

# Quadratic response function calculations using relativistic four-component TD-DFT and a non-collinear description of the spin density

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## Abstract

A theory, implementation and first application of relativistic four-component TD-DFT-based for the treatment of quadratic response properties will be presented. The expressions are based on the non-collinear treatment of the spin density which has been shown to offer the highest amount of reliability in previous studies. The non-collinear ansatz for the spin density leads to a large amount of complexity in the expressions for the perturbed analogs of the spin density which additionally suffer from definition problems for the closed-shell case (spin density approaching zero). This is overcome by proper modification of the working equations which are implemented to calculate the third-order derivative of the exchange-correlation energy and the corresponding spin density contributions.

In a first application study, first hyperpolarizabilities of *ortho*- and *meta*-diiodobenzene are calculated and compared with results obtained with one-component TD-DFT calculations with and without use of effective core potentials (ECPs). It has been found that the deviation between the four-component and the one-component/ECP results is not larger than 6% and that therefore the latter offers an efficient tool for calculations of quadratic

response properties while the four-component ansatz is useful for validation of the lower-order results.

## 1 Introduction

The last years have seen an increasing interest in non-linear optical (NLO) molecular properties both in science and technology. In general, NLO is a wide field compiling a lot of different molecular properties which have in common that their strength is not independent of radiation intensity as in linear optics. This dependency is the reason that normally, NLO are only observed at high radiation intensities connecting their experimental realization and technical use to a large extent to the availability of lasers. Therefore, experimental observation of NLO has started after lasers had become available.[1]

Although there is a big variety of NLO properties they have in common that they are considered more or less exotic. As for linear optical properties, in a first step resonant- and non-resonant NLO properties can be distinguished. With this distinction, NLO properties can often be interpreted as higher-order analogs of linear optical properties. Consider for example the interaction of a molecule with a homogeneous electric field with a frequency  $\omega$ . As long as  $\omega$  does not match an excitation energy, the interaction between the molecule and the field (the induced dipole moment) is described by a frequency-dependent polarizability  $\alpha_\omega$  which corresponds to the refractive index of a macroscopic sample. For  $\omega \rightarrow \omega_r$  with  $\omega_r$  being an excitation energy,  $\alpha_\omega$  becomes infinite and light absorption can be observed which can be described by a one-photon transition dipole moment.

The higher-order analogs of these well-known properties are the frequency-dependent first-order hyperpolarizability  $\beta_\omega$  and two-photon absorption (TPA) which correspond to either the conversion of two photons of frequencies  $\omega_1$  and  $\omega_2$  to one photon of frequency  $\omega_1 + \omega_2$  (second harmonic generation, SHG) or the absorption of two photons with frequencies  $\omega_1 + \omega_2 = \omega_r$  (TPA).

While TPA sees a lot of promising applications in 3D data storage, multiphoton microscopy, photodynamic cancer therapy, photochromic layers and drug delivery,[2, 3, 4, 5] materials with good SHG properties are indispensable for frequency upconversion of lasers.[6] For example, every green laser pointer contains a crystal which upconverts the radiation of an infrared laser diode to the second harmonic and therefore shifts it into the visible range of light. Apart from this, also imaging techniques based on SHG have been considered,[7] namely of biological tissues[8]. These few examples illustrate the big interest in materials with non-linear optical properties.

Development of such materials is often hampered by non-trivial structure-property relations which have been investigated in a lot of experimental and theoretical studies.[9, 10, 11, 12, 13, 14]

Calculations of non-linear optical properties are still quite an exotic field of quantum chemistry although there is a variety of implementations available which can calculate e.g. SHG and TPA using either time-dependent density functional theory (TD-DFT)[15], multiconfigurational SCF[16] as well as coupled cluster methods[17, 18, 19]. Higher-order NLO properties such as three-photon absorption and second hyperpolarizabilities have also been made available.[20] In recent years, recursive calculation techniques have been introduced which allow for NLO calculations to in principle infinite order.[21, 22, 23]

All these implementations have in common that they use response theory to describe light-matter interactions[24, 25] and one-component wave functions which offer an efficient and reliable treatment of organic molecules which do not contain atoms heavier than e.g. chlorine. For elements from the fourth period on, relativistic effects can no longer be neglected. However, for the fourth and fifth period, the use of effective core potentials (ECPs) for scalar relativistic effects still leads to reasonable results, also for NLO properties.[26]

Turning to even heavier elements, however, a treatment of relativistic effects through the Hamiltonian is required which necessitates use of a more-component wave function. Implementations of NLO using four-component (relativistic) wave functions are scarce and limited to Hartree-Fock[26, 27] and TD-DFT[28]. As the first implementations of linear optical properties using four-component wave functions[29], these implementations use the so-called *collinear* approach for the description of the spin density[30, 31] (*vide infra*). However, it has already been shown by van Wüllen in 2002,[30] that the collinear approach does not provide a proper description of the spin density as it is e.g. not orientation invariant. For this reason, both van Wüllen[30] and Wang and Liu[31] recommend use of the non-collinear approach for the description of the spin density. First implementations of excitation energies[32] as well as linear-optical properties using this approach[33, 34] have been presented.

In this work the first TD-DFT implementation of non-linear optical properties using a non-collinear description of the spin density will be presented.

This article will be organized as follows: In Section 2 the theory of NLO properties for four-component relativistic quantum chemistry will be derived, in section 3 the implementation will be presented. Section 4 will address technical details of the calculations. In section 5, the results of first application calculations are shown and in section 6 the results will be discussed and section 7 will give some concluding remarks.

## 2 Theory

### 2.1 Response theory

Time-dependent molecular properties are derived from the time-dependent Schrödinger equation

$$\left(\mathbf{H} - i\frac{\partial}{\partial t}\right)|\bar{0}(t)\rangle = 0, \quad (1)$$

where  $\mathbf{H}$  is the Hamiltonian and  $|\bar{0}(t)\rangle$  is the time-dependent wave function according to

$$|\bar{0}(t)\rangle = \exp[-iF(t)]|\tilde{0}(t)\rangle, \quad (2)$$

with  $F$  being a purely time-dependent function.[29] Following the lines of Christiansen et al.[25],  $|\bar{0}(t)\rangle$  is the complete wave function and  $|\tilde{0}(t)\rangle$  its phase-isolated part which in principle remains time-dependent. However it contains time dependence only through the perturbation and is stationary in the unperturbed limit. The phase-isolated form of the time-dependent Schrödinger equation can then be written as

$$\left(\mathbf{H} - i\frac{\partial}{\partial t}\right)|\tilde{0}(t)\rangle = \frac{\partial}{\partial t}F(t) = \mathcal{Q}(t), \quad (3)$$

where  $\mathcal{Q}(t)$  is the time-dependent quasienergy, a quantity which is a time-dependent analog of the energy and which approaches the energy in the static case. In the following, time dependence of  $|\tilde{0}(t)\rangle$  will be suppressed for brevity.

The time-dependent quasienergy allows for the formulation of a time-dependent Hellmann-Feynman theorem[25] according to

$$\frac{d\mathcal{Q}(t)}{d\epsilon_a} = \left\langle \tilde{0} \left| \frac{\partial \mathbf{H}}{\partial \epsilon_a} \right| \tilde{0} \right\rangle - i\frac{\partial}{\partial t} \left\langle \tilde{0} \left| \frac{\partial \tilde{0}}{\partial \epsilon_a} \right\rangle. \quad (4)$$

The time (and perturbation) dependence of the Hamiltonian is described by a one-particle perturbation operator  $\mathbf{V}_x(t)$  according to

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}_x(t). \quad (5)$$

As long as the perturbations considered are periodic in time, time dependency can be treated by time averaging. An important premiss for this is that the frequencies of all perturbations involved are integer multiples of one fundamental frequency according to[25]

$$\omega_k = n_k\omega_0, \quad n_k \in \mathbb{Z}, \quad (6)$$

$$\omega_0 = \frac{2\pi}{\tau}, \quad (7)$$

with  $\tau$  being the time period. This enables Fourier transformation of the perturbation operator following the lines of Christiansen and coworkers[25]

$$\mathbf{V}_x(t) = \sum_{k=-N}^N \exp[-i\omega_k t] \mathbf{V}_x(\omega_k). \quad (8)$$

However  $\omega_0$  can be chosen as small as necessary and therefore, this premiss is not very restrictive.[29] Time averaging of a function  $f(t)$  can then be performed according to

$$\{f(t)\}_\tau = \frac{1}{\tau} \int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} f(t) dt, \quad (9)$$

yielding  $\{f(t)\}_\tau$ , the time average of  $f(t)$ . Following those lines, the time-averaged quasienergy

$$Q = \{\mathcal{Q}\}_\tau, \quad (10)$$

is obtained allowing for the formulation of a time-averaged time-dependent Hellman-Feynman theorem

$$\frac{dQ}{d\epsilon_a} = \left\{ \left\langle \tilde{0} \left| \frac{\partial \mathbf{H}}{\partial \epsilon_a} \right| \tilde{0} \right\rangle \exp[-i\omega_a t] \right\}_\tau, \quad (11)$$

$$= \left\{ \left\langle \tilde{0} \left| \mathbf{V}_{\epsilon_a} \right| \tilde{0} \right\rangle \exp[-i\omega_a t] \right\}_\tau, \quad (12)$$

where it has been used that the time average of a time-differentiated periodic function is zero according to[25]

$$\left\{ \frac{\partial Z(t)}{\partial t} \right\}_T = 0. \quad (13)$$

The expectation values can now be expanded in orders of the perturbation according to

$$\begin{aligned} \langle \tilde{0} | V_{\epsilon_a} | \tilde{0} \rangle &= \langle 0 | V_{\epsilon_a} | 0 \rangle + \sum_{b_1=-N}^N \langle \langle \mathbf{V}_{\epsilon_a}; \mathbf{V}_1(\omega_{b_1}) \rangle \rangle \exp[-i\omega_{b_1} t] + \\ &\sum_{b_1, b_2=-N}^N \langle \langle \mathbf{V}_{\epsilon_a}; \mathbf{V}_1(\omega_{b_1}), \mathbf{V}_2(\omega_{b_2}) \rangle \rangle \exp[-i(\omega_{b_1} + \omega_{b_2}) t] + \dots \end{aligned} \quad (14)$$

This expansion can be inserted in Eq. (11). Averaging over time yields

$$\begin{aligned} \frac{dQ}{d\epsilon_a} &= \langle 0 | V_{\epsilon_a} | 0 \rangle \delta(\omega) + \sum_{b_1=-N}^N \langle \langle \mathbf{V}_{\epsilon_a}; \mathbf{V}_1(\omega_{b_1}) \rangle \rangle \exp[-i\omega_{b_1} t] \delta(\omega + \omega_{b_1}) + \\ &\sum_{b_1, b_2=-N}^N \langle \langle \mathbf{V}_{\epsilon_a}; \mathbf{V}_1(\omega_{b_1}), \mathbf{V}_2(\omega_{b_2}) \rangle \rangle \exp[-i(\omega_{b_1} + \omega_{b_2}) t] \delta(\omega + \omega_{b_1} + \omega_{b_2}) + \dots, \end{aligned} \quad (15)$$

where  $\delta(\mu)$  is zero for  $\mu \neq 0$  and unity for  $\mu = 0$ . The expansion coefficients in Eq. (15) are called response functions to order  $n$  with  $\langle \langle \mathbf{V}_{\epsilon_a}; \mathbf{V}_1(\omega_{b_1}) \rangle \rangle$  being the linear and  $\langle \langle \mathbf{V}_{\epsilon_a}; \mathbf{V}_1(\omega_{b_1}), \mathbf{V}_2(\omega_{b_2}) \rangle \rangle$  being the quadratic response function.

## 2.2 Time-dependent density functional theory

### 2.2.1 Density functional theory

Following the Hohenberg-Kohn-theorem, the energy  $E$  of a molecular system can completely be described as a functional of the electron density  $\rho$ . [35] Using the Kohn-Sham-approach, the energy can be obtained using a self-consistent field procedure analog to Hartree-Fock theory with the exchange and correlation contributions to the energy being described by the exchange-correlation functional  $E_{xc}(\rho)$ . [36] Turning now from the energy to the time-dependent quasienergy, the exchange-correlation functional is replaced by the exchange-correlation action  $A_{xc}(\rho)$ . [32] In the adiabatic approximation, however, which will be used in the following, the (static) exchange-correlation functional  $E_{xc}(\rho)$  is used instead of the time-dependent exchange-correlation action  $A_{xc}(\rho)$  to describe the time-dependent quasienergy. [37, 31, 32] In the adiabatic approximation, the time-dependent quasienergy reads

$$Q[\rho] = T[\rho] + V[\rho] + J[\rho] + (1 - \xi)K[\rho] + \xi E_{xc}[\rho] - S[\rho], \quad (16)$$

with  $T$  and  $V$  being the kinetic and potential energy contributions (one-electron part) and  $J$ ,  $K$ ,  $Q_{xc}$  and  $S$  the Coulomb, (Hartree-Fock) exchange, exchange-correlation (two-electron) and time-dependent contributions, respectively. The coefficient  $\xi$  is a scalar between 0 and 1 indicating the portion of Hartree-Fock-exchange energy in the system. For density functionals of the LDA and GGA-types,  $\xi$  is 1.

The one-electron, Coulomb and exchange terms are evaluated as analytical integrals while  $Q_{xc}[\rho]$  is evaluated by numerical integration.

### 2.2.2 The density

Up to now, the density as an input to the exchange-correlation functional has been termed  $\rho$ . The two key contributions to  $\rho$  are the charge density  $n$  and the spin density  $\zeta$ . The definition of the charge density is well-established according to

$$n(\mathbf{r}) = \sum_{pq} \Omega_{pq}(\mathbf{r}) D_{pq} = \sum_i \Omega_{ii}, \quad (17)$$

$$= \sum_{pq} \phi_p^* \phi_q D_{pq}, \quad (18)$$

with  $D_{pq}$  being the elements of the density matrix,  $\mathbf{r}$  is the position vector and  $\phi_q$  a basis function. In the following, the letters  $p, q, r, s, t, u$  will be used for arbitrary molecular orbitals,  $a, b, c, \dots$  for virtual and  $i, j, k, \dots$  for occupied orbitals. The quantity  $\mathbf{\Omega}(\mathbf{r})$  is

called orbital distribution. Note that both the number density  $n$  and  $\mathbf{\Omega}(\mathbf{r})$  are position dependent.

The most intuitive definition of the spin density is the so-called collinear approach which interpretes the electron charge of a system to be the sum of the densities of its electrons with  $\alpha$ - and  $\beta$ -spin, hence

$$n = \rho_\alpha + \rho_\beta. \quad (19)$$

In this simple picture, the spin density  $s$  is the difference of the  $\alpha$ - and  $\beta$ -electron densities,

$$\zeta = \rho_\alpha - \rho_\beta, \quad (20)$$

and is therefore zero in the closed-shell case.

This approach, which of course requires that electrons have either  $\alpha$ - oder  $\beta$ -spin is called the "collinear approach" for the definition of the spin density as it assumes that all electron spins are either parallel or antiparallel to each other. However, as the  $z$ -component of the spin is no longer a good quantum number as soon as relativistic effects and spin-orbit coupling come into play, this requirement is inappropriate for a proper relativistic treatment of molecular properties. This has also been proven in several studies either theoretically[30] or by comparison of calculated results[31, 38]. All these studies have shown that the non-collinear treatment of the spin density yields much better results than the collinear one.

In the non-collinear treatment, the spin density is no longer the difference between  $\rho_\alpha$  and  $\rho_\beta$  but the norm of the spin magnetization vector  $\mathbf{m}$  according to

$$\zeta^2 = \mathbf{m} \cdot \mathbf{m} = \sum_{i=x,y,z} \sum_{pq} D_{pq} \phi_p^* \sigma_i \phi_q = \sum_{i=x,y,z} \sum_{pq} D_{pq} \Omega_{pq,i} \quad (21)$$

where  $\sigma_i$  are the components of the vector of Pauli spin matrices. The elements of the density matrix are defined as

$$D_{pq} = \langle \tilde{0} | a_p^\dagger a_q | \tilde{0} \rangle, \quad (22)$$

where  $a_p^\dagger$  and  $a_q$  are the creation and annihilation operators of 2nd quantization.[39] It is important to note that the collinear approach can be interpreted as a simplification of the non-collinear case where only one spatial component of the vector  $\mathbf{m}$  has been taken into account.[30]

Furthermore, it is important to note that the non-collinear spin density can never be negative due to its definition as a norm (Eq. (21)).

### 2.2.3 Perturbation behaviour of the density

As discussed in the previous section, both the number and spin densities are constructed from the orbital distribution or its spin-magnetization analog and the density matrix. In the following, the time- and therefore also the perturbation dependency of the density will be considered.

In the previous sections, it was already mentioned that the phase-isolated wave function  $|\tilde{0}\rangle$  depends on time only through the perturbation. For a proper parametrization, the time-dependent orbital rotation operator  $\hat{\kappa}(t)$  is introduced

$$\hat{\kappa} = \sum_{pq} \kappa_{pq} a_p^\dagger a_q, \quad (23)$$

which is unitary and enters the wave function expression through an exponential function according to

$$|\tilde{0}\rangle = \exp[-\hat{\kappa}(t)|0\rangle. \quad (24)$$

The orbital rotation parameters  $\boldsymbol{\kappa}$  will carry the whole time- and perturbation dependence of the wave function. They can be interpreted as perturbation corrections to the wave function. Therefore, the unperturbed parameters  $\boldsymbol{\kappa}$  will be chosen zero, hence there is no correction in the unperturbed case.

In accordance with the Fourier transform of the perturbation discussed in 2.1, the time dependence of the orbital rotation parameters can be written as

$$\kappa_{pq} = \sum_{k=-N}^N \kappa_{pq} \exp[i\omega_k t]. \quad (25)$$

The quasienergy is assumed to be stationary with respect to the orbital rotation parameters

$$\left. \frac{dQ}{d\kappa_{pq}} \right|_{\epsilon=0} = 0, \quad (26)$$

at a perturbation strength of zero.

Applying this to the definition of the number and spin densities (Eqs. (17) and (21)), it is noted that the position dependence is completely located in the orbital distribution while time- and perturbation dependencies are condensed in the density matrix according to

$$\rho(\mathbf{r}, \boldsymbol{\kappa}) = \langle \tilde{0} | \boldsymbol{\rho} | \tilde{0} \rangle = \sum_{pq} \Omega_{pq}^*(\mathbf{r}) D_{pq}(\boldsymbol{\kappa}), \quad (27)$$



with  $\rho$  being the general density operator. This expression holds for both the number density and the components of the spin magnetization vector depending on the definition of the orbital distribution. This is indicated by the asterisk. As  $\kappa$  depends on time, all time dependencies will be substituted by dependencies on  $\kappa$  in the following for the description of the perturbation dependency of the density matrix. Invoking Eq. (24) in Eq. (22) and performing a Baker-Campbell-Hausdorff expansion of the exponential terms, the density matrix can be written as

$$D_{pq}(\kappa) = \langle 0|a_p^\dagger a_q|0\rangle + \langle 0|[\hat{\kappa}, a_p^\dagger a_q]|0\rangle + \frac{1}{2}\langle 0|[\hat{\kappa}, [\hat{\kappa}, a_p^\dagger a_q]]|0\rangle + \dots, \quad (28)$$

showing the dependence of the density matrix on the orbital rotation parameters. Inserting Eq. (28) into the definition of the (number or spin) density, Eq. (27), and collecting terms to first order, we get[29]

$$\langle 0|[\hat{\kappa}, \kappa]|0\rangle = \kappa_{ai}\Omega_{ai} - \Omega_{ia}\kappa_{ai}, \quad (29)$$

which is a one-index transformation of the orbital distribution with the orbital rotation parameters.

In a similar manner, also the higher-order nested commutators shown in Eq. (28) can be written in terms of nested one-index transformations of the orbital distribution.

It is important to recall that this theory works completely analogous for both the "primitive" orbital distribution corresponding to the number density  $n$  as well as the orbital distributions involving the Pauli spin matrices which lead to the components of the spin magnetization vector. Hence, the perturbation behaviour of the number and the spin densities can be treated completely analogous.

With this, the quasienergy can be written as a function of  $\rho$  and a functional of  $\kappa$  according to

$$Q[\rho(\kappa)] = Q_0 + \sum_{k=-N}^N \sum_x \epsilon_x(\omega_k) Q_x(\omega_k), \quad (30)$$

where the first term is the unperturbed quasienergy

$$Q_0 = \left\{ h_{pq} D_{pq}(\kappa) + \frac{1}{2} [(pq|rs) - \xi(ps|rq)] D_{pq}(\kappa) D_{rs}(\kappa) + E_{xc}[\rho(\kappa)] + V_{NN} - S[\rho(\kappa)] \right\}_\tau, \quad (31)$$

with the time-dependent contribution

$$S[\rho] = \left\{ \langle \tilde{0} | i \frac{\partial}{\partial t} | \tilde{0} \rangle \right\}, \quad (32)$$

and the second term is the perturbation contribution

$$Q_x(\omega_k) = \{ \langle \tilde{0} | \mathbf{V}_{\epsilon_a} | \tilde{0} \rangle \exp[-i\omega t] \}_T. \quad (33)$$

The quadratic response function can be obtained by differentiating the time-dependent quasienergy w.r.t. the perturbations. After some simplifications following the lines of Ref. 25, the expression reads

$$\begin{aligned} \frac{d^3 Q}{d\epsilon_a d\epsilon_b d\epsilon_c} \Big|_{\epsilon_a=\epsilon_b=\epsilon_c=0} &= \frac{\partial^3 Q}{\partial \epsilon_a \partial \epsilon_b \partial \epsilon_c} + \frac{\mathcal{P}_{abc}}{2} \left( \frac{\partial^3 Q}{\partial \epsilon_a \partial \kappa_{pq} \partial \kappa_{rs}} \frac{\partial \kappa_{pq}}{\partial \epsilon_b} \frac{\partial \kappa_{rs}}{\partial \epsilon_c} + \frac{\partial^3 Q}{\partial \epsilon_a \partial \epsilon_b \partial \kappa_{pq}} \frac{\partial \kappa_{pq}}{\partial \epsilon_c} \right) + \\ &\frac{\partial^3 Q}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} \frac{\partial \kappa_{pq}}{\partial \epsilon_a} \frac{\partial \kappa_{rs}}{\partial \epsilon_b} \frac{\partial \kappa_{tu}}{\partial \epsilon_c}, \end{aligned} \quad (34)$$

where  $\mathcal{P}_{abc}$  is a permutation operator which interchanges perturbations  $\epsilon_a$ ,  $\epsilon_b$ ,  $\epsilon_c$ . Note that in this formulation, the quadratic response function only depends on first-order derivatives of the orbital rotation parameters obtained by solving the response equations

$$\frac{d^2 Q}{d\kappa_{pq} d\epsilon_a} = \frac{\partial^2 Q}{\partial \kappa_{pq} \partial \kappa_{rs}} \kappa_{pq}^a + \frac{\partial^2 Q}{\partial \kappa_{pq} \partial \epsilon_a} = 0, \quad (35)$$

where the short-hand notation  $\kappa_{pq}^a$  for the derivatives of the orbital rotation parameters has been introduced. Eq. (35) can be considered a perturbed version of the variational condition, Eq. (26). Eqs. (26) and (35) have also been used to eliminate all higher-order derivatives of the orbital rotation parameters from Eq. (34) in accordance with the 2n+1-rule of response theory.[25] This means that only the first-order response of the orbital rotation parameters is needed for the calculation of the quadratic response function.

Recalling now the definition of the time-dependent quasienergy  $Q[\rho(\boldsymbol{\kappa})]$  (Eqs. (30)  $f$ ), it is noted that apart from the perturbation contribution  $Q_x$  the complete perturbation dependency of  $Q$  is through the orbital rotation parameters  $\boldsymbol{\kappa}$ . This is of special interest for the exchange-correlation contribution  $E_{xc}[\rho]$ .

#### 2.2.4 Derivatives of the exchange-correlation density functional

As the exchange-correlation energy depends on the perturbation only through the orbital rotation parameters  $\boldsymbol{\kappa}$  and the derivatives of  $\boldsymbol{\kappa}$  are known, the different orders of  $E_{xc}[\rho]$  in  $\boldsymbol{\kappa}$  have to be evaluated which afterwards are combined with the responses of  $\boldsymbol{\kappa}$ .

The first derivative of the exchange-correlation functional is called the *exchange-correlation potential*

$$\frac{\partial e_{xc}}{\partial \kappa_{pq}} = \frac{\delta e_{xc}}{\delta \rho} \frac{\partial \rho}{\partial \kappa_{pq}}, \quad (36)$$

and is already needed to set up the unperturbed Kohn-Sham matrix.[40] In these expressions,  $\delta$  indicates the derivative of a functional and  $\partial$  the partial derivative of a function.

For the treatment of linear response properties and excitation energies, also the exchange-correlation kernel is needed which is the second derivative of the exchange-correlation functional w.r.t. the orbital rotation parameters according to[29, 38, 32, 41]

$$\frac{\partial^2 e_{xc}}{\partial \kappa_{pq} \partial \kappa_{rs}} = \frac{\delta^2 e_{xc}}{\delta \rho^2} \frac{\partial \rho}{\partial \kappa_{pq}} \frac{\partial \rho}{\partial \kappa_{rs}}. \quad (37)$$

Note that in the previous two equations  $\rho$  has been used as a general parameter for the unperturbed number or spin density or (in the case of GGA functionals) its gradient. In contrast to the exchange-correlation potential, the exchange-correlation kernel is never calculated explicitly but always as contraction either with a trial vector[32] (calculation of excitation energies or solution of response equations like Eq. (35)) giving a matrix or with two perturbed  $\kappa$  vectors giving a scalar[42] (for calculation of molecular properties). In these cases, e.g. the second derivative of the xc-functional w.r.t. the perturbations is calculated according to

$$\frac{e_{xc}}{d\epsilon_a d\epsilon_b} \quad (38)$$

where the term depending on the second-order perturbed orbital rotation parameters  $\kappa_{pq}^{ab}$  is zero due to the variational condition (Eq. (26)).

For the treatment of the quadratic response function, which is the third derivative of the energy, the *second exchange correlation kernel* is needed which in the following will be discussed in detail. In this work, the second exchange-correlation kernel will only be needed in a full contraction with three perturbed orbital rotation vectors. The derivation of the second kernel is based on the expressions for the kernel presented by Bast and coworkers[32] and Komorovsky and coworkers[42] which in contrast to Eq. 37 already show explicit dependencies on number and spin densities.

An expression for the second kernel involving number and spin densities as well as their gradients becomes extremely long. Therefore, for the sake of brevity, the derivation will only be shown for the case of an LDA functional (i.e. without density gradients). As the definition of the quadratic response function used in this work explicitly excludes terms which depend on the orbital rotation parameters higher than first order, also terms which will use such high-order derivatives are excluded from the beginning. However, a treatment including density gradients is completely analogous and its final results will also be shown.

For an LDA functional, the complete third derivative of the exchange-correlation energy is

$$\begin{aligned}
\frac{\partial^3 e_{xc}}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} = & \int \left( \frac{\delta^3 e_{xc}}{\delta n^3} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial n}{\partial \kappa_{rs}} \frac{\partial n}{\partial \kappa_{tu}} + \mathcal{P}_{pq,rs,tu} \frac{\delta^3 e_{xc}}{\delta n^2 \delta \zeta} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial n}{\partial \kappa_{rs}} \frac{\partial \zeta}{\partial \kappa_{tu}} + \right. \\
& \mathcal{P}_{pq,rs,tu} \frac{\delta^3 e_{xc}}{\delta n \delta \zeta^2} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial \zeta}{\partial \kappa_{rs}} \frac{\partial \zeta}{\partial \kappa_{tu}} + \frac{\delta^3 e_{xc}}{\delta \zeta^3} \frac{\partial \zeta}{\partial \kappa_{pq}} \frac{\partial \zeta}{\partial \kappa_{rs}} \frac{\partial \zeta}{\partial \kappa_{tu}} + \\
& \mathcal{P}_{pq,rs,tu} \frac{\delta^2 e_{xc}}{\delta n^2} \frac{\partial n}{\partial \kappa_{pq}} \frac{\delta^2 n}{\partial \kappa_{rs} \partial \kappa_{tu}} + \mathcal{P}_{pq,rs,tu} \frac{\delta^2 e_{xc}}{\delta n \delta \zeta} \left( \frac{\partial^2 n}{\partial \kappa_{pq} \partial \kappa_{rs}} \frac{\partial \zeta}{\partial \kappa_{tu}} + \frac{\partial^2 \zeta}{\partial \kappa_{pq} \partial \kappa_{rs}} \frac{\partial n}{\partial \kappa_{tu}} \right) + \\
& \left. \mathcal{P}_{pq,rs,tu} \frac{\delta^2 e_{xc}}{\delta \zeta^2} \frac{\partial \zeta}{\partial \kappa_{pq}} \frac{\partial^2 \zeta}{\partial \kappa_{rs} \partial \kappa_{tu}} + \frac{\delta e_{xc}}{\delta n} \frac{\partial^3 n}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} + \frac{\delta e_{xc}}{\delta \zeta} \frac{\partial^3 \zeta}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} \right) d\mathbf{r}. \tag{39}
\end{aligned}$$

The functional derivatives in (39) can be calculated using the well-established automatic differentiation scheme presented which is based on a Taylor expansion of the corresponding expressions and allows also for the calculation of functional derivatives to arbitrary order.[43, 44] This scheme receives the differentiated densities as an input which in four-component theory have to be formed from the complete manifold of wave functions.

For the derivatives of the charge density  $n$ , this is straightforward using the nested commutators exemplified in Eq. (29) while especially for closed-shell systems, this requires special treatment of the spin density.

### 2.2.5 Derivatives of the non-collinear spin density

Differentiation of the non-collinear spin density w.r.t. either geometrical distortions (e.g. for treatment in GGA density functionals) or external fields (for the treatment of spectroscopical properties) requires differentiation of the expression in Eq. (21). Expressions for the first and second derivatives of the non-collinear spin density have already been introduced in Ref. 32. As the spin density is the norm of the spin magnetization vector, these derivatives require use of the chain rule and, to higher-order than one, also use of the quotient rule.

Starting point is the derivative of a norm w.r.t. the corresponding vector

$$\frac{\partial \zeta}{\partial \mathbf{m}} = \frac{\mathbf{m}}{\zeta}, \tag{40}$$

which is nothing more but the normalized vector and can be obtained from straightforward differentiation of every vector component using the chain rule. Eq. (40) is an important building block for the differentiation of the spin density following the lines of Ref. 32. Using these relations, the first and second derivatives with respect to the parameters  $\kappa_{pq}$

$\kappa_{rs}$ , respectively, are obtained according to[32]

$$\frac{\partial \zeta}{\partial \kappa_{pq}} = \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}}, \quad (41)$$

$$\frac{\partial^2 \zeta}{\partial \kappa_{pq} \partial \kappa_{rs}} = \frac{1}{\zeta} \left( \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \right) - \frac{1}{\zeta} \left( \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \right) \left( \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \right) + \frac{\mathbf{m}}{\zeta} \frac{\partial^2 \mathbf{m}}{\partial \kappa_{pq} \partial \kappa_{rs}}. \quad (42)$$

Note that already between Eqs. (41) and (42), there is an strong increase in complexity due to the use of the quotient rule which is necessary to get Eq. (42). Formulation of the third derivative of  $\zeta$  requires extensive use of the quotient, product and chain rules and yields

$$\begin{aligned} \frac{\partial \zeta}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} &= \frac{\mathbf{m}}{\zeta} \frac{\partial^3 \mathbf{m}}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} + \frac{3}{\zeta^2} \left( \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \right) \left( \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \right) \left( \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{tu}} \right) + \\ &\mathcal{P}_{pq,rs,tu} \frac{1}{2\zeta} \left( \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial^2 \mathbf{m}}{\partial \kappa_{rs} \partial \kappa_{tu}} \right) - \mathcal{P}_{pq,rs,tu} \frac{1}{2\zeta} \left( \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \right) \left( \frac{\mathbf{m}}{\zeta} \frac{\partial^2 \mathbf{m}}{\partial \kappa_{rs} \partial \kappa_{tu}} \right) - \\ &\mathcal{P}_{pq,rs,tu} \frac{1}{2\zeta^2} \left( \frac{\mathbf{m}}{\zeta} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \right) \left( \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \frac{\partial \mathbf{m}}{\partial \kappa_{tu}} \right). \end{aligned} \quad (43)$$

For closed-shell systems, this expression is running into defintion problems as  $\zeta \rightarrow 0$  and all terms apart from the first one depend on a division by  $\zeta$ . The treatment in the closed shell case will be discussed in the following.

### 2.2.6 Simplification for the closed shell-case

The treatment of the second xc-kernel in the closed shell case allows for simplification of both the functional derivatives and the perturbed spin density. Modifications of the exchange-correlation functional derivatives is explained most easily using a technique introduced by Wang and coworkers in 2003 who modify the charge and spin densities according to[31]

$$\rho_{\pm} = \frac{1}{2} (n \pm \zeta), \quad (44)$$

such that

$$n = \rho_+ + \rho_-; \quad \zeta = \rho_+ - \rho_-, \quad (45)$$

which is analogous to the collinear definition of the spin density. Using these expressions, the derivatives of the exchange-correlation functional can be rewritten.[31, 38] For the first derivative w.r.t. the spin density, this e.g. yields

$$\frac{\delta e_{xc}}{\delta \zeta} = \frac{1}{2} \frac{\delta e_{xc}}{\delta (\rho_+ - \rho_-)} = \frac{1}{2} \left( \frac{\delta e_{xc}}{\delta \rho_+} - \frac{\delta e_{xc}}{\delta \rho_-} \right). \quad (46)$$

For  $\zeta \rightarrow 0$ , this expression becomes zero, as well as the mixed second derivative of the xc-functional w.r.t.  $n$  and  $\zeta$ . [38, 32] The third-order derivative w.r.t. the spin density, is

$$\frac{\delta^3 e_{xc}}{\delta \zeta^3} = \frac{1}{8} \left( \frac{\delta^3 e_{xc}}{\delta^3 \rho_+} - 3 \frac{\delta^3 e_{xc}}{\delta^2 \rho_+ \delta \rho_-} + 3 \frac{\delta^3 e_{xc}}{\delta \rho_+ \delta \rho_-^2} - \frac{\delta^3 e_{xc}}{\delta^3 \rho_-} \right), \quad (47)$$

which is zero as well for the closed-shell case. Analyzing the other expressions from Eq. (39) using this technique, it is noted that, that all terms vanish which depend on an odd-order derivative w.r.t. the spin density. This holds also for expressions depending on the spin density gradient if GGA functionals are involved.

In order to have the second xc-kernel defined properly in the closed-shell case, divisions by the spin density can be removed using the following relation which originate from de l'Hôpital's rule: [38, 32]

$$\frac{1}{\zeta} \frac{\delta e_{xc}}{\delta \zeta} = \frac{\delta^2 e_{xc}}{\delta \zeta^2} \quad \text{for } \zeta \rightarrow 0. \quad (48)$$

In the following, also the higher analog to this expression will be used,

$$\frac{1}{\zeta} \frac{\delta^2 E_{xc}}{\delta \zeta \delta n} = \frac{\delta^3 e_{xc}}{\delta n \delta \zeta^2} \quad \text{for } \zeta \rightarrow 0, \quad (49)$$

as well as the a modification of Eq. (48),

$$\frac{1}{\zeta} \frac{\delta^2 E_{xc}}{\delta \zeta^2} = \frac{1}{\zeta} \left( \frac{1}{\zeta} \frac{\delta e_{xc}}{\delta \zeta} \right) \quad \text{for } \zeta \rightarrow 0. \quad (50)$$

Using these expressions, Eq. (39) can be simplified for the closed shell case to

$$\begin{aligned} \frac{\delta^3 E_{xc}}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} = \int & \left( \frac{\delta^3 e_{xc}}{\delta n^3} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial n}{\partial \kappa_{rs}} \frac{\partial n}{\partial \kappa_{tu}} + \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\delta^2 e_{xc}}{\delta n^2} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial^2 n}{\partial \kappa_{rs} \partial \kappa_{tu}} + \right. \\ & \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\delta^3 e_{xc}}{\delta n \delta \zeta^2} \left( \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \right) \frac{\partial n}{\partial \kappa_{tu}} + \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\delta^2 E_{xc}}{\delta \zeta^2} \left( \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial^2 \mathbf{m}}{\partial \kappa_{rs} \partial \kappa_{tu}} \right) + \\ & \left. \frac{\delta e_{xc}}{\delta n} \frac{\partial^3 n}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} \right) d\mathbf{r} \quad \text{for } \zeta \rightarrow 0. \end{aligned} \quad (51)$$

Note that this expression does no longer depend on the spin density  $\zeta$  at all but just on the spin magnetization vector  $\mathbf{m}$ . This allows for diving Eq. (51) into two parts: A *scalar* one which just contains dependencies on  $n$  and its derivatives as well as the *vectorial* part which depends on  $\mathbf{m}$ . [32] As all  $\mathbf{m}$ -dependencies are in pairs, their contributions can be interpreted as scalar products of differentiated spin magnetization vectors.

The expression for the derivative of a GGA-functional can be evaluated in a similar manner as leads to

$$\begin{aligned}
\frac{\partial^3 E_{xc}}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} = & \int \left[ \frac{\delta^3 e_{xc}}{\delta n^3} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial n}{\partial \kappa_{rs}} \frac{\partial n}{\partial \kappa_{tu}} + \frac{\delta^2 e_{xc}}{\delta n^2} \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial^2 n}{\partial \kappa_{rs} \partial \kappa_{tu}} + \frac{\delta e_{xc}}{\delta n} \frac{\partial^3 n}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} + \right. \\
& \frac{\delta^3 e_{xc}}{\delta n^2 \delta \nabla n} \mathcal{P}_{pq,rs,tu} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial n}{\partial \kappa_{rs}} \frac{\partial \nabla n}{\partial \kappa_{tu}} + \frac{\delta^3 e_{xc}}{\delta n \delta \nabla n^2} \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial \nabla n}{\partial \kappa_{rs}} \frac{\partial \nabla n}{\partial \kappa_{tu}} + \\
& \frac{\delta^3 e_{xc}}{\delta \nabla n^3} \frac{\partial \nabla n}{\partial \kappa_{pq}} \frac{\partial \nabla n}{\partial \kappa_{rs}} \frac{\partial \nabla n}{\partial \kappa_{tu}} + \frac{\delta^2 e_{xc}}{\delta n \delta \nabla n} \frac{\mathcal{P}_{pq,rs,tu}}{2} \left( \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial^2 \nabla n}{\partial \kappa_{rs} \partial \kappa_{tu}} + \frac{\partial^2 n}{\partial \kappa_{pq} \partial \kappa_{rs}} \frac{\partial \nabla n}{\partial \kappa_{tu}} \right) + \\
& \frac{\delta^2 e_{xc}}{\delta \nabla n^2} \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\partial \nabla n}{\partial \kappa_{pq}} \frac{\partial^2 \nabla n}{\partial \kappa_{rs} \partial \kappa_{tu}} + \frac{\delta e_{xc}}{\delta \nabla n} \frac{\partial^3 \nabla n}{\partial \kappa_{pq} \partial \kappa_{rs} \partial \kappa_{tu}} + \\
& \frac{\delta^3 e_{xc}}{\delta n \delta \zeta^2} \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \frac{\partial \mathbf{m}}{\partial \kappa_{tu}} + \frac{\delta^2 e_{xc}}{\delta \zeta^2} \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial^2 \mathbf{m}}{\partial \kappa_{rs} \partial \kappa_{tu}} + \quad (52) \\
& \frac{\delta^3 e_{xc}}{\delta \zeta^2 \delta \nabla n} \frac{\mathcal{P}_{pq,rs,tu}}{2} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \frac{\partial \nabla n}{\partial \kappa_{tu}} + \frac{\delta^3 e_{xc}}{\delta n \delta \zeta \delta \nabla \zeta} \mathcal{P}_{pq,rs,tu} \frac{\partial n}{\partial \kappa_{pq}} \frac{\partial \mathbf{m}}{\partial \kappa_{rs}} \frac{\partial \nabla \mathbf{m}}{\partial \kappa_{tu}} + \\
& \frac{\delta^3 e_{xc}}{\delta s \delta \nabla n \delta \nabla s} \mathcal{P}_{pq,rs,tu} \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial \nabla n}{\partial \kappa_{rs}} \frac{\partial \nabla \mathbf{m}}{\partial \kappa_{tu}} + \\
& \left. \frac{\delta^2 e_{xc}}{\delta s \delta \nabla s} \frac{\mathcal{P}_{pq,rs,tu}}{2} \left( \frac{\partial \mathbf{m}}{\partial \kappa_{pq}} \frac{\partial^2 \nabla \mathbf{m}}{\partial \kappa_{rs} \partial \kappa_{tu}} + \frac{\partial^2 \mathbf{m}}{\partial \kappa_{pq} \partial \kappa_{rs}} \frac{\partial \nabla \mathbf{m}}{\partial \kappa_{tu}} \right) \right] d\mathbf{r} \quad \text{for } s \rightarrow 0.
\end{aligned}$$

Analogous to the LDA-case, also for the GGA expression, scalar and vectorial parts can be formulated which depend on either  $n$  and  $\nabla n$  or  $n$ ,  $\nabla n$ ,  $\mathbf{m}$  and  $\nabla \mathbf{m}$ , respectively.

## 3 Impementation

### 3.1 The quadratic response function

In contrast to the theory, which was completely derived in the MO basis, property calculations will be carried out in the AO basis. AO-basis and density-matrix based approaches for molecular property calculations have become increasingly popular during the past years, especially as they promise a better scaling behaviour for larger molecular systems.[39, 45, 46, 47] For molecular property calculations, the shift from MO to AO basis is quite straightforward as in all cases matrices and vectors are contracted to a scalar. This might be exemplified on the expression for the number density  $n$  (Eq. (17))

$$n = \sum_i \phi_i^* \phi_i = \sum_i \sum_{\mu\nu} c_{i\mu}^* \phi_\mu^* c_{i\nu} \phi_\nu = \sum_{\mu\nu} \phi_\mu \phi_\nu \sum_i c_{i\mu}^* c_{i\nu} = \sum_{\mu\nu} \Omega_{\mu\nu} D_{\mu\nu}, \quad (53)$$

where  $c$  are the LCAO transformation coefficients and greek letters indicate the atomic orbital indices. Also in the AO basis, the integrals will carry the position dependence

while the density matrix carries the dependence on time and perturbation. The quadratic response function will be described in the AO basis based on the approach presented by Kjærgaard et al. in 2008.[39] This formulation was for non-relativistic theory, however it can straightforwardly be generalized to four-component theory. Following the lines of Kjærgaard and coworkers, the so-called supermatrix notation will be used, where index pairs are collapsed to one index resulting in a more compact notation. Vectors and matrices in supermatrix notation will be written in italic boldface and their elements will be indicated by uppercase indices while matrices and vectors in classical notation will be written in roman boldface and their elements will be indicated by lowercase indices. The quadratic response function can then be written as

$$\begin{aligned} \langle\langle \mathbf{A}; \mathbf{B}, \mathbf{C} \rangle\rangle = & \sum_{IJ} (A_{IJ}^{[2]} + A_{JI}^{[2]}) \kappa_I^b \kappa_J^c + \sum_{IJ} X_I^A B_{IJ}^{[2]} \kappa_J^c + \sum_{IJ} \kappa_I^a \kappa_J^b C_{IJ}^{[2]} + \\ & \sum_{IJK} \kappa_I^a (E_{IJK}^{[3]} + E_{IKJ}^{[3]} - \omega_i S_{IJK}^{[3]} - \omega_i S_{IKJ}^{[3]}) \kappa_J^b \kappa_K^c, \end{aligned} \quad (54)$$

where the numbers in square brackets denote the order of derivative w.r.t. the unperturbed parameters  $\boldsymbol{\kappa}$ . The quantities  $\mathbf{E}^{[2]}$ ,  $\mathbf{E}^{[3]}$ ,  $\mathbf{S}^{[2]}$ ,  $\mathbf{S}^{[3]}$  and  $\mathbf{A}^{[2]}$  can be obtained from the expression for the time-dependent quasienergy (Eq. (16) according to

$$\mathbf{E}^{[2]} = \frac{\partial^2}{\partial \boldsymbol{\kappa}^2} (T[\rho] + V[\rho] + J[\rho] + E_{xc}[\rho]), \quad (55)$$

$$\mathbf{E}^{[3]} = \frac{\partial^3}{\partial \boldsymbol{\kappa}^3} (T[\rho] + V[\rho] + J[\rho] + E_{xc}[\rho]), \quad (56)$$

$$\mathbf{S}^{[2]} = \frac{\partial^2}{\partial \boldsymbol{\kappa}^2} (S[\rho]), \quad (57)$$

$$\mathbf{S}^{[3]} = \frac{\partial^3}{\partial \boldsymbol{\kappa}^3} (S[\rho]), \quad (58)$$

$$\mathbf{A}^{[2]} = \frac{\partial^2}{\partial \boldsymbol{\kappa} \partial \epsilon_a} (T[\rho] + V[\rho] + J[\rho] + E_{xc}[\rho]). \quad (59)$$

Note that the derivative of  $S[\rho]$  w.r.t.  $\epsilon_a$  is always zero and hence, there is no  $S[\rho]$ -dependency in  $\mathbf{A}^{[2]}$ . For a detailed description of the derivation of Eq. (54), the reader is referred to Ref. 39.

In this work, the focus will not be on the implementation of the shown matrices as such but on their complete contractions with the perturbation parameters to a scalar value. Therefore, the following types of contractions can be identified:

1. Contraction of the  $\mathbf{A}^{[2]}$ -type matrices with two perturbation parameter vectors
2. Contraction of the  $\mathbf{E}^{[3]}$ -type matrices with three perturbation parameter vectors



3. Contraction of the  $\mathbf{S}^{[3]}$ -type matrices with three perturbation parameter vectors.

As Kjærgaard et al. have shown, the contractions of the  $\mathbf{S}^{[3]}$ -type matrices are always zero and hence, they will not further be discussed here.

The contraction of the  $\mathbf{A}^{[2]}$ -type matrices can be written as

$$\sum_{IJ} A_{IJ}^{[2]} \kappa_I^b \kappa_J^c = \text{Tr}[\mathbf{S}^T, [\mathbf{S}^T, \mathbf{A}]_{\kappa^b}]_{D^T} \kappa^c, \quad (60)$$

where the commutator[39, 45]

$$[\mathbf{A}, \mathbf{C}]_B = \mathbf{ABC} - \mathbf{CBA}, \quad (61)$$

has been introduced.  $\mathbf{D}$  is the unperturbed one-electron density matrix,  $\mathbf{S}$  is the overlap matrix.

In a computationally advantageous treatment, the nested commutator in Eq. (60) is decomposed according to

$$\sum_{IJ} A_{IJ}^{[2]} \kappa_I^b \kappa_J^c = \text{Tr}[\mathbf{S}^T, \mathbf{M}^{ab}]_{D^T} \kappa^c = \text{Tr} \mathbf{M}^{ab} [\mathbf{S}^T, \kappa^{c,T}]_{D^T} = \text{Tr} \mathbf{M}^{ab} \mathbf{D}^c, \quad (62)$$

$$\mathbf{M}^{ab} = [\mathbf{S}^T, \mathbf{A}]_{\kappa^b} \quad \mathbf{D}^c = [\mathbf{S}^T, \mathbf{D}]_{\kappa^c}, \quad (63)$$

where  $\mathbf{A}$  is the matrix of first-order perturbed one-electron integrals (e.g. electric dipole integrals in case the considered perturbation is an electric field). Using this formulation, the nested commutator can be simplified remarkably.

The contraction of the  $\mathbf{E}^{[3]}$ -type matrices can be written as

$$\begin{aligned} \sum_{IJK} E_{IJK}^{[3]} \kappa_I^a \kappa_J^b \kappa_K^c = & \text{Tr} \left( \frac{1}{2} [\mathbf{S}^T, [\mathbf{S}^T, [\mathbf{S}^T, (\mathbf{F}^{\text{KS}})^T]_{\kappa^a}]_{\kappa^b}]_{D^T} \kappa^c + \right. \\ & [\mathbf{S}^T, [\mathbf{S}^T, (\mathbf{G}^{\text{KS}})^T (\mathbf{D}^a)]_{\kappa^b, T}]_{D^T} \kappa^c + \\ & \frac{1}{2} [\mathbf{S}^T, (\mathbf{G}^{\text{KS}})^T ([\kappa^a, \mathbf{D}^b]_S)]_{D^T} \kappa^c + \\ & \left. \frac{1}{2} [\mathbf{S}^T, (\mathbf{T}^{xc})^T (\mathbf{D}^a, \mathbf{D}^b)]_{D^T} \kappa^c \right), \end{aligned} \quad (64)$$

where  $\mathbf{F}^{\text{KS}}$ ,  $\mathbf{G}^{\text{KS}}(\mathbf{M})$  and  $\mathbf{T}^{xc}$  are the Kohn-Sham matrix, the complete two-electron contribution to the Kohn-Sham matrix contracted with the matrix  $\mathbf{M}$  (see below) and the second kernel of the exchange-correlation functional, respectively. The latter term requires a special treatment which will be discussed in the next section.

The first term of Eq. (64) will be zero due to the variational condition.

The two-electron integral contributions  $\mathbf{G}(\mathbf{M})$  can in general be written as

$$G_{\mu\nu} = \sum_{\lambda\kappa} \left( g_{\mu\nu\lambda\kappa} - (1 - \xi)g_{\mu\kappa\lambda\nu} \right) M_{\lambda\kappa}, \quad (65)$$

where  $g_{\mu\nu\lambda\kappa}$  is the Coulomb contribution to the Kohn-Sham matrix,  $g_{\mu\kappa\lambda\nu}$  is the exact exchange contribution and  $M_{\lambda\kappa}$  is the one-electron density matrix (perturbed or unperturbed) used for the contraction.

Comparing the second and the third term in Eq. (64) it is noted that in both cases, the two-electron integral contributions once are contracted with a density matrix transformed with one first-order perturbation parameter vector and once with a density matrix transformed with two first-order perturbation parameter vectors. Expanding and rearranging the nested commutators the second term can be written according to

$$\text{Tr}[\mathbf{S}^T, [\mathbf{S}^T, (\mathbf{G}^{\text{KS}})^T(\mathbf{D}^a)]_{\boldsymbol{\kappa}^{b,T}}]_D \boldsymbol{\kappa}^c = \text{Tr}(\mathbf{G}^{\text{KS}})^T(\mathbf{D}^a)[\boldsymbol{\kappa}^{b,T}, \mathbf{D}^c]_{\mathbf{S}}, \quad (66)$$

$$= \text{Tr}(\mathbf{G}^{\text{KS}})^T(\mathbf{D}^a)\mathbf{D}^{bc}, \quad (67)$$

where the second-order perturbed density matrix and  $\mathbf{D}^{bc}$  have been introduced.

In a similar manner, the third term of Eq. (64) can be rewritten to get

$$\text{Tr}[\mathbf{S}^T, (\mathbf{G}^{\text{KS}})^T([\boldsymbol{\kappa}^a, \mathbf{D}^b]_{\mathbf{S}})]_{D^T} \boldsymbol{\kappa}^c = \text{Tr}(\mathbf{G}^{\text{KS}})^T(\mathbf{D}^{ab})\mathbf{D}^c, \quad (68)$$

which according to Eq. (65) would mean that the two-electron integral contributions contracted with the second-order perturbed density matrix are needed. However, re-writing the contraction in component-wise form according to

$$\text{Tr}(\mathbf{G}^{\text{KS}})^T(\mathbf{D}^{ab})\mathbf{D}^c = \sum_{\mu\nu\kappa\lambda} (g_{\mu\nu\lambda\kappa} - (1 - \xi)g_{\mu\kappa\lambda\nu}) D_{\mu\nu}^{ab} D_{\kappa\lambda}^c, \quad (69)$$

$$= \sum_{\mu\nu} G_{\mu\nu}^C D_{\mu\nu}^{ab}, \quad (70)$$

$$= \text{Tr}(\mathbf{G}^{\text{KS}})^T(\mathbf{D}^c)\mathbf{D}^{ab}. \quad (71)$$

Contractions of the two-electron integrals with second-order perturbed density matrices can completely be avoided which reduces both operation count and memory demand of the program as the amount of second-order perturbations is much larger than the one of first-order ones.

The contribution of the second kernel in Eq. (64) can be rewritten as

$$[\mathbf{S}^T, (\mathbf{T}^{xc})^T(\mathbf{D}^a, \mathbf{D}^b)]_D \boldsymbol{\kappa}^c = \text{Tr}(\mathbf{T}^{xc})^T(\mathbf{D}^A, \mathbf{D}^B)\mathbf{D}^C. \quad (72)$$

With these findings, Eq. (64) can be written according to

$$\sum_{IJK} \mathbf{E}_{IJK}^{[3]} X_I^A X_J^B X_K^C = \text{Tr} \left( (\mathbf{G}^{\text{KS}})^T (\mathbf{D}^C) \mathbf{D}^{AB} + (\mathbf{G}^{\text{KS}})^T (\mathbf{D}^B) \mathbf{D}^{AC} + \right. \quad (73)$$

$$\left. (\mathbf{G}^{\text{KS}})^T (\mathbf{D}^A) \mathbf{D}^{BC} + (\mathbf{T}^{xc})^T (\mathbf{D}^A, \mathbf{D}^B) \mathbf{D}^C \right).$$

This contribution can be calculated using the XCFun program library[48] and the proper first-order perturbed number- and spin densities following the lines of Eq. (51). The term in Eq. (74) covers all terms of Eq. (51) which contain a third-order derivative of the xc-functional. Terms with lower-order derivatives in Eq. (51) contribute to the exchange-correlation contributions to the terms in Eqs. (67) and (71).

### 3.2 The vectorial contribution to the second kernel using XCFun

In 2.2.6 it was shown that for the closed-shell case, the second kernel contribution has been divided in a scalar and a vectorial part with the scalar part just depending on the number density  $n$  and its gradients and derivatives while the contributions depending on the spin density and its derivatives and gradients are contained in the vectorial part which does not contain the spin density  $\zeta$  itself but the spin magnetization vector  $\mathbf{m}$  or its gradients or derivatives.

For the calculation of the functional derivatives in Eqs. (51) and (52) the XCFun library is used. This program module differentiates density functionals using the automatic differentiation technique based on a Taylor expansion of the density functional.[43, 44] It also provides the infrastructure for the multiplication of the functional derivative with the perturbed input densities. For the scalar part, this is straightforward as it contains all possible derivatives w.r.t.  $n$  and  $\nabla n$  and can therefore be considered "complete". As a consequence, calculation of the scalar contribution can be done in one single step.

With the modifications for the closed-shell case, calculation of the vectorial part is less straightforward as some contributions have been eliminated and the scalar value of  $s$  has been replaced by the vector  $\mathbf{m}$ . Inspecting Eqs. (51) and (52) it is noted that terms depending on  $\mathbf{m}$  always appear in pairs. Therefore, they can be interpreted as dot products which allows for an evaluation in a loop over components of  $\mathbf{m}$ .

As the vectorial part is in addition "incomplete" in that sense that several xc-functional derivatives have been eliminated in the modification process, XCFun requires a modification either in the source code or in the input to make sure that only the sought after terms are calculated. This problem is solved by dividing the vectorial part of Eq. (52) into three different sub-parts which are then calculated with selective density inputs.

The first sub-part contains all terms which depend on a second-order derivative w.r.t.  $\zeta$  which are the 10th, 11th and 12th term in Eq. (52), hence

$$\frac{\delta^3 e_{xc}}{\delta n \delta \zeta^2} n^k \mathbf{m}^l \mathbf{m}^m, \quad (74)$$

$$\frac{\delta^3 e_{xc}}{\delta \nabla n \delta \zeta^2} \nabla n^k \mathbf{m}^l \mathbf{m}^m, \quad (75)$$

$$\frac{\delta^2 e_{xc}}{\delta \delta \zeta^2} \mathbf{m}^{kl} \mathbf{m}^m. \quad (76)$$

In this example,  $k$ ,  $l$  and  $m$  represent three different combinations of perturbations (electric field directions) and their corresponding frequencies. For the calculation of these three contractions, the XCFun library is called in a loop over the three spatial components of  $\mathbf{m}$  with the unperturbed number density  $n$  and gradient  $\nabla n$ , the unperturbed spin density  $\zeta$  and gradient  $\nabla \zeta$  (which are zero in the closed-shell case), and the first-order number density  $n^k$  and gradient  $\nabla n^k$  as well as with the corresponding components of the spin magnetization vectors  $\mathbf{m}^l$  and  $\mathbf{m}^m$  as well as the second-order spin magnetization vector  $\mathbf{m}^{kl}$ . All other input quantities to the XCFun library are set to zero in order to make sure that only the listed contributions will be calculated.

Another looped call of the XCFun library calculates the contributions

$$\frac{\delta^2 e_{xc}}{\delta d \delta \nabla \zeta} (\mathbf{m}^k \nabla \mathbf{m}^{lm} + \mathbf{m}^{kl} \nabla \mathbf{m}^m). \quad (77)$$

Apart from the unperturbed input densities named earlier, this call only contains the corresponding elements of the spin magnetization vector  $\mathbf{m}^k$ ,  $\mathbf{m}^{kl}$  and its gradients  $\nabla \mathbf{m}^m$  and  $\nabla \mathbf{m}^{kl}$ .

The last looped call of the XCFun library calculates the contributions

$$\frac{\delta^3 e_{xc}}{\delta n \delta \zeta \delta \nabla \zeta} n^k \mathbf{m}^l \nabla \mathbf{m}^m, \quad (78)$$

$$\frac{\delta^3 e_{xc}}{\delta \nabla n \delta \zeta \delta \nabla \zeta} \nabla n^k \mathbf{m}^l \nabla \mathbf{m}^m. \quad (79)$$

## 4 Computational details

Benchmark calculations have been carried out on the *ortho*- and *meta*-diiodobenzene molecules. Molecular geometries have been optimized using the TURBOMOLE program package[49], the PBE density functional[50, 51] and the TZVP basis set[52]. On the iodine

atoms, Stuttgart-type ECPs have been used.[53] The molecules have been oriented such that the dipole moment vector is oriented parallel to the  $z$  axis.

Hyperpolarizability calculations have been carried out using the uncontracted Dyall-cvdz basis set.[54, 55, 56] For the four-component calculations, perturbation parameters, MO coefficients, perturbation parameters and perturbed and unperturbed one- and two-electron integrals have been calculated using the ReSpect program.[34, 57] One-component calculations have been carried out using the Dyall-cvdz basis set, Stuttgart-type ECPs and TURBOMOLE[49]. Molecular property calculations have been carried out using the PBE and BLYP[58, 59, 60] density functionals.

Contributions of the second kernel have been calculated by a standalone program which received the mentioned quantities as an input and performed the numerical calculation of the exchange-correlation contributions on an integration grid consisting of a radial[61] and an angular part[62] in an open-source implementation module[63].

## 5 Applications

As ECP techniques are well established for the treatment of scalar relativistic effects, in a first application study of the newly implemented four-component code, results from the four-component (4c) code will be compared with numbers obtained using non-relativistic one-component TD-DFT with ECPs for the treatment of scalar relativistic effects (1c/ECP) and without ECPs (1c)

In Table 1 an overview is given of the non-zero tensor elements of both the polarizability  $\alpha$  and the hyperpolarizability  $\beta$ .

Comparing the results in general it is noted immediately that the difference between the three approaches is much more significant for  $\beta$  than for  $\alpha$ . For  $\alpha$ , the deviations between the 4c results and the 1c results with or without ECPs is in the range of 1% or lower while deviations for  $\beta$  are up to 8% with deviations between 4c and 1c/ECP results being up to 6%. This is in line with the results of Henriksson et al.[64, 27, 28] who have reported similar differences in the influence of relativistic effects on  $\alpha$  and  $\beta$  for calculations using the collinear approach for the description of the spin density.

For all  $\alpha$  values as well as for most  $\beta$  values, the results from 1c/ECPs calculations have found to be the lowest values. For most  $\beta_{xxz}$  and  $\beta_{zzz}$  values, the 4c results are found to be between the 1c/ECP and the 1c results with the 1c calculations yielding the highest values in most cases.

Comparing the deviations for the  $\beta_{xxz}$ ,  $\beta_{yyz}$  and  $\beta_{zzz}$  elements it is noted that the

Table 1: Overview of the calculation results on diiodobenzenes.

	Polarizability [a.u.]			First Hyperpolarizability [a.u.]		
	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\beta_{xxz}$	$\beta_{yyz}$	$\beta_{zzz}$
<i>ortho</i> -diiodobenzene, BLYP						
4c	140.7	63.4	164.1	234.3	68.8	486.8
1c/ECP	139.5	63.1	163.1	220.2	68.4	461.4
1c	140.6	63.2	164.1	241.5	73.5	495.8
<i>ortho</i> -diiodobenzene, PBE						
4c	140.7	63.6	164.0	230.3	67.4	479.7
1c/ECP	139.6	63.3	163.1	218.9	67.5	458.5
1c	140.7	63.4	164.0	236.9	72.2	488.3
<i>meta</i> -diiodobenzene, BLYP						
4c	189.2	64.5	127.7	247.2	43.5	231.6
1c/ECP	187.0	64.2	127.0	238.6	43.3	220.4
1c	188.4	64.5	127.0	265.3	47.2	225.2
<i>meta</i> -diiodobenzene, PBE						
4c	189.4	64.7	127.4	250.0	42.3	223.7
1c/ECP	187.5	64.4	126.8	243.5	42.5	215.3
1c	188.6	64.5	127.1	269.6	45.6	227.2

4c and 1c/ECP results for the  $\beta_{yyz}$  values are much more similar than for the  $\beta_{xxz}$  and  $\beta_{zzz}$  elements. It appears that spin-orbit coupling effects on  $\beta_{yyz}$  elements are much less pronounced than for the  $\beta_{xxz}$  and  $\beta_{zzz}$  elements.

## 6 Discussion and Outlook

Comparison of the results for  $\beta$  obtained with 4c, 1c/ECP and 1c calculations have shown that the discrepancy between 1c/ECP and 1c calculations is significant and hence that there are reasonable relativistic effects on the elements of the first hyperpolarizability while the relativistic effects on the polarizability are low. In the case of large deviations between 4c and 1c/ECP results, 4c results have been found to be in between the 1c/ECP and the 1c results which indicates that use of ECP overestimates relativistic effects which is compensated by the spin-orbit coupling which is introduced by the four-component ansatz for the Hamiltonian.

On the other hand, non-linear optical property calculations have just moderate requirements regarding accuracy in most cases as they usually support molecular design and are to give semi-quantitative assessments of proposed materials prior to synthesis. As the deviations found between the 4c and the 1c/ECP-results has been found to be in the range of 6% it appears reasonable that the use of 1c/ECP is an efficient tool for such calculations which also offers an acceptable amount of reliability. However, the 4c method can serve as a reference for 1c/ECP calculations and in addition offers a reliable opportunity to treat compounds of even heavier elements.

Furthermore, a four-component treatment can be useful for the calculation of properties of open-shell systems. The present code is not yet able to treat open-shell systems but offers the potential of extension.

## 7 Conclusion

Theory and implementation of a four-component relativistic TD-DFT method for calculations of quadratic response properties using the non-collinear formulation of the spin density have been presented. As in the non-collinear formulation, the spin density is interpreted as the norm of the spin magnetization vector, every degree of differentiation of the spin density with respect to perturbations leads to a significant increase in complexity. Expressions have been reformulated to avoid definition problems for the closed-shell case (spin density approaching zero).

The expressions have been implemented into an own program code which reads orbital and perturbation parameters as well as one- and two-electron integrals from a previous run of the RESPECT program. A first series of application calculations has been carried out on *meta*- and *ortho*-diiodobenzene in order to compare the non-zero hyperpolarizability tensor elements from the four-component code with results from one-component calculations with and without use of effective core potentials. In the examples under consideration it has been found that the deviation between four-component and one-component results is up to 8%.

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