Electron correlation in a relativistic perspective

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with thanks to ....




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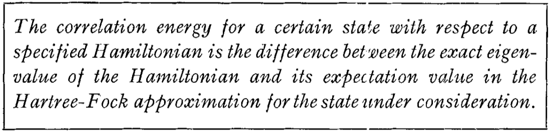
(Odense)	(Toulouse/Homs)	(Zürich)	(Portland)

Per-Olov Löwdin and correlation energy

Per-Olov Löwdin (1916 - 2000)



The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation for the state under consideration.

Adv. Chem. Phys. **2** (1958) 207

Problem: The relativistic many-electron Hamiltonian has no bound solutions !

Egil Hylleraas and helium atom

Egil Andersen Hylleraas (1898 - 1965)

- Bohr [Philos. Mag. 26, 476 (1913)]:

$$E = -3.065\, E_h$$

- Hylleraas [Z. Phys. 48, 469 (1928)]:

$$E = -2.895\, E_h$$

- Hylleraas [Z. Phys. 54, 347 (1929)]:

$$E = -2.9037\, E_h$$

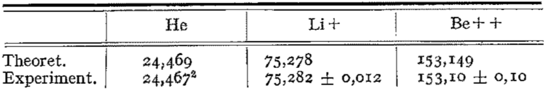
- Nakashima and Nakatsuji [J. Chem. Phys. 127, 224104 (2007)]:

$$E = -2.903724377034119598311159245194404446696905 37\, E_h$$

Egil Hylleraas and the helium isoelectronic series

Bengt Edlén (1906 -1993)

Ionization energies (eV):



	He	Li+	Be++
Theoret.	24,469	75,278	153,149
Experiment.	24,467[2]	75,282 ± 0,012	153,10 ± 0,10

E. A. Hylleraas, Naturwissenschaften 17, 982 (1929)

- “Exact” energy [E. Hylleraas, Naturwissenschaften 17, 982 (1929)]:

$$E^{exact} = -Z^2 + \frac{5}{8}Z - 0.15767 + O\left(Z^{-1}\right)\ E_h$$

- Hartree-Fock energy [J. Linderberg, Phys. Rev. 121, 816 (1961)]:

$$E^{HF} = -Z^2 + \frac{5}{8}Z - 0.11100 + O\left(Z^{-1}\right)\ E_h$$

- Correlation energy:

$$E_c = E^{exact} - E^{HF} = -0.04667 + O\left(Z^{-1}\right)\ E_h$$

- In the relativistic case the correlation energy is **not** constant along the series.

Non-relativistic two-electron atom

- One-electron problem (point nucleus)

$$\left[-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right]\varphi_Z\left(\mathbf{r}\right)=\varepsilon_Z\varphi_Z\left(\mathbf{r}\right)$$

- Coordinate scaling $r\rightarrow Z^{-1}r$:

$$\left[-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{r}\right]\varphi_{Z=1}\left(\mathbf{r}\right)=\varepsilon_{Z=1}\varphi_{Z=1}\left(\mathbf{r}\right);\quad \varepsilon_Z=Z^2\varepsilon_{Z=1}$$

- Two-electron problem:

$$\left[\hat{h}_{Z=1}\left(1\right)+\hat{h}_{Z=1}\left(2\right)+\frac{1}{Z}V_{ee}\right]\Psi\left(1,2\right)=E'\Psi\left(1,2\right);\quad E=Z^2E'$$

- The two-electron interaction appears as perturbation with Z^{-1} as corresponding perturbation parameter

Variational perturbation theory

T. Helgaker and P. Jørgensen, in Methods in Computational Molecular Physics S. Wilson and G. H. F. Diercksen (eds.), Plenum Press, New York (1992) 353

- Partitioned Hamiltonian:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1; \quad \hat{H}_0 = \hat{h}_Z(1) + \hat{h}_Z(2); \quad \hat{H}_1 = \frac{1}{r_{12}}$$

- Variational solution:

$$E \equiv E(\tilde{\varsigma}, \lambda); \quad \tilde{\varsigma} \text{ - variational parameters}$$

- Variational condition:

$$\left.\frac{\partial E}{\partial \varsigma_i}\right|_{\lambda} = 0 \quad \Rightarrow \quad \varsigma \equiv \varsigma(\lambda)$$

- Perturbation expansion

$$E(\lambda) = E_0 + \left.\frac{dE}{d\lambda}\right|_{\lambda=0} \lambda + \frac{1}{2} \left.\frac{d^2E}{d\lambda^2}\right|_{\lambda=0} \lambda^2 + \dots$$

- The variational parameters obey the $2n+1$ rule [Hylleraas (1930), Wigner (1935)]

Variational perturbation theory

Non-relativistic case 1

- Wave function parametrization

$$\begin{aligned}
|HF\rangle &= \exp\left[-\hat{\kappa}\right]|0\rangle; \quad \hat{\kappa} = \sum_{p>q}\left\{\kappa_{pq}\hat{p}^{\dagger}\hat{q} - \kappa^{*}_{pq}\hat{q}^{\dagger}\hat{p}\right\} \\
|CI\rangle &= \exp\left[-\hat{S}\right]|0\rangle; \quad \hat{S} = \sum_{M\in\{|M\rangle\}/\{|0\rangle\}}\left\{s_M|M\rangle\langle 0| - s^{*}_{M}|0\rangle\langle M|\right\} \\
|MCSCF\rangle &= \exp\left[-\hat{\kappa}\right]\exp\left[-\hat{S}\right]|0\rangle
\end{aligned}$$

- In the present case all methods start from the same zeroth-order function

$$\Phi_0 = \left|\varphi^{(0)}_{1s}\alpha\varphi^{(0)}_{1s}\beta\right|$$

- ... so that zeroth and first-order energy corrections are identical

$$\begin{aligned}
E_0 &= \left\langle 0\left|\hat{H}_0\right|0\right\rangle = 2\varepsilon_{1s} = -Z^2 \\
E_1 &= \left\langle \Phi_0\left|\hat{H}_1\right|\Phi_0\right\rangle = \left\langle\varphi^{(0)}_{1s}\varphi^{(0)}_{1s}|\varphi^{(0)}_{1s}\varphi^{(0)}_{1s}\right\rangle = \frac{5}{8}Z
\end{aligned}$$

Variational perturbation theory

Non-relativistic case 2

- Hartree-Fock perturbation theory:

$$E_2^{HF} = \sum_{ia} \frac{\left\langle \Phi_0 \left| \hat{H} \right| \Phi_i^a \right\rangle \left\langle \Phi_i^a \left| \hat{H} \right| \Phi_0 \right\rangle}{E_0 - E_i^a} = \sum_{ia} \frac{|F_{ia}|^2}{\varepsilon_i - \varepsilon_a}$$

- CI perturbation theory:

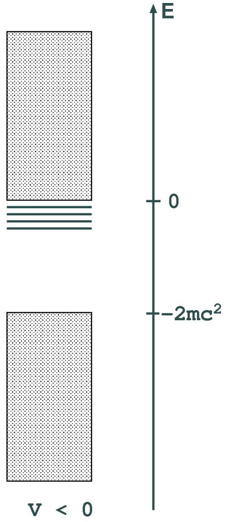
$$E_2^{CI} = E_2^{HF} + \sum_{ia} \frac{\left\langle \Phi_0 \left| \hat{H} \right| \Phi_{ij}^{ab} \right\rangle \left\langle \Phi_{ij}^{ab} \left| \hat{H} \right| \Phi_0 \right\rangle}{E_0 - E_{ij}^{ab}} = E_2^{MCSCF}$$

- Correlation energy:

$$E_c = E_2^{CI} - E_2^{HF} + O\left(Z^{-1}\right) = \sum_{ia} \frac{\langle ij \parallel ab \rangle \langle ab \parallel ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + O\left(Z^{-1}\right)$$

(the MP2-like expression is evaluated using the orbitals of the one-electron problem)

Relativistic two-electron atoms



- Dirac-Coulomb (DC) Hamiltonian

$$H = \hat{h}_D(1) + \hat{h}_D(2) + \frac{1}{r_{12}}; \quad \hat{h}_D = \beta mc^2 + c\,(\boldsymbol{\alpha}\cdot\mathbf{p}) + V_{eN}$$

- One-electron problem (point nucleus)

$$\left[\beta mc^2 + c\,(\boldsymbol{\alpha}\cdot\mathbf{p}) - \frac{Ze^2}{r}\right]\varphi_Z = \varepsilon_Z\varphi_Z$$

- Coordinate scaling $r \rightarrow Z^{-1}r$:

$$\left[\beta mc^2 + Zc\,(\boldsymbol{\alpha}\cdot\mathbf{p}) - \frac{Z^2e^2}{r}\right]\varphi_Z = \varepsilon_Z\varphi_Z,$$

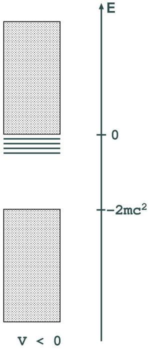
- ...implies velocity scaling

$$v^{nrel} = \frac{\mathbf{p}}{m} \rightarrow Z\frac{\mathbf{p}}{m}; \quad v^{rel} = c\boldsymbol{\alpha},$$

- in the relativistic case scaling down the speed of light

$$Z^2\left[\beta m\,(c/Z)^2 + (c/Z)\,(\boldsymbol{\alpha}\cdot\mathbf{p}) - \frac{e^2}{r}\right]\varphi_Z = Z^2\varepsilon_Z\varphi_Z,$$

Variational perturbation theory



- Proceeding as before

$$E_c = \sum_{ia} \frac{\langle ij \parallel ab\rangle \langle ab \parallel ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + O\left(Z^{-1}\right)$$

- **Problem:**
  An infinite number of doubly excited Slater determinants Φ_{ij}^{ab} are degenerate with the reference determinant Φ_0

- The Dirac-Coulomb Hamiltonian has no bound solutions !
  [G. E. Brown and D. G. Ravenhall, Proc. Roy. Soc. London A **208** (1951) 552]

The no-pair approximation

- Continuum dissolution can be avoided by embedding the DC Hamiltonian by projection operators onto positive energy orbitals [J. Sucher, Phys. Rev. A 22 (1980) 348]

$$H^{DC} \quad \rightarrow \quad \Lambda_+ H^{DC} \Lambda_+$$

- There are several choices of projectors:

Z	DC(Λ_+^{HF})	DC(Λ_+^{bare})	DC(Λ_+^{free})
2	-2.861813	-2.861813	-2.861820
10	-93.982761	-93.982762	-94.002680
18	-314.199521	-314.199525	-314.513907
36	-1296.165168	-1296.165234	-1303.570815
54	-3002.947488	-3002.947788	-3049.385180
86	-8245.261661	-8245.263456	-8674.425715
118	-18090.944596	-18090.952854	-20767.807429

HF energies of two-electron rare gas atoms

No-pair full CI

- Conventional correlated relativistic calculations develop the N-particle basis in positive-energy HF orbitals only
    - Λ_+^{HF} is kept frozen at the correlated level
- The second-order HF energy reflects the min-max variational principle

$$E_{2;rel}^{HF} = \underbrace{\sum_{a^+i^+} \frac{\left|F_{i^+a^+}\right|^2}{\varepsilon_i^+ - \varepsilon_a^+}}_{(-)} + \underbrace{\sum_{a^-i^+} \frac{\left|F_{i^+a^-}\right|^2}{\varepsilon_i^+ - \varepsilon_a^-}}_{(+)}$$

- The second-order correlation energy from CI variational perturbation theory

$$E_{2,corr;CI} = E_{2;rel}^{CI} - E_{2;rel}^{HF} = -\frac{1}{4}\sum_{i^+j^+}\sum_{a^+b^+} \frac{\left|\langle ij||ab\rangle\right|^2}{\varepsilon_a^+ + \varepsilon_b^+ - \varepsilon_i^+ - \varepsilon_j^+} - \sum_{a^-i^+} \frac{\left|F_{i^+a^-}^{(2)}\right|^2}{\varepsilon_i^+ - \varepsilon_a^-}$$

contains a relaxation contribution from the negative-energy orbitals.

No-pair full MCSCF

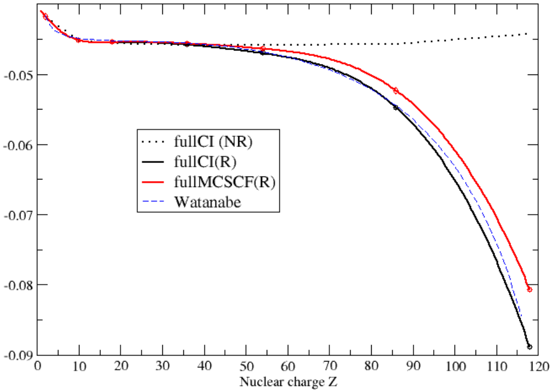
- Full optimization of the projection operator at the correlated level is possible by a *no-pair full MCSCF calculation:*
  - an MCSCF calculation based on a no-pair full CI expansion, but including orbital rotations κ_{ai}^{-+} between positive-energy occupied orbitals and negative-energy virtual orbitals.
- The second-order correlation energy from MCSCF variational perturbational theory

$$E_{corr;MCSCF} \approx E_{2;rel}^{MCSCF} - E_{2;rel}^{HF} = -\frac{1}{4}\sum_{i^+j^+}\sum_{a^+b^+}\frac{\left|\langle ij||ab\rangle\right|^2}{\varepsilon_a^+ + \varepsilon_b^+ - \varepsilon_i^+ - \varepsilon_j^+}$$

reduces to a pure MP2-like correlation expression,
as in the non-relativistic case

Numerical example

Correlation energies (in E_h) of the two-electron rare gas atoms as a function of nuclear charge Z, using the dyall_1s2.6z basis.



Full MCSCF within the no-pair approximation reduces the correlation energy in accordance with the minmax-principle, but only slightly.

Basis set convergence

Non-relativistic case

- Partial wave expansion

  [C. Schwartz, Phys. Rev. 126, 1015 (1962); R. N. Hill, J. Chem. Phys. 83, 1173 (1985)]

  $$E_{corr,L} \approx E_{corr,\infty} + a' \left(L+1\right)^{-3}.$$

- Principal (quantum number) expansion

  [T. Helgaker, W. Klopper, H. Koch, and J. Noga, J. Chem. Phys. 106, 9639 (1997)]

  $$E_{corr,X} = E_{corr,\infty} + aX^{-3}.$$

Basis set convergence

Relativistic case

- Using results of correlated relativistic calculations using the dyall_1s2Xz basis sets (X=2...7) we fit

$$E_{corr,X} = E_{corr,\infty} + aX^{-b}$$

	full CI			full MSCF		
Z	$E_{corr,\infty}$	a	b	$E_{corr,\infty}$	a	b
2	-0.042120	0.05706	2.8761	-0.042098	0.05776	2.8976
10	-0.045781	0.06512	2.5963	-0.045779	0.06513	2.5966
18	-0.046121	0.06641	2.5892	-0.046102	0.06655	2.5926
36	-0.046486	0.06785	2.5943	-0.046303	0.06900	2.6161
54	-0.047756	0.06887	2.5515	-0.047128	0.07083	2.5767
86	-0.055768	0.07214	2.3652	-0.053210	0.08089	2.4900
118	-0.091747	0.07422	1.8187	-0.082685	0.08907	2.0924

Conclusion

Adel Almoukhalalati, Stefan Knecht, Hans Jørgen Aagaard Jensen, Kenneth G. Dyall and Trond Saue, J. Chem. Phys. 145 (2016) 074104

- Present-day relativistic molecular electronic structure calculations treat the negative-energy orbitals as an orthogonal complement which is continuously updated at the SCF level and frozen at the correlated level.
- A complete relaxation of the electronic wave function within the no-pair approximation is possible at the MCSCF level as demonstrated in the present study.
- Full optimization of the projection operator

  $$\Lambda_{+}^{HF} \rightarrow \Lambda_{+}^{MCSCF}$$

  reduces the correlation energy in accordance with the underlying minmax-principle.
- The relativistic full MCSCF correlation energy scales at worst as X^{-2} (cardinal number)

Perspectives

- In order to reproduce our full MCSCF results at the coupled cluster level, full orbital relaxation is required.
- Orbital relaxation involving the negative-energy orbitals is crucial for getting magnetic properties right.
- Beyond the no-pair approximation: connect present days relativistic quantum chemical variational methods to QED

There is more work to do !