Static and Dynamic First Hyperpolarizabilities from Time-Dependent Auxiliary Density Perturbation Theory

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A new approach for the calculation of static and dynamic hyperpolarizabilities in the framework of auxiliary density perturbation theory is derived. It takes advantage of the Wigner's $2n + 1$ rule. As a byproduct dynamic quadratic response equations are obtained. Even though the final equations are similar to other approaches they present subtle differences due to their rooting in auxiliary density functional theory. The numerical stability and accuracy of the new approach is validated with respect to other theoretical and experimental results. © 2012 Wiley Periodicals, Inc.

Introduction

Many molecular properties are obtained as higher order perturbation corrections to the molecular energy with respect to a perturbation parameter. Unfortunately, the perturbation problem has to be solved in most cases iteratively due to the large size of the corresponding equation system. In the framework of Kohn–Sham density functional theory (DFT)[1,2] the coupled perturbed Kohn–Sham (CPKS) method,[3–6] which is a variant of the coupled-perturbed Hartree–Fock method,[7–10] is usually used for this purpose. In this approach, the computational demand increases with the perturbation order. For this reason Wigner's $2n + 1$ rule[11] is often employed. Therefore, third-order derivatives are available from first-order perturbations. In the particular case of the perturbation with an electric field the first-order perturbed density matrix can be used for the calculation of polarizabilities, α, and first hyperpolarizabilities, β. However, different to time-dependent Hartree–Fock[9] an extra response term arises in Kohn–Sham first hyperpolarizability calculations from the exchange-correlation functional.[12–15] Thus, extra care has to be taken to include properly the effects of this term.

DFT static and dynamic polarizabilities and hyperpolarizabilities of small molecules are usually in good agreement with correlated wave function methods and gas-phase experimental data.[5,6,12–14,16–26] However, for one-dimensional conjugated systems, such as polyacetylene chains, large overestimations have been found.[27,28] It is argued that this failure is rooted in the wrong asymptotic behavior of the local and gradient corrected density approximations commonly used for exchange functionals. This argumentation is supported by the increase of the DFT polarizability and second hyperpolarizability errors with the size of the one-dimensional conjugated systems.[29,30] Moreover, the error can be reduced by the inclusion of Hartree–Fock exchange in the exchange-correlation functional. Similar results are found for β in elongated push–pull polyenes.[31–34] In contrast, we showed recently that static and dynamic α values of C_{60} from local and gradient corrected DFT calculations[35] are in excellent agreement with their CCSD[36] and experimental[37,38] counterparts. Thus, the failure of conventional DFT functionals is not only size but also shape dependent. Clearly a better understanding

of the density response in large conjugated molecules to an external field in DFT calculations is needed.

Recently, we presented a new methodology for the calculation of static and dynamic first-order perturbed density matrices[35,39] in the framework of auxiliary density functional theory (ADFT).[40] ADFT is based on the variational fitting of the Coulomb potential[41,42] and the further use of the resulting approximated density for the calculation of the exchange-correlation energy and its derivatives.[43] Thus, it is well suited for the calculation of large molecules with hundreds to more than thousand atoms. Higher-order analytic energy derivatives can be easily accesed. Our ADFT implementation in deMon2k[44] is based on the linear combination of Gaussian type orbital (LCGTO) approximation. In the ADFT framework an alternative formulation of the CPKS approach is possible due to the use of the approximated density. The resulting perturbation equation system possesses only the dimension of the number of auxiliary functions[35,39] used to expand the approximated density. Therefore, a direct, noniterative, solution of the perturbation equation system is feasible. In correspondence to ADFT, we have named this new approach auxiliary density perturbation theory (ADPT) and its time-dependent variant time-dependent auxiliary density perturbation theory (TDADPT). TDADPT is well suited for dynamic polarizability calculations on large systems with hundreds of atoms. Examples are the calculation of the dynamic polarizability of the C_{180} and C_{240} fullerenes.[35] Note that the static polarizabilities of these fullerenes have been also calculated by various finite-field approaches and sum-over-states perturbation

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theory.[45, 46] So far, ADPT has been used successfully for the calculation of static and dynamic dipole–dipole polarizabilities,[35, 47] static dipole-quadrupole polarizabilities,[48] Fukui functions,[49, 50] and nuclear magnetic shielding tensors.[51]

In this contribution, we extend the application range of ADPT to the calculation of dynamic first hyperpolarizabilities employing Wigner's $2n+1$ rule. For this purpose, we first discuss the quadratic response of the density and Kohn–Sham matrices in the context of hyperpolarizability calculations. We then derive the working equations for the second-order response of the auxiliary density and show how Wigner's $2n+1$ rule can be incorporated into the TDADPT framework. After some further simplifications, we obtain a very compact formulation for TDADPT first hyperpolarizability calculations. To validate our new methodology, we calculate TDADPT static and dynamic first hyperpolarizabilities as well as the corresponding electro-optical Pockels effect for a test set of small molecules for which theoretical and experimental results are available in the literature. The article is organized in the following manner. The "Theory" section gives a detailed derivation of the ADPT working equations for the calculation of hyperpolarizabilities. The computational details of the validation calculations are given in "Computational Methodology" section. The validation results are discussed in the "Results and Discussion" section and conclusions are drawn in the last section.

Theory

A general expression for hyperpolarizability tensor elements that covers the calculation of second harmonic generation (SHG), electro-optical Pockels effect (EOPE), and optical rectification (OR) is given by the following formula[9]:

$$\beta_{abc}(-\omega_3; \omega_1, \omega_2) = -\sum_{\mu,\nu} P_{\mu\nu}^{(bc)}(\omega_1, \omega_2) H_{\mu\nu}^{(a)} \tag{1}$$

Here, $P_{\mu\nu}^{(bc)}(\omega_1, \omega_2)$ is the second-order perturbed density matrix, ω_1 and ω_2 are the frequencies of the two external dynamical electric fields, b and c represent components of these two fields and $\omega_3 = \omega_1 + \omega_2$ holds. $H_{\mu\nu}^{(a)}$ is an element of the dipole moment matrix. The three nonlinear optical properties SHG, EOPE, and OR are characterized by the following frequency combinations:

$$
\begin{array}{cccc}
\text{SHG} & \omega_1 = \pm\omega & \omega_2 = \pm\omega & \omega_3 = \pm 2\omega, \\
\text{EOPE} & \omega_1 = 0 & \omega_2 = \pm\omega & \omega_3 = \pm\omega, \\
\text{OR} & \omega_1 = \pm\omega & \omega_2 = \mp\omega & \omega_3 = 0.
\end{array}
$$

We now derive working formulas for the calculation of hyperpolarizability tensor elements according to Eq. (1) in the framework of ADPT.

Quadratic response of the density matrix

We start our derivation with the quadratic response of the density matrix in the framework of McWeeny's self-consistent perturbation (SCP) theory.[52–57] This follows our recent work on dynamic ADPT polarizability calculations.[35] For the idempotent relation

of the frequency dependent projector operator, $\breve{\Pi}$, follows up to second-order:

$$\breve{\Pi}\,\breve{\Pi} = \breve{\Pi} \tag{2}$$

$$\breve{\Pi}\,\breve{\Pi}^{(\lambda)}(\omega_1) + \breve{\Pi}^{(\lambda)}(\omega_1)\,\breve{\Pi} = \breve{\Pi}^{(\lambda)}(\omega_1) \tag{3}$$

$$
\begin{aligned}
&\breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2)\,\breve{\Pi} + \breve{\Pi}^{(\lambda)}(\omega_1)\,\breve{\Pi}^{(\eta)}(\omega_2) + \\
&\breve{\Pi}^{(\eta)}(\omega_2)\,\breve{\Pi}^{(\lambda)}(\omega_1) + \breve{\Pi}\,\breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2) = \breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2) \quad (4)
\end{aligned}
$$

Similarly, we find for the corresponding commutator between Kohn–Sham, $\breve{K}$, and projector matrix, $\breve{\Pi}$:

$$\breve{K}\,\breve{\Pi} - \breve{\Pi}\,\breve{K} = 0 \tag{5}$$

$$\breve{K}^{(\lambda)}(\omega_1)\,\breve{\Pi} - \breve{\Pi}\,\breve{K}^{(\lambda)}(\omega_1) + \breve{K}\,\breve{\Pi}^{(\lambda)}(\omega_1) - \breve{\Pi}^{(\lambda)}(\omega_1)\,\breve{K} = \omega_1\,\breve{\Pi}^{(\lambda)}(\omega_1) \tag{6}$$

$$
\begin{aligned}
&[\breve{K}^{(\lambda\eta)}(\omega_1, \omega_2), \breve{\Pi}] + [\breve{K}^{(\lambda)}(\omega_1), \breve{\Pi}^{(\eta)}(\omega_2)] + [\breve{K}^{(\eta)}(\omega_2), \breve{\Pi}^{(\lambda)}(\omega_1)] \\
&+ [\breve{K}, \breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2)] = \omega_3\,\breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2) \quad (7)
\end{aligned}
$$

The breve marks quantities in the orthogonalized basis set. Projection of Eq. (4) yields the following two nonvanishing matrix equations for the occupied–occupied (oo) and unoccupied–unoccupied (uu) blocks:

$$-\breve{\Pi}_{ou}^{(\lambda)}(\omega_1)\,\breve{\Pi}_{uo}^{(\eta)}(\omega_2) - \breve{\Pi}_{ou}^{(\eta)}(\omega_2)\,\breve{\Pi}_{uo}^{(\lambda)}(\omega_1) = \breve{\Pi}_{oo}^{(\lambda\eta)}(\omega_1, \omega_2) \tag{8}$$

$$\breve{\Pi}_{uo}^{(\lambda)}(\omega_1)\,\breve{\Pi}_{ou}^{(\eta)}(\omega_2) + \breve{\Pi}_{uo}^{(\eta)}(\omega_2)\,\breve{\Pi}_{ou}^{(\lambda)}(\omega_1) = \breve{\Pi}_{uu}^{(\lambda\eta)}(\omega_1, \omega_2) \tag{9}$$

The appearing first-order perturbed projector blocks are given as[35]:

$$\breve{\Pi}_{ou}^{(\lambda)}(\omega_1) = \sum_{i}^{occ} \sum_{a}^{uno} \frac{\mathcal{K}_{ia}^{(\lambda)}(\omega_1)}{\varepsilon_i - \varepsilon_a - \omega_1}\,\breve{c}_i\,\breve{c}_a^{\dagger}, \tag{10}$$

and

$$\breve{\Pi}_{uo}^{(\lambda)}(\omega_1) = \sum_{i}^{occ} \sum_{a}^{uno} \frac{\mathcal{K}_{ai}^{(\lambda)}(\omega_1)}{\varepsilon_i - \varepsilon_a + \omega_1}\,\breve{c}_a\,\breve{c}_i^{\dagger}. \tag{11}$$

Thus, no second-order quantities are needed for the calculation of the oo and uu blocks of $\breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2)$. The projection of Eq. (7) yields the following matrix equations for the occupied–unoccupied (ou) and the unoccupied–occupied (uo) blocks:

$$
\begin{aligned}
&-\breve{K}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) + \breve{K}_{oo}^{(\lambda)}(\omega_1)\,\breve{\Pi}_{ou}^{(\eta)}(\omega_2) \\
&-\breve{\Pi}_{ou}^{(\eta)}(\omega_2)\,\breve{K}_{uu}^{(\lambda)}(\omega_1) + \breve{K}_{oo}^{(\eta)}(\omega_2)\,\breve{\Pi}_{ou}^{(\lambda)}(\omega_1) \\
&-\breve{\Pi}_{ou}^{(\lambda)}(\omega_1)\,\breve{K}_{uu}^{(\eta)}(\omega_2) + \breve{K}\,\breve{\Pi}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) \\
&-\breve{\Pi}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2)\,\breve{K} = \omega_3\,\breve{\Pi}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) \quad (12)
\end{aligned}
$$

and

$$
\begin{aligned}
&\breve{K}_{uo}^{(\lambda\eta)}(\omega_1, \omega_2) + \breve{K}_{uu}^{(\lambda)}(\omega_1)\,\breve{\Pi}_{uo}^{(\eta)}(\omega_2) \\
&-\breve{\Pi}_{uo}^{(\eta)}(\omega_2)\,\breve{K}_{oo}^{(\lambda)}(\omega_1) + \breve{K}_{uu}^{(\eta)}(\omega_2)\,\breve{\Pi}_{uo}^{(\lambda)}(\omega_1) \\
&-\breve{\Pi}_{uo}^{(\lambda)}(\omega_1)\,\breve{K}_{oo}^{(\eta)}(\omega_2) + \breve{K}\,\breve{\Pi}_{uo}^{(\lambda\eta)}(\omega_1, \omega_2) \\
&-\breve{\Pi}_{uo}^{(\lambda\eta)}(\omega_1, \omega_2)\,\breve{K} = \omega_3\,\breve{\Pi}_{uo}^{(\lambda\eta)}(\omega_1, \omega_2) \quad (13)
\end{aligned}
$$

As for the calculation of the first-order perturbed projector matrix, we use as ansatz for the second-order perturbed projector matrix:

$$\breve{\Pi}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) = \sum_i^{occ} \sum_a^{uno} x_{ia}(\omega_1, \omega_2) \, \breve{c}_i \, \breve{c}_a^\dagger. \tag{14}$$

Inserting this ansatz for $\breve{\Pi}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2)$ into Eq. (12) yields:

$$-\breve{K}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) + \Omega_{ou}^{(\lambda,\eta)}(\omega_1, \omega_2) + \Omega_{ou}^{(\eta,\lambda)}(\omega_2, \omega_1)$$
$$+ \sum_i^{occ} \sum_a^{uno} x_{ia}(\omega_1, \omega_2)\left(\breve{K} \, \breve{c}_i \, \breve{c}_a^\dagger - \breve{c}_i \, \breve{c}_a^\dagger \, \breve{K} - \omega_3 \, \breve{c}_i \, \breve{c}_a^\dagger\right) = 0 \tag{15}$$

Here, we have collected the first-order contributions (note comma in superscript) as:

$$\Omega_{ou}^{(\lambda,\eta)}(\omega_1, \omega_2) = \breve{K}_{oo}^{(\lambda)}(\omega_1) \, \breve{\Pi}_{ou}^{(\eta)}(\omega_2) - \breve{\Pi}_{ou}^{(\eta)}(\omega_2) \, \breve{K}_{uu}^{(\lambda)}(\omega_1) \tag{16}$$

Thus, we obtain from Eq. (15):

$$x_{ia}(\omega_1, \omega_2) = \frac{\breve{c}_i^\dagger \, \breve{K}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) \, \breve{c}_a}{\varepsilon_i - \varepsilon_a - \omega_3} - \frac{\breve{c}_i^\dagger \, \breve{\Omega}_{ou}^{(\lambda,\eta)}(\omega_1, \omega_2) \, \breve{c}_a}{\varepsilon_i - \varepsilon_a - \omega_3}$$
$$- \frac{\breve{c}_i^\dagger \, \breve{\Omega}_{ou}^{(\eta,\lambda)}(\omega_2, \omega_1) \, \breve{c}_a}{\varepsilon_i - \varepsilon_a - \omega_3} \tag{17}$$

Inserting this result into Eq. (14) yields for the *ou* block of the second-order perturbed projector matrix:

$$\breve{\Pi}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) = \sum_i^{occ} \sum_a^{uno} \frac{\mathcal{K}_{ia}^{(\lambda\eta)}(\omega_1, \omega_2)}{\varepsilon_i - \varepsilon_a - \omega_3} \, \breve{c}_i \, \breve{c}_a^\dagger$$
$$- \sum_i^{occ} \sum_a^{uno} \frac{\Omega_{ia}^{(\lambda,\eta)}(\omega_1, \omega_2)}{\varepsilon_i - \varepsilon_a - \omega_3} \, \breve{c}_i \, \breve{c}_a^\dagger$$
$$- \sum_i^{occ} \sum_a^{uno} \frac{\Omega_{ia}^{(\eta,\lambda)}(\omega_2, \omega_1)}{\varepsilon_i - \varepsilon_a - \omega_3} \, \breve{c}_i \, \breve{c}_a^\dagger. \tag{18}$$

Similarly, we find for the *uo* block of the second-order perturbed projector matrix:

$$\breve{\Pi}_{uo}^{(\lambda\eta)}(\omega_1, \omega_2) = \sum_i^{occ} \sum_a^{uno} \frac{\mathcal{K}_{ai}^{(\lambda\eta)}(\omega_1, \omega_2)}{\varepsilon_i - \varepsilon_a + \omega_3} \, \breve{c}_a \, \breve{c}_i^\dagger$$
$$+ \sum_i^{occ} \sum_a^{uno} \frac{\Omega_{ai}^{(\lambda,\eta)}(\omega_1, \omega_2)}{\varepsilon_i - \varepsilon_a + \omega_3} \, \breve{c}_a \, \breve{c}_i^\dagger$$
$$+ \sum_i^{occ} \sum_a^{uno} \frac{\Omega_{ai}^{(\eta,\lambda)}(\omega_2, \omega_1)}{\varepsilon_i - \varepsilon_a + \omega_3} \, \breve{c}_a \, \breve{c}_i^\dagger \tag{19}$$

Here, the nominators are given by:

$$\mathcal{K}_{ia}^{(\lambda\eta)}(\omega_1, \omega_2) = \breve{c}_i^\dagger \, \breve{K}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) \, \breve{c}_a = \sum_{\mu,\nu} c_{\mu i} K_{\mu\nu}^{(\lambda\eta)}(\omega_1, \omega_2) \, c_{\nu a}$$
$$\Omega_{ia}^{(\lambda,\eta)}(\omega_1, \omega_2) = \breve{c}_i^\dagger \, \breve{\Omega}_{ou}^{(\lambda,\eta)}(\omega_1, \omega_2) \, \breve{c}_a = \sum_{\mu,\nu} c_{\mu i} \, \Omega_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2) \, c_{\nu a}$$

$$\tag{20}$$

The full second-order perturbed projector matrix then is given by:

$$\breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2) = \breve{\Pi}_{oo}^{(\lambda\eta)}(\omega_1, \omega_2) + \breve{\Pi}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2) + \breve{\Pi}_{uo}^{(\lambda\eta)}(\omega_1, \omega_2)$$
$$+ \breve{\Pi}_{uu}^{(\lambda\eta)}(\omega_1, \omega_2) \tag{21}$$

From the perturbed projector matrix the closed-shell second-order perturbed density matrix is obtained as:

$$\mathbf{P}^{(\lambda\eta)}(\omega_1, \omega_2) = 2 \, \mathbf{S}^{-1/2} \, \breve{\Pi}^{(\lambda\eta)}(\omega_1, \omega_2) \, \mathbf{S}^{-1/2} \tag{22}$$

Thus it follows:

$$P_{\mu\nu}^{(\lambda\eta)}(\omega_1, \omega_2) = 2 \sum_i^{occ} \sum_a^{uno} \frac{\mathcal{K}_{ia}^{(\lambda\eta)}(\omega_1, \omega_2)}{\varepsilon_i - \varepsilon_a - \omega_3} \, c_{\mu i} \, c_{\nu a}$$
$$+ 2 \sum_i^{occ} \sum_a^{uno} \frac{\mathcal{K}_{ia}^{(\lambda\eta)}(\omega_1, \omega_2)}{\varepsilon_i - \varepsilon_a + \omega_3} \, c_{\mu a} \, c_{\nu i}$$
$$+ 2 \, P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2) \tag{23}$$

Here $P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2)$ collects all first-order perturbation terms (note comma in superscript) and is given by:

$$\mathbf{P}^{(\lambda,\eta)}(\omega_1, \omega_2) = \mathbf{P}_{oo}^{(\lambda\eta)}(\omega_1, \omega_2) + \mathbf{P}_{uu}^{(\lambda\eta)}(\omega_1, \omega_2) + \mathbf{P}_{ou}^{(\lambda\eta)}(\omega_1, \omega_2)$$
$$+ \mathbf{P}_{uo}^{(\lambda,\eta)}(\omega_1, \omega_2) \tag{24}$$

As Eq. (24) shows the *oo* and *uu* blocks of the second-order perturbed density matrix contain only first-order perturbation terms. This is in accordance with Eqs. (8)–(11) for the corresponding blocks of the second-order perturbed projector matrix. For convenience of notation, we now introduce the transformation matrix,

$$W_{\mu\nu}^{(\lambda)}(\omega) = \sum_i^{occ} \sum_a^{uno} \frac{\mathcal{K}_{ia}^{(\lambda)}(\omega)}{\epsilon_i - \epsilon_a - \omega} c_{\mu i} \, c_{\nu a}. \tag{25}$$

With this transformation matrix, we can express the *oo* and *uu* blocks of the second-order perturbed density matrix as:

$$\mathbf{P}_{oo}^{(\lambda\eta)}(\omega_1, \omega_2) = -\mathbf{W}^{(\lambda)}(\omega_1) \, \mathbf{S} \, \mathbf{W}^{(\eta)\dagger}(-\omega_2)$$
$$- \mathbf{W}^{(\eta)}(\omega_2) \, \mathbf{S} \, \mathbf{W}^{(\lambda)\dagger}(-\omega_1) \tag{26}$$

and

$$\mathbf{P}_{uu}^{(\lambda\eta)}(\omega_1, \omega_2) = \mathbf{W}^{(\lambda)\dagger}(-\omega_1) \, \mathbf{S} \, \mathbf{W}^{(\eta)}(\omega_2)$$
$$+ \mathbf{W}^{(\eta)\dagger}(-\omega_2) \, \mathbf{S} \, \mathbf{W}^{(\lambda)}(\omega_1). \tag{27}$$

According to Eq. (18) the first-order perturbation terms of the *ou* block of the second-order perturbed density matrix are given by:

$$\mathbf{P}_{ou}^{(\lambda,\eta)}(\omega_1, \omega_2) = - \sum_i^{occ} \sum_a^{uno} \frac{\Omega_{ia}^{(\lambda,\eta)}(\omega_1, \omega_2) + \Omega_{ia}^{(\eta,\lambda)}(\omega_2, \omega_1)}{\epsilon_i - \epsilon_a - \omega_3} \, c_i \, c_a^\dagger$$

$$\tag{28}$$

with

$$\Omega_{ia}^{(\lambda,\eta)}(\omega_1,\omega_2) = \mathbf{c}_i^\dagger \left(\mathbf{K}^{(\lambda)}(\omega_1)\,\mathbf{W}^{(\eta)}(\omega_2)\,\mathbf{S} - \mathbf{S}\,\mathbf{W}^{(\eta)}(\omega_2)\,\mathbf{K}^{(\lambda)}(\omega_1) \right) \mathbf{c}_a. \tag{29}$$

Similarly, we find for the corresponding *uo* block from Eq. (19):

$$\mathbf{P}_{uo}^{(\lambda,\eta)}(\omega_1,\omega_2) = \sum_i^{occ} \sum_a^{uno} \frac{\Omega_{ai}^{(\lambda,\eta)}(\omega_1,\omega_2) + \Omega_{ai}^{(\eta,\lambda)}(\omega_2,\omega_1)}{\epsilon_i - \epsilon_a + \omega_3}\, \mathbf{c}_a\, \mathbf{c}_i^\dagger \tag{30}$$

with

$$\Omega_{ai}^{(\lambda,\eta)}(\omega_1,\omega_2) = \mathbf{c}_a^\dagger \left(\mathbf{K}^{(\lambda)}(\omega_1)\,\mathbf{W}^{(\eta)\dagger}(-\omega_2)\,\mathbf{S} - \mathbf{S}\,\mathbf{W}^{(\eta)\dagger}(-\omega_2)\,\mathbf{K}^{(\lambda)}(\omega_1) \right) \mathbf{c}_i. \tag{31}$$

To simplify the implementation of these expressions the following relation can be employed:

$$\mathbf{P}_{uo}^{(\lambda,\eta)\dagger}(\omega_1,\omega_2) = \mathbf{P}_{ou}^{(\lambda,\eta)}(-\omega_1,-\omega_2). \tag{32}$$

This completes the discussion of the $P_{\mu\nu}^{(\lambda,\eta)}(\omega_1,\omega_2)$ calculation. As Eq. (23) shows the only other quantity missing for the calculation of the second-order perturbed density matrix is the second-order perturbed Kohn-Sham matrix. Thus, we now turn to the quadratic response of the Kohn-Sham matrix.

Quadratic response of the Kohn-Sham matrix

For perturbation independent basis sets, a general expression for the calculation of the second-order perturbed Kohn-Sham matrix in the framework of ADFT is given by[58]:

$$K_{\mu\nu}^{(\lambda\eta)}(\omega_1,\omega_2) = \sum_{\bar{k}} \langle \mu\nu || \bar{k} \rangle \left(x_{\bar{k}}^{(\lambda,\eta)}(\omega_1,\omega_2) + z_{\bar{k}}^{(\lambda,\eta)}(\omega_1,\omega_2) \right) \tag{33}$$

In the above expression $\mathbf{x}^{(\lambda,\eta)}(\omega_1,\omega_2)$ corresponds to the second-order perturbed Coulomb fitting coefficients. The corresponding second-order perturbed exchange-correlation fitting coefficients are given by:

$$\begin{aligned} z_{\bar{k}}^{(\lambda\eta)}(\omega_1,\omega_2) &= \sum_{\bar{l},\bar{m}} G_{\bar{k}\bar{l}}^{-1}\, f_{\bar{l}\bar{m}}\, x_{\bar{m}}^{(\lambda\eta)}(\omega_1,\omega_2) + \sum_{\bar{l},\bar{m}} G_{\bar{k}\bar{l}}^{-1}\, f_{\bar{l}\bar{m}}^{(\eta)}(\omega_2)\, x_m^{(\lambda)}(\omega_1) \\ &= \sum_{\bar{l},\bar{m}} G_{\bar{k}\bar{l}}^{-1}\, f_{\bar{l}\bar{m}}\, x_{\bar{m}}^{(\lambda\eta)}(\omega_1,\omega_2) \\ &\quad + \sum_{\bar{l},\bar{m},\bar{n}} G_{\bar{k}\bar{l}}^{-1}\, g_{\bar{l}\bar{m}\bar{n}}\, x_{\bar{m}}^{(\lambda)}(\omega_1)\, x_{\bar{n}}^{(\eta)}(\omega_2) \end{aligned} \tag{34}$$

Here, $G_{\bar{k}\bar{l}}^{-1}$ denotes an element of the inverse Coulomb matrix.[59] The calculation of the exchange-correlation kernel integral elements,

$$f_{\bar{l}\bar{m}} = \int \int f_{xc}[\tilde{\rho};\mathbf{r},\mathbf{r}']\bar{l}(\mathbf{r})\,\bar{m}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}', \tag{35}$$

is described in.[47] In deMon2k these kernel integrals are available for all implemented local and gradient-corrected functionals. The $g_{\bar{l}\bar{m}\bar{n}}$ integral elements are defined by:

$$g_{\bar{l}\bar{m}\bar{n}} = \iiint g_{xc}[\tilde{\rho};\mathbf{r},\mathbf{r}',\mathbf{r}'']\bar{l}(\mathbf{r})\,\bar{m}(\mathbf{r}')\,\bar{n}(\mathbf{r}'')\,d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'' \tag{36}$$

The $g_{xc}[\tilde{\rho}]$ is the third functional derivative of the exchange-correlation energy functional. The first-order perturbed fitting coefficients are obtained by TDADPT as outlined in.[35] Because the second term in Eq. (34) depends only on first-order quantities we introduce (note comma in superscript):

$$x_{\bar{k}}^{(\lambda,\eta)}(\omega_1,\omega_2) \equiv \sum_{\bar{l},\bar{m},\bar{n}} G_{\bar{k}\bar{l}}^{-1}\, g_{\bar{l}\bar{m}\bar{n}}\, x_{\bar{m}}^{(\lambda)}(\omega_1)\, x_{\bar{n}}^{(\eta)}(\omega_2). \tag{37}$$

The second-order perturbed Kohn-Sham matrix can be written then as:

$$K_{\mu\nu}^{(\lambda\eta)}(\omega_1,\omega_2) = \sum_{\bar{k}} \langle \mu\nu || \bar{k} \rangle \left(x_{\bar{k}}^{(\lambda,\eta)}(\omega_1,\omega_2) + \sum_{\bar{l}} M_{\bar{k}\bar{l}}\, x_{\bar{l}}^{(\lambda,\eta)}(\omega_1,\omega_2) \right) \tag{38}$$

with

$$M_{\bar{k}\bar{l}} = \delta_{\bar{k}\bar{l}} + \sum_{\bar{m}} G_{\bar{k}\bar{m}}^{-1}\, \langle \bar{m} | f_{xc}[\tilde{\rho}] | \bar{l} \rangle. \tag{39}$$

Inserting Eq. (23) and Eq. (38) for the second-order perturbed density and Kohn–Sham matrix, respectively, into the expression for the hyperpolarizability tensor elements, Eq. (1), yields:

$$\begin{aligned} \beta_{\xi\lambda\eta}(-\omega_3;\omega_1,\omega_2) = &-2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda,\eta)}(\omega_1,\omega_2) H_{\mu\nu}^{(\xi)} \\ &-4 \sum_{\bar{k}} b_{\bar{k}}^{(\xi)}(\omega_3)\, x_{\bar{k}}^{(\lambda,\eta)}(\omega_1,\omega_2) \\ &-4 \sum_{\bar{k},\bar{l}} b_{\bar{k}}^{(\xi)}(\omega_3)\, M_{\bar{k}\bar{l}}\, x_{\bar{l}}^{(\lambda,\eta)}(\omega_1,\omega_2). \end{aligned} \tag{40}$$

Here we have introduced,

$$b_{\bar{k}}^{(\xi)}(\omega) \equiv \sum_i^{occ} \sum_a^{uno} \frac{H_{ia}^{(\xi)}\,\omega_{ia}}{\omega_{ia}^2 - \omega^2}\, \langle ia || k \rangle, \tag{41}$$

with $\omega_{ia} = \varepsilon_i - \varepsilon_a$. This represents an element of the first-order perturbation vector as defined in.[35] Thus, what remains to be done is the calculation of the second-order perturbed Coulomb coefficients $\mathbf{x}^{(\lambda,\eta)}$.

Quadratic response of the fitting coefficients

Because of the direct relation between the density matrix and the Coulomb fitting coefficients it is possible to define a second-order fitting equation system. If the basis and auxiliary functions

are perturbation independent, as it is here the case, this equation system takes the form:

$$\sum_{\bar{l}} G_{\bar{k}\bar{l}} x_{\bar{l}}^{(\lambda\eta)}(\omega_1, \omega_2) = \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda\eta)}(\omega_1, \omega_2) \langle \mu\nu || \bar{k} \rangle. \quad (42)$$

Similar to the derivation of the first-order response in ADPT we now substitute the second-order perturbed density matrix in Eq. (42) by its explicit expression from Eq. (23). Expanding the second-order Kohn–Sham matrices according to Eq. (38) then yields:

$$\sum_{\bar{l}} G_{\bar{k}\bar{l}} x_{\bar{l}}^{(\lambda\eta)}(\omega_1, \omega_2) = 2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda\eta)}(\omega_1, \omega_2) \langle \mu\nu || \bar{k} \rangle$$
$$+ 4 \sum_{\bar{l}} A_{\bar{k}\bar{l}}(\omega_3) x_{\bar{l}}^{(\lambda\eta)}(\omega_1, \omega_2)$$
$$+ 4 \sum_{\bar{l},\bar{m}} A_{\bar{k}\bar{l}}(\omega_3) M_{\bar{l}\bar{m}} x_{\bar{m}}^{(\lambda\eta)}(\omega_1, \omega_2). \quad (43)$$

The appearing Coulomb coupling matrix has the same form as in the first-order TDADPT response. Its matrix elements are given by:

$$A_{\bar{k}\bar{l}}(\omega) \equiv \sum_{i}^{occ} \sum_{a}^{uno} \frac{\langle \bar{k} || ia \rangle \, \omega_{ia} \, \langle ai || \bar{l} \rangle}{\omega_{ia}^2 - \omega^2}. \quad (44)$$

We now introduce a second-order perturbation vector defined as:

$$b_{\bar{k}}^{(\lambda,\eta)}(\omega_1, \omega_2) = 2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2) \langle \mu\nu || \bar{k} \rangle$$
$$+ 4 \sum_{\bar{l}} A_{\bar{k}\bar{l}}(\omega_3) x_{\bar{l}}^{(\lambda,\eta)}(\omega_1, \omega_2). \quad (45)$$

This vector depends only on first-order quantities as denoted by the commas in the superscripts. Thus, we can formulate the following equation system for the calculation of the second-order perturbed Coulomb fitting coefficients:

$$(\mathbf{G} - 4\,\mathbf{A}(\omega_3)\,\mathbf{M})\mathbf{x}^{(\lambda\eta)}(\omega_3) = \mathbf{R}(\omega_3)\,\mathbf{x}^{(\lambda\eta)}(\omega_1, \omega_2) = \mathbf{b}^{(\lambda,\eta)}(\omega_1, \omega_2) \quad (46)$$

Note that the response matrix has the same form as for the calculation of the first-order Coulomb fitting coefficients. This is in line with previous discussions of perturbation theory in the context of the variational fitting.[60,61] The direct solution of this equation system is given by:

$$x_{\bar{k}}^{(\lambda\eta)}(\omega_1, \omega_2) = \sum_{\bar{l}} R_{\bar{k}\bar{l}}^{-1}(\omega_3)\, b_{\bar{l}}^{(\lambda,\eta)}(\omega_1, \omega_2) \quad (47)$$

Substituting Eq. (47) in (40) eliminates the perturbed second-order Coulomb fitting coefficients from the hyperpolarizability

tensor element expression:

$$\beta_{\xi\lambda\eta}(-\omega_3; \omega_1, \omega_2) = -2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2)\, H_{\mu\nu}^{(\xi)}$$
$$- 4 \sum_{\bar{k}} b_{\bar{k}}^{(\xi)}(\omega_3)\, x_{\bar{k}}^{(\lambda,\eta)}(\omega_1, \omega_2)$$
$$- 4 \sum_{\bar{k},\bar{l},\bar{m}} b_{\bar{k}}^{(\xi)}(\omega_3)\, M_{\bar{k}\bar{l}}\, R_{\bar{l}\bar{m}}^{-1}(\omega_3)\, b_{\bar{m}}^{(\lambda,\eta)}(\omega_1, \omega_2)$$
$$(48)$$

With the equality,

$$\mathbf{M}\,\mathbf{R}^{-1}(\omega) = (\mathbf{R}^{-1}(\omega))^{\dagger}\, \mathbf{M}^{\dagger}, \quad (49)$$

and the first-order TDADPT equation system,[35]

$$\mathbf{R}(\omega_3)\, \mathbf{x}^{(\xi)}(\omega_3) = 4\, \mathbf{b}^{(\xi)}(\omega_3), \quad (50)$$

follows further:

$$\beta_{\xi\lambda\eta}(-\omega_3; \omega_1, \omega_2) = -2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2)\, H_{\mu\nu}^{(\xi)}$$
$$- 4 \sum_{\bar{k}} b_{\bar{k}}^{(\xi)}(\omega_3)\, x_{\bar{k}}^{(\lambda,\eta)}(\omega_1, \omega_2)$$
$$- \sum_{\bar{k},\bar{l}} x_{\bar{l}}^{(\xi)}(\omega_3)\, M_{\bar{k}\bar{l}}\, b_{\bar{k}}^{(\lambda,\eta)}(\omega_1, \omega_2). \quad (51)$$

This represent Wigner's $2n+1$ rule in the TDADPT framework. Thus, only first-order quantities are needed to calculate an element of the hyperpolarizability tensor.

Simplification

Inserting the explicit form of the second-order perturbation vector, Eq. (45) in (51) yields:

$$\beta_{\xi\lambda\eta}(-\omega_3; \omega_1, \omega_2)$$
$$= -2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2) \left(H_{\mu\nu}^{(\xi)} + \sum_{\bar{k},\bar{l}} \langle \mu\nu || \bar{k} \rangle M_{\bar{k}\bar{l}} x_{\bar{l}}^{(\xi)}(\omega_3) \right)$$
$$- \sum_{\bar{k}} (4\, \mathbf{b}^{(\xi)}(\omega_3) + 4\mathbf{A}(\omega_3)\, \mathbf{M}\, \mathbf{x}^{(\xi)}(\omega_3))_{\bar{k}}\, x_{\bar{k}}^{(\lambda,\eta)}(\omega_1, \omega_2) \quad (52)$$

The parenthesis in the first term of Eq. (52) is equal to $K_{\mu\nu}^{(\xi)}(\omega_3)$. The parenthesis in the second term is equal to $\mathbf{G}\,\mathbf{x}^{(\xi)}(\omega_3)$. Thus, Eq. (52) can be written as:

$$\beta_{\xi\lambda\eta}(-\omega_3; \omega_1, \omega_2) = -2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2)\, K_{\mu\nu}^{(\xi)}(\omega_3)$$
$$- \sum_{\bar{k},\bar{l}} G_{\bar{k}\bar{l}}\, x_{\bar{l}}^{(\xi)}(\omega_3)\, x_{\bar{k}}^{(\lambda,\eta)}(\omega_1, \omega_2) \quad (53)$$

Expressing $x_{\bar{k}}^{(\lambda,\eta)}(\omega_1, \omega_2)$ by its explicit form Eq. (37) yields the final form of the ADPT hyperpolarizability tensor elements:

$$\beta_{\xi\lambda\eta}(-\omega_3; \omega_1, \omega_2) = -2 \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda,\eta)}(\omega_1, \omega_2)\, K_{\mu\nu}^{(\xi)}(\omega_3)$$
$$- \sum_{\bar{k},\bar{l},\bar{m}} g_{\bar{k}\bar{l}\bar{m}}\, x_{\bar{k}}^{(\lambda)}(\omega_1)\, x_{\bar{l}}^{(\eta)}(\omega_2)\, x_{\bar{m}}^{(\xi)}(\omega_3) \quad (54)$$

Note that the second term in Eq. (54) can be expressed as:

$$\iiint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \tilde{\rho}^{(\lambda)}(\mathbf{r}) \, \tilde{\rho}^{(\xi)}(\mathbf{r}') \, \tilde{\rho}^{(\eta)}(\mathbf{r}'') \, d\mathbf{r} \, d\mathbf{r}' \, d\mathbf{r}'' \quad (55)$$

The calculation of this term by finite differences of exchange-correlation potentials is described in the Appendix. This concludes the calculation of static and dynamic ADPT hyperpolarizabilities tensor elements. By the choice of the frequencies in Eq. (54) SHG, EOPE, and OR nonlinear optical properties can be calculated.

Computational Methodology

All calculations are performed with the LCGTO-DFT code deMon2k.[44] As it is well documented in the literature basis sets for polarizability and hyperpolarizability calculations must contain diffuse functions.[62] An economical strategy for constructing these basis sets is to augment valence basis sets of reasonable quality with additional polarization functions.[63–66] The TZVP-FIP1 basis set used here[26,67] is built on the triple zeta valence plus polarization (TZVP) basis set optimized for local DFT calculations.[68] The atomic TZVP basis sets are augmented by field-induced polarization (FIP) functions as proposed by Zeis et al.[64] The exponents of the FIP functions are found by optimizing the atomic polarizabilities to their experimental reference values.[69,70] These basis sets are available from the deMon2k basis set library.[71] To avoid the contamination of the valence basis sets with the diffuse FIP functions spherical basis functions are used.

For the expansion of the auxiliary function density, used for the calculation of the Coulomb and exchange-correlation contributions, primitive Hermite Gaussian auxiliary functions[72,73] are employed. In all hyperpolarizability calculations the GEN-A2* auxiliary function set[74] is used. It contain s, p, d, f, and g auxiliary functions that are grouped together in sets with common exponents.[75,76] The combination of TZVP-FIP1 basis sets and GEN-A2* auxiliary functions sets has already been successfully used for ADPT polarizability calculations.[35,39,47] The obtained polarizabilities are in good agreement with available experimental results, particularly in the low frequency range.

For the local density approximation (LDA), we combined the exchange functional from Dirac[77] with the VWN correlation functional.[78] For the generalized gradient approximation (GGA) the PBE[79] and BP86[80,81] functionals were used. To investigate the sensitivity of the hyperpolarizabilities with respect to the parametrization of the exchange-correlation functional we introduced a modified B88 exchange functional in which the enhancement function was changed to:

$$f(x_\sigma) = 1 + \beta \frac{x_\sigma^2}{1 + 3\beta x_\sigma \sinh^{-1}(x_\sigma)} \quad (56)$$

Here, σ denotes the spin manifold and x_σ is defined as:

$$x_\sigma = |\nabla \rho_\sigma| / \rho_\sigma^{4/3} \quad (57)$$

The parameter β (not to be confused with the hyperpolarizability) is set to 0.05. The functional form of (56) was motivated by the model potential from Leeuwen and Baerends.[82] However, it represents a true GGA because (56) is used for the exchange energy rather than the potential. In our validation calculations we have combined this modified B88 exchange functional with the P86 correlation functional[81] and named it mBP86. The effect of this modification can be directly seen by comparison with the BP86 results. For all functionals the corresponding kernel and kernel derivatives were used in the hyperpolarizability calculations, i.e., the so-called adiabatic local density approximations to the kernel and kernel derivative were not employed. The finite field hyperpolarizabilities were calculated as described in.[26]

The exchange-correlation energy, potential, kernel and kernel derivative were numerically integrated on an adaptive grid[83] with a grid tolerance of 10^{-6} a.u. (GRID FINE). For all other deMon2k input keywords the default settings are used. In order to ensure the numerical stability of the presented results we also performed all calculations with the so-called reference grid in deMon2k. In this grid, every atom is surrounded by 200 radial shells, each carrying a Lebedev grid with 1202 points ($L = 59$). Moreover, we tightened the SCF convergence to 10^{-9} a.u. in these calculations. The difference to the here reported hyperpolarizabilities are well below 1% in all calculations. This documents the numerical stability of our results.

To simplify comparison of the calculated TDADPT hyperpolarizabilities with experimental and theoretical values from the literature all calculations are performed in the so-called EFISH (electric-field-induced second-harmonic) orientation. In this orientation, the dipole moment of the molecule is aligned along the z axis. The average hyperpolarizability is calculated by the following expression:

$$\bar{\beta}(-\omega_3; \omega_1, \omega_2) = \frac{1}{5} \sum_i (\beta_{zii} + \beta_{izi} + \beta_{iiz}) \quad (58)$$

Results and Discussion

In all validation calculations the experimental molecular structures[84–86] were used. In Table 1 static VWN (TD)ADPT hyperpolarizability tensor elements are compared with their finite-field counterparts. The two TDADPT columns refer to the analytical and numerical kernel, f_{xc}, and kernel derivative, g_{xc}, calculations. The differences between these results is in all cases below 1.0 a.u. with a maximum of 0.85 a.u. for the average hyperpolarizability of NH_3. This reflects the intrinsic accuracy of the numerical f_{xc} and g_{xc} calculation. A detailed analysis shows that the largest part of the error arises from the numerical g_{xc} calculation. In any case this error is considerably smaller than the one introduced by the so-called adiabatic local density approximations which can reach several atomic units. The symmetry breaking of individual β tensor elements, e.g., β_{xxz} and β_{yyz} in NH_3, CO and HF (see also Table 2), is also well below 1.0 a.u. and can be reduced by improving the grid quality. The two finite-field columns in Table 1 list results from finite-field calculations with field strengths of 0.01 (default setting in deMon2k) and 0.001 a.u., respectively. The comparison of these values shows the numerical stability of the finite-field procedure, which is usually better than a few atomic

Table 1. Comparison of static VWN (TD)ADPT and finite-field hyperpolarizabilities (a.u.) of small molecules.

Molecule	Value	TDADPT Analytical	TDADPT Numerical	Finite field 0.01	Finite field 0.001
H$_2$O	β_{xxz}	−13.68	−13.19	−13.68	−13.06
	β_{yyz}	−5.20	−5.17	−5.30	−7.74
	β_{zzz}	−17.20	−16.88	−17.62	−17.57
	$\bar{\beta}$	−21.66	−21.15	−21.97	−23.03
NH$_3$	β_{xxz}	−11.50	−11.95	−11.73	−12.31
	β_{yyz}	−11.66	−12.10	−11.76	−12.82
	β_{zzz}	−27.86	−28.57	−26.91	−31.45
	$\bar{\beta}$	−30.61	−31.56	−30.25	−33.95
CO	β_{xxz}	5.34	5.43	5.46	5.47
	β_{yyz}	5.34	5.31	5.46	5.47
	β_{zzz}	27.31	27.42	27.51	27.50
	$\bar{\beta}$	22.80	22.81	23.07	23.07
HF	β_{xxz}	−2.03	−2.06	−1.97	−3.15
	β_{yyz}	−2.03	−2.06	−1.97	−3.15
	β_{zzz}	−12.08	−12.08	−11.98	−10.65
	$\bar{\beta}$	−9.69	−9.71	−9.56	−10.18
H$_2$S	β_{xxz}	−14.29	−14.49	−13.87	45.97
	β_{yyz}	6.10	5.82	6.52	7.48
	β_{zzz}	−2.38	−2.82	−0.74	−3.22
	$\bar{\beta}$	−6.35	−6.89	−4.86	30.14

The Analytical and Numerical colums under TDADPT list results from analytical and numerical kernel, f_{xc}, and kernel derivative, g_{xc}, calculations, respectively. The columns with the numbers 0.01 and 0.001 under Finite-Field list results from finite-field calculations with 0.01 and 0.001 a.u. field strenghs, respectively.

Table 2. Comparison of static LDA and GGA (TD)ADPT hyperpolarizabilities (a.u.) with Hartree-Fock and CCSD(T) results from the literature.[87]

Molecule	Value	VWN	PBE	BP86	mBP86	TDHF	CCSD(T)
H$_2$O	β_{xxz}	−13.68	−13.94	−15.63	−13.37	−9.40	−10.20
	β_{yyz}	−5.20	−4.86	−4.60	−2.54	−1.40	−6.20
	β_{zzz}	−17.20	−15.75	−16.94	−13.93	−7.10	−13.70
	$\bar{\beta}$	−21.66	−20.69	−21.59	−17.94	−10.80	−18.00
NH$_3$	β_{xxz}	−11.50	−11.55	−12.34	−14.63	−7.00	−8.80
	β_{yyz}	−11.66	−11.74	−12.38	−14.10	−7.00	−8.80
	β_{zzz}	−27.86	−26.70	−26.32	−24.95	−11.10	−39.60
	$\bar{\beta}$	−30.61	−29.93	−30.58	−32.12	−15.20	−34.30
CO	β_{xxz}	5.34	5.64	5.06	3.27	3.50	6.60
	β_{yyz}	5.34	5.73	4.92	3.27	3.50	6.60
	β_{zzz}	27.31	26.93	26.89	24.12	28.20	26.00
	$\bar{\beta}$	22.80	23.08	22.13	18.41	21.20	23.50
HF	β_{xxz}	−2.03	−1.94	−1.90	−1.63	−0.28	−1.27
	β_{yyz}	−2.03	−1.99	−1.79	−1.66	−0.28	−1.27
	β_{zzz}	−12.08	−12.44	−12.36	−12.62	−8.40	−9.62
	$\bar{\beta}$	−9.69	−9.82	−9.63	−9.64	−5.38	−7.20
H$_2$S	β_{xxz}	−14.29	−15.18	−14.65	−13.96	−9.90	−9.50
	β_{yyz}	6.10	4.38	9.02	7.91	5.60	−4.40
	β_{zzz}	−2.38	−1.61	0.02	−3.85	7.90	1.10
	$\bar{\beta}$	−6.35	−7.40	−3.39	−5.87	2.20	−7.70

units. However, the β_{xxz} element of H$_2$S molecule changes from −13.87 to 45.97 a.u. in these finite-field calculations. This shows once again the problematic of finite-field results. Altogether the (TD)ADPT and finite-field results using a field strength of 0.01 a.u. compare very favorable with each other. The maximum deviation is around 2 a.u. for the $\bar{\beta}$ of H$_2$S.

Table 2 compares static LDA and GGA (TD)ADPT hyperpolarizabilities with Hartree-Fock (TDHF) and CCSD(T) results. In general, the agreement between DFT and CCSD(T) hyperpolarizabilities is good. The (TD)HF results show often large deviations from these data sets. This underlines the importance of correlation contributions to the hyperpolarizabilities. The LDA, PBE, and BP86 hyperpolarizabilities are usually close together. An exception is the BP86 average hyperpolarizability of H$_2$S which is significantly less negative than the VWN and PBE results. On the other hand the mBP86 functional yields for many molecules significantly different hyperpolarizabilities. In some cases (H$_2$O and NH$_3$) this improves the agreement with the CCSD(T) results whereas in others (CO and H$_2$S) larger discrepancies are observed. In any case this demonstrates that the hyperpolarizabilities are indeed sensitive to the parametrization of the functional.

Table 3 compares calculated and measured second harmonic generation (SHG) values. All data refer to a wavelength of 694.3 nm. As for static values listed in Table 2 the LDA and GGA TDADPT SHG values compare reasonably well with the CCSD(T) and experimental values. In particular, the large overestimations of hyperpolarizabilities as reported in other works[13] is not observed with the here used methodology. We attribute this mainly to the used basis set that contains FIP functions optimized for atomic polarizabilities. As for the static hyperpolarizabilities TDHF results are not reliable. The largest discrepancy

Table 3. Comparison of dynamic LDA and GGA TDADPT hyperpolarizabilities (a.u.) with TDHF, CCSD(T), and experimental results.

Molecule	Value	VWN	PBE	BP86	mBP86	TDHF[a]	CCSD(T)[a]	Exp.
H$_2$O	SHG	−28.07	−28.07	−27.72	−22.25	−12.57	−21.10	−22.00 ± 6.0[b]
	OR/EOPE	−23.49	−22.51	−23.23	−19.03	−11.29	−19.00	
NH$_3$	SHG	−51.76	−51.76	−51.52	−48.60	−21.97	−49.10	−48.40 ± 1.2[b]
	OR/EOPE	−35.64	−34.82	−35.65	−36.34	−16.74	−38.30	
CO	SHG	27.16	27.16	26.55	21.65	24.10	27.00	29.90 ± 3.2[b]
	OR/EOPE	24.13	24.32	23.47	19.52	21.90	24.60	
HF	SHG	−11.15	−11.15	−10.84	−10.80	−5.85	−8.00	−10.90 ± 1.0[c]
	OR/EOPE	−10.14	−10.16	−9.85	−9.95	−5.52	−7.50	
H$_2$S	SHG	−8.82	−8.82	−4.21	−7.16	2.38	−8.80	−9.95 ± 2.1[b]
	OR/EOPE	−6.86	−7.98	−3.36	−6.11	2.12	−8.20	

All values refer to a wavelenght of 694.3 nm.
[a] Calculations from Ref. [87].
[b] SHG measured from Ref. [88].
[c] SHG measured from Ref. [89].

between DFT and experimental results are observed for water where VWN, PBE, and BP86 severely overestimate the measured value. Unfortunately, the experimental value possesses a rather large error bar, in the same range as the overestimation. However, the CCSD(T) result indicates that the VWN, PBE and BP86 overestimations exist in this molecule. With the mBP86 functional the 6 a.u. overestimation by VWN, PBE and BP86 is removed!. The same trend, but less dramatic, is observed for NH_3. Again the mBP86 functional yields a TDADPT SHG value in excellent agreement with experiment and the CCSD(T) result. However, for CO the mBP86 SHG value severely underestimates the experimental and CCSD(T) results. This underestimation is rooted in the static mBP86 result for CO as Table 2 shows. For HF all TDADPT results compare favorable with experiment. The VWN and PBE SHG values for H_2S are in excellent agreement with the reported CCSD(T) value and in the error range of the experimental measured value. The BP86 and mBP86 values are in absolute too small. Table 3 also list the optical rectification (OR) and the electro-optical Pockels effect (EOPE) which are the same for the here studied molecules. Comparison with the corresponding CCSD(T) results reveals a very similar trend as for the just discussed SHG values.

Table 4 compares static LDA and GGA (TD)ADPT hyperpolarizabilities of methane analogs with other theoretical results from the literature. The listed Hartree-Fock values are only given for completeness. Because of their unreliability, we will not further discuss them. For CH_3OH the VWN, PBE and BP86 hyperpolarizabilities severely overestimate the CCSD literature value.[90] With the mBP86 functional a significant improvement is obtained. The difference to the CCSD value reduces to around 10%. In CH_3F the sign of our calculated average hyperpolarizabilities, using EFISH orientation as described in the "Computational Methodology" section, differs from the other theoretical results in the literature. If we compare absolute values our LDA value is in fair agreement with corresponding result from Lee and Colwell,[6] whereas the mBP86 value is closed to their Hartree–Fock hyperpolarizability. Our VWN, PBE, and BP86 TDADPT hyperpolarizabilities of CH_3CN are in good agreement with the LDA results from.[6] The mBP86

average hyperpolarizability is larger and in better agreement with the CCSD(T) value from.[6]

Table 5 compares calculated and measured SHG results for the same set of methane analogs as in Table 4. Our calculated DFT SHG values were determined at the same wavelength as the experimental values. For CH_3OH the VWN, PBE, and BP86 SHG values severely overestimate the CCSD result from[90] and the experimental value from.[92] This overestimation is considerably reduced by the mBP86 functional. A similar trend is observed for CH_3F. Here, the mBP86 value is in good agreement with a MP2 hyperpolarizability augmented with Hartree–Fock dispersion.[93] Moreover, the experimental SHG value is considerably larger (in absolute) and lies just in between the TDADPT VWN, PBE, BP86, and mBP86 values. However, there is no doubt about the sign of the SHG value which confirms our negative static average hyperpolarizability for CH_3F in Table 4. For the CH_3CN the TDADPT SHG values are all quite similar. The mBP86 result is in particular good agreement with the CCSD(T) hyperpolarizability augmented with MP2 dispersion for a wavelength of 514.5 nm. Because our calculations refer to 1064 nm this literature value can be considered as a lower bound for our calculations. The experimental SHG value for CH_3CN seems considerably too low. For CH_3Cl we find a sign inversion between the VWN and PBE TDADPT result on one side and the corresponding BP86 and mBP86 results on the other side. Comparison with experiment reveals that the BP86 and mBP86 sign is correct. In CHF_3 we find larger absolute values for TDADPT VWN, PBE, and BP86 than for mBP86. Again the mBP86 value is in better agreement with experiment. The theoretical TDHF value determines a lower bound for the SHG value of CHF_3. The TDADPT SHG values for CF_3Cl are all closed together and significantly larger than the experimental measured value. Unfortunately, no other theoretical reference values are available for this system. In $CHCl_3$ we find again a sign inversion between the TDADPT results. Surprisingly, only the BP86 SHG value is positive whereas all other TDADPT SHG values are negative. Considering the relative large error bars on the experimental value our best assumption is a SHG value around zero for $CHCl_3$ which is best predicted by the PBE functional. Unfortunately, no other theoretical SHG values are available for this system. The TDADPT SHG values of $CFCl_3$ are all larger, in absolute, than the available experimental reference value. The VWN and PBE results are within the experimental error bars. The mBP86 SHG result is just a little bit outside this range. In Table 5 we also list OR and EOPE values for the studied molecules and wavelength. By and large they follow the same trend as the just discussed SHG results.

Table 4. Comparison of static LDA and GGA (TD) ADPT hyperpolarizabilities (a.u.) of methane analogs with other theoretical results from the literature.

Molecule	VWN	PBE	BP86	mBP86	Other theoretical results
CH_3OH	−47.04	−46.75	−44.57	−36.55	−33.52[a]
CH_3F	−56.29	−57.54	−56.23	−39.53	36.23[b]; 62.22[c]
CH_3CN	21.23	22.49	22.73	25.72	4.09[d]; 22.76[e]; 24.24[f]
CH_3Cl	−1.83	−3.06	5.72	14.46	
CHF_3	−31.20	−31.34	−30.78	−26.28	−19.04[g]
CF_3Cl	−69.34	−71.60	−80.61	−73.69	
$CHCl_3$	−4.80	−2.53	4.18	−4.55	
$CFCl_3$	−32.32	−36.35	−39.49	−38.67	

[a] CCSD, from Ref. [90].
[b] Hartree-Fock, from Ref. [6].
[c] LDA, from Ref. [6].
[d] Hartree-Fock, from Ref. [6].
[e] LDA, from Ref. [6].
[f] CCSD(T), from Ref. [6].
[g] Hartree-Fock, from Ref. [91].

Conclusions

The working equations for static and dynamic first hyperpolarizability calculations in the framework of (TD)ADPT are derived on the basis of Wigner's $2n + 1$ rule for perturbation theory. The final formula is similar to other approaches but introduces the third-order functional derivative of the exchange-correlation energy in terms of auxiliary functions. For the calculations of the kernel and kernel derivative integrals we employ finite difference formulas of the corresponding potential. Thus, for all LDA

Table 5. Comparison of dynamic LDA and GGA TDADPT hyperpolarizabilities (a.u.) of methane analogs with other theoretical and experimental results.

Molecule	Value	VWN	PBE	BP86	mBP86	Theor.	Exp.
CH_3OH	SHG	−61.11	−61.05	−58.16	−45.31	−40.61[a]	−35.0 ± 2.1[b]
	OR/EOPE	−51.04	−50.87	−48.61	−39.21		
CH_3F	SHG	−67.66	−69.19	−67.85	−46.57	−46.30[c]	−57.0 ± 4.2[d]
	OR/EOPE	−59.68	−60.91	−59.83	−42.12	23.45[e]	
CH_3CN	SHG	22.63	23.63	25.00	26.94	27.48[f]	17.9 ± 1.1[g]
	OR/EOPE	21.69	22.63	23.92	25.85		
CH_3Cl	SHG	−2.65	−4.44	6.32	17.48		13.3 ± 1.4[h]
	OR/EOPE	−2.12	−3.54	5.61	15.61		
CHF_3	SHG	−36.21	−36.09	−35.74	−29.99	−20.20[i]	−25.2 ± 0.9[j]
	OR/EOPE	−32.73	−32.59	−32.29	−27.46	−19.40[k]	
CF_3Cl	SHG	−81.85	−82.55	−94.19	−84.65		−69.2 ± 2.8[l]
	OR/EOPE	−73.15	−73.74	−84.01	−75.95		
$CHCl_3$	SHG	−5.44	−2.69	5.50	−6.77		1.2 ± 2.6[m]
	OR/EOPE	−5.00	−2.53	4.52	−5.66		
$CFCl_3$	SHG	−34.81	−37.44	−44.98	−42.47		−30.9 ± 9.6[n]
	OR/EOPE	−33.24	−35.70	−41.91	−39.42		

The TDADPT values were calculated at the same wavelength as for the corresponding experiments.
[a] Dynamic value at $\lambda = 694.3$ nm, CCSD, from Ref. [90].
[b] Dynamic value at $\lambda = 694.3$ nm, ESHG, from Ref. [92].
[c] Dynamic value at $\lambda = 632.8$ nm, static β from MP2 with SCF percentage dispersion from Ref. [93].
[d] Dynamic value at $\lambda = 694.3$ nm, ESHG, from Ref. [94].
[e] Dynamic value at $\lambda = 694.3$ nm, TDHF, from Ref. [91].
[f] Dynamic value at $\lambda = 514.5$ nm, static β from CCSD(T) with MP2 additive dispersion from Ref. [93].
[g] EFISH at $\lambda = 1064$ nm from Ref. [95].
[h] Dynamic value at $\lambda = 694.3$ nm, ESHG, from Ref. [96].
[i] Dynamic value at $\lambda = 694.3$ nm, TDHF, from Ref. [91].
[j] Dynamic value at $\lambda = 694.3$ nm, ESHG, from Ref. [94].
[k] Dynamic value at $\lambda = 694.3$ nm, TDHF, from Ref. [91].
[l] Dynamic value at $\lambda = 694.3$ nm, ESHG, from Ref. [94].
[m] Dynamic value at $\lambda = 694.3$ nm, ESHG, from Ref. [96].
[n] Dynamic value at $\lambda = 694.3$ nm, ESHG, from Ref. [96].

and GGA functionals implemented in deMon2k these integrals are available. This avoids the so-called adiabatic local density approximation for these integrals in case of GGA functionals. Our validation calculations show that this implementation is numerically stable and possesses maximum errors well below 1.0 a.u. in all cases. This error is significantly smaller than the one introduced by the adiabatic local density approximation which can reach several atomic units.

Even though it was not the main purpose of this article our validation calculations show that accurate hyperpolarizabilities can be obtained with the TZVP-FIP1 basis and GEN-A2* auxiliary function set. In particular, the systematical large overestimations of hyperpolarizabilities by LDA and GGA functionals in the basis set limit is not observed here. We attribute this mainly to the used basis set that contains FIP functions optimized for atomic polarizabilities. Thus, it is likely that the observed large overestimation of LDA and GGA hyperpolarizabilities in the literature is rooted in overestimations of atomic polarizabilities which can be easily and systematically removed by adequate basis sets. This also eliminates the numerical difficulties associated with basis set limit calculations. As a result our TZVP-FIP1/GEN-A2* LDA and GGA hyperpolarizabilities are usually in fair to good agreement with correlated wave function results.

In accordance with other studies in the literature, we find that LDA and conventional GGA TDADPT hyperpolarizabilities are very similar. Significant differences are found with the newly introduced mBP86 functional. This shows that hyperpolarizabilities are sensitive to the parametrization of the functional. Unfortunately, the mBP86 hyperpolarizabilities improve not for all systems but certainly for the majority. At this point, it is important to emphasize that this improvement is not always a reduction of the hyperpolarizability value as obtained by mixing Hartree–Fock into the exchange-correlation functional. Certainly, there is still room for improvement in this direction.

Appendix: Calculation of g_{xc} Integrals by Finite Differences

We now describe the calculation of the $g_{xc}[\tilde{\rho}]$ integral, Eq. (55), by finite differences of exchange-correlation potentials as implemented in deMon2k. This permits calculation of the g_{xc} term in Eq. (54) for all implemented local and gradient corrected functionals. To avoid cluttering the notation, we skip the external field frequencies. We start our derivation with the following second-order expansion of the exchange-correlation potential:

$$v_{xc}[\tilde{\rho} \pm \delta\tilde{\rho}^{(\lambda)} \pm \delta\tilde{\rho}^{(\eta)}; \mathbf{r}] \cong v_{xc}[\tilde{\rho}; \mathbf{r}] \pm \int f_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}'] \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \, d\mathbf{r}'$$

$$\pm \int f_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}'] \delta\tilde{\rho}^{(\eta)}(\mathbf{r}') \, d\mathbf{r}'$$

$$+ \frac{1}{2} \iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$

$$+ \frac{1}{2} \iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \delta\tilde{\rho}^{(\eta)}(\mathbf{r}') \, \delta\tilde{\rho}^{(\eta)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$

$$+ \iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \, \delta\tilde{\rho}^{(\eta)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$

Here $\delta\tilde{\rho}^{(\lambda)}$ denotes a variation of the perturbed auxiliary density $\tilde{\rho}^{(\lambda)}$. The positive and negative expansions are combined and indicated by the $\pm$ sign. The addition of these two expansions yields:

$$2 \iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \, \delta\tilde{\rho}^{(\eta)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$
$$\cong -2 v_{xc}[\tilde{\rho}; \mathbf{r}] + v_{xc}[\tilde{\rho} + \delta\tilde{\rho}^{(\lambda)} + \delta\tilde{\rho}^{(\eta)}; \mathbf{r}]$$
$$+ v_{xc}[\tilde{\rho} - \delta\tilde{\rho}^{(\lambda)} + \delta\tilde{\rho}^{(\eta)}; \mathbf{r}]$$
$$- \iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$
$$- \iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \delta\tilde{\rho}^{(\eta)}(\mathbf{r}') \, \delta\tilde{\rho}^{(\eta)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$

To express the last two terms in the above expression by exchange-correlation potentials, we now introduce the following second-order expansions:

$$v_{xc}[\tilde{\rho} \pm \delta\tilde{\rho}^{(\lambda)}; \mathbf{r}] \cong v_{xc}[\tilde{\rho}; \mathbf{r}] \pm \int f_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}'] \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \, d\mathbf{r}'$$
$$+ \frac{1}{2} \iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$

Addition of these two expansions then yields:

$$\iint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \, \delta\tilde{\rho}^{(\lambda)}(\mathbf{r}'') \, d\mathbf{r}' \, d\mathbf{r}''$$
$$\cong -2 v_{xc}[\tilde{\rho}; \mathbf{r}] + v_{xc}[\tilde{\rho} + \delta\tilde{\rho}^{(\lambda)}; \mathbf{r}] + v_{xc}[\tilde{\rho} - \delta\tilde{\rho}^{(\lambda)}; \mathbf{r}]$$

Inserting this expansion in the last two terms in Eq. (A1) and substituting the perturbed density variations by their finite difference counterparts,

$$\delta\tilde{\rho}^{(\lambda)}(\mathbf{r}') \cong \epsilon \tilde{\rho}^{(\lambda)}(\mathbf{r}'), \tag{A1}$$

yields the following expression for the $g_{xc}[\tilde{\rho}]$ integral in Eq. (55):

$$\iiint g_{xc}[\tilde{\rho}; \mathbf{r}, \mathbf{r}', \mathbf{r}''] \, \tilde{\rho}^{(\xi)}(\mathbf{r}) \, \tilde{\rho}^{(\lambda)}(\mathbf{r}') \, \tilde{\rho}^{(\eta)}(\mathbf{r}'') \, d\mathbf{r} \, d\mathbf{r}' \, d\mathbf{r}''$$
$$\cong \int \frac{\tilde{\rho}^{(\xi)}(\mathbf{r}) \, v_{xc}[\tilde{\rho}; \mathbf{r}]}{\epsilon^2} \, d\mathbf{r} + \int \frac{\tilde{\rho}^{(\xi)}(\mathbf{r}) \, v_{xc}[\tilde{\rho} + \epsilon(\tilde{\rho}^{(\lambda)} + \tilde{\rho}^{(\eta)}); \mathbf{r}]}{2\epsilon^2} \, d\mathbf{r}$$
$$+ \int \frac{\tilde{\rho}^{(\xi)}(\mathbf{r}) \, v_{xc}[\tilde{\rho} - \epsilon(\tilde{\rho}^{(\lambda)} + \tilde{\rho}^{(\eta)}); \mathbf{r}]}{2\epsilon^2} \, d\mathbf{r}$$
$$- \int \frac{\tilde{\rho}^{(\xi)}(\mathbf{r}) \, v_{xc}[\tilde{\rho} + \epsilon\tilde{\rho}^{(\lambda)}; \mathbf{r}]}{2\epsilon^2} \, d\mathbf{r} - \int \frac{\tilde{\rho}^{(\xi)}(\mathbf{r}) \, v_{xc}[\tilde{\rho} - \epsilon\tilde{\rho}^{(\lambda)}; \mathbf{r}]}{2\epsilon^2} \, d\mathbf{r}$$
$$- \int \frac{\tilde{\rho}^{(\xi)}(\mathbf{r}) \, v_{xc}[\tilde{\rho} + \epsilon\tilde{\rho}^{(\eta)}; \mathbf{r}]}{2\epsilon^2} \, d\mathbf{r} - \int \frac{\tilde{\rho}^{(\xi)}(\mathbf{r}) \, v_{xc}[\tilde{\rho} - \epsilon\tilde{\rho}^{(\eta)}; \mathbf{r}]}{2\epsilon^2} \, d\mathbf{r}$$

This equation was implemented for LDA and GGA functionals in deMon2k. For the calculation of the g_{xc} integral the same grid as for the energy calculation is used. However, the density cutoff is enlarged to 10^{-6} and 10^{-4} a.u. for LDA and GGA, respectively, to guarantee stable results. The finite difference value ϵ is set to 10^{-8} in all calculations.

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