}$$

Equation (19.13b) turns out to be yet another version of the gradient formula and is used to derive a set of coupled first-order differential equations from equation (19.3): $h_D\,\psi = E\,\psi$ yields $[\boldsymbol{\alpha}\cdot\boldsymbol{p} + (\beta-\mathbb{1})/\alpha + \alpha(V-E)]\,\psi = 0$, or in matrix notation:

$$\begin{pmatrix}\alpha(V-E) & (\boldsymbol{\sigma}\cdot\boldsymbol{p}) \\ (\boldsymbol{\sigma}\cdot\boldsymbol{p}) & \alpha(V-E) - 2/\alpha\end{pmatrix}\quad\begin{vmatrix}F/r\,|\kappa m\rangle \\ iG/r\,|\overline{\kappa}m\rangle\end{pmatrix} = 0 \to \tag{19.14}$$

$$F' + \kappa\cdot F/r + (\alpha(V-E) - 2/\alpha)\cdot G = 0 \tag{19.15a}$$

$$G' - \kappa\cdot G/r - \alpha(V-E)\cdot F = 0 \tag{19.15b}$$

In the Pauli limit $\alpha\to 0$, $F_{nj} \to (1-\frac{1}{4}\alpha^2\cdot T)P_{nl}$ after renormalization with the kinetic energy operator $T = -\frac{1}{2}\mathrm{d}^2/\mathrm{d}r^2 + l(l+1)/2r^2$ and, using $\alpha(V-E) \ll 2/\alpha$:

$$G_{nj} \to \tfrac{1}{2}\alpha(P'_{nl} + \kappa\cdot P_{nl}/r) \tag{19.16}$$

The reader is referred to [Froese Fischer et al., 2016] for a topical review of the *ab initio* multi-configuration methods in this field.
Alternatively, the Pauli spin matrices are also directly related to the 4 by 4 Hermitian and traceless matrices γ^μ satisfying $\{\gamma^\mu,\gamma^\nu\} = 2g^{\mu\nu}$, with $\gamma^0\gamma^i = \boldsymbol{\alpha}_i$ or $\boldsymbol{\gamma} = \beta\boldsymbol{\alpha}$.
The known metric tensor $g_{\mu\nu}$ is given by:

$$g_{\mu\nu} = \begin{pmatrix}1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1\end{pmatrix} \tag{19.17}$$

where $\gamma_\mu = g_{\mu\nu}\gamma^\nu \rightarrow \gamma_0 = \gamma^0$ and $\gamma_i = -\gamma^i$.

$$\gamma^0 = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} = \beta = \beta^{-1} = \gamma^4 \qquad \gamma^i = \begin{pmatrix} 0 & \boldsymbol{\sigma}_i \\ -\boldsymbol{\sigma}_i & 0 \end{pmatrix} \tag{19.18}$$

The γ^μ appear in the covariant form of the Dirac equation:

$$[\gamma^\mu(i\hbar\partial_\mu - eA_\mu) - mc]\,\psi = 0 \tag{19.19}$$

The Dirac representation of the four contravariant gamma matrices is:

$$\gamma^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad \gamma^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$
$$\gamma^2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix} \qquad \gamma^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \tag{19.20}$$

To define a pseudo- or axial vector and a pseudoscalar that both appear in PNC, the product of all four gamma matrices is used: $\gamma^5 = \gamma_5 = i\gamma^0\gamma^1\gamma^2\gamma^3$, where $\{\gamma^5, \gamma^\mu\} = 0$.

$$\gamma^5 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \mathbb{1} \\ \mathbb{1} & 0 \end{pmatrix} \tag{19.21}$$

The upper or lower position of the index 5 is therefore of no significance. Whereas $\psi^\dagger\psi$ is a scalar, $\psi^\dagger\gamma_5\psi$ is a pseudoscalar as it changes sign under parity inversion. Similarly, while $\psi^\dagger\gamma_\mu\psi$ yields a (polar) vector, $\psi^\dagger\gamma_5\gamma_\mu\psi$ classifies as an axial or pseudovector. Other conventions such as $\gamma_i = \begin{pmatrix} 0 & -i\boldsymbol{\sigma}_i \\ i\boldsymbol{\sigma}_i & 0 \end{pmatrix}$ and $\gamma_5 = \pm\gamma_0\gamma_1\gamma_2\gamma_3$ are also in use, where e.g. $\gamma_5 = \begin{pmatrix} 0 & -\mathbb{1} \\ -\mathbb{1} & 0 \end{pmatrix}$. Apparently, γ_5 interchanges the upper and lower component of the relativistic wavefunction.

Chapter 20

Reduced matrix elements

The matrix elements of an operator set between the large and small components of the wavefunctions (19.6), may always be written as (a sum of) diagonal or anti-diagonal contributions.
For a diagonal operator with respective matrix elements $u_{11}^{(t)}$ and $u_{22}^{(t)}$ one finds for the reduced matrix element:

$$\left(p \parallel \hat{U}^{(t)} \parallel q\right) = \left\langle l_1 j_1 \parallel u^{(t)} \parallel l_2 j_2 \right\rangle \int_0^\infty F_1 F_2 U(r)\,\mathrm{d}r + \left\langle \bar{l}_1 j_1 \parallel u^{(t)} \parallel \bar{l}_2 j_2 \right\rangle \int_0^\infty G_1 G_2 U(r)\,\mathrm{d}r \tag{20.1a}$$

and for an anti-diagonal operator with respective matrix elements $v_{12}^{(t)}$ and $v_{21}^{(t)}$:

$$\left(p \parallel \hat{V}^{(t)} \parallel q\right) = i\left\langle l_1 j_1 \parallel v^{(t)} \parallel \bar{l}_2 j_2 \right\rangle \int_0^\infty F_1 G_2 V(r)\,\mathrm{d}r - i\left\langle \bar{l}_1 j_1 \parallel v^{(t)} \parallel l_2 j_2 \right\rangle \int_0^\infty F_2 G_1 V(r)\,\mathrm{d}r \tag{20.1b}$$

[Grant, 1970] names the diagonal operators from equation (20.1a) type A and the anti-diagonal operators from equation (20.1b) type B, respectively.
Both the product of two diagonal and the product of two anti-diagonal operators yield a diagonal operator. The product of a diagonal and an anti-diagonal operator is anti-diagonal with $w_{12} = u_{11}v_{12}$ and $w_{21} = u_{22}v_{21}$. The same is true for the product of an anti-diagonal and a diagonal operator, but here $w_{12} = u_{22}v_{12}$ and $w_{21} = u_{11}v_{21}$.

20.1 Diagonal

An important example of equation (20.1a) for $\hat{U}^{(t)} = f(r)\cdot C^{(t)}$:

$$\begin{aligned}
\left(l_1 j_1 \parallel f(r)\cdot C^{(t)} \parallel l_2 j_2\right) &= \left\langle l_1 j_1 \parallel C^{(t)} \parallel l_2 j_2 \right\rangle \int_0^\infty F_1 F_2 \cdot f(r)\,\mathrm{d}r \\
&+ \left\langle \bar{l}_1 j_1 \parallel C^{(t)} \parallel \bar{l}_2 j_2 \right\rangle \int_0^\infty G_1 G_2 \cdot f(r)\,\mathrm{d}r \\
&= \left\langle j_1 \parallel C^{(t)} \parallel j_2 \right\rangle \int_0^\infty (F_1 F_2 + G_1 G_2)\cdot f(r)\,\mathrm{d}r \\
&= (-1)^{j_1-\frac{1}{2}} \cdot [j_1, j_2]^{\frac{1}{2}} \cdot \begin{pmatrix} j_1 & t & j_2 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \int_0^\infty (F_1 F_2 + G_1 G_2)\cdot f(r)\,\mathrm{d}r \\
&\equiv (-1)^{j_1-\frac{1}{2}} \cdot [j_1, j_2]^{\frac{1}{2}} \cdot \begin{pmatrix} j_1 & t & j_2 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \cdot U_f
\end{aligned} \tag{20.2}$$

In the last steps, use is made of equation (3.51b) and identity (C.52) from [Brink and Satchler, 1968], Appendix II:

$$\begin{aligned}\left\langle \tfrac{1}{2}lj \parallel C^{(t)} \parallel \tfrac{1}{2}l'j' \right\rangle &= (-1)^{\frac{1}{2}+l+j}\,[j,j']^{\frac{1}{2}} \begin{Bmatrix} j & t & j' \\ l' & \frac{1}{2} & l \end{Bmatrix} \left\langle l \parallel C^{(t)} \parallel l' \right\rangle \\ &= (-1)^{j-\frac{1}{2}} \cdot [j,j']^{\frac{1}{2}} \cdot \begin{pmatrix} j & t & j' \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \end{aligned} \tag{20.3}$$

As a result, $\langle j \parallel C^{(t)} \parallel j' \rangle$ explicitly depends on j only as long as $l + t + l'$ is even.
By definition:

$$\int_0^\infty (F_1F_2 + G_1G_2) \cdot f(r)\,\mathrm{d}r = U_f \tag{20.4}$$

and U_k is used for $f(r) = r^k$, such that $U_0 = 1$ if bra and ket are equal. An important example, in accordance with the WE theorem for $k = q = 0$, being:

$$\left\langle \tfrac{1}{2}lj \parallel \mathbb{1} \parallel \tfrac{1}{2}l'j' \right\rangle = \delta(j,j') \cdot [j]^{\frac{1}{2}} \rightarrow \left(\tfrac{1}{2}lj \parallel \mathbb{1} \parallel \tfrac{1}{2}lj \right) = [j]^{\frac{1}{2}} \tag{20.5}$$

20.2 Anti-diagonal

A second, somewhat more complicated example of physical interest is the anti-diagonal operator $\hat{V}^{(t)} = f(r)\,(\boldsymbol{\alpha} C^{(k)})^{(t)}$ with $k = t, t \pm 1$.
With differing conventions and notations, the reduced matrix element is calculated by a number of authors [Bhalla, 1970, Grant, 1970, Grant, 1974, Armstrong, 1966, Armstrong, 1968, Feneuille, 1971, Lindgren and Rosén, 1974].
Below, equation (20.1b) and subsequent techniques are applied to find the more explicit expression (20.10) for the reduced matrix element of this operator:

$$\begin{aligned}&\left(\tfrac{1}{2}l_1j_1 \parallel f(r)(\boldsymbol{\alpha} C^{(k)})^{(t)} \parallel \tfrac{1}{2}l_2j_2 \right) = \\ &i \left\langle \tfrac{1}{2}l_1j_1 \parallel (\boldsymbol{\sigma} C^{(k)})^{(t)} \parallel \tfrac{1}{2}\bar{l}_2j_2 \right\rangle \int_0^\infty F_1G_2 \cdot f(r)\,\mathrm{d}r - i \left\langle \tfrac{1}{2}\bar{l}_1j_1 \parallel (\boldsymbol{\sigma} C^{(k)})^{(t)} \parallel \tfrac{1}{2}l_2j_2 \right\rangle \int_0^\infty G_1F_2 \cdot f(r)\,\mathrm{d}r \end{aligned} \tag{20.6}$$

In turn, $\left\langle \tfrac{1}{2}lj \parallel (\boldsymbol{\sigma} C^{(k)})^{(t)} \parallel \tfrac{1}{2}l'j' \right\rangle$ is found from equations (3.49), (C.55), (C.56) and (C.57), with $\left\langle \frac{1}{2} \parallel \sigma^{(1)} \parallel \frac{1}{2} \right\rangle = \sqrt{6}$:

$$\begin{aligned}\left\langle \tfrac{1}{2}lj \parallel (\sigma^{(1)}C^{(k)})^{(t)} \parallel \tfrac{1}{2}l'j' \right\rangle &= \left\langle \tfrac{1}{2} \parallel \sigma^{(1)} \parallel \tfrac{1}{2} \right\rangle \cdot \left\langle l \parallel C^{(k)} \parallel l' \right\rangle \cdot [j,t,j']^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l' & k \\ j & j' & t \end{Bmatrix} \\ &= \delta(k,t) \cdot (-1)^l \cdot [j,j']^{\frac{1}{2}} \cdot \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} + (-1)^{j'-\frac{1}{2}+t} \cdot [j,j']^{\frac{1}{2}} \cdot \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \\ &\cdot \left\{ \delta(k,t-1) \cdot [\kappa + \kappa' - t] \cdot (t(2t-1))^{-\frac{1}{2}} + \delta(k,t+1) \cdot [\kappa + \kappa' + t + 1] \cdot ((t+1)(2t+3))^{-\frac{1}{2}} \right\} \end{aligned} \tag{20.7}$$

The following recursion formula is a direct result of the above:

$$\left\langle \tfrac{1}{2}lj \parallel (\sigma^{(1)}C^{(t+1)})^{(t)} \parallel \tfrac{1}{2}l'j' \right\rangle = \frac{[\kappa + \kappa' - t]}{[\kappa + \kappa' + t + 1]} \cdot \left(\frac{t(2t-1)}{(t+1)(2t+3)} \right)^{\frac{1}{2}} \cdot \left\langle \tfrac{1}{2}lj \parallel (\sigma^{(1)}C^{(t-1)})^{(t)} \parallel \tfrac{1}{2}l'j' \right\rangle \tag{20.8}$$

To substitute equation (20.7) into equation (20.6), use is made of $\overline{\kappa} = -\kappa$ and $-(-1)^{\bar{l}} = (-1)^{l}$. The following abbreviation is introduced:

$$\int_0^\infty (F_1 G_2 \pm F_2 G_1) \cdot f(r)\,\mathrm{d}r = E_f^{\pm} \tag{20.9}$$

The two RHS terms of equation (20.6) are redistributed to express $\left\langle j \parallel f(r)\,(\boldsymbol{\alpha} C^{(k)})^{(t)} \parallel j' \right\rangle$ in terms of these integrals:

$$a \cdot \int_0^\infty F_1 G_2 \cdot f(r)\,\mathrm{d}r + b \cdot \int_0^\infty G_1 F_2 \cdot f(r)\,\mathrm{d}r = \tfrac{1}{2}(a+b) \cdot E_f^{+} + \tfrac{1}{2}(a-b) \cdot E_f^{-}$$

For the case $k = t \to a = b$, and only E_f^+ is retained. $E_k^{\pm}$ is used for $f(r) = r^k$.
The three options $k = t, t \pm 1$ are listed separately below.

$$\begin{aligned}\left(\tfrac{1}{2} l j \parallel f(r)(\boldsymbol{\alpha} C^{(t-1)})^{(t)} \parallel \tfrac{1}{2} l' j'\right) &= i\,[j,j']^{\frac{1}{2}} \cdot (t(2t-1))^{-\frac{1}{2}} \\ &\cdot (-1)^{j'-\frac{1}{2}+t} \cdot \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot \left[(\kappa - \kappa') E_f^{+} - t \cdot E_f^{-}\right]\end{aligned} \tag{20.10a}$$

$$\left(\tfrac{1}{2} l j \parallel f(r)(\boldsymbol{\alpha} C^{(t)})^{(t)} \parallel \tfrac{1}{2} l' j'\right) = i\,[j,j']^{\frac{1}{2}} \cdot (-1)^{l} \cdot \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \cdot E_f^{+} \tag{20.10b}$$

$$\begin{aligned}\left(\tfrac{1}{2} l j \parallel f(r)(\boldsymbol{\alpha} C^{(t+1)})^{(t)} \parallel \tfrac{1}{2} l' j'\right) &= i\,[j,j']^{\frac{1}{2}} \cdot ((t+1)(2t+3))^{-\frac{1}{2}} \\ &\cdot (-1)^{j'-\frac{1}{2}+t} \cdot \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot \left[(\kappa - \kappa') E_f^{+} + (t+1) E_f^{-}\right]\end{aligned} \tag{20.10c}$$

Examples of frequent interest are found for $\{1kt\} = \{101\}$, $\{110\}$ and $\{111\}$.
The case $\{1kt\} = \{101\}$ and $f(r) = r^0 = 1$ yields $\hat{V}^{(t)} = \boldsymbol{\alpha}$ and turns out to be closely related to the velocity transition operator or the linear momentum operator:

$$\left(\tfrac{1}{2} l j \parallel \boldsymbol{\alpha} \parallel \tfrac{1}{2} l' j'\right) = i\,[j,j']^{\frac{1}{2}} \cdot (-1)^{j'+\frac{1}{2}} \cdot \begin{pmatrix} j & j' & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot \left[(\kappa - \kappa') E_0^{+} - E_0^{-}\right] \tag{20.11}$$

For the important case $f(r) = r^k$, it is often imperative to work out the non-relativistic approximation of the integrals $E_f^{\pm} \equiv E_k^{\pm}$.
Substitution of the Pauli limit $G_j \to \frac{1}{2}\alpha\,(F' + \kappa \cdot F/r)$ yields after integration by parts [1]:

$$E_k^{+} \to \tfrac{1}{2}\alpha \cdot (\kappa_1 + \kappa_2 - k) \cdot \int_0^\infty F_1 F_2 \cdot r^{k-1}\,\mathrm{d}r \tag{20.12a}$$

$$E_k^{-} \to -\tfrac{1}{2}\alpha \cdot (\kappa_1 - \kappa_2 - k) \cdot \int_0^\infty F_1 F_2 \cdot r^{k-1}\,\mathrm{d}r + \alpha \cdot \int_0^\infty F_1 F_2' \cdot r^{k}\,\mathrm{d}r \tag{20.12b}$$

[1] For E_{-2}^{+} and $l = l' = 0$, the boundary term at $r = 0$ does not vanish; the non-relativistic limit becomes: $E_{-2}^{+} \to -\frac{1}{2}\alpha \left\langle \delta(r)/r^2 \right\rangle$ as derived in the below equation (22.23).

It will be interesting to use equations (20.11), (20.12a) and (20.12b) plus the relation $\kappa(\kappa+1) = l(l+1)$ to find the non-relativistic limit of $\left(\frac{1}{2}l_1 j_1 \parallel \boldsymbol{\alpha} \parallel \frac{1}{2}l_2 j_2\right)$:

$$\left(\tfrac{1}{2}lj \parallel \boldsymbol{\alpha} \parallel \tfrac{1}{2}l'j'\right) \approx -i\alpha \cdot [j,j']^{\frac{1}{2}} (-1)^{j'+\frac{1}{2}} \cdot \begin{pmatrix} j & j' & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r}\right] P_{n'l'}\, \mathrm{d}r \tag{20.13}$$

On the other hand, the linear momentum reduced matrix element is, from equations (3.51b), (7.47) and (C.52), given by:

$$\begin{aligned} \left\langle \tfrac{1}{2}lj \parallel \boldsymbol{p} \parallel \tfrac{1}{2}l'j' \right\rangle &= i \cdot (-1)^{\frac{1}{2}+l'+j} \cdot [j,j']^{\frac{1}{2}} \cdot \begin{Bmatrix} j & 1 & j' \\ l' & \frac{1}{2} & l \end{Bmatrix} \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \\ &\quad \cdot \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r}\right] P_{n'l'}\, \mathrm{d}r \\ &= i \cdot [j,j']^{\frac{1}{2}} (-1)^{j'+\frac{1}{2}} \cdot \begin{pmatrix} j & j' & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r}\right] P_{n'l'}\, \mathrm{d}r \end{aligned} \tag{20.14}$$

Comparison of equations (20.13) and (20.14) yields the important non-relativistic limit of the Dirac matrix operator[2]:

$$\left(\tfrac{1}{2}lj \parallel \boldsymbol{\alpha} \parallel \tfrac{1}{2}l'j'\right) \to -\alpha \left\langle \tfrac{1}{2}lj \parallel \boldsymbol{p} \parallel \tfrac{1}{2}l'j' \right\rangle \tag{20.15}$$

The substitution $\boldsymbol{\alpha}_i \to -\alpha \boldsymbol{p}_i$ in equation (19.5) yields the orbit-orbit term (5.122).

For the case $\{1kt\} = \{111\}$, the angular part may by means of equation (3.49) and identity (C.55) due to [Brink and Satchler, 1968], be reduced to:

$$\begin{aligned} \left\langle \tfrac{1}{2}lj \parallel \left(\sigma^{(1)} C^{(1)}\right)^{(1)} \parallel \tfrac{1}{2}l'j' \right\rangle &= \left\langle \tfrac{1}{2} \parallel \sigma^{(1)} \parallel \tfrac{1}{2} \right\rangle \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot [j,1,j']^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l' & 1 \\ j & j' & 1 \end{Bmatrix} \\ &= (-1)^l \cdot [j,j']^{\frac{1}{2}} \cdot \begin{pmatrix} j & j' & 1 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \end{aligned} \tag{20.16}$$

As before with $k = 0$, equation (20.16) is a straightforward special case of equation (20.7) for $k = 1$.

20.3 Continuity equation

The standard form of the continuity equation reads:

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \boldsymbol{v}) = 0 \tag{20.17}$$

The continuity equation for the local conservation of the Dirac charge-current operator $j^\mu = ec\,\psi^\dagger \gamma^0 \gamma^\mu \psi = \{c\rho, \boldsymbol{j}\}$ is given by:

$$\partial_\mu j^\mu = \frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j} = 0 \tag{20.18}$$

[2]The minus sign is the consequence of the now widely adopted sign convention of the small component G_{nj}.

According to (19.6), $\psi = \begin{pmatrix}\Phi\\ \chi\end{pmatrix}$ is a four-component spinor consisting of a large component Φ and a small component χ.
Furthermore, $\rho = \psi^\dagger\psi = |\psi|^2$ is the charge density and $\boldsymbol{j} = c\,\psi^\dagger\gamma^0\gamma^i\psi = \psi^\dagger c\boldsymbol{\alpha}\psi$ the current density. Apparently, $c\boldsymbol{\alpha}$ may be regarded as a relativistic velocity operator. After multiplication with $\alpha = c^{-1}$, it follows:

$$\alpha\cdot\frac{\partial\left(\psi^\dagger\psi\right)}{\partial t} + \boldsymbol{\nabla}\cdot\left(\psi^\dagger\boldsymbol{\alpha}\psi\right) = 0 \tag{20.19}$$

If the bra and ket involve different wavefunctions ψ_i and ψ_f, the continuity equation still applies, but now w.r.t. the transition current density:

$$\alpha\cdot\frac{\partial\left(\psi_i^\dagger\psi_f\right)}{\partial t} + \boldsymbol{\nabla}\cdot\left(\psi_i^\dagger\boldsymbol{\alpha}\psi_f\right) = 0 \tag{20.20}$$

$\partial/\partial t$ is a diagonal operator that explicitly factors out the harmonic time dependence $\exp(-iEt)$ of the wavefunctions. Given that $\langle\kappa_1\,m_1|\kappa_2\,m_2\rangle = \langle\overline{\kappa}_1\,m_1|\overline{\kappa}_2\,m_2\rangle$, this yields the following result:

$$\alpha\cdot\frac{\partial\left(\psi_1^\dagger\,\psi_2\right)}{\partial t} = i\alpha\cdot(E_1-E_2)\cdot\frac{F_1F_2+G_1G_2}{r^2} = -\frac{i}{r^2}\cdot k\,(F_1F_2+G_1G_2)\cdot\langle\kappa_1\,m_1|\kappa_2\,m_2\rangle \tag{20.21a}$$

As $\boldsymbol{\nabla}\cdot\boldsymbol{\alpha}$ is an anti-diagonal operator, one obtains:

$$\begin{aligned}\boldsymbol{\nabla}\cdot\left(\psi_1^\dagger\,\boldsymbol{\alpha}\,\psi_2\right) &= \boldsymbol{\nabla}\cdot\left(\Phi_1^\dagger\,\boldsymbol{\sigma}\,\chi_2+\chi_1^\dagger\,\boldsymbol{\sigma}\,\Phi_2\right)\\ &= \left(\boldsymbol{\sigma}\cdot\nabla\Phi_1^\dagger\right)\chi_2+\left(\boldsymbol{\sigma}\cdot\nabla\chi_1^\dagger\right)\Phi_2+\Phi_1^\dagger\,(\boldsymbol{\sigma}\cdot\nabla\,\chi_2)+\chi_1^\dagger\,(\boldsymbol{\sigma}\cdot\nabla\Phi_2)\\ &= \frac{i}{r^2}\left[(G_1F_2-F_1G_2)'+\frac{\kappa_2-\kappa_1}{r}\,(F_1G_2+G_1F_2)\right]\cdot\langle\kappa_1\,m_1|\kappa_2\,m_2\rangle\end{aligned} \tag{20.21b}$$

where equation (19.13b) is applied fourfold to the second line.
Adding the terms 20.21a and 20.21b and dividing by $-i/r^2\cdot\langle\kappa_1\,m_1|\kappa_2\,m_2\rangle$ gives the continuity equation for the transition current density in terms of the pertinent radial integrals:

$$\frac{\mathrm{d}}{\mathrm{d}r}\,(F_1G_2-G_1F_2)+\frac{\kappa_1-\kappa_2}{r}\cdot(F_1G_2+G_1F_2)+k\cdot(F_1F_2+G_1G_2) = 0 \tag{20.22}$$

Equation (20.22) can e.g. be employed to translate transition amplitudes in the Coulomb gauge to the Babushkin gauge and demonstrate their theoretical equivalence.

Chapter 21

Transformation

Given that, according to equation (5.27):

$$\left(p\left(\tfrac{1}{2}lj\right) \parallel \left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)t} \parallel q\left(\tfrac{1}{2}l'j'\right)\right) = -[\kappa,k]^{\frac{1}{2}} \cdot [j,j',t]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l' & k \\ j & j' & t \end{Bmatrix} \tag{21.1}$$

and the result corresponding to equation (5.20):

$$\left(p \parallel \left(\mathbf{p}^\dagger\mathbf{q}\right)^{(t)} \parallel q\right) = -[t]^{\frac{1}{2}} \tag{21.2}$$

plus the elementary $SL \rightarrow jj$ recoupling following equation (2.37), one finds:

$$\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)t} = \sum_{j,j'} [j,j',\kappa,k]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l' & k \\ j & j' & t \end{Bmatrix} \left(\mathbf{p}^\dagger\mathbf{q}\right)^{(t)} \tag{21.3}$$

where primed quantum numbers refer to the ket state and $\kappa + k + t$ is even for reasons of Hermiticity.
Obviously, combination of two out of the above three equations yields the third.

The operator $\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)t}$ may thus be interpreted as a sum over j-dependent creation-annihilation operators $\mathbf{p}^\dagger/\mathbf{q}$ that operate on the $(2j+1)$ eigenstates $\psi = |nljm)$ of a (central field) Dirac electron. Neglecting coupling of the small components, it follows that $\mathbf{p}^\dagger$ is a tensor operator with ranks $(sl)j$.

In analogy to its non-relativistic counterpart in equation (5.53), each relativistic j-dependent one-electron operator may be written in terms of second quantization as:

$$\hat{F}^{(t)} = -[t]^{-\frac{1}{2}} \left(p \parallel \hat{F}^{(t)} \parallel q\right) \left(\mathbf{p}^\dagger\mathbf{q}\right)^{(t)} = -\hat{S}(p,q) \left(\mathbf{p}^\dagger\mathbf{q}\right)^{(t)} \tag{21.4}$$

From equations (5.68) and (5.69), it follows that a every 'complete' one-particle operator is given by:

$$F^{(\kappa k)t} = -[\kappa,k]^{-\frac{1}{2}} \left\langle a \parallel F^{(\kappa k)} \parallel b\right\rangle \left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)t} = -S(a,b) \left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)t} \tag{21.5}$$

implicitly defining the radial part as:

$$S(a,b) = [\kappa,k]^{-\frac{1}{2}} \left\langle a \parallel F^{(\kappa k)} \parallel b \right\rangle = \int_0^\infty a(r)R(r)b(r)\,\mathrm{d}r \tag{21.6}$$

To find the relativistic expression for $S(a,b)$ as a sum over j-dependent relativistic radial terms $\hat{S}(p,q)$, one multiplies both sides of equation (21.1) with:

$$-S(a,b)\sum_{j,j'}[j,j']^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l' & k \\ j & j' & t \end{Bmatrix}$$

and applies the orthogonality of 9j-symbols, equation (2.19), yielding
$S(a,b) = \sum_{j,j'}[j,j',\kappa,k]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l' & k \\ j & j' & t \end{Bmatrix} \hat{S}(p,q)$ to finally arrive at:

$$S(a,b) \;=\; [t]^{-\frac{1}{2}} \sum_{j,j'} [j,j',\kappa,k]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l' & k \\ j & j' & t \end{Bmatrix} \left(p \parallel \hat{F}^{(t)} \parallel q\right) \tag{21.7}$$

Comparing equations (21.3) and (21.7), one concludes that both the spin-angular and the radial part are transformed in the same way in terms of the underlying j-dependent, relativistic quantities. To include full relativity, however, it suffices to replace just the radial parts by means of equation (21.7).

Chapter 22

Electromagnetic fields

Consider an atom exposed to an electromagnetic field, described by Maxwell's equations $\mathbf{B} = \nabla \times \mathbf{A}$ and $\mathbf{E} = -\nabla\Phi - \partial\mathbf{A}/\partial t$ where Φ and $\mathbf{A}$ denote the usual scalar and vector potential, respectively: $A_\mu = (\Phi, -c\mathbf{A})$. The Hamiltonian for the interaction of an electron with the corresponding vector potential $\mathbf{A}$ reads in au:

$$H = -(\alpha)^{-1} \sum_i \boldsymbol{\alpha}_i \cdot \mathbf{A}(\mathbf{r}_i) \tag{22.1}$$

The Zeeman effect is produced by a constant external magnetic field, whereas hyperfine structure is produced by the nuclear magnetic point dipole. The expressions for these effects turn out to be quite similar. To derive relativistic formulae from equation (21.7), the Hamiltonian is to be converted into tensor operator form first. The Hamiltonians of both the hyperfine structure and the Zeeman effect are split into an electronic and a nuclear (or external magnetic) part. According to equation (21.5), the electronic part is written as:

$$T_e^{(t)} = \sum_{\kappa k} F^{(\kappa k)t} = - \sum_{\kappa k, nl} S_{nl}^{\kappa k} \cdot (\mathbf{a}^\dagger \mathbf{a})^{(\kappa k)t} \tag{22.2}$$

For the magnetic dipole hyperfine structure and the Zeeman effect, $t = 1$.
For the electric quadrupole hyperfine interaction, described by the quadrupole term in the expansion of the electrostatic potential, $t = 2$.

22.1 Hyperfine structure(2)

This is the relativistic sequel of section 3.8. The below derivation of the magnetic dipole and electric quadrupole interactions is based on their relativistic Hamiltonian expressions, transformed to second quantized form by equation (21.7) and equation (20.1b) or (20.1a), respectively.

22.1.1 Magnetic dipole

Using the expression for the potential of a nuclear magnetic point dipole gives:

$$\mathbf{A}(\mathbf{r}) = \alpha^2 \left(\nabla \times \frac{\boldsymbol{\mu}_I}{r} \right) = \frac{\alpha^2}{r^3} \cdot (\boldsymbol{\mu}_I \times \boldsymbol{r})$$

and $\boldsymbol{\mu}_I = (\mu_I/I)\cdot\boldsymbol{I}$ one arrives at:

$$\mathbf{A}_{M_1} = \frac{\mu_I}{I}\cdot\frac{\alpha^2}{r^3}\cdot(\boldsymbol{I}\times\boldsymbol{r}) \tag{22.3}$$

Again using $\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) = -(\mathbf{a}\times\mathbf{c})\cdot\mathbf{b}$ with $\boldsymbol{r}_i = r_i C_i^{(1)}$ and equation (3.17) for the cross product, one obtains the magnetic dipole interaction in spherical tensor form, in au:

$$H_D = -i\sqrt{2}\cdot\frac{\mu_I}{I}\cdot\alpha\ \sum_i\left(\frac{\left(\alpha_i^{(1)}C_i^{(1)}\right)^{(1)}}{r_i^2}\cdot I^{(1)}\right) \tag{22.4}$$

In accordance with [Andersson and Jönsson, 2008, Li et al., 2020], the electronic part is now taken to be:

$$T^{(1)} = -i\sqrt{2}\cdot\alpha\sum_i\ \frac{\left(\alpha_i^{(1)}C_i^{(1)}\right)^{(1)}}{r_i^2} \tag{22.5}$$

Again, equation (20.1b) is used for this anti-diagonal operator:

$$\begin{aligned}&\left(p\parallel T^{(1)}\parallel q\right) = -i\sqrt{2}\cdot\alpha\cdot\left(\tfrac{1}{2}lj\parallel\left(\alpha^{(1)}C^{(1)}\right)^{(1)}\cdot r^{-2}\parallel\tfrac{1}{2}lj'\right)\\ &= \sqrt{2}\cdot\alpha\left(\left\langle\tfrac{1}{2}lj\parallel\left(\sigma^{(1)}C^{(1)}\right)^{(1)}\parallel\tfrac{1}{2}\bar{l}j'\right\rangle\int_0^\infty r^{-2}F_jG_{j'}\,\mathrm{d}r - \left\langle\tfrac{1}{2}\bar{l}j\parallel\left(\sigma^{(1)}C^{(1)}\right)^{(1)}\parallel\tfrac{1}{2}lj'\right\rangle\int_0^\infty r^{-2}G_jF_{j'}\,\mathrm{d}r\right)\end{aligned} \tag{22.6}$$

The (anti-diagonal) radial integrals $P_{jj'}$ are defined by:

$$P_{jj'} = \int_0^\infty\frac{F_{nlj}\,G_{nlj'} + G_{nlj}\,F_{nlj'}}{r^2}\,\mathrm{d}r = E^+_{-2} \tag{22.7}$$

Finally, equation (20.16) with $(-1)^{\bar{l}} = -(-1)^l$ is used to find:

$$\left(p\parallel T^{(1)}\parallel q\right) = \sqrt{2}\cdot\alpha\cdot[j,j']^{\frac{1}{2}}\cdot(-1)^l\cdot\begin{pmatrix} j & j' & 1\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot P_{jj'} \tag{22.8}$$

In second quantized form, the electronic magnetic dipole operator is given by:

$$T^{(1)} = -\sum_{\kappa k}S^{\kappa k}_{nl}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)1}\qquad\text{with } \kappa + k \text{ odd} \tag{22.9}$$

After application of equation (21.7), one arrives for the magnetic dipole case at:

$$S^{\kappa k}_{nl} = \tfrac{1}{3}\sqrt{6}\cdot\alpha\ \sum_{jj'}[j,j']\cdot[\kappa,k]^{\frac{1}{2}}\cdot\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \kappa\\ l & l & k\\ j & j' & 1\end{Bmatrix}(-1)^l\cdot\begin{pmatrix} j & j' & 1\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot P_{jj'} \tag{22.10}$$

Using equations (5.66) to put H_D into second quantized form, the magnetic dipole hyperfine Hamiltonian is effectively written as:

$$\begin{aligned}H_D &= \frac{\mu_I}{I}\left(T^{(1)}\cdot I^{(1)}\right) = -\frac{\mu_I}{I}\sum_{\kappa k}S^{\kappa k}_{nl}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(\kappa k)1}\cdot I^{(1)}\\ &= \sum_i\left(a^{01}_{nl}\,l_i^{(1)} - (10)^{\frac{1}{2}}\cdot a^{12}_{nl}\left(s_iC_i^{(2)}\right)^{(1)} + a^{10}_{nl}\,s_i^{(1)}\right)\cdot\boldsymbol{I}\end{aligned} \tag{22.11}$$

with μ_I in nuclear magnetons and $a^{\kappa k}_{nl}$ in cm^{-1}, the parameters are defined in equation (3.87): $a^{\kappa k}_{nl} = 3.1825571\times10^{-3}\cdot\mu_I/I\cdot\langle r^{-3}\rangle^{\kappa k}_{nl}$.

22.1.2 Electric quadrupole

The electronic part of the electric quadrupole interaction is the diagonal operator:

$$T^{(2)} = -\sum_i C_i^{(2)} r_i^{-3} \tag{22.12}$$

A direct application of equations (20.2) and (20.3) now yields:

$$\begin{aligned} \left(p \parallel \hat{U}^{(t)} \parallel q\right) &= \left(\tfrac{1}{2}lj \parallel -C^{(2)} \cdot r^{-3} \parallel \tfrac{1}{2}lj'\right) \\ &= (-1)^{j+\frac{1}{2}} \cdot [j,j']^{\frac{1}{2}} \cdot \begin{pmatrix} j & 2 & j' \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \cdot T_{jj'} \end{aligned} \tag{22.13}$$

Here, the (diagonal) radial integrals $T_{jj'}$ are defined by:

$$T_{jj'} = \int_0^\infty \frac{F_{nlj}\,F_{nlj'} + G_{nlj}\,G_{nlj'}}{r^3}\,\mathrm{d}r = U_{-3} \tag{22.14}$$

In second quantized form, the electric quadrupole operator is given by:

$$T^{(2)} = -\sum_{\kappa k} S_{nl}^{\kappa k} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(\kappa k)2} \qquad \text{with } \kappa + k \text{ even} \tag{22.15}$$

In combination with equation (21.7), this gives for the electric quadrupole case:

$$S_{nl}^{\kappa k} = \frac{1}{\sqrt{5}} \cdot \sum_{jj'} [j,j'] \cdot [\kappa,k]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l & k \\ j & j' & 2 \end{Bmatrix} (-1)^{j'-\frac{1}{2}} \cdot \begin{pmatrix} j & j' & 2 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot T_{jj'} \tag{22.16}$$

22.1.3 S integrals

The quantities $S_{nl}^{\kappa k}$ may be identified from equations (22.9) and (22.15), and compared to equation (5.66) for the dipole part and equation (5.58) for the quadrupole part, to extract the required relativistic expressions for $\langle r^{-3} \rangle_{nl}^{\kappa k}$ from the proportionality factors.
Below, the contributions of the six parameters to the radial electronic part are written using the explicit expressions from appendices C.1, C.2 and C.3.

As usual, the signs + and − refer to the cases $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$, respectively.

$$S^{01}_{nl} = -\frac{2}{3}\sqrt{3}\cdot[2l(l+1)(2l+1)]^{\frac{1}{2}}\cdot\frac{\alpha}{(2l+1)^2}\cdot[(l+1)P_{++} - P_{+-} - lP_{--}]$$
$$= \alpha^2\cdot\left[\frac{2l(l+1)(2l+1)}{3}\right]^{\frac{1}{2}}\cdot\left\langle r^{-3}\right\rangle^{01}_{nl} \tag{22.17a}$$

$$S^{12}_{nl} = \frac{2}{3}\cdot\left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\cdot\frac{\alpha}{(2l+1)^2}\cdot[2(l+1)(2l-1)P_{++} - (2l-1)(2l+3)P_{+-} + 2l(2l+3)P_{--}]$$
$$= \alpha^2\cdot\left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\cdot\left\langle r^{-3}\right\rangle^{12}_{nl} \tag{22.17b}$$

$$S^{10}_{nl} = -\frac{2}{3}\cdot[2(2l+1)]^{\frac{1}{2}}\cdot\frac{\alpha}{(2l+1)^2}\cdot\left[(l+1)^2P_{++} + 2l(l+1)P_{+-} + l^2P_{--}\right]$$
$$= \alpha^2\cdot\left[\frac{2l+1}{2}\right]^{\frac{1}{2}}\cdot\left\langle r^{-3}\right\rangle^{10}_{nl} \tag{22.17c}$$

$$S^{02}_{nl} = \left[\frac{2\,l(l+1)(2l+1)}{5(2l-1)(2l+3)}\right]^{\frac{1}{2}}\cdot\frac{1}{(2l+1)^2}\cdot[(l+2)(2l-1)T_{++} + 6T_{+-} + (l-1)(2l+3)T_{--}]$$
$$= -\sqrt{\frac{2}{5}}\cdot\left\langle l\parallel C^{(2)}\parallel l\right\rangle\cdot\left\langle r^{-3}\right\rangle^{02}_{nl} = \left[\frac{2\,l(l+1)(2l+1)}{5(2l-1)(2l+3)}\right]^{\frac{1}{2}}\cdot\left\langle r^{-3}\right\rangle^{02}_{nl} \tag{22.17d}$$

$$S^{11}_{nl} = \frac{2}{5}\cdot[l(l+1)(2l+1)]^{\frac{1}{2}}\cdot\frac{1}{(2l+1)^2}\cdot[(l+2)T_{++} - 3T_{+-} - (l-1)T_{--}]$$
$$= \frac{1}{\sqrt{30}}\cdot\left\langle r^{-3}\right\rangle^{11}_{nl} \tag{22.17e}$$

$$S^{13}_{nl} = -\frac{1}{5}\left[\frac{6(l-1)l(l+1)(l+2)(2l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\cdot\frac{1}{(2l+1)^2}\cdot[(2l-1)T_{++} + 4T_{+-} - (2l+3)T_{--}]$$
$$= \frac{1}{\sqrt{70}}\cdot\left\langle r^{-3}\right\rangle^{13}_{nl} \tag{22.17f}$$

The hfs operators are now fully defined by equations (21.5) and (22.17), but the partitioning of S^{11}_{nl} and S^{13}_{nl} into a prefactor and $\langle r^{-3}\rangle^{\kappa k}_{nl}$ is somewhat arbitrary, as they both vanish in the non-relativistic limit. Here, we follow the convention of [Lindgren and Rosén, 1974], later adopted by [Büttgenbach, 1982], to multiply these operators, next to the existing factor $[\kappa,k]^{-\frac{1}{2}}$ due to relation 5.57 between the $U_i^{(\kappa k)t}$ and the $w_i^{(\kappa k)t}$ operators, with an additional factor of $(3/10)^{\frac{1}{2}}$. The partitioning of [Feneuille and Armstrong, 1973] seems in fact more elegant, but has not commonly been used.

22.1.4 The hfs parameter $\langle r^{-3}\rangle$

Based on a formalism of equivalent operators rather than on the more transparent framework of second quantization, [Sandars and Beck, 1965] derived explicit expressions for the effective radial parameters $a^{\kappa k}_{nl}$ and $b^{\kappa k}_{nl}$ appearing in equations (3.87)

and (3.102), in terms of relativistic expressions for $\langle r^{-3}\rangle_{nl}^{\kappa k}$.
In 1982, the work of Sandars and Beck was summarized by [Büttgenbach, 1982]. Although unfortunately not explicitly formulated, both Sandars and Beck and Büttgenbach defined $P_{jj'}$ (or G_{nlj}) with an opposite sign. Therefore, all their magnetic dipole expressions differ from ours by an overall minus sign; other than that, their results agree with the results of section 22.1.3, derived within the overarching structure of second quantization.
In our notation, the $F_{jj'}$ integrals of Sandars and Beck are given as:

$$F_{jj'} = \frac{2}{\alpha(\kappa+\kappa'+2)} \cdot P_{jj'} \tag{22.18}$$

The expressions for $\langle r^{-3}\rangle_{nl}^{\kappa k}$ are readily recognizable in the above results directly derived by second quantization.

for $l \neq 0$:

$$\left\langle r^{-3}\right\rangle_{nl}^{01} = -\frac{2}{\alpha}\cdot\frac{1}{(2l+1)^2}\cdot[(l+1)P_{++} - P_{+-} - lP_{--}] \tag{22.19a}$$

$$\left\langle r^{-3}\right\rangle_{nl}^{12} = \frac{1}{3}\cdot\frac{2}{\alpha}\cdot\frac{1}{(2l+1)^2}[2(l+1)(2l-1)P_{++} - (2l-1)(2l+3)P_{+-} + 2l(2l+3)P_{--}] \tag{22.19b}$$

$$\left\langle r^{-3}\right\rangle_{nl}^{10} = \frac{2}{3}\cdot -\frac{2}{\alpha}\cdot\frac{1}{(2l+1)^2}\left[(l+1)^2P_{++} + 2l(l+1)P_{+-} + l^2P_{--}\right] \tag{22.19c}$$

$$\left\langle r^{-3}\right\rangle_{nl}^{02} = \frac{1}{(2l+1)^2}[(l+2)(2l-1)T_{++} + 6T_{+-} + (2l+3)(l-1)T_{--}] \tag{22.19d}$$

$$\left\langle r^{-3}\right\rangle_{nl}^{11} = \frac{2}{(2l+1)}\left[\frac{6\,l(l+1)}{5(2l+1)}\right]^{\frac{1}{2}}[(l+2)T_{++} - 3T_{+-} - (l-1)T_{--}] \tag{22.19e}$$

$$\left\langle r^{-3}\right\rangle_{nl}^{13} = -\frac{2}{(2l+1)}\left[\frac{21(l+2)(l-1)l(l+1)}{5(2l+3)(2l+1)(2l-1)}\right]^{\frac{1}{2}}[(2l-1)T_{++} + 4T_{+-} - (2l+3)T_{--}]$$

for $l = 0$: (22.19f)

$$\left\langle r^{-3}\right\rangle_{ns}^{01} = \left\langle r^{-3}\right\rangle_{ns}^{12} = 0 \tag{22.19g}$$

$$\left\langle r^{-3}\right\rangle_{ns}^{10} = -\frac{2}{\alpha}\cdot\frac{2}{3}P_{++} = -\frac{8}{3\alpha}\int\frac{F_{ns}G_{ns}}{r^2}\,\mathrm{d}r \to \text{N-R}: \frac{2}{3}\left\langle\frac{\delta(r)}{r^2}\right\rangle_{ns} \tag{22.19h}$$

Likewise, the off-diagonal contact term appearing in spin polarization, is given by:

$$\left\langle n_1 s\left|(r^{-3})^{10}\right|n_2 s\right\rangle = -\frac{4}{3\alpha}\int_0^\infty\frac{F_1G_2+F_2G_1}{r^2}\,\mathrm{d}r \to \text{N-R}: \frac{2}{3}\left\langle n_1 s\left|\frac{\delta(r)}{r^2}\right|n_2 s\right\rangle \tag{22.20}$$

Non-relativistic limits

The non-relativistic limit of the magnetic dipole terms is either found from equation (20.12a) or directly by inserting the P-integrals reduced to their Pauli limit, using $G_j \to \frac{1}{2}\alpha\,(F' + \kappa\cdot F/r)$. Considering the function $f = F/r$, it follows:

$\frac{1}{2}\quad \left[f^2\right]_0^\infty = \int_0^\infty f\,f'\,\mathrm{d}r$ with $f' = \left(\frac{F'}{r} - \frac{F}{r^2}\right)$ and therefore:

$$\frac{1}{2}\quad \left[\frac{F^2}{r^2}\right]_0^\infty = \int_0^\infty\frac{F}{r}\left(\frac{F'}{r} - \frac{F}{r^2}\right)\mathrm{d}r = \int_0^\infty\left(\frac{F\,F'}{r^2} - \frac{F^2}{r^3}\right)\mathrm{d}r = \frac{1}{2}\left(0 - \lim_{r\to 0}\frac{F(r)^2}{r^2}\right) = -\frac{1}{2}\left\langle\frac{\delta(r)}{r^2}\right\rangle.$$

For $l \neq 0$, $\langle \delta(r)/r^2 \rangle = 0$ and therefore $\int_0^\infty FF' \cdot r^{-2}\,\mathrm{d}r = \int_0^\infty F^2 \cdot r^{-3}\,\mathrm{d}r = \langle r^{-3} \rangle$:

$$P_{++} \to \tfrac{1}{2}\alpha \int_0^\infty \frac{2 \cdot F(F' - (l+1) \cdot F/r)}{r^2}\mathrm{d}r \qquad = -\alpha \cdot l \cdot \left\langle r^{-3} \right\rangle \tag{22.21a}$$

$$P_{+-} \to \tfrac{1}{2}\alpha \int_0^\infty \frac{F(2 \cdot F' - F/r)}{r^2}\mathrm{d}r \qquad = \tfrac{1}{2}\alpha \cdot \left\langle r^{-3} \right\rangle \tag{22.21b}$$

$$P_{--} \to \tfrac{1}{2}\alpha \int_0^\infty \frac{2 \cdot F(F' + l \cdot F/r)}{r^2}\mathrm{d}r \qquad = \alpha \cdot (l+1) \cdot \left\langle r^{-3} \right\rangle \tag{22.21c}$$

According to equation (20.12a) the expressions (22.21) for $l \neq 0$ all correspond to:

$$P_{jj'} = E^+_{-2} \to \tfrac{1}{2}\alpha \cdot (\kappa + \kappa' + 2) \cdot \left\langle r^{-3} \right\rangle \tag{22.22}$$

From equations (22.18) and (22.22), it is now readily verified that all $F_{jj'}$ integrals used by [Sandars and Beck, 1965] indeed tend to $\langle r^{-3} \rangle$ in the non-relativistic limit.

Substitution into the $(\kappa k) = (01)$ orbital term (22.19a) gives: $\langle r^{-3} \rangle^{01}_{nl} \to \langle r^{-3} \rangle$.
The similar substitution into the $(\kappa k) = (12)$ spin-dipole term (22.19b) yields again: $\langle r^{-3} \rangle^{12}_{nl} \to \langle r^{-3} \rangle$.
For the contact term $(\kappa k) = (10)$, the result is: $-\frac{4}{3}(\int_0^\infty FF'/r^2\,\mathrm{d}r - \int_0^\infty F^2/r^3\,\mathrm{d}r)$, which becomes zero for $l \neq 0$.

For $l = 0$, it can directly be seen from equations (22.17) that both the orbital and the spin-dipole term vanish .
The non-relativistic reduction of the contact term in the last step in equation (22.19h), may be derived using $G_+ = G_{ns} = \frac{1}{2}\alpha\,(F' - F/r)$:

$$\left\langle r^{-3} \right\rangle^{10}_{ns} \approx -\frac{4}{3}\int_0^\infty \frac{F_{ns}\,(F'_{ns} - F_{ns}/r)}{r^2}\,\mathrm{d}r = -\frac{4}{3}\int_0^\infty \left(\frac{F\,F'}{r^2} - \frac{F^2}{r^3}\right)\,\mathrm{d}r = \frac{2}{3}\left\langle \frac{\delta(r)}{r^2} \right\rangle \tag{22.23}$$

The non-relativistic limit of the off-diagonal contact term (22.20) is found in a similar way:

$$\left\langle n_1 s \left| (r^{-3})^{10} \right| n_2 s \right\rangle \approx \frac{2}{3}\int_0^\infty \left(\frac{2F_1F_2}{r^3} - \frac{(F_1F_2)'}{r^2}\right)\,\mathrm{d}r = -\frac{2}{3}\left[\frac{F_1F_2}{r^2}\right]_0^\infty = \frac{2}{3}\left\langle n_1 s \left| \frac{\delta(r)}{r^2} \right| n_2 s \right\rangle \tag{22.24}$$

For the electric quadrupole terms, non-relativistic limits are obtained from:
$T_{++} = T_{+-} = T_{--} = \langle r^{-3} \rangle$.
Using this, it is straightforward to find from equation (22.19d): $\langle r^{-3} \rangle^{02}_{nl} \to \langle r^{-3} \rangle$.
In the remaining two parameters, the non-relativistic contributions of $T_{jj'}$ cancel:
$\langle r^{-3} \rangle^{11}_{nl} \to 0$ and $\langle r^{-3} \rangle^{13}_{nl} \to 0$.

In summary, for the non-relativistic case one finds for $l \neq 0$:

$$\left\langle r^{-3} \right\rangle^{01}_{nl} = \left\langle r^{-3} \right\rangle^{12}_{nl} = \left\langle r^{-3} \right\rangle^{02}_{nl} = \left\langle r^{-3} \right\rangle_{nl} \text{ and}$$
$$\left\langle r^{-3} \right\rangle^{10}_{nl} = \left\langle r^{-3} \right\rangle^{11}_{nl} = \left\langle r^{-3} \right\rangle^{13}_{nl} = 0. \tag{22.25}$$

22.1.5 Extended nucleus

For contact interactions that take place inside the nucleus, the point nucleus model may easily be oversimplified.

Nuclear size effects are determined by the RMS nuclear radius $\langle r^2 \rangle^{\frac{1}{2}}$, where:

$$\langle r^2 \rangle = \frac{1}{Z} \int \rho(r) \cdot r^2 \, \mathrm{d}^3 r \tag{22.26}$$

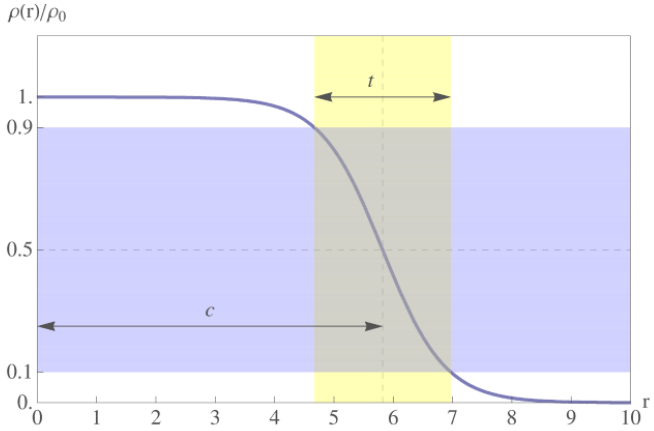
Instead of the point nuclear model, extended nuclear descriptions can be used, the most important being the homogeneous and the two-parameter Fermi charge distribution:

$$\rho(r) = \frac{\rho_0}{1 + e^{(r-c)/a}} = \frac{\rho_0}{1 + \exp\left[4 \ln 3 \cdot \left(\frac{r-c}{t}\right)\right]} \tag{22.27}$$

In the Fermi distribution model, $t = a \cdot 4 \ln 3$ is the surface thickness; typically, $t \approx 2.30$ fm for all nuclei with $A > 9$. In addition, c is the half-density radius: the distance to the $r-$value at which the nuclear charge density is one-half of its maximum.

$$c^2 = \frac{5}{3} \cdot \langle r^2 \rangle - \frac{7}{3} \cdot a^2 \pi^2 \rightarrow \langle r^2 \rangle = \frac{3}{5} \cdot c^2 + \frac{7}{5} a^2 \pi^2 \tag{22.28}$$

$$\rho_0 = \frac{3}{4\pi c^3} \left(1 + \frac{a^2 \pi^2}{c^2}\right)^{-1} \tag{22.29}$$



For nuclei with $A > 9$, the following empirical (in the unit fm) is commonly used:

$$\langle r^2 \rangle^{\frac{1}{2}} = 0.836 \cdot M_{\mathrm{nucl}}^{\frac{1}{3}} + 0.570 \text{ where } M_{\mathrm{nucl}} = A - Z \cdot m_e. \tag{22.30}$$

The homogeneous case is retrieved for $t = a = 0 \rightarrow R = c$.
Then, ρ_0 represents the homogeneous charge density of the nucleus:

$$\rho_0 = \frac{Z}{\frac{4}{3}\pi R^3} \tag{22.31}$$

Inside the nucleus, the potential $V_{\mathrm{out}}(r) = -Z/r$ will as a result be replaced by:

$$V_{\mathrm{in}}(r) = \frac{Z}{2R} \left(\frac{r^2}{R^2} - 3\right) \tag{22.32}$$

Thus, in the homogeneous model one obtains $\langle r^2\rangle = 3R^2/5 \rightarrow c = \sqrt{5/3}\cdot\langle r^2\rangle^{\frac{1}{2}}$.

In table 22.1, the dominant radial hfs parameter a_{6s}^{10} calculated from equations (22.19h) and (3.87) is much closer to experiment with an extended nucleus:

Table 22.1: The hfs parameter a_{6s}^{10} in cm^{-1} for Bi VI and Tl IV compared with experiment.

	MCDF[a]	MCDF[b]	Expt
Bi VI	3.13	2.75	2.87(3)
Pb V	3.29	2.92	-
Tl IV	7.17	6.40	6.43(5)

[a] MCDF, point nucleus model

[b] MCDF, two-parameter Fermi nuclear charge distribution

22.2 Zeeman effect(2)

For a constant magnetic field $\mathbf{B}_0$, one may choose the vector potential:
$\mathbf{A}(\mathbf{r}) = \frac{1}{2}(\mathbf{B}_0\times\mathbf{r})$. This choice may simply be verified for $\mathbf{B}_0 = B_0\,\mathbf{k}$ with the Maxwell equation $\mathbf{B} = \nabla\times\mathbf{A}$:

$$\mathbf{A}(\mathbf{r}) = \tfrac{1}{2}\begin{vmatrix}\mathbf{i} & \mathbf{j} & \mathbf{k}\\ 0 & 0 & B_0\\ x & y & x\end{vmatrix} = -(\tfrac{1}{2}yB_0)\,\mathbf{i} + (\tfrac{1}{2}xB_0)\,\mathbf{j} \rightarrow$$

$$\mathbf{B} = \nabla\times\mathbf{A} = \begin{vmatrix}\mathbf{i} & \mathbf{j} & \mathbf{k}\\ \partial/\partial x & \partial/\partial y & \partial/\partial z\\ -\frac{1}{2}yB_0 & \frac{1}{2}xB_0 & 0\end{vmatrix} = (\tfrac{1}{2}B_0 + \tfrac{1}{2}B_0)\,\mathbf{k} = B_0\,\mathbf{k}$$

This leads to the following relativistic Hamiltonian for the Zeeman effect:

$$H_Z = -\tfrac{1}{2}(\alpha)^{-1}\sum_i \boldsymbol{\alpha}_i\cdot(\mathbf{B}_0\times\mathbf{r}_i) = -\tfrac{1}{2}\cdot\frac{i\sqrt{2}}{\alpha}\cdot\sum_i\left(r_i\left(\alpha_i^{(1)}C_i^{(1)}\right)^{(1)}\cdot B_0^{(1)}\right) \tag{22.33}$$

where in the last step, use is made from $\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) = -(\mathbf{a}\times\mathbf{c})\cdot\mathbf{b}$ with $\vec{r}_i = r_i C_i^{(1)}$ and equation (3.17) for the cross product and H_Z, like H_D in equation (22.4), is given in au.
Again in accordance with [Andersson and Jönsson, 2008, Li et al., 2020], the (anti-diagonal) electronic part is defined as:

$$\left(p \parallel N^{(1)} \parallel q\right) \;=\; -\tfrac{1}{2}\cdot\frac{i\sqrt{2}}{\alpha}\cdot\left(\tfrac{1}{2}lj \parallel r\left(\alpha^{(1)}C^{(1)}\right)^{(1)} \parallel \tfrac{1}{2}lj'\right) \tag{22.34}$$

The radial integrals that arise are defined as:

$$D_{jj'} = \tfrac{1}{2}\int_0^\infty r\,(F_{nlj}\,G_{nlj'} + G_{nlj}\,F_{nlj'})\;\mathrm{d}r = \tfrac{1}{2}\cdot E_1^+ \tag{22.35}$$

Equation (20.1b) gives:

$$\begin{aligned}&\left(\tfrac{1}{2}lj \parallel r\left(\alpha^{(1)}C^{(1)}\right)^{(1)} \parallel \tfrac{1}{2}lj'\right)\\&= i\left\langle \tfrac{1}{2}lj \parallel \left(\sigma^{(1)}C^{(1)}\right)^{(1)} \parallel \tfrac{1}{2}\bar{l}j'\right\rangle \int_0^\infty rF_jG_{j'}\,\mathrm{d}r - i\left\langle \tfrac{1}{2}\bar{l}j \parallel \left(\sigma^{(1)}C^{(1)}\right)^{(1)} \parallel \tfrac{1}{2}lj'\right\rangle \int_0^\infty rG_jF_{j'}\,\mathrm{d}r\end{aligned} \tag{22.36}$$

Equation (20.16) with $(-1)^{\bar{l}} = -(-1)^l$ is used to find:

$$\left(p \parallel N^{(1)} \parallel q\right) = \frac{\sqrt{2}}{\alpha}\cdot[j,j']^{\frac{1}{2}}\cdot(-1)^l\cdot\begin{pmatrix} j & j' & 1\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot D_{jj'} \tag{22.37}$$

Radial factors $S^{\kappa k}$ associated with a relativistic tensor operator $F^{(\kappa k)t}$ are defined by equation (21.5):

$$F^{(\kappa k)t} = -S^{\kappa k}\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)t}$$

After application of equation (21.7), one arrives at:

$$S^{Z,\kappa k}_{nl} = \frac{\sqrt{6}}{3\alpha}\cdot\sum_{jj'}[j,j']\cdot[\kappa,k]^{\frac{1}{2}}\cdot\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \kappa\\ l & l & k\\ j & j' & 1\end{Bmatrix}(-1)^l\cdot\begin{pmatrix} j & j' & 1\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot D_{jj'} \tag{22.38}$$

Here, the three allowed values are $\kappa k = 01, 10$ and 12. As the non-relativistic atomic magnetic moment is given by $\vec{\mu} = -\mu_B M^{(1)} = -\frac{1}{2}\cdot(L^{(01)1} + g_s S^{(10)1})$, it is immediately clear that the spin-dipole term $\kappa k = 12$ is purely relativistic. Obviously, equation (22.38) bears a striking resemblance to equation (22.10), and the three radial factors may be written accordingly:

$$\begin{aligned}S^{01}_{nl} &= -\frac{2}{3\alpha}\sqrt{3}\cdot[2l(l+1)(2l+1)]^{\frac{1}{2}}\cdot\frac{1}{(2l+1)^2}\cdot[(l+1)D_{++} - D_{+-} - lD_{--}]\\&= \left[\frac{l(l+1)(2l+1)}{6}\right]^{\frac{1}{2}}\cdot a^{01}\end{aligned} \tag{22.39a}$$

$$\begin{aligned}S^{10}_{nl} &= -\frac{2}{3\alpha}\cdot[2(2l+1)]^{\frac{1}{2}}\cdot\frac{1}{(2l+1)^2}\cdot\left[(l+1)^2D_{++} + 2l(l+1)D_{+-} + l^2D_{--}\right]\\&= \left[\frac{2l+1}{2}\right]^{\frac{1}{2}}\cdot a^{10}\end{aligned} \tag{22.39b}$$

$$\begin{aligned}S^{12}_{nl} &= \frac{2}{3\alpha}\cdot\left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\cdot\frac{1}{(2l+1)^2}\cdot[2(l+1)(2l-1)D_{++} - (2l-1)(2l+3)D_{+-} + 2l(2l+3)D_{--}]\\&= \left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{\frac{1}{2}}\cdot a^{12}\end{aligned} \tag{22.39c}$$

Equations (22.17) transform into (22.39) by the substitution $\alpha^2\left\langle r^{-3}\right\rangle^{\kappa k}_{nl}\cdot P_{jj'} \to \frac{1}{2}a^{\kappa k}\cdot D_{jj'}$, bearing in mind that the Zeeman operators for $\kappa k = (10)$ and (12) carry

an additional factor of two.
Summarizing, the relativistic expression in tensor operator form is written:

$$H_Z = \mathbf{B_0} \cdot \sum_{\kappa,k} F^{(\kappa k)1} = -\mathbf{B_0} \cdot \sum_{\kappa,k} S^{\kappa k}_{nl} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(\kappa k)1}$$
$$= -\mathbf{B_0} \cdot \left\{ S^{01}_{nl} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(01)1} + S^{10}_{nl} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(10)1} + S^{12}_{nl} \left(\mathbf{a}^\dagger \mathbf{a}\right)^{(12)1} \right\} \quad (22.40)$$

$H_Z = -\vec{\mu} \cdot \vec{B}_0 = \mathbf{B_0} \cdot \frac{1}{2} M^{(1)}$ may be rewritten to facilitate comparison with its non-relativistic counterpart:

$$H_Z = \mathbf{B_0} \cdot \tfrac{1}{2} \left(a^{01} L^{(01)1} + \left[2a^{10} + (g_s - 2)\right] S^{(10)1} - 2(10)^{\frac{1}{2}} a^{12} \sum_i \left(sC^{(2)}\right)^{(1)}_i \right) \quad (22.41)$$

where the $a^{\kappa k}$ coefficients are related to the $S^{\kappa k}_{nl}$ factors through equations (5.66):

$$a^{01} = -\frac{4}{\alpha} \cdot \frac{1}{(2l+1)^2} \cdot \left[(l+1)D_{++} - D_{+-} - lD_{--}\right] \quad (22.42a)$$

$$a^{10} = -\frac{4}{3\alpha} \cdot \frac{1}{(2l+1)^2} \cdot \left[(l+1)^2 D_{++} + 2l(l+1)D_{+-} + l^2 D_{--}\right] \quad (22.42b)$$

$$a^{12} = \frac{2}{3\alpha} \cdot \frac{1}{(2l+1)^2} \cdot \left[2(l+1)(2l-1)D_{++} - (2l-1)(2l+3)D_{+-} + 2l(2l+3)D_{--}\right] \quad (22.42c)$$

The Landé g-factor is defined as: $g_J = \left[J(J+1)(2J+1)\right]^{-\frac{1}{2}} \cdot \langle \alpha J \parallel M^{(1)} \parallel \alpha J \rangle$.
To find a relativistic expression for the g-factor, it suffices to replace the non-relativistic form $M^{(1)}_{NR} = \left(L^{(01)1} + g_s \cdot S^{(10)1}\right)$ with its relativistic equivalent: $M^{(1)}_R = \left(a^{01} L^{(01)1} + \left[2a^{10} + (g_s - 2)\right] S^{(10)1} - 2(10)^{\frac{1}{2}} a^{12} \sum_i \left(sC^{(2)}\right)^{(1)}_i \right)$.

22.2.1 Non-relativistic limit

The non-relativistic limit of the Zeeman terms is found from equation (20.12a) with $k = 1$:

$$D_{jj'} = \tfrac{1}{4}\alpha \cdot (\kappa + \kappa' - 1) \quad (22.43)$$

This leads to the radially independent expressions:

$$D_{++} = \tfrac{1}{4}\alpha \int_0^\infty 2 \cdot r \left[F(F' - (l+1) \cdot F/r)\right] \mathrm{d}r = -\tfrac{1}{4}\alpha \cdot (2l+3) \quad (22.44a)$$

$$D_{+-} = \tfrac{1}{4}\alpha \int_0^\infty r \left[F(2 \cdot F' - F/r)\right] \quad \mathrm{d}r = -\tfrac{1}{2}\alpha \quad (22.44b)$$

$$D_{--} = \tfrac{1}{4}\alpha \int_0^\infty 2 \cdot r \left[F(F' + l \cdot F/r)\right] \quad \mathrm{d}r = \tfrac{1}{4}\alpha \cdot (2l-1) \quad (22.44c)$$

Inserting the above non-relativistic expressions into equations (22.39) and (22.42) yields:

$$S^{01}_{nl} = \left[\frac{l(l+1)(2l+1)}{6}\right]^{\frac{1}{2}} \rightarrow a^{01} = 1 \quad (22.45a)$$

$$S^{10}_{nl} = \left[\frac{2l+1}{2}\right]^{\frac{1}{2}} \rightarrow a^{10} = 1 \quad (22.45b)$$

$$S^{12}_{nl} = 0 \rightarrow a^{12} = 0 \quad (22.45c)$$

These results may have also directly been retrieved by comparing equation (22.40) with the second quantized form of the non-relativistic expression for H_Z using equations (5.66) and dropping the QED[1] correction $\frac{1}{2}(g_s-2)\sigma^{(1)} = (g_s-2)S^{(1)}$ for the moment so that $g_s \to 2$:

$$\begin{aligned} H_Z &= -\vec{\mu}\cdot\vec{B}_0 = \mathbf{B_0}\cdot\tfrac{1}{2}M^{(1)} \\ &= -\mathbf{B_0}\cdot\left\{\left[\frac{l(l+1)(2l+1)}{6}\right]^{\frac{1}{2}}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(01)1} + \left[\frac{2l+1}{2}\right]^{\frac{1}{2}}\left(\mathbf{a}^\dagger\mathbf{a}\right)^{(10)1}\right\} \end{aligned} \tag{22.46}$$

To compare all of the above with [Armstrong and Feneuille, 1974], one should be aware that they define both κ and G_{nlj} with the opposite sign; they use Gaussian CGS units in which the Bohr magneton μ_0 corresponds $\mu_B/c = \frac{1}{2}\alpha$ in atomic units.

[1] The operator $\frac{1}{2}(g_s-2)\begin{pmatrix}\boldsymbol{\sigma} & 0\\ 0 & -\boldsymbol{\sigma}\end{pmatrix}$ in question is sometimes called Schwinger's QED correction.

Chapter 23

Transition probabilities(2)

The transition operator T for the transition between two electron states is once again given by the interaction of the electron in question and the field of free photons given by the scalar potential Φ and the vector potential $\mathbf{A}$:

$$T = \left[-(\alpha)^{-1} \sum_i \boldsymbol{\alpha}_i \cdot \mathbf{A}(\mathbf{r}_i) + \Phi(\mathbf{r}_i) \right] \cdot \exp(-i\omega t) \tag{23.1}$$

Recall that $A_\mu = (\Phi, -c\mathbf{A})$, satisfying $\Box A_\mu = \left[(\partial/\partial ct)^2 - \nabla^2 \right] A_\mu = 0$.
In the following, the harmonic time dependence is factored out and only spatial components are considered. According to equation (8.22), the vector potential for a photon $(\omega, \mathbf{k})$ with a polarization vector $\mathbf{e}$ (equations (3.10)) is given in the Coulomb (transverse) gauge by the plane wave description:

$$\mathbf{A}(\mathbf{r}, \omega) = \mathbf{e} \cdot \exp(i\, \mathbf{k} \cdot \mathbf{r}) \tag{23.2}$$

while the scalar potential $\Phi(\mathbf{r}, \omega)$ vanishes. Thereby:

$$T = -(\alpha)^{-1} \sum_i (\boldsymbol{\alpha}_i \cdot \mathbf{e}) \exp(i\, \mathbf{k_i} \cdot \mathbf{r_i}) \tag{23.3}$$

Next, the vector potential $\mathbf{A}$ may be expanded in terms of Vector Spherical Harmonics (VSH, equation (3.8)), separating radial and angular dependence.
First, the plane wave expansion is used:

$$\begin{aligned} \exp(i\, \mathbf{k} \cdot \mathbf{r}) &= \sum_\lambda i^\lambda \cdot [4\pi(2\lambda+1)]^{\frac{1}{2}} \cdot j_\lambda(kr) \cdot Y_{\lambda 0} \\ &= \sum_\lambda i^\lambda \cdot [\lambda] \cdot j_\lambda(kr) \cdot C_0^{(\lambda)} \end{aligned} \tag{23.4}$$

The radial transition operator may therefore be expressed in terms of spherical Bessel functions of the first kind $j_\lambda(kr) = j_\lambda(\omega r/c) = j_\lambda(\alpha\omega r)$.
They are related to the ordinary Bessel functions by: $j_\lambda(kr) = \sqrt{\pi/2kr} \cdot J_{\lambda+\frac{1}{2}}(kr)$.
They satisfy the recurrence relations:

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\lambda+1}{r} \right) j_\lambda(kr) = k \cdot j_{\lambda-1}(kr) \tag{23.5a}$$

$$\left(-\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\lambda}{r} \right) j_\lambda(kr) = k \cdot j_{\lambda+1}(kr) \tag{23.5b}$$

It follows directly from the above:

$$j_{\lambda-1}(kr) + j_{\lambda+1}(kr) = \frac{2\lambda+1}{kr} \cdot j_\lambda(kr) \tag{23.6a}$$

$$\lambda j_{\lambda-1}(kr) - (\lambda+1) j_{\lambda+1}(kr) = \frac{2\lambda+1}{k} \cdot \frac{\mathrm{d}\, j_\lambda(kr)}{\mathrm{d}r} \tag{23.6b}$$

In the long wavelength approximation $kr \ll 1$, they reduce to the below first term of the Taylor expansion:

$$j_\lambda(kr) \approx \frac{(kr)^\lambda}{(2\lambda+1)!!} \rightarrow j_1(kr) \approx \frac{kr}{3} \text{ and } j_2(kr) \approx \frac{(kr)^2}{15} \tag{23.7}$$

Multiplication with $\mathbf{e}_q^{(1)}$ and use of equations (3.9) and (3.8) now yields the required expansion of a plane wave in terms of VSH:

$$\begin{aligned} \mathbf{e}_q^{(1)} \exp(i\,\mathbf{k}\cdot\mathbf{r}) &= \sum_\lambda i^\lambda \cdot [4\pi(2\lambda+1)]^{\frac{1}{2}} \cdot j_\lambda(kr) \cdot Y_{\lambda 0} \cdot \mathbf{e}_q^{(1)} \\ &= \sum_{K,\lambda} i^\lambda \cdot [4\pi(2\lambda+1)]^{\frac{1}{2}} \cdot j_\lambda(kr) \cdot (\lambda 0\; 1q|Kq) \mathbf{Y}_{K\lambda q} \end{aligned} \tag{23.8}$$

Here also, [Brink and Satchler, 1968, Grant, 1970] and [Feneuille, 1971] put equation (3.9) to use, with the pertinent $3j$–symbols $\begin{pmatrix} \lambda & 1 & K \\ 0 & q & -q \end{pmatrix}$ in appendix C.4:

$$\begin{aligned} \alpha_q^{(1)} C_0^{(\lambda)} &= \sum_K (1q\;\lambda 0|Kq) \cdot \left(\alpha^{(1)} C^{(\lambda)}\right)_q^{(K)} \\ &= \sum_K (-1)^{K+q} \cdot [K]^{\frac{1}{2}} \cdot \begin{pmatrix} \lambda & 1 & K \\ 0 & q & -q \end{pmatrix} \cdot \left(\alpha^{(1)} C^{(\lambda)}\right)_q^{(K)} \end{aligned} \tag{23.9}$$

23.1 Vector multipole fields

However, the required result can be found in a more direct way by application of the three vector field operators ∇, $(\nabla \times \mathbf{L})$ and $\mathbf{L}$ to the below spherical tensor form of the scalar potential field [Edmonds, 1957]:

$$\Phi_{LM} = i^L \cdot [L] \cdot j_L(kr) \cdot C_M^{(L)} \tag{23.10}$$

This operation yields three mutually orthogonal multipole fields directly associated with the longitudinal, electric and magnetic vector field, respectively: $\mathbf{A}^l_{LM}, \mathbf{A}^e_{LM}$ and $\mathbf{A}^m_{LM}$. Both Φ_{LM} and the three vector potentials $\mathbf{A}_k$ satisfy the Helmholtz wave equation with wave number k:

$$\begin{aligned} \nabla^2 \Phi_k + k^2 \Phi_k &= 0 \\ \nabla^2 \mathbf{A}_k + k^2 \mathbf{A}_k &= 0 \end{aligned} \tag{23.11}$$

With the same normalization as Φ_{LM}, one obtains [1]:

$$c\mathbf{A}^l_{LM} = (ik)^{-1} \nabla\, \Phi_{LM} \tag{23.12a}$$

$$c\mathbf{A}^e_{LM} = \left[k\sqrt{L(L+1}\right]^{-1} (\nabla \times \mathbf{L})\, \Phi_{LM} \tag{23.12b}$$

$$c\mathbf{A}^m_{LM} = \left[\sqrt{L(L+1}\right]^{-1} \mathbf{L}\, \Phi_{LM} \tag{23.12c}$$

[1] The vector potentials $c\mathbf{A}$ rather than $\mathbf{A}$ are used here for agreement with [Grant, 2007].

From equation (23.11), it follows that they are interrelated as:

$$\mathbf{A}^e_{LM} = k^{-1}\left(\nabla \times \mathbf{A}^m_{LM}\right) \tag{23.13a}$$
$$\mathbf{A}^m_{LM} = k^{-1}\left(\nabla \times \mathbf{A}^e_{LM}\right) \tag{23.13b}$$

The properties of (V)SH, listed e.g. in equations 5.9.14-23 of [Edmonds, 1957], are now utilized to find the effect of the three operators ∇, $(\nabla\times\mathbf{L})$ and $\mathbf{L}$ on $j_L(kr)Y_{LM}$:

$$\nabla\, j_L(kr)Y_{LM} = \frac{k}{\sqrt{2L+1}}\left[\sqrt{L}\cdot j_{L-1}(kr)\mathbf{Y}_{L\,L-1\,M} + \sqrt{L+1}\cdot j_{L+1}(kr)\mathbf{Y}_{L\,L+1\,M}\right] \tag{23.14a}$$

$$(\nabla\times\mathbf{L})\, j_L(kr)Y_{LM} = ik\sqrt{\frac{L(L+1)}{2L+1}}\left[\sqrt{L+1}\cdot j_{L-1}(kr)\mathbf{Y}_{L\,L-1\,M} - \sqrt{L}\cdot j_{L+1}(kr)\mathbf{Y}_{L\,L+1\,M}\right] \tag{23.14b}$$

$$\mathbf{L}\, j_L(kr)Y_{LM} = [L(L+1)]^{\frac{1}{2}}\cdot j_L(kr)\mathbf{Y}_{LLM} \tag{23.14c}$$

Below, the VSH below are written in a slightly adapted version [Grant, 1974]:

$$\left(e^{(1)}C^{(k)}\right)^{(L)}_M = (-1)^{1+k-L}\cdot\left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}}\cdot\left(Y^{(k)}e^{(1)}\right)^{(L)}_M = (-1)^{1+k-L}\cdot\left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}}\cdot\mathbf{Y}_{LkM} \tag{23.15}$$

Alternatively, [Bhalla, 1970] uses $T^M_{L,k} = (-1)^{1+k-L}\cdot\mathbf{Y}_{LkM}$ and [Lindgren and Rosén, 1974] $C^{Lk}_M = (4\pi/2k+1)^{\frac{1}{2}}\cdot\mathbf{Y}_{LkM} = \left(C^{(k)}e^{(1)}\right)^{(L)}_M$.

Combining equations 23.12 and 23.14, the vector multipole fields are finally [2]:

$$\begin{aligned} c\mathbf{A}^l_{LM} &= i^{L-1}[L(2L-1)]^{\frac{1}{2}} j_{L-1}(kr)\left(e^{(1)}C^{(L-1)}\right)^{(L)}_M \\ &\quad -i^{L+1}[(L+1)(2L+3)]^{\frac{1}{2}} j_{L+1}(kr)\left(e^{(1)}C^{(L+1)}\right)^{(L)}_M \end{aligned} \tag{23.16a}$$

$$\begin{aligned} c\mathbf{A}^e_{LM} &= -i^{L-1}[(L+1)(2L-1)]^{\frac{1}{2}} j_{L-1}(kr)\left(e^{(1)}C^{(L-1)}\right)^{(L)}_M \\ &\quad -i^{L+1}[L(2L+3)]^{\frac{1}{2}} j_{L+1}(kr)\left(e^{(1)}C^{(L+1)}\right)^{(L)}_M \end{aligned} \tag{23.16b}$$

$$c\mathbf{A}^m_{LM} = -i^L(2L+1) j_L(kr)\left(e^{(1)}C^{(L)}\right)^{(L)}_M \tag{23.16c}$$

$\mathbf{A}^l_{LM}$ and $\mathbf{A}^e_{LM}$ have parity $(-1)^{L+1}$, while Φ_{LM} and $\mathbf{A}^m_{LM}$ have parity $(-1)^L$.
$\mathbf{A}^e_{LM}$ and $\mathbf{A}^m_{LM}$ are transverse as $\nabla\cdot\mathbf{A}^e_{LM} = \nabla\cdot\mathbf{A}^m_{LM} = 0$, which can directly be seen from equations (23.12).
Similarly, $\mathbf{A}^l_{LM}$ turns out to be longitudinal: $\nabla\cdot c\mathbf{A}^l_{LM} = ik\cdot\Phi_{LM}$ and $\nabla\times\mathbf{A}^l_{LM} = 0$.
As a result, both $\mathbf{A}^l_{LM}$ and Φ_{LM} do not contribute in the Coulomb gauge $\nabla\cdot\mathbf{A} = 0$.
In the Coulomb gauge, with the gauge parameter $G_L = 0$ [Grant, 1974], the expansion of a plane wave traveling in the $z-$direction becomes [Brink and Satchler, 1968], equation (4.47):

$$\mathbf{e}^{(1)}_q \exp(ikz) = -\frac{1}{\sqrt{2}}\sum_L\left(q\mathbf{A}^m_{Lq} + \mathbf{A}^e_{Lq}\right) \tag{23.17}$$

[2] Expressions 23.16 all agree with [Grant, 1974, Grant, 2007] except for two misprints in the longitudinal potential in the last reference.

However, the potential $A_\mu = (\Phi, -c\mathbf{A})$ is not uniquely defined, as gauge transformations $A_\mu \to A_\mu + \partial_\mu \Lambda$, with $\Box\Lambda = 0$, leave the Maxwell equations unchanged.
In terms of spherical tensors: $\Lambda_L = G_L \cdot \Phi_{LM} \exp(-i\omega t)$.
The potentials in any gauge then become:

$$\Phi_{LM} \to \Phi_{LM} + \frac{\partial \Lambda_L}{\partial t} = (1 - ik\, G_L)\, \Phi_{LM}$$
$$\mathbf{A}^e_{LM} \to \mathbf{A}^e_{LM} - \nabla\Lambda_L = \mathbf{A}^e_{LM} + G_L \mathbf{A}^l_{LM} \tag{23.18}$$

23.2 Multipole radiation matrix elements

The multipole expansion of the transition operator $T = \Phi - c\boldsymbol{\alpha}\cdot\mathbf{A}$ is written as:

$$T = \sum_L T^{(L)l} + T^{(L)e} + T^{(L)m} = \sum_L (\Phi_{LM} - \boldsymbol{\alpha}\cdot c\mathbf{A}^l_{LM}) - \boldsymbol{\alpha}\cdot(c\mathbf{A}^e_{LM} + c\mathbf{A}^m_{LM}) \tag{23.19}$$

Electric multipoles can be found in any gauge of choice by adding $G_L \cdot T^{(L)l}$ to $T^{(L)e}$.
Judging from equations (23.16), T may always be reduced to operators of the type $j_\lambda(kr)\left(\boldsymbol{\alpha}\cdot(e^{(1)}C^{(\lambda)})^{(L)}_M\right) = j_\lambda(kr)\,(\boldsymbol{\alpha}C^{(\lambda)})^{(L)}_M$ with $\lambda = L, L\pm 1$. The corresponding matrix elements may therefore directly be evaluated with equations (20.10).
The occurring radial integrals are defined as in [Bhalla, 1970]:

$$I^\pm_\lambda(k) = \int_0^\infty (F_1 G_2 \pm G_1 F_2)\, j_\lambda(kr)\mathrm{d}r \approx \frac{k^\lambda}{(2\lambda+1)!!}\cdot E^\pm_\lambda \tag{23.20a}$$

and for the matrix elements involving the scalar potential to be included in $T^{(L)l}$:

$$J_\lambda(k) = \int_0^\infty (F_1 F_2 + G_1 G_2)\, j_\lambda(kr)\mathrm{d}r \approx \frac{k^\lambda}{(2\lambda+1)!!}\cdot U_\lambda \tag{23.20b}$$

Combining equations (20.2) and (23.10), one obtains:

$$\left(\tfrac{1}{2} lj \parallel \Phi_L \parallel \tfrac{1}{2} l'j'\right) = -i^L [j,j']^{\frac{1}{2}} (-1)^{j'-\frac{1}{2}+L} \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} [L]\cdot J_L(k) \tag{23.21}$$

Inserting (23.16) into (23.19) and application of equation (20.10) yields the following reduced transition operator matrix elements:

$$\left(\tfrac{1}{2} lj \parallel T^{(L)l} \parallel \tfrac{1}{2} l'j'\right) = -i^L [j,j']^{\frac{1}{2}} (-1)^{j'-\frac{1}{2}+L} \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}$$
$$\left[(\kappa-\kappa')(I^+_{L-1} + I^+_{L+1}) - L I^-_{L-1} + (L+1) I^-_{L+1} + (2L+1) J_L\right] \tag{23.22a}$$

$$\left(\tfrac{1}{2} lj \parallel T^{(L)e}_C \parallel \tfrac{1}{2} l'j'\right) = -i^L [j,j']^{\frac{1}{2}} (-1)^{j'-\frac{1}{2}+L} \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}$$
$$\left[-\left(\frac{L+1}{L}\right)^{\frac{1}{2}} \left[(\kappa-\kappa') I^+_{L-1} - L I^-_{L-1}\right] + \left(\frac{L}{L+1}\right)^{\frac{1}{2}} \left[(\kappa-\kappa') I^+_{L+1} + (L+1) I^-_{L+1}\right]\right] \tag{23.22b}$$

$$\left(\tfrac{1}{2}lj \parallel T^{(L)m} \parallel \tfrac{1}{2}l'j'\right) = i^{L+1}\cdot[L]\cdot[j,j']^{\frac{1}{2}}(-1)^{l}\begin{pmatrix} j & j' & L \\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot I_L^+$$

$$= -i^{L+1}\cdot\frac{2L+1}{\sqrt{L(L+1)}}\cdot[j,j']^{\frac{1}{2}}(-1)^{j'-\frac{1}{2}+L}\begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0\end{pmatrix}(\kappa+\kappa')\cdot I_L^+ \tag{23.22c}$$

where in the very last line, equation (C.9a) has been used to comply with Grant's radial factor $M_{jj'}^{(L)}$ [Grant, 2007] in all three cases [3]:

$$\left(\tfrac{1}{2}lj \parallel T^{(L)} \parallel \tfrac{1}{2}l'j'\right) = [j,j']^{\frac{1}{2}}(-1)^{j'-\frac{1}{2}+L}\begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0\end{pmatrix}\cdot M_{jj'}^{(L)} \tag{23.23}$$

For reasons of parity, $l+l'+L$ is even for electric multipole radiation and odd for magnetic multipole radiation.
One is now in the position to apply equation (21.7) and find the radial factors $S^{(L)}$ associated with relativistic tensor operators $T^{(\kappa k)L} = -S^{(L)}\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\kappa k)L}$:

$$S^{(L)} = [L]^{-\frac{1}{2}}\sum_{jj'}[j,j',\kappa,k]^{\frac{1}{2}}\cdot\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l & l' & k \\ j & j' & L\end{Bmatrix}\left(\tfrac{1}{2}lj \parallel T^{(L)} \parallel \tfrac{1}{2}l'j'\right) \tag{23.24}$$

The full matrix element of the transition operator is written $\left(\frac{1}{2}ljm\,|T_M^{(L)}|\,\frac{1}{2}l'j'm'\right)$. Fermi's golden rule then gives:

$$g_2\cdot A_{21} = \sum_{m_1m_2}2k\cdot\left|\left(j_1m_1|T_M^{(L)}|j_2m_2\right)\right|^2 = 2k\cdot[L]^{-1}\cdot\left|\left(j_1 \parallel T^{(L)} \parallel j_2\right)\right|^2 \tag{23.25}$$

In the non-relativistic formulation, the usual transition operator $T_{NR}^{(L)}$ is purely the electronic part whereas relativistically, the EM field factor $c_L^{e,m}$ is already automatically included. The relativistic transition operator $T^{(L)}$ appearing in equations (23.22) is related to its non-relativistic analogue $T_{NR}^{(L)}$ by this factor $c_L^{e,m}$ as:

$$T^{(L)} \to c_L^{e,m}\cdot T_{NR}^{(L)} \text{ or equivalently for the radial factors: } S^{(L)} \to c_L^{e,m}\cdot S_{NR}^{(L)} \tag{23.26}$$

Using $\forall x,y\in\mathbb{N}:\ \left|(-1)^x\cdot i^y\right|^2 = 1$, comparison of equation (23.25) with equations (7.72) and (7.80) yields in the long wavelength approximation:

$$c_L^e = \frac{i^L\cdot k^L}{(2L-1)!!}\cdot\left[\frac{L+1}{L}\right]^{\frac{1}{2}} \quad \text{and: } c_L^m = \tfrac{1}{2}\alpha\cdot\frac{i^{L+1}\cdot k^L}{(2L-1)!!}\cdot\left[\frac{L+1}{L}\right]^{\frac{1}{2}} \tag{23.27}$$

23.3 Electric multipole radiation(2)

To conserve the freedom of choice for any given gauge transformation $T^{(L)e} \to T^{(L)e} + G_L\cdot T^{(L)l}$, the matrix element $\left(\frac{1}{2}lj \parallel T^{(L)l} \parallel \frac{1}{2}l'j'\right)$ should vanish identically. [Grant, 1974] proved this with explicit radial integrals for the first time.
The recurrence relations (23.6) may be used to avoid mixed ranks in $j_\lambda(kr)$ and express $\left(\frac{1}{2}lj \parallel T^{(L)l} \parallel \frac{1}{2}l'j'\right)$ in terms of $j_L(kr)$ only:

$$I_{L-1}^+ + I_{L+1}^+ = \frac{2L+1}{k}\cdot\int_0^\infty\frac{(F_1G_2+G_1F_2)}{r}\cdot j_L(kr)\,\mathrm{d}r \tag{23.28a}$$

[3] The quantity $\overline{M}_{jj'}^{(L)}$ originally introduced by [Grant, 1974] differs from $M_{jj'}^{(L)}$ by a minus sign.

$$-LI^-_{L-1} + (L+1)I^-_{L+1} = -\frac{2L+1}{k} \cdot \int_0^\infty (F_1G_2 - G_1F_2) \cdot \frac{\mathrm{d}}{\mathrm{d}r} j_L(kr)\,\mathrm{d}r$$
$$= \frac{2L+1}{k} \cdot \int_0^\infty \frac{\mathrm{d}}{\mathrm{d}r}\,(F_1G_2 - G_1F_2) \cdot j_L(kr)\,\mathrm{d}r \qquad (23.28b)$$

Using the above in equation (23.22a), the matrix element of the longitudinal transition operator is rewritten as:

$$\left(\tfrac{1}{2}lj \parallel T^{(L)l} \parallel \tfrac{1}{2}l'j'\right) = -i^L[j,j']^{\frac{1}{2}}(-1)^{j'-\frac{1}{2}+L}\begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot \frac{2L+1}{k} \cdot$$
$$\int_0^\infty \left[\frac{\mathrm{d}}{\mathrm{d}r}\,(F_1G_2 - G_1F_2) + \frac{\kappa_1 - \kappa_2}{r} \cdot (F_1G_2 + G_1F_2) + k \cdot (F_1F_2 + G_1G_2)\right] \cdot j_L(kr)\,\mathrm{d}r \qquad (23.29)$$

The expression in square brackets equals zero as it matches exactly the LHS of the continuity equation for radial integrals (20.22): $\left(\frac{1}{2}lj \parallel T^{(L)l} \parallel \frac{1}{2}l'j'\right)$ vanishes indeed!

The gauge parameter G_L can assume the values $G_L = \sqrt{L+1/L}$ for the Babushkin (B) or length gauge and $G_L = 0$ for the Coulomb (C) or transverse gauge, leading to the length and the velocity formulation, respectively.
In the Babushkin gauge, the contributions of $I^{\pm}_{L-1}$ (important in the Coulomb gauge) are eliminated and $\left(\frac{1}{2}lj \parallel T^{(L)e}_C \parallel \frac{1}{2}l'j'\right)$ is replaced by:

$$\left(\tfrac{1}{2}lj \parallel T^{(L)e}_B \parallel \tfrac{1}{2}l'j'\right) = - i^L \cdot \frac{2L+1}{\sqrt{L(L+1)}} \cdot [j,j']^{\frac{1}{2}}(-1)^{j'-\frac{1}{2}+L}\begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}$$
$$\cdot \left[(\kappa - \kappa')I^+_{L+1} + (L+1)(I^-_{L+1} + J_L)\right] \qquad (23.30)$$

The radial factors $S^{(L)e}$ associated with $T^{(L)e} = -S^{(L)e}\,(\mathbf{a}^\dagger\mathbf{b})^{(\kappa k)L}$ are subsequently found by application of equation (21.7) for $(\kappa k)L = (0L)L$:

$$S^{(L)e} = [\tfrac{1}{2}, L]^{-\frac{1}{2}} \sum_{jj'} [j,j']^{\frac{1}{2}} \cdot (-1)^{j+l'+\frac{1}{2}+L} \cdot \begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2} \end{Bmatrix} \left(\tfrac{1}{2}lj \parallel T^{(L)e} \parallel \tfrac{1}{2}l'j'\right) \qquad (23.31)$$

23.3.1 Babushkin gauge

Using equations (20.3) and (23.23) plus the fact that $l + l' + L + 1$ is always odd, $S^{(L)e}$ reduces in the Babushkin gauge to:

$$S^{(L)e}_B = i^L \left[\frac{2L+1}{2L(L+1)}\right]^{\frac{1}{2}} \left\langle l \parallel C^{(L)} \parallel l' \right\rangle \sum_{jj'} [j,j'] \cdot \begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \left[(\kappa - \kappa')I^+_{L+1} + (L+1)(I^-_{L+1} + J_L)\right]$$
$$\approx \frac{(ik)^L}{(2L-1)!!} \left[\frac{L+1}{2L(2L+1)}\right]^{\frac{1}{2}} \left\langle l \parallel C^{(L)} \parallel l' \right\rangle \sum_{jj'} [j,j'] \cdot \begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \cdot U_L \qquad (23.32)$$

In the above last line, the long wavelength limit is used plus the fact that J_L makes the dominant contribution.

This then yields the following result, to be compared with equation (7.70):

$$\begin{aligned} T^{(L)e}_{B,NR} &= -\frac{(ik)^L}{(2L-1)!!}\left[\frac{2(L+1)}{L(2L+1)}\right]^{\frac{1}{2}}\left\langle l \parallel C^{(L)} \parallel l'\right\rangle \int_0^\infty P_1P_2\cdot r^L \mathrm{d}r\cdot\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(0L)L} \\ &= \underbrace{\frac{(ik)^L}{(2L-1)!!}\left[\frac{L+1}{L}\right]^{\frac{1}{2}}}\cdot\underbrace{-\left[\frac{2}{(2L+1)}\right]^{\frac{1}{2}}\left\langle l \parallel C^{(L)} \parallel l'\right\rangle L^{(L)}_{NR}\cdot\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(0L)L}} \\ &= c^e_L\cdot T^{(L)}_{NR} \end{aligned} \tag{23.33}$$

The first LHS factor of the last line satisfies equation (23.27) exactly.
By Fermi's golden rule (23.25), the electric multipole transition probability thus becomes in a.u.:

$$g_2\cdot A_{21} = \left(\frac{2(L+1)\cdot(2\pi)^{2L+1}}{L(2L+1)(2L-1)!!(2L-1)!!}\right)\cdot\sigma^{2L+1}\cdot\left|\left(j_1 \parallel T^{(L)} \parallel j_2\right)\right|^2 \tag{23.34}$$

Here, $T^{(L)}$ can either be the non-relativistic transition operator $T^{(L)}_{NR}$ or the corresponding relativistic expression given below. In the non-relativistic limit, the $G_1G_2\cdot r^L$ term in U_L may be discarded and the summation over j, j' in equation (23.32) can therefore be carried out independently: $\sum_{jj'}[j,j']\cdot\begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2}\end{Bmatrix}^2 = 2$.
The correct relativistic analogue $L^{(L)}$ that replaces the length formulation of the multipole transition integral $L^{(L)}_{NR}$ in an $SL-$coupled framework is thus found from equation (23.32):

$$\begin{aligned} L^{(L)} &= \tfrac{1}{2}\cdot\sum_{jj'}[j,j']\cdot\begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2}\end{Bmatrix}^2\cdot\int_0^\infty(F_1F_2+G_1G_2)\cdot r^L\,\mathrm{d}r \\ &= \tfrac{1}{2}\cdot\sum_{jj'}[j,j']\cdot\begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2}\end{Bmatrix}^2\cdot U_L \end{aligned} \tag{23.35}$$

$L^{(L)}$ is an inherently 'long wavelength' quantity; letting go of this approximation but still neglecting $I^{\pm}_{L+1}$, the expression for the multipole transition integral will be given by:

$$L^{(L)} = \frac{(2L+1)!!}{k^L}\cdot\tfrac{1}{2}\cdot\sum_{jj'}[j,j']\cdot\begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2}\end{Bmatrix}^2\cdot J_L \tag{23.36}$$

with the obvious non-relativistic limit:

$$L^{(L)}_{NR} = \int_0^\infty P_1P_2\cdot r^L\mathrm{d}r \tag{23.37}$$

23.3.2 Coulomb gauge

In the Coulomb gauge, the radial factor $S^{(L)e}$ becomes:

$$\begin{aligned} S_C^{(L)e} &= i^L \left[\frac{1}{2(2L+1)}\right]^{\frac{1}{2}} \left\langle l \parallel C^{(L)} \parallel l' \right\rangle \sum_{jj'} [j,j'] \cdot \begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \\ &\cdot \left[-\left(\frac{L+1}{L}\right)^{\frac{1}{2}} \left[(\kappa-\kappa')I_{L-1}^{+} - LI_{L-1}^{-}\right] + \left(\frac{L}{L+1}\right)^{\frac{1}{2}} \left[(\kappa-\kappa')I_{L+1}^{+} + (L+1)I_{L+1}^{-}\right] \right] \\ &\approx \frac{k^{-1}(ik)^L}{(2L-1)!!} \left[\frac{L+1}{2L(2L+1)}\right]^{\frac{1}{2}} \left\langle l \parallel C^{(L)} \parallel l' \right\rangle \sum_{jj'} [j,j'] \cdot \begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \cdot \left[LE_{L-1}^{-} - (\kappa-\kappa')E_{L-1}^{+} \right] \end{aligned} \tag{23.38}$$

The long wavelength limit is again used in the last line. Comparison of equations (23.32) and (23.38) reveals the relation between the relativistic transition integrals of the two gauges:

$$U_L \leftrightarrow k^{-1} \cdot \left[LE_{L-1}^{-} - (\kappa-\kappa')E_{L-1}^{+} \right] \tag{23.39}$$

The U_L and $E_L^{\pm}$ integrals are defined in equations (20.4) and (20.9), respectively. The relativistic replacement in the velocity formulation of the multipole transition integral $V_{NR}^{(L)}$ in an SL–framework becomes:

$$V^{(L)} = \tfrac{1}{2}k^{-1} \cdot \sum_{jj'} [j,j'] \cdot \begin{Bmatrix} j & j' & L \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \cdot \left[LE_{L-1}^{-} - (\kappa-\kappa')E_{L-1}^{+} \right] \tag{23.40}$$

In the non-relativistic limit, the Coulomb transition integral becomes after application of equations (20.12a) and (20.12b) with $k = \alpha\omega = \alpha(\varepsilon_2 - \varepsilon_1) > 0$:

$$V_{NR}^{(L)} = \omega^{-1} \cdot \left[L \int_0^{\infty} P_1 P_2' \cdot r^{L-1} \mathrm{d}r - \tfrac{1}{2}\left[l(l+1) - l'(l'+1) - L(L-1) \right] \int_0^{\infty} P_1 P_2 \cdot r^{L-2} \mathrm{d}r \right] \tag{23.41}$$

23.4 Electric dipole radiation(2)

For the electric dipole radiation $L = 1$, the expression in the Babushkin or length gauge becomes:

$$\left(\tfrac{1}{2} lj \parallel T_B^{(1)e} \parallel \tfrac{1}{2} l'j' \right) = -i \cdot \frac{3}{\sqrt{2}} \cdot [j,j']^{\frac{1}{2}} \cdot (-1)^{j'+\frac{1}{2}} \cdot \begin{pmatrix} j & j' & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \left[(\kappa-\kappa')I_2^{+} + 2(I_2^{-} + J_1) \right] \tag{23.42}$$

where in the long wavelength limit $I_2^{\pm} = 4\pi^2/15\lambda^2 \cdot E_2^{\pm}$ are relatively small. The radial quantity $S_B^{(1)e}$ in $T_B^{(1)e} = -S_B^{(1)e} \left(\mathbf{a}^{\dagger}\mathbf{b}\right)^{(01)1}$ is found from equation (23.32):

$$\begin{aligned} S_B^{(1)e} &= \tfrac{1}{2} i\sqrt{3} \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \sum_{jj'} [j,j'] \cdot \begin{Bmatrix} j & j' & 1 \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \cdot \left[(\kappa-\kappa')I_2^{+} + 2(I_2^{-} + J_1) \right] \\ &\approx 2i\sqrt{3} \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \frac{(l+2)(2l+1)J_{1++} + J_{1+-} + l(2l+3)J_{1--}}{(2l+1)(2l+3)} \\ &\approx \tfrac{2}{3} i\sqrt{3} \cdot k \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot \frac{(l+2)(2l+1)U_{1++} + U_{1+-} + l(2l+3)U_{1--}}{(2l+1)(2l+3)} \end{aligned} \tag{23.43}$$

Without loss of generality, $l' = l + 1$ is taken here in above last lines.

23.4.1 Non-relativistic limit

The non-relativistic limit $S^{(1)e}_{B,NR}$ is directly obtained by equating the fraction in equation (23.43) to $L^{(1)}_{NR} = \int P_1 P_2\, r\mathrm{d}r$:

$$S^{(1)e}_{B,NR} = \tfrac{2}{3} i\sqrt{3} \cdot k \cdot \left\langle l \parallel C^{(1)} \parallel l' \right\rangle \cdot L^{(1)}_{NR} \tag{23.44}$$

In the Coulomb gauge, equation (23.41) gives for $L = 1$ the known velocity form (7.36), to be compared with $L^{(1)}_{NR}$:

$$V^{(1)}_{NR} = \omega^{-1} \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1) - l'(l'+1)}{2r} \right] P_{n'l'}\, \mathrm{d}r = \omega^{-1} \int_0^\infty P_{nl} \left[\frac{\mathrm{d}}{\mathrm{d}r} + \frac{l_>}{r} \right] P_{n'l'}\, \mathrm{d}r \tag{23.45}$$

Substituting $L = 1$ in equation (23.34), the non-relativistic electric dipole transition probability becomes in a.u.:

$$g_2 \cdot A_{21} = \tfrac{4}{3} \cdot (2\pi)^3 \cdot \sigma^3 \cdot \left| \left(j_1 \parallel T^{(1)}_{NR} \parallel j_2 \right) \right|^2 \tag{23.46}$$

This corresponds exactly to the original non-relativistic expression (7.7), except for the conversion from a.u. to SI by the factor $fe^2/\hbar \cdot a_0^2 \cdot 10^6$.
The substitution $T^{(1)}_{NR} \to T^{(1)}_R$ using equation (23.35) or (23.40) for the transition integral yields the completely relativistic form.

23.5 Electric quadrupole radiation(2)

In the Babushkin gauge, one finds for the radial electric quadrupole factor:

$$\begin{aligned} S^{(2)e}_B &= i^2 \left[\frac{5}{12} \right]^{\frac{1}{2}} \left\langle l \parallel C^{(2)} \parallel l' \right\rangle \sum_{jj'} [j, j'] \cdot \begin{Bmatrix} j & j' & 2 \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \left[(\kappa - \kappa') I_3^+ + 3(I_3^- + J_2) \right] \\ &\approx \frac{(ik)^2}{2} \left[\frac{1}{15} \right]^{\frac{1}{2}} \left\langle l \parallel C^{(2)} \parallel l' \right\rangle \sum_{jj'} [j, j'] \cdot \begin{Bmatrix} j & j' & 2 \\ l' & l & \frac{1}{2} \end{Bmatrix}^2 \cdot U_2 \end{aligned} \tag{23.47}$$

Given the triangular condition $\{ll'2\}$ and the parity condition of even $l + l' + 2$, l' is restricted to: $l' = l(\neq 0), l \pm 2$.

23.5.1 Non-relativistic limit

The non-relativistic limit $S^{(2)e}_{B,NR}$ is obtained after the summation over j and j' under the assumption the $L^{(2)}_{NR} = \int P_1 P_2\, r^2\, \mathrm{d}r$ is j–independent:

$$S^{(2)e}_{B,NR} = \frac{(ik)^2}{\sqrt{15}} \left\langle l \parallel C^{(2)} \parallel l' \right\rangle \cdot L^{(2)}_{NR} \tag{23.48}$$

The velocity form corresponding to the length form $L^{(2)}_{NR}$ is directly obtained from equation (23.41):

$$V^{(2)}_{NR} = \omega^{-1} \cdot \left[2 \int_0^\infty P_1 P_2' \cdot r\, \mathrm{d}r - \tfrac{1}{2} \left\{ l(l+1) - l'(l'+1) - 2 \right\} \cdot \int_0^\infty P_1 P_2\, \mathrm{d}r \right] \tag{23.49}$$

For $P_1 \neq P_2$, this reduces to:

$$\begin{aligned} V_{NR}^{(2)\ (l'=l)} &= \frac{2}{\omega} \cdot \int_0^\infty P_1 \left(r\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{2} \right) P_2 \, \mathrm{d}r \\ V_{NR}^{(2)\ (l'=l+2)} &= \frac{2}{\omega} \cdot \int_0^\infty P_1 \left(r\frac{\mathrm{d}}{\mathrm{d}r} + l + 2 \right) P_2 \, \mathrm{d}r \\ V_{NR}^{(2)\ (l'=l-2)} &= \frac{2}{\omega} \cdot \int_0^\infty P_1 \left(r\frac{\mathrm{d}}{\mathrm{d}r} - l + 1 \right) P_2 \, \mathrm{d}r \end{aligned} \tag{23.50}$$

while for $P_1 = P_2$, the non-relativistic velocity formulation yields an indeterminate result as: $V_{NR}^{(2)} = \omega^{-1} \cdot \left[\int_0^\infty (P^2)' \cdot r \, \mathrm{d}r + 1 \right] \approx 0/0$. Derived from the off-diagonal hypervirial theorem, equations (23.50) were already given by [Godefroid, 1978].

Substituting $L = 2$ in equation (23.34), the non-relativistic electric quadrupole transition probability becomes in a.u.:

$$g_2 \cdot A_{21} = \frac{1}{15} \cdot (2\pi)^5 \cdot \sigma^5 \cdot \left| \left(j_1 \parallel T_{NR}^{(2)} \parallel j_2 \right) \right|^2 \tag{23.51}$$

This corresponds exactly to the original non-relativistic expression (7.77), except for the conversion from a.u. to SI by the factor $fe^2/\hbar \cdot a_0^4 \cdot 10^{10}$.
The substitution $T_{NR}^{(2)} \to T_R^{(2)}$ using equation (23.35) or (23.40) for the transition integral yields the completely relativistic form again.

23.6 Magnetic multipole radiation(2)

The magnetic multipole transition operator $T^{(L)m}$ is given in equation (23.22c); parity requires that $l + l' + L$ is odd.
The radial factors $S^{(L)m}$ associated with $T^{(L)m} = -S^{(L)m} \left(\mathbf{a}^\dagger \mathbf{b} \right)^{(\nu k)L}$ are found by application of equation (21.7):

$$\begin{aligned} S^{(L)m} &= [L]^{-\frac{1}{2}} \sum_{jj'} [j, j', \nu, k]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \nu \\ l & l' & k \\ j & j' & L \end{Bmatrix} \left(\tfrac{1}{2} l j \parallel T^{(L)m} \parallel \tfrac{1}{2} l' j' \right) \\ &= i^{L+1} [L]^{\frac{1}{2}} \sum_{jj'} [j, j'] \cdot [\nu, k]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \nu \\ l & l' & k \\ j & j' & L \end{Bmatrix} \cdot (-1)^l \cdot \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \cdot I_L^+ \\ &\approx \frac{i^{L+1} \cdot k^L}{(2L-1)!!} \cdot [\nu, k]^{\frac{1}{2}} \cdot [L]^{-\frac{1}{2}} \sum_{jj'} [j, j'] \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \nu \\ l & l' & k \\ j & j' & L \end{Bmatrix} \cdot (-1)^l \cdot \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \cdot E_L^+ \end{aligned} \tag{23.52}$$

In the last line, the long wavelength limit $I_L^+ = k^L/(2L+1)!! \cdot E_L^+$ is used.
Here and in the following, tensor ranks $(\nu k)L$ with $\nu = 0, 1$ instead of the usual $(\kappa k)L$ are used to avoid confusion with the quantum numbers κ.
Allowed values are: $(\nu k)L = (0\,L)L, (1\,L-1)L$ and $(1\,L+1)L$. Non-relativistically, only the orbital term $(\nu k)L = (0\,L)L$ and the spin term $(1\,L-1)L$ remain, as can be seen from equations (7.82).

23.6.1 Non-relativistic limit

In the non-relativistic limit, equation (20.12a) gives:
$E_L^+ \to \frac{1}{2}\alpha \cdot (\kappa + \kappa' - L) \cdot \int_0^\infty F_1 F_2\, r^{L-1} \mathrm{d}r$. This implies that the summations over j, j' can be carried out explicitly for all allowed values of (νk):

$$\sum_{jj'} [j,j'] \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ l & l' & L \\ j & j' & L \end{Bmatrix} \cdot (-1)^l \cdot \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \cdot (\kappa + \kappa' - L)$$

$$= -2\left[\frac{2l'(l'+1)(2l'+1)(2L-1)}{L+1}\right]^{\frac{1}{2}} \cdot \begin{Bmatrix} l & l' & L \\ 1 & L-1 & l' \end{Bmatrix} \cdot \left\langle l \parallel C^{(L-1)} \parallel l' \right\rangle \qquad (23.53a)$$

$$\sum_{jj'} [j,j'] \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l' & L-1 \\ j & j' & L \end{Bmatrix} \cdot (-1)^l \cdot \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \cdot (\kappa + \kappa' - L)$$

$$= \left[\frac{2(L+1)(2L+1)}{3(2L-1)}\right]^{\frac{1}{2}} \cdot \left\langle l \parallel C^{(L-1)} \parallel l' \right\rangle \qquad (23.53b)$$

$$\sum_{jj'} [j,j'] \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l' & L+1 \\ j & j' & L \end{Bmatrix} \cdot (-1)^l \cdot \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \cdot (\kappa + \kappa' - L) = 0 \qquad (23.53c)$$

As expected, the $(\nu k)L = (1\,L+1)L$ case vanishes in the non-relativistic limit. The above summations are less standard but may be verified with any dedicated computer algebra package.
Combining all of the foregoing, one obtains for the non-relativistic orbital term:

$$\begin{aligned} T^{(L)m}_{\mathrm{orb},NR} &= \tfrac{1}{2}\alpha \cdot \frac{i^{L+1} \cdot k^L}{(2L-1)!!} \cdot 2\left[\frac{2l'(l'+1)(2l'+1)(2L-1)}{L+1}\right]^{\frac{1}{2}} \cdot \begin{Bmatrix} l & l' & L \\ 1 & L-1 & l' \end{Bmatrix} \\ &\cdot \left\langle l \parallel C^{(L-1)} \parallel l' \right\rangle \cdot \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(0L)L} \cdot \int_0^\infty F_1 F_2\, r^{L-1} \mathrm{d}r \\ &= \underbrace{\tfrac{1}{2}\alpha \cdot \frac{i^{L+1} \cdot k^L}{(2L-1)!!} \cdot \left[\frac{L+1}{L}\right]^{\frac{1}{2}}} \cdot \underbrace{\frac{2}{L+1} \cdot [L(2L-1)]^{\frac{1}{2}} \sum_i r_i^{L-1} \left(C_i^{(L-1)} l_i\right)^{(L)}} \\ &= c_L^m \cdot M^{(L)}_{\mathrm{orb}} \end{aligned} \qquad (23.54)$$

where in the last lines, use is made of equations (7.81), (7.82a) and (23.27).
A similar derivation now with equation (7.82b) follows for the spin term:

$$\begin{aligned} T^{(L)m}_{\mathrm{spin},NR} &= \tfrac{1}{2}\alpha \cdot \frac{i^{L+1} \cdot k^L}{(2L-1)!!} \cdot -\left[\frac{3(2L-1)}{2L+1}\right]^{\frac{1}{2}} \cdot \left[\frac{2(L+1)(2L+1)}{3(2L-1)}\right]^{\frac{1}{2}} \\ &\cdot \left\langle l \parallel C^{(L-1)} \parallel l' \right\rangle \cdot \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(1\,L-1)L} \cdot \int_0^\infty F_1 F_2\, r^{L-1} \mathrm{d}r \\ &= \underbrace{\tfrac{1}{2}\alpha \cdot \frac{i^{L+1} \cdot k^L}{(2L-1)!!} \cdot \left[\frac{L+1}{L}\right]^{\frac{1}{2}}} \cdot \underbrace{\frac{2}{L+1} \cdot [L(2L-1)]^{\frac{1}{2}} \sum_i r_i^{L-1} (L+1) \left(C_i^{(L-1)} s_i\right)^{(L)}} \\ &= c_L^m \cdot M^{(L)}_{\mathrm{spin}} \end{aligned} \qquad (23.55)$$

As expected, $T_{NR}^{(L)m} = c_L^m \cdot M_{NR}^{(L)}$ with $M_{NR}^{(L)}$ identical to the non-relativistic magnetic multipole operator given in equation (7.81).
The relativistic analogue of the magnetic multipole operator is now given by:

$$M^{(L)} = -\frac{2}{\alpha}\sum_{\nu k}\left[\frac{L(2\nu+1)(2k+1)}{(L+1)(2L+1)}\right]^{\frac{1}{2}}\sum_{jj'}[j,j']\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \nu\\ l & l' & k\\ j & j' & L\end{Bmatrix}(-1)^l\begin{pmatrix}j & j' & L\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}E_L^+\cdot\left(\mathbf{a}^\dagger\mathbf{b}\right)^{(\nu k)L} \tag{23.56}$$

Note that this expression contains, next to the orbital and the spin term, an expectedly small, pure relativistic contribution for $(\nu k)L = (1\,L+1)L$.
The relativistic replacement of the radial integral $\int_0^\infty F_1F_2\,r^{L-1}\mathrm{d}r$ is somewhat more subtle to find than in the electric multipole case.
For the orbital case, comparison learns:

$$\begin{aligned}&\tfrac{1}{2}\alpha\cdot -2\left[\frac{2l'(l'+1)(2l'+1)(2L-1)}{L+1}\right]^{\frac{1}{2}}\cdot\begin{Bmatrix}l & l' & L\\ 1 & L-1 & l'\end{Bmatrix}\cdot\left\langle l\parallel C^{(L-1)}\parallel l'\right\rangle\cdot\int_0^\infty F_1F_2\,r^{L-1}\mathrm{d}r\\ &\quad\to\sum_{jj'}[j,j']\cdot\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & 0\\ l & l' & L\\ j & j' & L\end{Bmatrix}\cdot(-1)^l\cdot\begin{pmatrix}j & j' & L\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot E_L^+\end{aligned} \tag{23.57a}$$

Given the relativistic integrals E_L^+, only an elementary computer program is needed here to calculate the replacement of $\int_0^\infty F_1F_2\,r^{L-1}\mathrm{d}r$.
Similarly for the spin case:

$$\begin{aligned}&\tfrac{1}{2}\alpha\cdot\left[\frac{2(L+1)(2L+1)}{3(2L-1)}\right]^{\frac{1}{2}}\cdot\left\langle l\parallel C^{(L-1)}\parallel l'\right\rangle\cdot\int_0^\infty F_1F_2\,r^{L-1}\mathrm{d}r\\ &\quad\to\sum_{jj'}[j,j']\cdot\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & 1\\ l & l' & L-1\\ j & j' & L\end{Bmatrix}\cdot(-1)^l\cdot\begin{pmatrix}j & j' & L\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot E_L^+\end{aligned} \tag{23.57b}$$

With the equations (23.53), it is straightforward to check that the LHS and the RHS of both the above replacements are equal in the non-relativistic limit.
Note that if the j–dependency of E_L^+ is not negligible, the relativistic analogues of $\int_0^\infty F_1F_2\,r^{L-1}\mathrm{d}r$ will differ between the orbital and the spin term as a result of the different j–dependent weighting factors in the two cases.

23.7 Magnetic dipole radiation(2)

For magnetic dipole radiation, substitution of $L = 1$ in equation (23.52) yields:

$$S^{(1)m} = -\sqrt{3}\sum_{jj'}[j,j']\cdot[\nu,k]^{\frac{1}{2}}\cdot\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \nu\\ l & l & k\\ j & j' & 1\end{Bmatrix}(-1)^l\cdot\begin{pmatrix}j & j' & 1\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}I_1^+ \tag{23.58}$$

Equation (23.58) closely resembles equation (22.10) or (22.38), again with the three allowed values $\nu k = 01, 10$ and 12. Both the magnetic dipole radiation and the Zeeman effect originate from the same magnetic dipole operator, and are therefore

strongly interrelated. As the non-relativistic atomic magnetic moment is given by $\vec{\mu} = -\mu_B \cdot M^{(1)}_{NR} = -\frac{1}{2} \cdot [L^{(01)1} + g_s S^{(10)1}]$, the spin-dipole term $\nu k = 12$ turns out to be is purely relativistic again.
Comparing equations (23.20a) and (22.35), it follows that in the long wavelength approximation:

$$I^+_1 = \tfrac{1}{3} k \cdot E^+_1 = \tfrac{2}{3} k \cdot D_{jj'} \tag{23.59}$$

Comparison of the $S-$integrals (22.38) and (23.58) yields therefore:

$$S^{(1)m} = -\sqrt{2} \cdot \alpha k \cdot S^{Z,\kappa k} \text{ ,written below for each combination of } \kappa k : \tag{23.60}$$

$$S^{(01)m}_{nl} = -\sqrt{2} \cdot \alpha k \cdot \left[\frac{l(l+1)(2l+1)}{6} \right]^{\frac{1}{2}} \cdot a^{01} \tag{23.61a}$$

$$S^{(10)m}_{nl} = -\sqrt{2} \cdot \alpha k \cdot \left[\frac{2l+1}{2} \right]^{\frac{1}{2}} \cdot a^{10} \tag{23.61b}$$

$$S^{(12)m}_{nl} = -\sqrt{2} \cdot \alpha k \cdot \left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)} \right]^{\frac{1}{2}} \cdot a^{12} \tag{23.61c}$$

where the $a^{\kappa k}$ coefficients are the same as in equations (22.42):

$$a^{01} = -\frac{6}{\alpha k} \cdot \frac{1}{(2l+1)^2} \cdot \left[(l+1) I^+_{1,++} - I^+_{1,+-} - l I^+_{1,--} \right] \tag{23.62a}$$

$$a^{10} = -\frac{2}{\alpha k} \cdot \frac{1}{(2l+1)^2} \cdot \left[(l+1)^2 I^+_{1,++} + 2l(l+1) I^+_{1,+-} + l^2 I^+_{1,--} \right] \tag{23.62b}$$

$$a^{12} = \frac{1}{\alpha k} \cdot \frac{1}{(2l+1)^2} \cdot \left[2(l+1)(2l-1) I^+_{1,++} - (2l-1)(2l+3) I^+_{1,+-} + 2l(2l+3) I^+_{1,--} \right] \tag{23.62c}$$

To find the relativistic expression for the transition probability, one applies Fermi's golden rule (23.25) with:

$$T^{(1)m} = -\sum_{\kappa k} S^{\kappa k, m} \left(\mathbf{a}^\dagger \mathbf{a} \right)^{(\kappa k)1} = -\tfrac{1}{2} \sqrt{2} \cdot \alpha k \cdot M^{(1)}_R \tag{23.63}$$

giving:

$$g_2 \cdot A_{21} = \tfrac{1}{3} \alpha^2 \cdot k^3 \cdot \left| \left\langle j \parallel M^{(1)}_R \parallel j' \right\rangle \right|^2 = \tfrac{1}{3} \alpha^2 \cdot (2\pi)^3 \cdot \sigma^3 \cdot \left| \left\langle j \parallel M^{(1)}_R \parallel j' \right\rangle \right|^2 \tag{23.64}$$

where $M^{(1)}_R = \left(a^{01} L^{(01)1} + \left[2a^{10} + (g_s - 2) \right] S^{(10)1} - 2(10)^{\frac{1}{2}} a^{12} \sum_i \left(sC^{(2)} \right)^{(1)}_i \right)$.

23.7.1 Non-relativistic limit

As to be expected from the earlier non-relativistic treatment resulting in equation (7.85), I^+_1 is radially independent in the non-relativistic limit:

$$I^+_1 = \frac{1}{6} \cdot \alpha k \cdot (\kappa + \kappa' - 1) \quad \rightarrow \tag{23.65}$$

$$I^{+}_{1++} = -\frac{1}{6}\cdot\alpha k\cdot(2l+3) \tag{23.66a}$$

$$I^{+}_{1+-} = -\frac{1}{3}\cdot\alpha k \tag{23.66b}$$

$$I^{+}_{1--} = \frac{1}{6}\cdot\alpha k\cdot(2l-1) \tag{23.66c}$$

And similarly for the $S-$integrals:

$$S^{01,m} = -\sqrt{2}\cdot\alpha k\cdot\left[\frac{l(l+1)(2l+1)}{6}\right]^{\frac{1}{2}} \qquad \rightarrow a^{01}=1 \tag{23.67a}$$

$$S^{10,m}_{nl} = -\sqrt{2}\cdot\alpha k\cdot\left[\frac{2l+1}{2}\right]^{\frac{1}{2}} \qquad \rightarrow a^{10}=1 \tag{23.67b}$$

$$S^{12,m}_{nl} = 0 \qquad \rightarrow a^{12}=0 \tag{23.67c}$$

and therefore, as $M^{(1)} = -2\sum_{\kappa k} S^{Z,\kappa k}\left(\mathbf{a}^{\dagger}\mathbf{a}\right)^{(\kappa k)1}$, the magnetic dipole transition operator $T^{(1)m}$ becomes in the non-relativistic limit:

$$T^{(1)m} = -\sum_{\kappa k} S^{\kappa k,m}\left(\mathbf{a}^{\dagger}\mathbf{a}\right)^{(\kappa k)1} = -\tfrac{1}{2}\sqrt{2}\cdot\alpha k\cdot M^{(1)}_{NR} \tag{23.68}$$

and by Fermi's golden rule (23.25):

$$g_2\cdot A_{21} = \tfrac{1}{3}\alpha^2\cdot k^3\cdot\left|\left\langle j \parallel M^{(1)}_{NR}\parallel j'\right\rangle\right|^2 = \tfrac{1}{3}\alpha^2\cdot(2\pi)^3\cdot\sigma^3\cdot\left|\left\langle j \parallel M^{(1)}_{NR}\parallel j'\right\rangle\right|^2 \tag{23.69}$$

This corresponds exactly to the original non-relativistic expression (7.84), except for the conversion from a.u. to SI by the factor $fe^2/\hbar\cdot a_0^2\cdot 10^6$.

With $l'=l\neq 0$, the radial overlap integral $\int_0^{\infty}P_1P_2\,\mathrm{d}r$ may be replaced by its separate relativistic analogues:

$$\int_0^{\infty}P_1P_2\,\mathrm{d}r_{(\mathrm{orb})} \rightarrow \delta(l,l')\cdot(\alpha)^{-1}\left[\frac{3}{l(l+1)(2l+1)}\right]^{\frac{1}{2}}\sum_{jj'}[j,j']\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & 0\\ l & l & 1\\ j & j' & 1\end{Bmatrix}(-1)^{l}\begin{pmatrix}j & j' & 1\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}E^{+}_{1} \tag{23.70a}$$

$$\int_0^{\infty}P_1P_2\,\mathrm{d}r_{(\mathrm{spin})} \rightarrow \delta(l,l')\cdot(\alpha)^{-1}\left[\frac{1}{(2l+1)}\right]^{\frac{1}{2}}\sum_{jj'}[j,j']\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & 1\\ l & l & 0\\ j & j' & 1\end{Bmatrix}(-1)^{l}\begin{pmatrix}j & j' & 1\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}E^{+}_{1} \tag{23.70b}$$

23.8 Magnetic quadrupole radiation(2)

For magnetic quadrupole radiation, substitution of $L=2$ in equation (23.52) yields:

$$S^{(2)m} = \frac{i(ik)^2}{3\sqrt{5}}\cdot[\nu,k]^{\frac{1}{2}}\sum_{jj'}[j,j']\cdot\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \nu\\ l & l' & k\\ j & j' & 2\end{Bmatrix}\cdot(-1)^{l}\cdot\begin{pmatrix}j & j' & 2\\ -\frac{1}{2} & -\frac{1}{2} & 1\end{pmatrix}\cdot E^{+}_{2} \tag{23.71}$$

The three allowed values are $(\nu k)2 = (02)2, (11)2$ and $(13)2$; only $(02)2$ and $(11)2$ appear non-relativistically, as can be seen from comparison with equation (7.98).
To find the relativistic expression for the transition probability, one applies Fermi's golden rule (23.25) in a.u.:

$$g_2 \cdot A_{21} = \frac{2k}{5} \cdot \left|\left(j \parallel T^{(2)m} \parallel j'\right)\right|^2 = \left(\frac{\alpha}{2}\right)^2 \cdot \frac{(2\pi)^5}{15} \cdot \sigma^5 \cdot \left|\left\langle j \parallel M^{(2)} \parallel j' \right\rangle\right|^2 \tag{23.72}$$

where $M^{(2)}$ is given by equation (23.56) with $L = 2$. This matches exactly the non-relativistic expression (7.97), when the prefactor $fe^2/\hbar \cdot a_0^4 \cdot 10^{10}$ is added to ensure that A_{21} is in s^{-1} and σ in cm^{-1}.

23.8.1 Non-relativistic limit

The non-relativistic transition probability is found by the substitution $M_{NR}^{(2)} \to M^{(2)}$ where $M_{NR}^{(2)}$ is given by equation (7.98).
Assuming without loss of generality that $l' = l + 1$, the radial integral $\int_0^\infty P_1 P_2 \, r \, \mathrm{d}r$ may however straightforwardly be replaced by its relativistic analogue:

$$\int_0^\infty F_1 F_2 \, r \, \mathrm{d}r_{(\mathrm{orb})} \to -(\alpha)^{-1} \left[\frac{5}{l(l+1)(l+2)}\right]^{\frac{1}{2}} \sum_{jj'} [j, j'] \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ l & l+1 & 2 \\ j & j' & 2 \end{Bmatrix} (-1)^l \begin{pmatrix} j & j' & 2 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} E_2^+ \tag{23.73a}$$

$$\int_0^\infty F_1 F_2 \, r \, \mathrm{d}r_{(\mathrm{spin})} \to -(\alpha)^{-1} \left[\frac{6}{5(l+1)}\right]^{\frac{1}{2}} \sum_{jj'} [j, j'] \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l+1 & 1 \\ j & j' & 2 \end{Bmatrix} (-1)^l \begin{pmatrix} j & j' & 2 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} E_2^+ \tag{23.73b}$$

Chapter 24

Fine structure

We consider below the relativistic form of one of the common (orthogonal) parameters, namely the spin-orbit coupling constant $\zeta(a,b)$ given by equation (5.89):

$$H_{SO} = \sum_i \mathbf{s}_i \cdot \mathbf{l}_i \, \zeta(a,b) = \delta(l,l') \, (l(l+1)(2l+1)/2)^{\frac{1}{2}} \left(\mathbf{a}^\dagger \mathbf{b}\right)^{(11)0} \zeta(a,b)$$

In order to find the contribution of the nuclear attraction to $\zeta(a,b)$, we use equation (21.7) with $(\kappa,k,t) = (1,1,0)$, and calculate the reduced matrix element of the (even) operator $-Z/r$:

$$(p_j \parallel -Z/r \parallel q_{j'}) = \delta(j,j')[j]^{\frac{1}{2}} \, (p_j|-Z/r|q_{j'}) = \delta(j,j')[j]^{\frac{1}{2}} \int_0^\infty -\left(F_p F_q + G_p G_q\right) \frac{Z}{r} \, \mathrm{d}r$$

The final result thus becomes immediately:

$$\zeta(a,b) = \delta(l,l') \sum_j \delta(j,j')[j] \, \frac{l(l+1) + \frac{3}{4} - j(j+1)}{l(l+1)(2l+1)} \int_0^\infty \left(F_p F_q + G_p G_q\right) \frac{Z}{r} \, \mathrm{d}r \qquad (24.1)$$

Only j-dependent terms in the integral survive summation over j.
In the Pauli limit, this means only $G_j \approx \frac{1}{2}\alpha \left(F' + \kappa \cdot F/r\right)$ contributes.
After integration by parts, the well known non-relativistic limit appears, now derived without any explicit reference to magnetic effects:

$$\zeta(a,b) = \tfrac{1}{2}\alpha^2 Z \int_0^\infty a(r) \, r^{-3} \, b(r) \, \mathrm{d}r$$

Equation (14.33) being the most important part of $\Delta\zeta$, it may be interesting to trace its relativistic origin. The contribution comes from the spin-own-orbit part of MSO, and thus the relativistic Coulomb interaction; the result is found to be:

$$\begin{aligned} \Delta\zeta(a) \quad &= \quad -\sum_b \left(\frac{M}{4l'+2}\right) \sum_{j,j'} [j,j'] \frac{l(l+1) + \frac{3}{4} - j(j+1)}{l(l+1)(2l+1)} \\ &\times \quad \int_0^\infty \int_0^\infty (F_j^2 + G_j^2)_1 \, (r_>)^{-1} (F_{j'}^2 + G_{j'}^2)_2 \, \mathrm{d}r_1 \mathrm{d}r_2 \end{aligned} \qquad (24.2)$$

In the Pauli limit, again only G_j depends on j and therefore the integral $\int_0^\infty \int_0^\infty (G_j^2)_1 \, (r_>)^{-1} (F_{j'}^2)_2 \, \mathrm{d}r_1 \mathrm{d}r_2$ is the leading term surviving the summation over j. Integrating by parts to remove $\mathrm{d}F/\mathrm{d}r$ and carrying out the summations over j and j', one obtains exactly expression (14.33) as the Pauli limit of equation (24.2).

Chapter 25

Deltafunctions

As a second example, we consider the expectation value $|\Psi(0)|^2$ of the operator $\delta(\boldsymbol{r})$, that frequently appears in contact interactions. As:

$$\delta(\vec{r}) = -\frac{1}{4\pi}\cdot\nabla^2\left(\frac{1}{r}\right) \tag{25.1}$$

$$\text{N.B. } r\neq 0 : \nabla_r^2\left(\tfrac{1}{r}\right) = \left(\tfrac{\partial^2}{\partial r^2} + \tfrac{2}{r}\tfrac{\partial}{\partial r}\right)\tfrac{1}{r} = 0$$
$$\int \delta(\vec{r})\,\mathrm{d}V = 4\pi\int \delta(\vec{r})\cdot r^2\mathrm{d}r = 1 = \int \delta(r)\mathrm{d}r$$

$$\delta(\vec{r}) = \delta(\boldsymbol{r}) = \frac{1}{4\pi}\frac{\delta(r)}{r^2} \text{ with: } \langle\delta(\boldsymbol{r})\rangle = |\Psi(0)|^2 \text{ and: } \langle\bar{n}s|\delta(\boldsymbol{r})|n's\rangle = \Psi_{\bar{n}s}(0)\cdot\Psi_{n's}(0)$$

so, for the non-relativistic Coulomb limit $(\kappa k) = (00)$:

$$\delta(\boldsymbol{r}) = -\delta(ll')\cdot(\mathbf{a}^\dagger\mathbf{b})^{(00)}\frac{1}{4\pi}\int_0^\infty a\,\frac{\delta(r)}{r^2}b\,\mathrm{d}r \tag{25.2}$$

with the relativistic expectation value:

$$\langle\delta(\mathbf{r})\rangle = \sum_j [j]\cdot[\tfrac{1}{2},l]^{-1}\frac{1}{4\pi}\int_0^\infty\left(F_j^2+G_j^2\right)\frac{\delta(r)}{r^2}\,\mathrm{d}r \tag{25.3}$$

In fully relativistic calculations, one should take the finite extent of the nucleus into account and replace $\delta(r)/4\pi r^2$ by a nuclear charge distribution $\rho(r)$ e.g.:

$$\langle\delta(\mathbf{r})\rangle = \sum_j [j]\cdot[\tfrac{1}{2},l]^{-1}\int_0^\infty\left(F_j^2+G_j^2\right)\cdot\rho(r)\,\mathrm{d}r \tag{25.4}$$

In the field of HFS, the contact operator $(\kappa k) = (10)$ is, in analogy with the other HFS contributions and conform to equation (22.19h), frequently written as :

$$\left\langle r^{-3}\right\rangle_c = -\frac{8}{3\alpha}\int\frac{F_{ns}G_{ns}}{r^2}\,\mathrm{d}r \approx \frac{8\pi}{3}\langle\delta(\mathbf{r})\rangle_c = \frac{2}{3}\left\langle\frac{\delta(r)}{r^2}\right\rangle_c \tag{25.5}$$

From hydrogenic considerations, one has:

$$\lim_{r\to 0}\left(\frac{P_{ns}(r)}{r}\right)^2 = \lim_{r\to 0}\left(\frac{\mathrm{d}P_{ns}(r)}{\mathrm{d}r}\right)^2 = \frac{4Z^3}{n^3\,a_0^3} \leftrightarrow |\Psi(0)|^2 = \pi^{-1}\cdot\left(\frac{Z}{n\,a_0}\right)^3 \tag{25.6}$$

Chapter 26

Two-particle operators

For two-particle operators, a similar expression is found:

$$\begin{aligned} S(ab,cd) &= [t]^{-\frac{1}{2}}\,[k]^{\frac{1}{2}}\,[\kappa_1,k_1,\kappa_2,k_2]^{\frac{1}{2}} \sum_{j_a.j_b.j_c.j_d} [j_a,j_b,j_c,j_d]^{\frac{1}{2}} \\ &\times (-1)^{\kappa_2+k_1+k+t} \begin{Bmatrix} \kappa_1 & \kappa_2 & k \\ k_2 & k_1 & t \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa_1 \\ l_a & l_c & k_1 \\ j_a & j_c & t \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa_2 \\ l_b & l_d & k_2 \\ j_b & j_d & t \end{Bmatrix} \\ &\times \left(j_a j_b \parallel \left\{ A^{(t)} B^{(t)} \right\}^{(0)} \parallel j_c j_d \right) \end{aligned} \tag{26.1}$$

As long as $l_1 + k + l_2$ is even, the reduced matrix element of the $C^{(t)}$ tensor depends explicitly only on j_1 and j_2 as shown in equation (20.3). Using this and the fact that the instantaneous Coulomb interaction is an even operator, we obtain the relativistic form of the Slater integral from equation (26.1):

$$\begin{aligned} R^k(ab,cd) &= \tfrac{1}{4} \sum_{j_a,j_b,j_c,j_d} [j_a,j_b,j_c,j_d] \begin{Bmatrix} j_a & k & j_c \\ l_c & \frac{1}{2} & l_a \end{Bmatrix}^2 \begin{Bmatrix} j_b & k & j_d \\ l_d & \frac{1}{2} & l_b \end{Bmatrix}^2 \\ &\times \int_0^\infty \int_0^\infty \mathrm{d}r_1 \mathrm{d}r_2 \left(F_a F_c + G_a G_c\right)_1 r_<^k / r_>^{k+1} \left(F_b F_d + G_b G_d\right)_2 \end{aligned} \tag{26.2}$$

So in the most general case, the familiar R^k integral turns out to be a weighted sum over 16 relativistic integrals, each of which has the same non-relativistic limit. If these integrals were independent of j (which in the Pauli approximation means neglecting the G_j's) the prefacing factor can be calculated explicitly yielding unity. With the above relativistic definition, the two-body Darwin term will be included in the "cross-terms" $F_a F_c G_b G_d$ and $G_a G_c F_b F_d$ in the above integral.

Chapter 27

Relativistic core for B-spline excitations

A desirable extension of the basic B-spline program is to improve the quality of its results in more relativistic cases by including the capability of reading core orbitals generated by the MCDF package.
The MCDF package generates multi-configuration core orbitals using the Dirac-Fock equations. The Dirac-Fock equations are based upon the same principles as the Hartree-Fock equations, but instead of using classical quantum mechanics, the Dirac theory is used to build the equations. For the central force problem it is convenient to write down all equations in a two-component form. This leaves us with two-component eigenfunctions, referred to as large and small components that can be retrieved from the output of the MCDF program. Actually, our (non-relativistic) B-spline program is not designed to produce them directly. Using MCDF core orbitals as input and including the most important relativistic corrections for the series will however yield an equivalent improvement. It is therefore necessary to redefine the Hartree Y_k functions as they occur in the Hartree-Fock equations (10.3).

27.1 Knot-points and interpolation of MCDF orbitals

The points r_i on which the MCDF orbitals are calculated, are given by:

$$r(i) = \frac{1}{Z}\left(e^{-\frac{65}{16}+\frac{i}{16}} - e^{-\frac{65}{16}}\right) \tag{27.1}$$

Here, Z (NZ in the program) is the atomic charge: for high charge, it is important to have sufficient points close to the origin. The sequence is not very different from the sequence used in MCHF. The main difference is that the MCDF sequence has points much closer to $r = 0$ than MCHF has. For a proper interpolation of the MCDF orbitals, we can use the current routine that generates the knotpoint sequence. Important though is to change the parameter PREFIST to a much smaller value: $\left(e^{-\frac{65}{16}+\frac{1}{16}} - e^{-\frac{65}{16}}\right) \approx 1.1 \times 10^{-3}$.

27.2 Redefinition of the R^k and Y_k integrals

The MCDF core orbitals are composed from a large component $F(r)$ and a small component $G(r)$. From this, the relativistic definition of the Hartree function Y_k^R of the traditional Y_k integral, see equation (10.3), is given by:

$$\frac{1}{r}Y_k^R(ab,r) = \tfrac{1}{2}\sum_{j_a,j_b}[j_a,j_b]\begin{Bmatrix} j_a & k & j_b \\ l_b & \frac{1}{2} & l_a \end{Bmatrix}^2 \int_0^\infty \frac{r_<^k}{r_>^{k+1}}\left(F_a(s)F_b(s)+G_a(s)G_b(s)\right)\,\mathrm{d}s \tag{27.2}$$

As an example, the expression for the direct interaction for s-electrons $|b\rangle$ from the core reduces to:

$$\frac{1}{r}Y_k^R(bb,r) = \delta(k,0)\int_0^\infty \frac{r_<^k}{r_>^{k+1}}\left(F_b(s)^2+G_b(s)^2\right)\,\mathrm{d}s \tag{27.3}$$

These redefinitions are to be applied to the B-spline expression (11.11), with the use of Bentley's method [Bentley, 1994] without off-diagonal Lagrange multipliers:

$$H_{ij} = \langle B_i|H_{BN}|B_j\rangle + \sum_b q_b\left\langle B_i\left|\frac{1}{r}Y_0(bb,r)\right|B_j\right\rangle - \frac{1}{2}\sum_k \frac{\langle l_a\parallel C^{(k)}\parallel l_b\rangle^2}{(2l_a+1)(2l_b+1)}\langle B_i|Y_k(B_jb,r)|b\rangle \tag{27.4}$$

One concludes that the core itself is determined by the second term in the above; equation (27.2) for equivalent electrons is inserted.
If a is associated with the channel electron and b with the core electrons, one uses the expansion:

$$Y_k^R(ab,r) = \sum_i c_i Y_k^R(B_ib,r) \tag{27.5}$$

For the third term, one needs to calculate $Y_k^R(B_jb,r)$ with B_j a B-spline. Given that small components of B-spline functions are not (yet) defined and therefore neglected, expression (27.2) now reduces to:

$$\frac{1}{r}Y_k^R(B_jb,r) = \tfrac{1}{2}\sum_{j_a,j_b}[j_a,j_b]\begin{Bmatrix} j_a & k & j_b \\ l_b & \frac{1}{2} & l_a \end{Bmatrix}^2 \int_0^\infty \frac{r_<^k}{r_>^{k+1}}B_j(s)F_b(s)\,\mathrm{d}s \tag{27.6}$$

There is no j_a-value associated with the channel (with $\{|B_j\rangle\}$ as basis), so the sum over j_a can be carried out directly by means of equation (2.11), and the above is reduced to:

$$\frac{1}{r}Y_k^R(B_jb,r) = \tfrac{1}{2}\sum_{j_b}[j_b]\cdot[l_b]^{-1}\int_0^\infty \frac{r_<^k}{r_>^{k+1}}B_j(s)F_b(s)\,\mathrm{d}s \tag{27.7}$$

For core s-electrons $|b\rangle$ this simply reduces to:

$$\frac{1}{r}Y_k^R(B_jb,r) = \frac{1}{r}Y_k(B_jb,r) \tag{27.8}$$

In accordance with equation (26.2), the relativistic R^k-integral is given by:

$$\left\langle c(r)\left|\frac{1}{r}Y_k^R(ab,r)\right|d(r)\right\rangle = \tfrac{1}{2}\sum_{j_c,j_d}[j_c,j_d]\begin{Bmatrix} j_c & k & j_d \\ l_d & \frac{1}{2} & l_c \end{Bmatrix}^2 \cdot \int_0^\infty \frac{1}{r}Y_k^R(ab,r)\left(F_c(r)F_d(r)+G_c(r)G_d(r)\right)\,\mathrm{d}r \tag{27.9}$$

In the program Basis, only $\left\langle B_i(r)\left|\frac{1}{r}Y_k^R(ab,r)\right|b(r)\right\rangle$ is needed. Again neglecting small omponents and averaging over possible values of j_a, this reduces to:

$$\left\langle B_i(r)\left|\frac{1}{r}Y_k^R(ab,r)\right|b(r)\right\rangle = \tfrac{1}{2}\sum_{j_b}[j_b]\cdot[l_b]^{-1}\int_0^\infty \frac{1}{r}Y_k^R(ab,r)B_i(r)F_b(r)\,\mathrm{d}s \tag{27.10}$$

Again, for core s-electrons, the RHS factor prefacing the integral equals 1.
A similar expression is valid for all core electrons $|b\rangle$:

$$\left\langle B_i(r)\left|\frac{1}{r}Y_k^R(bb,r)\right|a(r)\right\rangle = \int_0^\infty \frac{1}{r}Y_k^R(bb,r)B_i(r)F_a(r)\,\mathrm{d}s \tag{27.11}$$

Appendices

Appendix A

Other useful Coulomb matrix elements

A.1 $l^N \leftrightarrow l^{N-2}l'^2$

$$\left\langle l^N(SL)\,|\,C\,|\,l^{N-2}\,(S_1L_1),l'^2(S_2L_2)\,(S'L')\right\rangle = \sqrt{\tfrac{1}{2}N(N-1)}\cdot\delta(SS')\cdot\delta(LL')$$
$$\cdot\sum_k(-1)^k\left\langle l\parallel C^{(k)}\parallel l'\right\rangle^2\cdot\mathbf{R^k}(\mathbf{l^2},\mathbf{l'^2})\cdot\sum_{\tilde{S}\tilde{L}}\cdot[\tilde{L},L_2,\tilde{S},S_2]^{\frac{1}{2}}\cdot(-1)^{L+L_2+L_1}\cdot(-1)^{1+S_1+S}$$
$$\cdot\begin{Bmatrix}S_2 & \frac{1}{2} & \frac{1}{2}\\ \tilde{S} & S & S_1\end{Bmatrix}\begin{Bmatrix}\tilde{L} & L & l\\ L_2 & l & L_1\end{Bmatrix}\begin{Bmatrix}l & L_2 & l\\ l' & k & l'\end{Bmatrix}\left(l^N\,SL\{|l^{N-1}\tilde{S}\tilde{L}\right)\left(l^{N-1}\,\tilde{S}\tilde{L}\{|l^{N-2}S_1L_1\right) \tag{A.1}$$

A.2 $l'^{\,2}l^N \leftrightarrow l^N l''^{\,2}$

$$\left\langle l'^2(S_1L_1)l^N(S_2L_2)SL\,|\,C\,|\,l^N(S_2L_2)l''^2(S_1L_1)SL\right\rangle = (-1)^{S_1+S_2-S}\cdot(-1)^{L_1+L_2-L}$$
$$\cdot\sum_k(-1)^k\left\langle l'\parallel C^{(k)}\parallel l''\right\rangle^2\cdot\mathbf{R^k}(\mathbf{l'^2},\mathbf{l''^2})\cdot(-1)^{L_1}\cdot\begin{Bmatrix}k & l' & l''\\ L_1 & l'' & l'\end{Bmatrix} \tag{A.2}$$

A.3 $l^N \leftrightarrow l^{N-2}l'l''$

$$\left\langle l^N(SL)\,|\,C\,|\,(l^{N-2}{}_{S_1L_1},l')_{S_{12}L_{12}}\,l''(S'L')\right\rangle \quad = \quad \sqrt{N(N-1)}\cdot\delta(SS')\cdot\delta(LL')$$
$$\cdot\sum_k\left\langle l\parallel C^{(k)}\parallel l'\right\rangle\left\langle l\parallel C^{(k)}\parallel l''\right\rangle\cdot\mathbf{R^k}(\mathbf{l^2},\mathbf{l'l''})\cdot(-1)^{L_1+L_{12}+L}\cdot\sum_{S_2L_2}\delta(S_2,S_{12})\cdot[L_2,L_{12}]^{\frac{1}{2}}$$
$$\cdot(-1)^{L_2}\begin{Bmatrix}k & L_{12} & L_2\\ L & l & l''\end{Bmatrix}\cdot\begin{Bmatrix}k & L_{12} & L_2\\ L_1 & l & l'\end{Bmatrix}\cdot\left(l^N\,SL\{|l^{N-1}S_2L_2\right)\left(l^{N-1}\,S_2L_2\{|l^{N-2}S_1L_1\right) \tag{A.3}$$

A.4 $l^N l' \leftrightarrow l^{N-1} l''^2$

$$\begin{aligned}
&\left\langle l^N (S_1 L_1)\, l'\, SL \,|\, C \,|\, l^{N-1} (S_1' L_1')\, l''^2 (S_2 L_2)\, S' L' \right\rangle = \sqrt{2N} \cdot \delta(SS') \cdot \delta(LL') \\
&\sum_k (-1)^k \left\langle l \parallel C^{(k)} \parallel l'' \right\rangle \left\langle l' \parallel C^{(k)} \parallel l'' \right\rangle \cdot \mathbf{R^k}(\mathbf{ll'}, \mathbf{l''^2}) \cdot [L_1, S_1, L_2, S_2]^{\frac{1}{2}} \left(l^N\, S_1 L_1 \{| l^{N-1} S_1' L_1' \right) \\
&\cdot (-1)^{1+S_1'+S} \begin{Bmatrix} S_2 & \frac{1}{2} & \frac{1}{2} \\ S_1 & S & S_1' \end{Bmatrix} (-1)^{L+L_2+L_1'} \begin{Bmatrix} L_1 & L & l' \\ L_2 & l & L_1' \end{Bmatrix} \begin{Bmatrix} l & L_2 & l' \\ l'' & k & l'' \end{Bmatrix}
\end{aligned} \tag{A.4}$$

A.5 $l^N l' \leftrightarrow l^{N-1} s l''$

$$\begin{aligned}
&\left\langle l^N (S_1 L_1)\, l' (SL) \,|\, C \,|\, l^{N-1} (S_2 L_2)\, s (S_1' L_2)\, l'' (S' L') \right\rangle = \sqrt{N} \cdot \delta(SS') \cdot \delta(LL') \cdot \delta(S_1, S_1') \\
&\cdot \left\langle l \parallel C^{(l)} \parallel s \right\rangle \left\langle l' \parallel C^{(l)} \parallel l'' \right\rangle \cdot \mathbf{R^l}(\mathbf{ll'}, \mathbf{sl''}) \cdot (-1)^{L_2+l''+L} \cdot [L_1]^{\frac{1}{2}} \cdot [l]^{-\frac{1}{2}} \\
&\cdot (-1)^l \cdot \left(l^N\, S_1 L_1 \nu_1 \{| l^{N-1} S_2 L_2 \nu_2 \right) \cdot \begin{Bmatrix} L_2 & l & L_1 \\ l' & L & l'' \end{Bmatrix} \\
&+\sqrt{N} \cdot \delta(SS') \cdot \delta(LL') \cdot \left\langle l \parallel C^{(l')} \parallel l'' \right\rangle \left\langle l' \parallel C^{(l')} \parallel s \right\rangle \cdot \mathbf{R^{l'}}(\mathbf{ll'}, \mathbf{l''s}) \cdot (-1)^{L_2+L} \cdot [L_1]^{\frac{1}{2}} \cdot [l']^{-\frac{1}{2}} \\
&\begin{Bmatrix} l'' & l & l' \\ L_1 & L & L_2 \end{Bmatrix} (-1)^{l'+l''} \cdot [S_1, S_1']^{\frac{1}{2}} \cdot (-1)^{S_1+S_1'} \cdot \begin{Bmatrix} S_2 & S_1 & \frac{1}{2} \\ S & S_1' & \frac{1}{2} \end{Bmatrix} \cdot \left(l^N\, S_1 L_1 \nu_1 \{| l^{N-1} S_2 L_2 \nu_2 \right)
\end{aligned} \tag{A.5}$$

A.6 $l^N l' \leftrightarrow l^{N-1} l'' l'''$

$$\begin{aligned}
&\left\langle l^N (S_1 L_1)\, l'\, SL \,|\, C \,|\, l^{N-1} (S_1' L_1')\, l'' (S_2 L_2)\, l''\, S' L' \right\rangle = \sqrt{N} \cdot \delta(SS') \cdot \delta(LL') \cdot \delta(S_1, S_2) \\
&\cdot \sum_k (-1)^k \cdot \left\langle l \parallel C^{(k)} \parallel l'' \right\rangle \left\langle l' \parallel C^{(k)} \parallel l''' \right\rangle \cdot \mathbf{R^k}(\mathbf{ll'}, \mathbf{l''l'''}) \cdot [L_1, L_2]^{\frac{1}{2}} \\
&\cdot \left(l^N\, S_1 L_1 \{| l^{N-1} S_1' L_1' \right) \cdot (-1)^{l+L_1+L_1'} \cdot \begin{Bmatrix} l & k & l'' \\ L_2 & L_1' & L_1 \end{Bmatrix} \cdot (-1)^{L_2+l'''+L} \cdot \begin{Bmatrix} k & l' & l''' \\ L & L_2 & L_1 \end{Bmatrix} \\
&+\sqrt{N} \cdot \delta(SS') \cdot \delta(LL') \cdot \sum_{k'} (-1)^{k'} \cdot \left\langle l \parallel C^{(k')} \parallel l''' \right\rangle \left\langle l' \parallel C^{(k')} \parallel l'' \right\rangle \cdot \mathbf{R^{k'}}(\mathbf{ll'}, \mathbf{l'''l''}) \\
&\cdot (-1)^{S_1+S_2} \cdot \begin{Bmatrix} S_1 & S & \frac{1}{2} \\ S_2 & S_1' & \frac{1}{2} \end{Bmatrix} \cdot [S_1, L_1, S_2, L_2]^{\frac{1}{2}} \cdot \begin{Bmatrix} l & k' & l''' \\ L_1 & l' & L \\ L_1' & l'' & L_2 \end{Bmatrix} \left(l^N\, S_1 L_1 \{| l^{N-1} S_1' L_1' \right)
\end{aligned} \tag{A.6}$$

A.7 $l^N l''^2 \leftrightarrow l^N l' l'''$, l^N spectator

$$\begin{aligned}\Big\langle l^N(S_1L_1)\,l''^{\,2}(S_2L_2)\,SL|\,C\,|\,l^N(S_1L_1)\,l'(S_{12}L_{12})\,l'''\,S'L'\Big\rangle &= \sqrt{2}\cdot\delta(SS')\cdot\delta(LL')\\
\cdot\sum_k(-1)^k\cdot\Big\langle l''\parallel C^{(k)}\parallel l'\Big\rangle\Big\langle l''\parallel C^{(k)}\parallel l'''\Big\rangle\cdot\mathbf{R^k}(\mathbf{l''^2},\mathbf{l'l'''})\cdot[S_{12},L_{12},S_2,L_2]^{\frac12}&\\
\cdot(-1)^{S_1+1+S}\cdot\begin{Bmatrix}S_1&\frac12&S_{12}\\\frac12&S&S_2\end{Bmatrix}\cdot(-1)^{L+L_1+L_2}\cdot\begin{Bmatrix}L_1&l'&L_{12}\\l'''&L&L_2\end{Bmatrix}\cdot\begin{Bmatrix}k&l''&l'''\\L_2&l'&l''\end{Bmatrix}&\quad(A.7)\end{aligned}$$

A.8 $l^N l' l'' \leftrightarrow l^N l''^2$, l'' spectator

$$\begin{aligned}\Big\langle l^N(S_1L_1)\,l'(S_{12}L_{12})\,l''SL|\,C\,|\,l^N(S_1'L_1')\,l''^2(S_2L_2)\,S'L'\Big\rangle &= N\sqrt{2}\cdot\delta(SS')\cdot\delta(LL')\cdot\delta(S_1,S_1')\\
\cdot(-1)^{S_1'+S+1}\cdot[S_{12},S_2]^{\frac12}\cdot\begin{Bmatrix}\frac12&S_1'&S_{12}\\S&\frac12&S_2\end{Bmatrix}\cdot\sum_k(-1)^k\cdot\Big\langle l\parallel C^{(k)}\parallel l\Big\rangle\Big\langle l'\parallel C^{(k)}\parallel l''\Big\rangle\cdot\mathbf{R^k}(\mathbf{ll'},\mathbf{ll''})&\\
\cdot[L_1,L_1',L_{12},L_2]^{\frac12}\cdot\begin{Bmatrix}l''&L_1'&L_{12}\\L&l''&L_2\end{Bmatrix}\cdot\begin{Bmatrix}L_1&L_1'&k\\l''&l'&L_{12}\end{Bmatrix}&\\
\cdot\sum_{\tilde S\tilde L}\Big(l^N\,S_1L_1\{|l^{N-1}\tilde S\tilde L\Big)\cdot\Big(l^N\,S_1'L_1'\{|l^{N-1}\tilde S\tilde L\Big)\cdot(-1)^{\tilde L+L+L_{12}+l+l''+L_1+k}\cdot\begin{Bmatrix}L_1&L_1'&k\\l&l&\tilde L\end{Bmatrix}&\\
-N\sqrt{2}\cdot\delta(SS')\cdot\delta(LL')\cdot\sum_{k'}(-1)^{k'}\cdot\Big\langle l\parallel C^{(k')}\parallel l''\Big\rangle\Big\langle l'\parallel C^{(k')}\parallel l\Big\rangle\cdot\mathbf{R^{k'}}(\mathbf{ll'},\mathbf{l''l})&\\
\cdot(-1)^{S_1-S}\cdot[S_1,S_1',S_{12},S_2]^{\frac12}\cdot\begin{Bmatrix}S_{12}&\frac12&S_1'\\S_2&S&\frac12\end{Bmatrix}\cdot(-1)^{L+L_1'}\cdot[L_1,L_1',L_{12},L_2]^{\frac12}\cdot\begin{Bmatrix}L_1'&L_{12}&l''\\l''&L_2&L\end{Bmatrix}&\\
\cdot\sum_{\tilde S\tilde L}\Big(l^N\,S_1L_1\{|l^{N-1}\tilde S\tilde L\Big)\cdot\Big(l^N\,S_1'L_1'\{|l^{N-1}\tilde S\tilde L\Big)\cdot\begin{Bmatrix}\frac12&\tilde S&S_1'\\\frac12&S_{12}&S_1\end{Bmatrix}\cdot\begin{Bmatrix}k'&l'&l\\l''&L_{12}&L_1'\\l&L_1&\tilde L\end{Bmatrix}&\end{aligned}$$

(A.8)

A.9 $l'^{4l'+2} l^{N-2} l'' \leftrightarrow l'^{4l'+1} l^N$

$$\begin{aligned}\Big\langle l'^{4l'+2}l^{N-2}(S_1L_1)\,l''\;SL|\,C\,|\,l'^{4l'+1}l^N(S_1'L_1')S'L'\Big\rangle &= \delta(SS')\delta(LL')(-1)^N\sqrt{N(N-1)}\\
\cdot[S_1',L_1']^{\frac12}\cdot\sum_k(-1)^k\Big\langle l\parallel C^{(k)}\parallel l'\Big\rangle\Big\langle l\parallel C^{(k)}\parallel l''\Big\rangle\cdot\mathbf{R^k}(\mathbf{l'l''},\mathbf{ll})&\\
\cdot\sum_{\tilde S\tilde L}(-1)^{1+\tilde S+S}\cdot[\tilde S,\tilde L]^{\frac12}\cdot\begin{Bmatrix}\frac12&S_1&S\\\frac12&S_1'&\tilde S\end{Bmatrix}\cdot\begin{Bmatrix}L_1&l''&L\\l&k&l'\\\tilde L&l&L_1'\end{Bmatrix}\cdot&\\
\cdot\Big(l^N\,(S_1'L_1')\{|l^{N-1}(\tilde S\tilde L)\Big)\Big(l^{N-1}(\tilde S\tilde L)\{|l^{N-2}(S_1L_1)\Big)&\end{aligned}$$

(A.9)

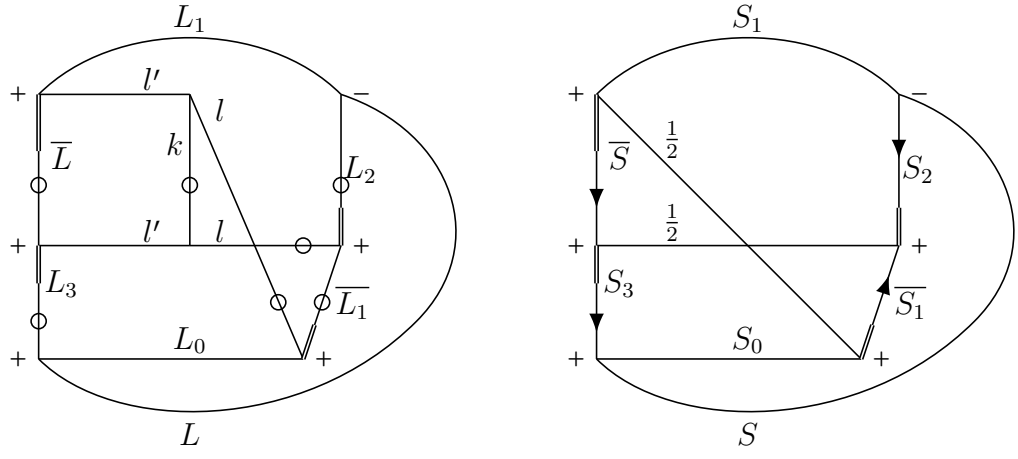
A.10 $l'^{4l'+2}l^N \leftrightarrow l'^{4l'}l^{N+2}$

$$\left\langle l'^{4l'+2}l^N(SL)\,|\,C\,|\,l'^{4l'}(S_1L_1)l^{N+2}(S_2L_2)S'L'\right\rangle = \delta(SS')\delta(LL')\sqrt{\frac{(N+2)(N+1)}{2}}\,[S,L]^{-\frac{1}{2}}$$
$$\cdot[S_1,L_1,S_2,L_2]^{\frac{1}{2}}\,(-1)^{1+S+S_2}\cdot(-1)^{L+L_1+L_2}\sum_k\left\langle l'\parallel C^{(k)}\parallel l\right\rangle^2(-1)^k\begin{Bmatrix} l' & l' & L_1\\ l & l & k\end{Bmatrix}\cdot\mathbf{R^k}(\mathbf{l'l'},\mathbf{ll})$$
$$\cdot\sum_{\tilde S\tilde L}[\tilde S,\tilde L]^{\frac{1}{2}}\cdot\begin{Bmatrix} l & l & L_1\\ L_2 & L & \tilde L\end{Bmatrix}\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & S_1\\ S_2 & S & \tilde S\end{Bmatrix}\cdot\left(l^{N+2}\,S_2L_2\{|l^{N+1}\tilde S\tilde L\right)\left(l^{N+1}\tilde S\tilde L\{|l^NSL\right) \tag{A.10}$$

A.11 $l'^{M+2}l^N \leftrightarrow l'^{M}l^{N+2}$

$$\left\langle l'^{M+2}(S_3L_3)l^N(S_0L_0)\,SL\,|\,C\,|\,l'^M(S_1L_1)l^{N+2}(S_2L_2)SL\right\rangle = \tfrac{1}{2}\sqrt{(M+2)(M+1)(N+2)(N+1)}$$
$$\cdot\sum_{\overline S\,\overline L}\sum_{\overline{S_1}\,\overline{L_1}}\left(l'^{M+2}\,S_3L_3\{|l'^{M+1}\overline S\,\overline L\right)\left(l'^{M+1}\overline S\,\overline L\{|l'^MS_1L_1\right)\cdot\left(l^{N+2}\,S_2L_2\{|l^{N+1}\overline{S_1}\,\overline{L_1}\right)\left(l^{N+1}\overline{S_1}\,\overline{L_1}\{|l^NS_0L_0\right)$$
$$\cdot(-1)^{S_3+S_0-S}\cdot\left[\overline S,S_3,\overline{S_1},S_2\right]^{\frac{1}{2}}\begin{Bmatrix} S_1 & S_2 & S\\ \frac{1}{2} & \overline{S_1} & S_0\\ \overline S & \frac{1}{2} & S_3\end{Bmatrix}\cdot(-1)^{L_2+L_1+\overline L+\overline{L_1}}\cdot\left[\overline L,L_3,\overline{L_1},L_2\right]^{\frac{1}{2}}$$
$$\sum_k\left\langle l'\parallel C^{(k)}\parallel l\right\rangle^2\cdot\mathbf{R^k}(\mathbf{l'l'},\mathbf{ll})\cdot\begin{Bmatrix} L_2 & L_1 & l' & l\\ L & \overline L & k & \overline{L_1}\\ L_0 & L_3 & l' & l\end{Bmatrix} \tag{A.11}$$

Graphically:



A.12 $l'^{4l'+2}l^N \leftrightarrow l'^{4l'+1}l^{N+1}$

Assuming that parity(l')=parity(l):

$$\begin{aligned}
&\left\langle l'^{4l'+2}\, l^N(SL)\,|\,C\,|\,l'^{4l'+1}\, l^{N+1}(S_1L_1)S'L'\right\rangle = \delta(SS')\delta(LL')(-1)^{N-1}N\sqrt{(4l'+2)(N+1)}\\
&\cdot[S_1,L_1]^{\frac{1}{2}}\cdot[\tfrac{1}{2},l']^{-\frac{1}{2}}\cdot\sum_k\left\langle l'\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k)}\parallel l\right\rangle\cdot\mathbf{R^k(l'l,ll)}\cdot\sum_{\tilde S\tilde L}\left(l^{N+1}\,S_1L_1\{|l^N\tilde S\tilde L\right)[\tilde S,\tilde L]^{\frac{1}{2}}\\
&\cdot\sum_{S_2L_2}\left(l^N\,SL\{|l^{N-1}S_2L_2\right)\left(l^N\,\tilde S\tilde L\{|l^{N-1}S_2L_2\right)(-1)^{1+\tilde S+S}\begin{Bmatrix}\tilde S & \frac{1}{2} & S_1\\ S & \frac{1}{2} & S_2\end{Bmatrix}\begin{Bmatrix}L_2 & l & \tilde L\\ l & k & l\\ L & l' & L_1\end{Bmatrix}\\
+\quad&\delta(l,l')\cdot(-1)^N(4l'+1)\sqrt{(4l'+2)(N+1)}\cdot[S_1,L_1]^{\frac{1}{2}}\cdot[\tfrac{1}{2},l']^{-\frac{1}{2}}\cdot[S,L]^{-\frac{1}{2}}\cdot\left(l^{N+1}\,S_1L_1\{|l^NSL\right)\\
&\sum_k(-1)^k\left\langle l'\parallel C^{(k)}\parallel l'\right\rangle\left\langle l'\parallel C^{(k)}\parallel l\right\rangle\mathbf{R^k(l'l',l'l)}\sum_{\tilde S\tilde L}[\tilde S,\tilde L]\left[(2l'+1)(4l'+1)\right]^{-1}(-1)^{l'+l+\tilde L}\begin{Bmatrix}k & l' & l\\ \tilde L & l' & l'\end{Bmatrix}
\end{aligned}\tag{A.12}$$

A.13 $l'^{4l'+2}l^N \leftrightarrow l'^{4l'+1}l^Nl''$

Given the condition that parity(l'') equals parity(l'), one obtains:

$$\begin{aligned}
&\left\langle l'^{4l'+2}l^N(SL)\,|\,C\,|\,l'^{4l'+1}l^N(S_3L_3)S_1L_1\; l''(S'L')\right\rangle = \delta(SS')\delta(LL')(-1)^{N-1}N\sqrt{4l'+2}\\
&\Bigg[\sum_k\left\langle l'\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k)}\parallel l''\right\rangle\cdot\mathbf{R^k(l'l,ll'')}\cdot[\tfrac{1}{2},l',S_1]^{-\frac{1}{2}}\cdot[S_3,L_3,L_1]^{\frac{1}{2}}\cdot(-1)^{k+L+L_3}\\
&\sum_{S_2L_2}\delta(S_1,S_2)\left(l^N\,SL\{|l^{N-1}S_2L_2\right)\left(l^N\,S_3L_3\{|l^{N-1}S_2L_2\right)\begin{Bmatrix}l & k & l'\\ L_1 & L_3 & L_2\end{Bmatrix}\begin{Bmatrix}k & l & l''\\ L & L_1 & L_2\end{Bmatrix}\\
&-\sum_{k'}\left\langle l'\parallel C^{(k')}\parallel l''\right\rangle\left\langle l\parallel C^{(k')}\parallel l\right\rangle\cdot\mathbf{R^{k'}(l'l,l''l)}\cdot[\tfrac{1}{2},l',S_3]^{-\frac{1}{2}}\cdot[S_1,L_1,L_3]^{\frac{1}{2}}\cdot\delta(S,S_3)\\
&\sum_{S_2L_2}\left(l^N\,SL\{|l^{N-1}S_2L_2\right)\left(l^N\,S_3L_3\{|l^{N-1}S_2L_2\right)(-1)^{l+l''+L_1+L_2}\begin{Bmatrix}l & k' & l\\ L_3 & L_2 & L\end{Bmatrix}\begin{Bmatrix}k' & l'' & l'\\ L_1 & L_3 & L\end{Bmatrix}\Bigg]
\end{aligned}\tag{A.13}$$

A.14 $l'^{4l'+1}l^Nl''\leftrightarrow l'^{4l'+2}l^{N-2}l''^{\,2}$

$$\begin{aligned}
&\left\langle\left(l'^{4l'+1}l^NS_2L_2\right)S_{123}L_{123}\,l''\,SL|\,C\,|\,l'^{4l'+2}l^{N-2}S_2'L_2'\,l''^{\,2}S_3'L_3'\,SL\right\rangle = (-1)^{N-1}\sqrt{2(4l'+2)N(N-1)}\\
&\cdot[S_2,L_2,S_{123},L_{123},S_3',L_3']^{\frac{1}{2}}\cdot[\tfrac{1}{2},l']^{-\frac{1}{2}}\cdot\sum_k(-1)^k\cdot\left\langle l\parallel C^{(k)}\parallel l'\right\rangle\left\langle l\parallel C^{(k)}\parallel l''\right\rangle\cdot\mathbf{R^k(l^2,l'l'')}\\
&\cdot\begin{Bmatrix}S_2' & \frac{1}{2} & S_{123}\\ \frac{1}{2} & S & S_3'\end{Bmatrix}\cdot\begin{Bmatrix}L_2' & l'' & L_{123}\\ l'' & L & L_3'\end{Bmatrix}\cdot\sum_{\overline{S}\,\overline{L}}[\overline{S},\overline{L}]^{\frac{1}{2}}\cdot\left(l^N\,S_2L_2\{|l^{N-1}\overline{S}\,\overline{L}\right)\left(l^{N-1}\overline{S}\,\overline{L}\{|l^{N-2}S_2'L_2'\right)\\
&\cdot(-1)^{S_{123}+S+S_2'+S_3'+1+\overline{S}}\cdot\begin{Bmatrix}\frac{1}{2} & S_2' & S_{123}\\ \frac{1}{2} & S_2 & \overline{S}\end{Bmatrix}\cdot(-1)^{L+L_2'+L_3'}\cdot\begin{Bmatrix}L_2' & l'' & L_{123}\\ l & k & l'\\ \overline{L} & l & L_2\end{Bmatrix}
\end{aligned}\tag{A.14}$$

A.15 $l'\,l^N l''' \leftrightarrow l^N l''^{\,2}$, l^N spectator

The phase factor w.r.t. A.7 equals $(-1)^x = (-1)^N \cdot (-1)^{S_2+\frac{1}{2}-S_{12}} \cdot (-1)^{L_2+l'-L_{12}}$.

$$\Big\langle l'\,l^N(S_2L_2)S_{12}L_{12}\,l'''\,SL\big|\,C\,\big|\,l^N(S_2L_2)\,l''^{\,2}(S'_3L'_3)\,SL\Big\rangle = (-1)^N\sqrt{2}\cdot[S_{12},L_{12},S'_3,L'_3]^{\frac{1}{2}}$$
$$\cdot(-1)^{S_{12}+S+\frac{1}{2}}\cdot\begin{Bmatrix} S_{12} & S & \frac{1}{2}\\ S'_3 & \frac{1}{2} & S_2\end{Bmatrix}\cdot(-1)^{L_{12}+L+l'''}\cdot\begin{Bmatrix} L_{12} & L & l'''\\ L'_3 & l' & L_2\end{Bmatrix}$$
$$\sum_k(-1)^k\cdot\Big\langle l'\parallel C^{(k)}\parallel l''\Big\rangle\Big\langle l'''\parallel C^{(k)}\parallel l''\Big\rangle\cdot\mathbf{R^k}(\mathbf{l'l'''},\mathbf{l''^{\,2}})\cdot(-1)^{L'_3}\cdot\begin{Bmatrix} k & l'' & l'''\\ L'_3 & l' & l''\end{Bmatrix} \tag{A.15}$$

A.16 $l'\,l^N l'' \leftrightarrow l^N l''^{\,2}$, l'' spectator

The phase factor w.r.t. A.8 is the same $(-1)^x$, see above.

$$\Big\langle l'\,l^N(S_2L_2)S_{12}L_{12}\,l''\,SL\big|\,C\,\big|\,l^N(S'_2L'_2)\,l''^{\,2}(S'_3L'_3)\,SL\Big\rangle = (-1)^{N-1}\cdot N\sqrt{2}\cdot[S_{12},L_{12},S'_3,L'_3]^{\frac{1}{2}}$$
$$\cdot[S_2,L_2,S'_2,L'_2]^{\frac{1}{2}}\cdot\sum_k(-1)^k\cdot\Big\langle l'\parallel C^{(k)}\parallel l\Big\rangle\Big\langle l\parallel C^{(k)}\parallel l''\Big\rangle\cdot\mathbf{R^k}(\mathbf{l'l},\mathbf{ll''})$$
$$\cdot(-1)^{2S'_2+\frac{1}{2}-S_{12}-S}\cdot(-1)^{L_2+L'_2+L_{12}+l'+L}\cdot\begin{Bmatrix} S'_2 & \frac{1}{2} & S_{12}\\ \frac{1}{2} & S & S'_3\end{Bmatrix}\cdot\begin{Bmatrix} L'_2 & l'' & L_{12}\\ l'' & L & L'_3\end{Bmatrix}$$
$$\sum_{\overline{S}\,\overline{L}}\begin{Bmatrix} \frac{1}{2} & S_2 & S_{12}\\ \frac{1}{2} & S'_2 & \overline{S}\end{Bmatrix}\cdot\begin{Bmatrix} L_2 & l & \overline{L}\\ L_{12} & l'' & L'_2\\ l' & k & l\end{Bmatrix}\cdot\Big(l^N\,S_2L_2\{|l^{N-1}\overline{S}\,\overline{L}\Big)\cdot\Big(l^N\,S'_2L'_2\{|l^{N-1}\overline{S}\,\overline{L}\Big)$$
$$-(-1)^{N-1}\cdot N\sqrt{2}\cdot\delta(S_2\,S'_2)\cdot[S_{12},L_{12},S'_3,L'_3]^{\frac{1}{2}}\cdot[L_2,L'_2]^{\frac{1}{2}}\cdot(-1)^{S_{12}+S+\frac{1}{2}}\cdot\begin{Bmatrix} S_{12} & S'_2 & \frac{1}{2}\\ S'_3 & \frac{1}{2} & S\end{Bmatrix}$$
$$\cdot\begin{Bmatrix} L_{12} & L'_2 & l''\\ L'_3 & l'' & L\end{Bmatrix}\cdot\sum_{k'}(-1)^{k'}\cdot\Big\langle l'\parallel C^{(k')}\parallel l''\Big\rangle\Big\langle l\parallel C^{(k')}\parallel l\Big\rangle\cdot\mathbf{R^{k'}}(\mathbf{l'l},\mathbf{l''l})\cdot\begin{Bmatrix} L_2 & k' & L'_2\\ l'' & L_{12} & l'\end{Bmatrix}$$
$$\sum_{\overline{S}\,\overline{L}}(-1)^{\overline{L}+l+L}\cdot\begin{Bmatrix} \overline{L} & l & L'_2\\ k' & L_2 & l\end{Bmatrix}\cdot\Big(l^N\,S_2L_2\{|l^{N-1}\overline{S}\,\overline{L}\Big)\cdot\Big(l^N\,S'_2L'_2\{|l^{N-1}\overline{S}\,\overline{L}\Big) \tag{A.16}$$

A.17 $s^2 l^{N-1} l' \leftrightarrow s\,l^N l''$

The parity condition is: $(-1)^{l+l'+l''} = 1$.

$$\Big\langle s^2l^{N-1}(S_2L_2)l'(SL)\,\big|\,C\,\big|\,\Big(s\,l^N(S_1L_1)\Big)\,S_{12}L_{12}\,l''(S'L')\Big\rangle = \delta(SS')\delta(LL')(-1)^{N-1}\sqrt{2N}$$
$$\cdot\delta(L_{12},L_1)\cdot\begin{Bmatrix} l & l' & l''\\ L & L_1 & L_2\end{Bmatrix}\cdot\Big(l^N S_1L_1\{|l^{N-1}S_2L_2\Big)$$
$$\cdot\Big[\delta(S_{12},S_2)\cdot\Big\langle l'\parallel C^{(l)}\parallel l''\Big\rangle\cdot\mathbf{R^l}(\mathbf{s\,l'},\mathbf{ll''})\cdot[\tfrac{1}{2},l]^{-\frac{1}{2}}\cdot[S_1,L_1]^{\frac{1}{2}}\cdot[S_2]^{-\frac{1}{2}}\cdot(-1)^{l'+L_2+L}$$
$$-\delta(S_1,S)\cdot\Big\langle l\parallel C^{(l'')}\parallel l'\Big\rangle\cdot\mathbf{R^{l''}}(\mathbf{s\,l'},\mathbf{l''l})\cdot[\tfrac{1}{2},l'']^{-\frac{1}{2}}\cdot[S_{12},L_1]^{\frac{1}{2}}\cdot[S_1]^{-\frac{1}{2}}\cdot(-1)^{l+L_2+L}\Big] \tag{A.17}$$

Appendix B

Some perturbation operators

Matrix elements of effective (2+1)-electron operators in the configuration l^2l'.
The orbital angular momenta $l, l', \bar{l}$ and l'' are respectively associated with the orbitals a, b, c, and v (the latter two referring to closed and virtual shells).
For a two-particle excitation $cb \to a^2$, we thus obtain for the configuration l^2l' the final equation:

$$\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3)\left|T(cb\to a^2)\right|l^2(S'L')l'(S_3L_3)\right\rangle \\
&= \sum_{k,k'} 2\left\langle \bar{l}\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k')}\parallel \bar{l}\right\rangle\left\langle l'\parallel C^{(k)}\parallel l\right\rangle\left\langle l\parallel C^{(k')}\parallel l'\right\rangle \\
&\times [S,L,S',L']^{\frac{1}{2}}\,(-1)^{S+S'+1}\begin{Bmatrix} S & \frac{1}{2} & \frac{1}{2}\\ S' & S_3 & \frac{1}{2}\end{Bmatrix} \\
&\times \begin{Bmatrix} L & \bar{l} & l'\\ k' & l & l\end{Bmatrix}\begin{Bmatrix} L' & \bar{l} & l'\\ k & l & l\end{Bmatrix}\begin{Bmatrix} L & \bar{l} & l'\\ L' & L_3 & l'\end{Bmatrix}\frac{R^k(cb;aa)R^{k'}(aa;bc)}{E_A-E_B}
\end{aligned} \tag{B.1}$$

All remaining three-particle operators arise from single electron excitations in the second order of perturbation theory.
Equations (B.2) represent the $a \to v$ excitation, equations (B.3) the $b \to v$ excitation. Below, the characters D and E indicate 'direct' and 'exchange' terms. Equations corresponding to closed shell excitations $c \to a$ and $c \to b$ with $\bar{l} = l''$ are obtained from equations (B.2) and (B.3) by adding a minus sign and replacing v with c.

$$\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3)|T(DD+DD)|l^2(S'L')l'(S_3L_3)\right\rangle \\
&= \sum_{k,k'} 2\left\langle l\parallel C^{(k)}\parallel l''\right\rangle\left\langle l\parallel C^{(k')}\parallel l''\right\rangle\left\langle l'\parallel C^{(k)}\parallel l'\right\rangle\left\langle l\parallel C^{(k')}\parallel l\right\rangle \\
&\times \delta(S,S')\,(-1)^{L+l'+L_3}\,[L,L']^{\frac{1}{2}} \\
&\times\left(\begin{Bmatrix} l & l & L'\\ l'' & l & k'\end{Bmatrix}\begin{Bmatrix} l & l'' & L'\\ k & L & l\end{Bmatrix}+\begin{Bmatrix} l & l & L\\ l'' & l & k'\end{Bmatrix}\begin{Bmatrix} l & l'' & L\\ k & L' & l\end{Bmatrix}\right) \\
&\times\begin{Bmatrix} L & k & L'\\ l' & L_3 & l'\end{Bmatrix}\sum\!\!\!\!\!\!\int_{a\to v}\frac{R^k(ab;vb)R^{k'}(aa;av)}{E_A-E_B}
\end{aligned} \tag{B.2a}$$

$$
\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3)|T(ED+DE)|l^2(S'L')l'(S_3L_3)\right\rangle \\
&= \sum_{k,k'} 2\left\langle l \parallel C^{(k)} \parallel l'\right\rangle \left\langle l \parallel C^{(k')} \parallel l\right\rangle \left\langle l' \parallel C^{(k)} \parallel l''\right\rangle \left\langle l \parallel C^{(k')} \parallel l''\right\rangle \\
&\times [S,L,S',L']^{\frac{1}{2}} (-1)^k \begin{Bmatrix} S_3 & \frac{1}{2} & S \\ \frac{1}{2} & \frac{1}{2} & S' \end{Bmatrix} \\
&\times \left((-1)^S \begin{Bmatrix} k & l & l'' \\ L' & l & l \end{Bmatrix} \begin{Bmatrix} l' & L_3 & L' \\ l & L & l \\ k & l' & l'' \end{Bmatrix} + (-1)^{S'} \begin{Bmatrix} k' & l & l'' \\ L & l & l \end{Bmatrix} \begin{Bmatrix} l' & L_3 & L \\ l & L' & l \\ k & l' & l'' \end{Bmatrix} \right) \\
&\times \sum\!\!\!\!\!\!\int_{a\to v} \frac{R^k(ab;bv)R^{k'}(aa;av)}{E_A - E_B}
\end{aligned} \tag{B.2b}
$$

$$
\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3)|U(DD)|l^2(S'L')l'(S_3L_3)\right\rangle \\
&= \sum_{k,k'} 2\left\langle l \parallel C^{(k)} \parallel l\right\rangle \left\langle l \parallel C^{(k')} \parallel l\right\rangle \left\langle l' \parallel C^{(k)} \parallel l''\right\rangle \left\langle l' \parallel C^{(k')} \parallel l''\right\rangle \\
&\times \delta(S,S')\ (-1)^{S_3+L_3-(1/2+l')}\ (-1)^{S_3+S-1/2}\ [L,L']^{\frac{1}{2}} \\
&\times \begin{Bmatrix} L_3 & L & l & k' \\ l' & l & l & l' \\ l'' & k & l & L' \end{Bmatrix} \sum\!\!\!\!\!\!\int_{b\to v} \frac{R^k(ab;av)R^{k'}(ab;av)}{E_A - E_B}
\end{aligned} \tag{B.3a}
$$

$$
\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3)|U(DE+ED)|l^2(S'L')l'(S_3L_3)\right\rangle \\
&= \sum_{k,k'} 2\left\langle l \parallel C^{(k)} \parallel l'\right\rangle \left\langle l \parallel C^{(k')} \parallel l\right\rangle \left\langle l \parallel C^{(k)} \parallel l''\right\rangle \left\langle l' \parallel C^{(k')} \parallel l''\right\rangle \\
&\times [S,L,S',L']^{\frac{1}{2}}\ (-1)^{S+S'} \begin{Bmatrix} S & \frac{1}{2} & \frac{1}{2} \\ S' & \frac{1}{2} & S_3 \end{Bmatrix} \\
&\times \left(\begin{Bmatrix} l & l & l & k \\ k' & L & l' & l \\ l'' & l' & L_3 & L' \end{Bmatrix} + \begin{Bmatrix} l & l & l & k \\ k' & L' & l' & l \\ l'' & l' & L_3 & L \end{Bmatrix} \right) \\
&\times \sum\!\!\!\!\!\!\int_{b\to v} \frac{R^k(av;ba)R^{k'}(ab;av)}{E_A - E_B}
\end{aligned} \tag{B.3b}
$$

$$
\begin{aligned}
&\left\langle l^2(SL)l'(S_3L_3)|U(EE)|l^2(S'L')l'(S_3L_3)\right\rangle \\
&= \sum_{k,k'} 2\left\langle l \parallel C^{(k)} \parallel l'\right\rangle \left\langle l \parallel C^{(k')} \parallel l'\right\rangle \left\langle l \parallel C^{(k)} \parallel l''\right\rangle \left\langle l \parallel C^{(k')} \parallel l''\right\rangle \\
&\times [S,L,S',L']^{\frac{1}{2}}\ (-1)^S \cdot (-1)^{L_3+L'+l'} \cdot (1-\tfrac{1}{2}\delta(k,k')) \cdot \begin{Bmatrix} S & \frac{1}{2} & \frac{1}{2} \\ S' & \frac{1}{2} & S_3 \end{Bmatrix} \\
&\times \left(\begin{bmatrix} k & L & l & l' \\ l'' & l & l & L_3 \\ l & k' & l' & L' \end{bmatrix} + \begin{bmatrix} k' & L & l & l' \\ l'' & l & l & L_3 \\ l & k & l' & L' \end{bmatrix} \right) \sum\!\!\!\!\!\!\int_{b\to v} \frac{R^k(ab;va)R^{k'}(av;ba)}{E_A - E_B}
\end{aligned} \tag{B.3c}
$$

$$\left\langle ll'(SL) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{ab1}/\Delta E \parallel ll'(S'L') \right\rangle_{a\to b} = \left\langle a \parallel F^{(\kappa k)} \parallel b \right\rangle \cdot [S, L, S', L']^{\frac{1}{2}}$$
$$\cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot (-1)^{\kappa+k+S'+L'} \cdot \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l' \right\rangle \left\langle l' \parallel C^{(k')} \parallel l' \right\rangle \cdot R^{k'}(ab, bb) \cdot \Delta E^{-1} \cdot$$
$$\left[(-1)^{S} \cdot \begin{Bmatrix} L & l' & l' \\ k' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l & l' & l' \end{Bmatrix} + (-1)^{S'} \cdot \begin{Bmatrix} L' & l' & l' \\ k' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L' & k & L \\ l & l' & l' \end{Bmatrix} \right] \qquad \text{(B.4a)}$$

$$\left\langle ll'(SL) \parallel -(C_{AB}T^{(t)}_{BA} + T^{(t)}_{AB}C_{BA})^{ab2}/\Delta E \parallel ll'(S'L') \right\rangle_{a\to b} = \left\langle a \parallel F^{(\kappa k)} \parallel b \right\rangle \cdot [S, L, S', L']^{\frac{1}{2}}$$
$$\cdot \begin{Bmatrix} S & \kappa & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \cdot (-1)^{\kappa+k} \cdot \sum_{k'} \left\langle l \parallel C^{(k')} \parallel l' \right\rangle \left\langle l' \parallel C^{(k')} \parallel l' \right\rangle \cdot R^{k'}(ab, bb) \cdot \Delta E^{-1} \cdot$$
$$\left[(-1)^{S+L+S'+L'} (-1)^{S} \cdot \begin{Bmatrix} L & l' & l' \\ k' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L & k & L' \\ l & l' & l' \end{Bmatrix} + (-1)^{S'} \cdot \begin{Bmatrix} L' & l' & l' \\ k' & l' & l \end{Bmatrix} \cdot \begin{Bmatrix} L' & k & L \\ l & l' & l' \end{Bmatrix} \right]$$
(B.4b)

Appendix C

Special nj-symbols

C.1 3j-symbols

$$\begin{pmatrix} j & k & j \\ -j & 0 & j \end{pmatrix} = \frac{(2j)!}{[(2j-k)!(2j+k+1)!]^{\frac{1}{2}}} \tag{C.1}$$

$$\begin{pmatrix} j & 1 & j \\ -j & 0 & j \end{pmatrix} = \left(\frac{j}{(j+1)(2j+1)}\right)^{\frac{1}{2}} \tag{C.2a}$$

$$\begin{pmatrix} j & 2 & j \\ -j & 0 & j \end{pmatrix} = \left(\frac{j(2j-1)}{(j+1)(2j+1)(2j+3)}\right)^{\frac{1}{2}} \tag{C.2b}$$

$$\begin{pmatrix} j & 0 & j \\ -m & 0 & m \end{pmatrix} = (-1)^{j-m}[j]^{-\frac{1}{2}} \tag{C.3a}$$

$$\begin{pmatrix} j & 1 & j \\ -m & 0 & m \end{pmatrix} = (-1)^{j-m}\frac{m}{\sqrt{j(j+1)(2j+1)}} \tag{C.3b}$$

$$\begin{pmatrix} l & 1 & l+1 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{l-1}\left[\frac{l+1}{(2l+1)(2l+3)}\right]^{\frac{1}{2}} \tag{C.4a}$$

$$\begin{pmatrix} l & 1 & l-1 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{l}\left[\frac{l}{(2l-1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.4b}$$

$$\begin{pmatrix} l & 1 & l \\ 0 & 1 & -1 \end{pmatrix} = (-1)^{l+1}\left[\frac{1}{2(2l+1)}\right]^{\frac{1}{2}} \tag{C.4c}$$

$$\begin{pmatrix} l & 1 & l-1 \\ 0 & 1 & -1 \end{pmatrix} = (-1)^l \left[\frac{l-1}{2(2l-1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.4d}$$

$$\begin{pmatrix} l & 1 & l+1 \\ 0 & 1 & -1 \end{pmatrix} = (-1)^l \left[\frac{l+2}{2(2l+1)(2l+3)}\right]^{\frac{1}{2}} \tag{C.4e}$$

$$\begin{pmatrix} j+\frac{1}{2} & \frac{1}{2} & j \\ m & \frac{1}{2} & -m-\frac{1}{2} \end{pmatrix} = (-1)^{j+m-\frac{1}{2}} \cdot \left[\frac{j-m+\frac{1}{2}}{2(j+1)(2j+1)}\right]^{\frac{1}{2}} \tag{C.5}$$

$$\begin{pmatrix} l-\frac{1}{2} & l-\frac{1}{2} & 1 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = (-1)^l \cdot \left[\frac{l}{(2l-1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.6a}$$

$$\begin{pmatrix} l+\frac{1}{2} & l-\frac{1}{2} & 1 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = (-1)^{l+1} \cdot \frac{1}{2} \cdot \left[\frac{1}{2l+1}\right]^{\frac{1}{2}} \tag{C.6b}$$

$$\begin{pmatrix} l+\frac{1}{2} & l+\frac{1}{2} & 1 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = (-1)^{l+1} \cdot \left[\frac{l+1}{(2l+1)(2l+3)}\right]^{\frac{1}{2}} \tag{C.6c}$$

$$\begin{pmatrix} j & j & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} = (-1)^{j-\frac{1}{2}} \cdot \frac{1}{2} \cdot \left[\frac{1}{j(j+1)(2j+1)}\right]^{\frac{1}{2}} \tag{C.7a}$$

$$\begin{pmatrix} j & j+1 & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} = (-1)^{j-\frac{1}{2}} \cdot \frac{1}{2} \cdot \left[\frac{1}{(j+1)}\right]^{\frac{1}{2}} \tag{C.7b}$$

$$\begin{pmatrix} j & j-1 & 1 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} = (-1)^{j+\frac{1}{2}} \cdot \frac{1}{2} \cdot \left[\frac{1}{j}\right]^{\frac{1}{2}} \tag{C.7c}$$

$$\sum_t [t] \cdot \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}^2 = \tfrac{1}{2} \qquad \Gamma_{jtj'} = 2 \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}^2 \text{ [Grant, 1961]} \tag{C.7d}$$

$$\begin{pmatrix} l-\frac{1}{2} & l-\frac{1}{2} & 2 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} = (-1)^{l+1} \cdot \left[\frac{(l-1)(l+1)}{2l(2l-1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.8a}$$

$$\begin{pmatrix} l+\frac{1}{2} & l-\frac{1}{2} & 2 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} = (-1)^{l} \cdot \left[\frac{3}{2(2l-1)(2l+1)(2l+3)}\right]^{\frac{1}{2}} \tag{C.8b}$$

$$\begin{pmatrix} l+\frac{1}{2} & l+\frac{1}{2} & 2 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} = (-1)^{l} \cdot \left[\frac{l(l+2)}{2(l+1)(2l+1)(2l+3)}\right]^{\frac{1}{2}} \tag{C.8c}$$

[Brink and Satchler, 1968], recursion formulae Appendix I:

$$\begin{pmatrix} j & j' & L \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot -\tfrac{1}{2} \cdot \frac{(-1)^{j+j'+L}[j]+[j']}{[L(L+1)]^{\frac{1}{2}}}$$

$$\text{for odd } l+l'+L: \quad = \begin{pmatrix} j & j' & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot \frac{(-1)^{j'-\frac{1}{2}+l'}(\kappa+\kappa')}{[L(L+1)]^{\frac{1}{2}}} \tag{C.9a}$$

For $a+b+c$ even:

$$\begin{pmatrix} a & b & c \\ 1 & -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b & c \\ 0 & 0 & 0 \end{pmatrix} \cdot \frac{c(c+1) - a(a+1) - b(b+1)}{2\left[a(a+1)b(b+1)\right]^{\frac{1}{2}}} \tag{C.9b}$$

C.2 6j-symbols

$$\begin{Bmatrix} 1 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} = -\tfrac{1}{3} \tag{C.10}$$

$$\begin{aligned} \begin{Bmatrix} a & b & c \\ 1 & c & b \end{Bmatrix} &= (-1)^{a+b+c}\,[b,c]^{-\frac{1}{2}} \cdot \frac{a(a+1) - b(b+1) - c(c+1)}{2\sqrt{b(b+1)\cdot c(c+1)}} \\ &= (-1)^{s} \cdot \frac{\frac{1}{2}C}{\sqrt{b(b+1)(2b+1)\cdot c(c+1)(2c+1)}} \end{aligned} \tag{C.11}$$

$$\begin{Bmatrix} a & b & c \\ 2 & c & b \end{Bmatrix} = 2(-1)^{s} \cdot \frac{\frac{3}{4}C(C+1) - b(b+1)c(c+1)}{\left[b(b+1)(2b+1)(2b-1)(2b+3)c(c+1)(2c+1)(2c-1)(2c+3)\right]^{\frac{1}{2}}} \tag{C.12}$$

$$\begin{Bmatrix} l & l & 1 \\ 2 & 1 & l \end{Bmatrix} = \left[\frac{(2l-1)(2l+3)}{30\cdot l(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.13}$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix} = (-1)^{S} \cdot \tfrac{1}{3} \cdot \left(\tfrac{3}{2} - S(S+1)\right) \tag{C.14}$$

$$\sum_{S,S'} [S,S'] \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix}^2 = 2 \tag{C.15a}$$

$$\sum_{S,S'} [S,S'] \cdot (-1)^{S} \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix}^2 = -1 \tag{C.15b}$$

$$\sum_{S,S'} [S,S'] \cdot (-1)^{S+S'} \cdot \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix}^2 = 0 \tag{C.15c}$$

$$\begin{Bmatrix} l-\frac{1}{2} & l & \frac{3}{2} \\ 1 & \frac{1}{2} & l \end{Bmatrix} = -\frac{1}{2}\left[\frac{2l-1}{3\,l(2l+1)}\right]^{\frac{1}{2}} \tag{C.16}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l & \frac{5}{2} \\ 3 & \frac{1}{2} & l \end{Bmatrix} = -\left[\frac{l-1}{14(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.17}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l & \frac{5}{2} \\ \frac{1}{2} & 2 & l+\frac{1}{2} \end{Bmatrix} = -\frac{1}{2}\left[\frac{2l-1}{5(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.18}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l+\frac{1}{2} & 1 \\ l & l & \frac{1}{2} \end{Bmatrix} = \frac{1}{2(2l+1)(l+1)} \cdot [2l(2l+3)]^{\frac{1}{2}} \tag{C.19}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l-\frac{1}{2} & 1 \\ l & l & \frac{1}{2} \end{Bmatrix} = \frac{-1}{2l+1} \cdot \left[\frac{1}{2l(l+1)}\right]^{\frac{1}{2}} \tag{C.20}$$

$$\begin{Bmatrix} l-\frac{1}{2} & l-\frac{1}{2} & 1 \\ l & l & \frac{1}{2} \end{Bmatrix} = \frac{-1}{4l(l+\frac{1}{2})} \cdot [2(2l-1)(l+1)]^{\frac{1}{2}} \tag{C.21}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l+\frac{1}{2} & 2 \\ l & l & \frac{1}{2} \end{Bmatrix} = \frac{-1}{(2l+1)(l+1)} \cdot \left[\frac{(l+2)(2l-1)}{2}\right]^{\frac{1}{2}} \tag{C.22}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l-\frac{1}{2} & 2 \\ l & l & \frac{1}{2} \end{Bmatrix} = \frac{1}{2(2l+1)} \cdot \left[\frac{6}{l(l+1)}\right]^{\frac{1}{2}} \tag{C.23}$$

$$\begin{Bmatrix} l-\frac{1}{2} & l-\frac{1}{2} & 2 \\ l & l & \frac{1}{2} \end{Bmatrix} = \frac{1}{l(2l+1)} \cdot \left[\frac{(2l+3)(l-1)}{2}\right]^{\frac{1}{2}} \tag{C.24}$$

$$\begin{Bmatrix} \frac{1}{2} & 2 & \frac{3}{2} \\ l+\frac{1}{2} & l & l+\frac{1}{2} \end{Bmatrix} = -\left[\frac{l+2}{10(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.25}$$

$$\begin{Bmatrix} \frac{1}{2} & 2 & \frac{3}{2} \\ l-\frac{1}{2} & l & l+\frac{1}{2} \end{Bmatrix} = \frac{1}{2}\left[\frac{3(2l+3)}{10(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.26}$$

$$\begin{Bmatrix} \frac{1}{2} & 2 & \frac{3}{2} \\ l-\frac{1}{2} & l & l-\frac{1}{2} \end{Bmatrix} = -\frac{1}{2}\left[\frac{2(l-1)}{5l(2l+1)}\right]^{\frac{1}{2}} \tag{C.27}$$

$$\begin{Bmatrix} \frac{1}{2} & 2 & \frac{5}{2} \\ l+\frac{1}{2} & l & l+\frac{1}{2} \end{Bmatrix} = -\frac{1}{2}\left[\frac{2l-1}{5\,(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.28}$$

$$\begin{Bmatrix} \frac{1}{2} & 2 & \frac{5}{2} \\ l+\frac{1}{2} & l & l-\frac{1}{2} \end{Bmatrix} = -\left[\frac{l+2}{15\,l(2l+1)}\right]^{\frac{1}{2}} \tag{C.29}$$

$$\begin{Bmatrix} \frac{1}{2} & 2 & \frac{5}{2} \\ l-\frac{1}{2} & l & l+\frac{1}{2} \end{Bmatrix} = \left[\frac{l-1}{15(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.30}$$

$$\begin{Bmatrix} \frac{1}{2} & 2 & \frac{5}{2} \\ l-\frac{1}{2} & l & l-\frac{1}{2} \end{Bmatrix} = \frac{1}{2}\left[\frac{2l+3}{5\,l(2l+1)}\right]^{\frac{1}{2}} \tag{C.31}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l & \frac{5}{2} \\ 3 & \frac{1}{2} & l \end{Bmatrix} = -\left[\frac{l-1}{14\,(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.32}$$

$$\begin{Bmatrix} l-\frac{1}{2} & l & \frac{5}{2} \\ 3 & \frac{1}{2} & l \end{Bmatrix} = -\left[\frac{l+2}{14\,l(2l+1)}\right]^{\frac{1}{2}} \tag{C.33}$$

$$\begin{Bmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ l+\frac{1}{2} & l & l+\frac{1}{2} \end{Bmatrix} = \frac{1}{2}\left[\frac{2l+3}{3(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.34}$$

$$\begin{Bmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ l+\frac{1}{2} & l & l-\frac{1}{2} \end{Bmatrix} = (-1)^{2l+1}\left[\frac{1}{3(2l+1)}\right]^{\frac{1}{2}} \tag{C.35}$$

$$\begin{Bmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ l-\frac{1}{2} & l & l-\frac{1}{2} \end{Bmatrix} = \frac{1}{2}\left[\frac{2l-1}{3l(2l+1)}\right]^{\frac{1}{2}} \tag{C.36}$$

$$\begin{Bmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ l+\frac{1}{2} & l & l+\frac{1}{2} \end{Bmatrix} = \left[\frac{l}{6(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.37}$$

$$\begin{Bmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ l-\frac{1}{2} & l & l+\frac{1}{2} \end{Bmatrix} = -\frac{1}{2}\cdot\left[\frac{2l-1}{6(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.38}$$

$$\begin{Bmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ l-\frac{1}{2} & l & l-\frac{1}{2} \end{Bmatrix} = -\left[\frac{l+1}{6l(2l+1)}\right]^{\frac{1}{2}} \tag{C.39}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l & \frac{3}{2} \\ 1 & \frac{1}{2} & l \end{Bmatrix} = \frac{1}{2}\left[\frac{2l+3}{3(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.40}$$

$$\begin{Bmatrix} l-\frac{1}{2} & l & \frac{3}{2} \\ 1 & \frac{1}{2} & l \end{Bmatrix} = -\frac{1}{2}\left[\frac{2l-1}{3l(2l+1)}\right]^{\frac{1}{2}} \tag{C.41}$$

$$\begin{Bmatrix} l+\frac{1}{2} & l & \frac{3}{2} \\ 2 & \frac{1}{2} & l \end{Bmatrix} = \frac{1}{2}\left[\frac{2l-1}{5(l+1)(2l+1)}\right]^{\frac{1}{2}} \tag{C.42}$$

$$\begin{Bmatrix} l-\frac{1}{2} & l & \frac{3}{2} \\ 2 & \frac{1}{2} & l \end{Bmatrix} = \frac{1}{2}\left[\frac{2l+3}{5l(2l+1)}\right]^{\frac{1}{2}} \tag{C.43}$$

$$\begin{Bmatrix} a & b & c \\ \frac{1}{2} & c-\frac{1}{2} & b+\frac{1}{2} \end{Bmatrix} = (-1)^s\left[\frac{(s-2b)(s-2c+1)}{(2b+1)(2b+2)(2c+1)2c}\right]^{\frac{1}{2}} \tag{C.44}$$

$$\begin{Bmatrix} a & b & c \\ \frac{1}{2} & c-\frac{1}{2} & b-\frac{1}{2} \end{Bmatrix} = (-1)^s\left[\frac{(s+1)(s-2a)}{2b(2b+1)2c(2c+1)}\right]^{\frac{1}{2}} \tag{C.45}$$

$$\begin{Bmatrix} j & j+\frac{1}{2} & \frac{1}{2} \\ J & J+\frac{1}{2} & g+\frac{1}{2} \end{Bmatrix} = (-1)^{1+g+j+J}\cdot\frac{1}{2}\left[\frac{(1+g+j-J)(1+g-j+J)}{(2j+1)(j+1)(2J+1)(J+1)}\right]^{\frac{1}{2}} \tag{C.46}$$

$$\begin{Bmatrix} j & j+\frac{1}{2} & \frac{1}{2} \\ J+\frac{1}{2} & J & g \end{Bmatrix} = (-1)^{1+g+j+J}\cdot\frac{1}{2}\left[\frac{(1-g+j+J)(2+g+j+J)}{(2j+1)(j+1)(2J+1)(J+1)}\right]^{\frac{1}{2}} \tag{C.47}$$

C.3 9j-symbols

Using equation (2.14) for the below 'stretched' cases:

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ 1 & 1 & 2 \end{Bmatrix} = \frac{1}{9} \tag{C.48}$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l & 2 \\ j & j' & 1 \end{Bmatrix} = -\frac{2}{\sqrt{3}} \begin{Bmatrix} \frac{1}{2} & 1 & \frac{3}{2} \\ j' & l & j \end{Bmatrix} \begin{Bmatrix} j' & l & \frac{3}{2} \\ 2 & \frac{1}{2} & l \end{Bmatrix} \tag{C.49}$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l & 1 \\ j & j' & 2 \end{Bmatrix} = -\frac{2}{\sqrt{3}} \begin{Bmatrix} \frac{1}{2} & 2 & \frac{3}{2} \\ j' & l & j \end{Bmatrix} \begin{Bmatrix} j' & l & \frac{3}{2} \\ 1 & \frac{1}{2} & l \end{Bmatrix} \tag{C.50}$$

$$\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l & 3 \\ j & j' & 2 \end{Bmatrix} = -\sqrt{2} \begin{Bmatrix} \frac{1}{2} & 2 & \frac{5}{2} \\ j' & l & j \end{Bmatrix} \begin{Bmatrix} j' & l & \frac{5}{2} \\ 3 & \frac{1}{2} & l \end{Bmatrix} \tag{C.51}$$

[Brink and Satchler, 1968], Appendix II, only for even $l + l' + t$:

$$\begin{Bmatrix} j & j' & t \\ l' & l & \frac{1}{2} \end{Bmatrix} \cdot \left\langle l \parallel C^{(t)} \parallel l' \right\rangle = (-1)^{l+1} \cdot (-1)^{j+j'+t} \cdot \begin{pmatrix} j & j' & t \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \tag{C.52}$$

[Brink and Satchler, 1968], Appendix III, p 144-145:

$$\begin{Bmatrix} a & b & c \\ d & e & c \\ g & g & 1 \end{Bmatrix} = \frac{a(a+1) - d(d+1) - b(b+1) + e(e+1)}{[4c(c+1)(2c+1)g(g+1)(2g+1)]^{\frac{1}{2}}} \times (-1)^{c+g+b+d} \cdot \begin{Bmatrix} a & b & c \\ e & d & g \end{Bmatrix} \quad \text{(C.53)}$$

For $g = \frac{1}{2}$ and $c + d + e$ even, this yields:

$$\sqrt{6} \cdot [c,d,e]^{\frac{1}{2}} \cdot \begin{pmatrix} c & d & e \\ 0 & 0 & 0 \end{pmatrix} \cdot \begin{Bmatrix} a & b & c \\ d & e & c \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix} = \begin{pmatrix} a & b & c \\ \frac{1}{2} & \frac{1}{2} & -1 \end{pmatrix} \quad \text{(C.54)}$$

assuming $t = k$ in the operator $\left(\sigma^{(1)} C^{(k)}\right)^{(t)}$, this gives:

$$\sqrt{6} \cdot (-1)^l \cdot \left\langle l \parallel C^{(k)} \parallel l' \right\rangle \cdot [k]^{\frac{1}{2}} \cdot \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l' & k \\ j & j' & k \end{Bmatrix} = \begin{pmatrix} j & j' & k \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} \quad \text{(C.55)}$$

For the other cases $t = k \pm 1$, two more relations (with $c + d + e$ odd) are needed:

$$\begin{aligned} & \sqrt{6} \cdot [c,d,e]^{\frac{1}{2}} \cdot \begin{pmatrix} c-1 & d & e \\ 0 & 0 & 0 \end{pmatrix} \cdot \begin{Bmatrix} a & b & c \\ d & e & c-1 \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix} \\ = \; & \frac{(-1)^{b+e+\frac{1}{2}} \cdot [(d-a)(2a+1) + (e-b)(2b+1) - c]}{(c(2c-1))^{\frac{1}{2}}} \cdot \begin{pmatrix} a & b & c \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \end{aligned} \quad \text{(C.56)}$$

$$\begin{aligned} & \sqrt{6} \cdot [c,d,e]^{\frac{1}{2}} \cdot \begin{pmatrix} c+1 & d & e \\ 0 & 0 & 0 \end{pmatrix} \cdot \begin{Bmatrix} a & b & c \\ d & e & c+1 \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix} \\ = \; & \frac{(-1)^{b+e+\frac{1}{2}} \cdot [(d-a)(2a+1) + (e-b)(2b+1) + c + 1]}{((c+1)(2c+3))^{\frac{1}{2}}} \cdot \begin{pmatrix} a & b & c \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \end{aligned} \quad \text{(C.57)}$$

Appendix D

Tables of electric dipole transition integrals

Table D.1: Values for the electric dipole transition integrals in Cr II calculated by means of MCDF including core polarization

Cr II	$3d^4 4p$	$3d^3 4s 4p$	$3d^2 4s^2 4p$	$3d^4 5p$	$3d^4 4f$
$3d^5$	1.05	-	-	.246	.345
$3d^4 4s$	-2.96	.828	-	.032	-
$3d^3 4s^2$	-	-2.740	.671	-	-
$3d^4 4d$	-3.32	-	-	6.30	-7.07
$3d^4 5s$	2.23	-	-	-6.87	-
$3d^4 5d$	-1.06	-	-	-5.69	6.42
$3d^4 6s$	0.607	-	-	5.02	-

Table D.2: Values for the electric dipole transition integrals in Mn II calculated by means of MCDF including core polarization

Mn II	$3d^6$	$3d^54s$	$3d^44s^2$	$3d^54d$	$3d^55s$	$3d^55d$	$3d^56s$
$3d^54p$	.95	-2.81	-	-3.36	2.08	-0.82	0.58
$3d^44s4p$	-	0.76	-2.62	-	-	-	-
$3d^34s^24p$	-	-	0.62	-	-	-	-
$3d^55p$	0.239	0.025	-	6.37	-6.70	-5.48	4.97
$3d^54f$	0.291	-	-	-6.38	-	6.80	-

Table D.3: Values for the electric dipole transition integrals in Fe II calculated by means of MCDF including core polarization

Fe II	$3d^7$	$3d^64s$	$3d^54s^2$	$3d^64d$	$3d^65s$	$3d^65d$	$3d^66s$	$3d^54p^2$	$3d^54s4d$	$3d^54s5d$
$3d^64p$	.863	-2.713	-	-3.283	2.048	-0.803	0.564	0.685	-	-
$3d^54s4p$	-	0.703	-2.531	-	-	-	-	-2.480	-2.940	-0.764
$3d^44s^24p$	-	-	0.586	-	-	-	-	-	-	-
$3d^65p$	0.221	0.038	-	4.938	-6.429	-6.119	4.780	-	-	-
$3d^64f$	0.238	-	-	-5.695	-	7.180	-	-	-	-

Table D.4: Values for the electric dipole transition integrals in Co II calculated by means of MCDF including core polarization

Co II	$3d^8$	$3d^74s$	$3d^64s^2$	$3d^74d$	$3d^75s$	$3d^75d$	$3d^76s$
$3d^74p$	.79	-2.65	-	-3.20	2.13	-0.79	0.57
$3d^64s4p$	-	0.65	-2.44	-	-	-	-
$3d^54s^24p$	-	-	0.55	-	-	-	-
$3d^75p$	0.22	0.03	-	4.88	-6.41	-6.00	4.89
$3d^74f$	0.19	-	-	-5.56	-	7.32	-

Table D.5: Values for the electric dipole transition integrals in Ni II calculated by means of MCDF including core polarization

Ni II	$3d^9$	$3d^84s$	$3d^74s^2$	$3d^84d$	$3d^85s$	$3d^85d$	$3d^86s$
$3d^84p$	0.734	-2.593	-	-3.11	2.21	-0.78	0.58
$3d^74s4p$	-	0.608	-2.402	-	-	-	-
$3d^64s^24p$	-	-	0.517	-	-	-	-
$3d^85p$	0.211	-0.001	-	4.82	-6.39	-5.88	4.95
$3d^84f$	0.160	-	-	-5.43	-	7.42	-

Table D.6: Values for the electric dipole transition integrals in Ti III calculated by means of MCDF including core polarization

Ti III	3d4p	4s4p	3d5p	3d4f	$3p^5 3d^3$
$3d^2$	.999	-	.231	.617	-1.02
3d4s	-2.880	.788	.150	-	-
$4s^2$	-	-2.700	-	-	-
3d5s	1.710	-	-5.830	-	-
3d6s	.501	-	3.550	-	-
3d4d	-3.270	-	3.790	-4.980	-
3d5d	-.625	-	-5.690	3.640	-
$4p^2$	.780	-2.670	-	-	-

Table D.7: Values for the electric dipole transition integrals in Fe III calculated by means of MCDF including core polarization

Fe III	$3d^6$	$3d^5 4s$	$3d^4 4s^2$
$3d^5 4p$	.681	-2.397	-

Table D.8: Values for the electric dipole transition integrals in V IV calculated by means of MCDF including core polarization

V IV	3d4p	4s4p	3d5p	3d4f	$3p^5 3d^3$
$3d^2$	.699	-	.185	.577	-0.898
3d4s	-2.464	.590	.204	-	-
$4s^2$	-	-2.343	-	-	-
3d5s	1.326	-	-4.835	-	-
3d6s	.398	-	2.764	-	-
3d4d	-2.892	-	2.589	-3.770	-
3d5d	-.317	-	-4.943	2.338	-
$4p^2$	.587	-2.325	-	-	-

Table D.9: Values for the electric dipole transition integrals in Cu IV calculated by means of MCDF including core polarization.

Cu IV	$3d^8$	$3d^7 4s$	$3d^6 4s^2$
$3d^7 4p$	.484	-1.967	-

Table D.10: Values for the electric dipole transition integrals in Cr V calculated by means of MCDF including core polarization

Cr V	3d4p	4s4p	3d5p	3d4f
$3d^2$	.538	-	.153	.533
3d4s	-2.159	.469	.235	-
$4s^2$	-	-2.067	-	-
3d5s	1.092	-	-4.157	-
3d6s	.340	-	2.128	-
3d4d	-2.430	-	1.924	-3.051
3d5d	-.128	-	-4.334	1.842
$4p^2$	.465	-2.056	-	-

Table D.11: Values for the electric dipole transition integrals in Mn V calculated by means of MCDF including core polarization

Mn V	$3d^3$	$3d^24s$	3d $4s^2$
$3d^24p$	.492	-2.020	-

Table D.12: Values for the electric dipole transition integrals in Fe V calculated by means of MCDF including core polarization

Fe V	$3d^4$	$3d^34s$	$3d^24s^2$
$3d^34p$	.469	-1.966	-

Table D.13: Values for the electric dipole transition integrals in Co V calculated by means of MCDF including core polarization

Co V	$3d^5$	$3d^44s$	$3d^34s^2$
$3d^44p$	.452	-1.901	-

Table D.14: Values for the electric dipole transition integrals in Ni V calculated by means of MCDF including core polarization

Ni V	$3d^6$	$3d^54s$	$3d^44s^2$
$3d^54p$	.434	-1.841	-

Table D.15: Values for the electric dipole transition integrals in Cu V calculated by means of MCDF including core polarization.

Cu V	$3d^7$	$3d^64s$	$3d^54s^2$
$3d^64p$	.419	-1.798	-

Table D.16: Values for the electric dipole transition integrals in Mn VI calculated by means of MCDF including core polarization

Mn VI	3d4p	4s4p	3d5p	3d4f
$3d^2$	.436	-	.129	.516
3d4s	-1.942	0.386	0.243	-
$4s^2$	-	-1.872	-	-
3d5s	0.916	-	-3.664	-
3d6s	.291	-	1.765	-
3d4d	-2.155	-	1.501	-2.558
3d5d	-.016	-	-3.852	1.400
$4p^2$	.385	-1.864	-	-

Table D.17: Values for the electric dipole transition integrals in Fe VI calculated by means of MCDF including core polarization

Fe VI	$3d^3$	$3d^24s$	$3d\ 4s^2$
$3d^24p$	.402	-1.831	-

Table D.18: Values for the electric dipole transition integrals in Co VI calculated by means of MCDF including core polarization

Co VI	$3d^4$	$3d^34s$	$3d^24s^2$
$3d^34p$	.389	-1.781	-

Table D.19: Values for the electric dipole transition integrals in Ni VI calculated by means of MCDF including core polarization

Ni VI	$3d^5$	$3d^44s$	$3d^34s^2$
$3d^44p$	.375	-1.727	-

Table D.20: Values for the electric dipole transition integrals in Cu VI calculated by means of MCDF including core polarization.

Cu VI	$3d^6$	$3d^54s$	$3d^44s^2$
$3d^54p$	.365	-1.672	-

Table D.21: Values for the electric dipole transition integrals in Fe VII calculated by means of MCDF including core polarization, $\alpha_d(3p) = 0.85(1.6)$ and $\alpha_d(3d) = 1.01(2.0)$.

Fe VII	3d4p	3d4f	$3p^53d^3$
$3d^2$	.348	.466	-.640
3d4s	-1.717	-	-

Table D.22: Values for the electric dipole transition integrals in Cu VII calculated by means of MCDF including core polarization, $\alpha_d(3p) = 0.50(1.5)$ and $\alpha_d(3d) = 0.72(1.7)$.

Cu VII	$3d^5$	$3d^4 4s$	$3d^3 4s^2$
$3d^4 4p$	.322	-1.580	-

Table D.23: Values for the electric dipole transition integrals in Ge VII calculated by means of MCDF including core polarization, $\alpha_d(3p) = 0.321(1.24)$ and $\alpha_d(3d) = 0.543(1.45)$

Ge VII	$3d^7 4p$	$3p^5 3d^9$	$3d^7 4f$
$3d^8$	.297	-0.527	.298
$3d^7 4s$	-1.462	-	-
$3d^6 4s^2$	-	-	-

Table D.24: Values for the electric dipole transition integrals in Fe IX calculated by means of MCDF including core polarization, $\alpha_d(3s) = 0.57(1.5)$ and $\alpha_d(3p) = 0.78(1.5)$

Fe IX	$3p^5 3d$	$3p^5 4s$	$3p^5 4d$	$3p^5 5s$	$3p^5 5d$	$3s3p^6 4p$
$3p^6$	-0.623	0.252	0.181	0.090	0.106	0.162
$3p^5 4p$	0.271	-1.484	-1.589	0.581	0.171	-0.629
$3p^5 4f$	0.487	-	-1.623	-	0.586	-
$3p^5 5p$	0.080	0.240	0.804	-2.791	-2.941	-
$3p^5 5f$	0.249	-	0.584	-	-3.159	-
$3s3p^6 3d$	-0.640	-	-	-	-	0.273

Table D.25: Values for the electric dipole transition integrals in Os IV calculated by means of MCDF including core polarization

Os IV	$5d^4 6p$	$5d^3 6s6p$	$5d^2 6s^2 6p$
$5d^5$	1.152	-	-
$5d^4 6s$	-2.573	1.103	-
$5d^3 6s^2$	-	-2.519	1.059

Table D.26: Values for the electric dipole transition integrals in Os V calculated by means of MCDF including core polarization

Os V	$5d^3 6p$	$5d^2 6s6p$	$5d\,6s^2 6p$
$5d^4$	1.061	-	-
$5d^3 6s$	-2.422	1.022	-
$5d^2 6s^2$	-	-2.38	0.99

Table D.27: Values for the electric dipole transition integrals in Os VI calculated by means of MCDF including core polarization

Os VI	$5d^26p$
$5d^3$	0.9854
$5d^26s$	-2.2989

Appendix E

Tables of electric quadrupole transition integrals

Table E.1: Values for the electric quadrupole transition integrals in Co II calculated by means of MCDF including core polarization. For $3d^7nd$, the upper row gives the 3d→3d and the lower row the nd→nd transition integrals.

Co II	$3d^8$	$3d^74s$	$3d^64s^2$	$3d^74d$	$3d^75s$	$3d^75d$	$3d^76s$
$3d^8$	1.60	-2.55	-	-1.55	0.20	-0.66	0.09
$3d^74s$	-2.55	1.31	-1.95	9.48	-	2.89	-
$3d^64s^2$	-	-1.95	1.12	-	-	-	-
$3d^74d$	-1.55	9.48	-	1.26	-38.26	-24.55	18.97
	-	-	-	35.53	-	-	-
$3d^75s$	0.20	-	-	-38.26	1.27	34.47	-
$3d^75d$	-0.66	2.89	-	-24.55	34.47	1.26	-141.78
	-	-	-	-	-	139.25	-
$3d^76s$	0.09	-	-	18.97	-	-141.78	1.26

Table E.2: Values for the electric quadrupole transition integrals in Ni II calculated by means of MCDF including core polarization. For $3d^8nd$, the upper row gives the 3d→3d and the lower row the nd→nd transition integrals.

Ni II	$3d^9$	$3d^84s$	$3d^74s^2$	$3d^84d$	$3d^85s$	$3d^85d$	$3d^86s$
$3d^9$	1.42	-2.29	-	-1.37	0.14	-0.60	0.07
$3d^84s$	-2.29	1.18	-1.76	8.96	-	2.79	-
$3d^74s^2$	-	-1.76	1.02	-	-	-	-
$3d^84d$	-1.37	8.96	-	1.14	-37.08	-24.07	19.98
	-	-	-	34.54	-	-	-
$3d^85s$	0.14	-	-	-37.08	1.15	32.86	-
$3d^85d$	-0.60	2.79	-	-24.07	32.86	1.14	-138.55
	-	-	-	-	-	136.58	-
$3d^86s$	0.07	-	-	19.98	-	-138.55	1.14

Table E.3: Values for the electric quadrupole transition integrals in Mn III calculated by means of MCDF including core polarization

Mn III	$3d^5$	$3d^44s$	$3d^34s^2$	$3d^44d$	$3d^45s$
$3d^5$	1.58	-2.25	-	-1.49	0.062
$3d^44s$	-2.25	1.34	1.24	8.57	-
$3d^34s^2$	-	1.24	1.64	-	-
$3d^44d$	-1.49	8.57	-	1.30	-24.3
$3d^45s$	0.062	-	-	-24.3	1.30

Table E.4: Values for the electric quadrupole transition integrals in Fe III calculated by means of MCDF including core polarization

Fe III	$3d^6$	$3d^5 4s$	$3d^4 4s^2$
$3d^6$	1.43	-2.01	-
$3d^5 4s$	-2.01	1.23	-1.64
$3d^4 4s^2$	-	-1.64	1.08

Table E.5: Values for the electric quadrupole transition integrals in Cr IV calculated by means of MCDF including core polarization

Cr IV	$3d^3$	$3d^2 4s$
$3d^3$	1.45	-1.88
$3d^2 4s$	-1.88	1.26

Table E.6: Values for the electric quadrupole transition integrals in Ni IV calculated by means of MCDF including core polarization

Ni IV	$3d^7$	$3d^6 4s$	$3d^5 4s^2$
$3d^7$	0.96	-1.27	-
$3d^6 4s$	-1.27	0.86	-1.08
$3d^5 4s^2$	-	-1.08	0.78

Table E.7: Values for the electric quadrupole transition integrals in Cr V calculated by means of MCDF including core polarization

Cr V	$3d^2$	$3d4s$
$3d^2$	1.23	-1.46
$3d4s$	-1.46	1.09

Table E.8: Values for the electric quadrupole transition integrals in Mn V calculated by means of MCDF including core polarization

Mn V	$3d^3$	$3d^2 4s$
$3d^3$	1.11	-1.33
$3d^2 4s$	-1.33	0.98

Table E.9: Values for the electric quadrupole transition integrals in Mn VI calculated by means of MCDF including core polarization

Mn VI	$3d^2$	$3d4s$
$3d^2$	0.97	-1.08
$3d4s$	-1.08	0.87

Table E.10: Values for the electric quadrupole transition integrals in Fe VI calculated by means of MCDF including core polarization

Fe VI	$3d^3$	$3d^24s$	$3d4s^2$
$3d^3$	0.88	-0.99	-
$3d^24s$	-0.99	0.81	-0.87
$3d4s^2$	-	-0.87	0.74

Table E.11: Values for the electric quadrupole transition integrals in Fe VII calculated by means of MCDF including core polarization

Fe VII	$3d^2$	3d4s
$3d^2$	0.80	-0.84
3d4s	-0.84	0.72

Chapter 28

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Complex Atoms

described by orthogonal operators

This textbook aims at explaining the basic ideas and concepts underlying the theory of orthogonal operators and its application to atomic spectroscopy. Embedded between two more general parts on angular momentum theory and relativity, the main principles are presented in chapter 14 of part II. With orthogonal operators, standard deviations of energy fits are frequently reduced by an order of magnitude and only elementary linear algebra is needed to project *ab initio* results of any provenance onto an orthogonal basis of operators. The framework of orthogonal operators is surely fortified with the support of Hartree-Fock calculations combined with perturbation theory; B-splines are a strong tool to calculate the occurring one- and two-electron excited states. These *ab initio* aspects are covered as well in part II for this reason. Second quantization in the coupled form as an elegant method to handle a wide variety of angular momentum problems is used throughout the book in all three parts. In part III, second quantization is also used to show how a $jj \rightarrow SL$ transformation yields fully relativistic results in SL–coupling. Hyperfine structure and electromagnetic radiation are treated in some detail to illustrate the potential of this formalism.

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