Nonlinear Response Time-Dependent Density Functional Theory Combined with the Effective Fragment Potential Method

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Abstract
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Keywords
Multiphoton processes, Solvents, Polarization, Density functional theory, Polarizability

Disciplines
Chemistry

Comments

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Nonlinear response time-dependent density functional theory combined with the effective fragment potential method

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This work presents an extension of the linear response TDDFT/EFP method to the nonlinear-response regime together with the implementation of nonlinear-response TDDFT/EFP in the quantum-chemistry computer package GAMESS. Included in the new method is the ability to calculate the two-photon absorption cross section and to incorporate solvent effects via the EFP method. The nonlinear-response TDDFT/EFP method is able to make correct qualitative predictions for both gas phase values and aqueous solvent shifts of several important nonlinear properties. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4867271]

I. INTRODUCTION

While the polarization of a molecular system under the influence of a relatively weak oscillating electric field can be well described by a linear correction to the Hamiltonian within time-dependent perturbation theory, stronger fields typical in present-day laser experiments necessitate higher-order corrections characterizing a multitude of nonlinear optical effects. The frequency-dependent coefficients of the linear, quadratic, etc., corrections are, respectively, known as the dynamic polarizability, dynamic first hyperpolarizability, etc.  

The nonlinear optical effects of molecular systems are of practical interest in many areas of science, technology, and medicine. The second harmonic generation (SHG), electro-optical Pockels effect (EOPE), and optical rectification (OR) are second-order effects characterized by the dynamic first hyperpolarizability. The dynamic first hyperpolarizability has two frequencies as independent variables and the aforementioned second-order effects are each characterized by a specific combination of these frequencies. The version of the dynamic first hyperpolarizability corresponding to the SHG, i.e., the frequency-doubling effect, can also describe the process of a concerted two-photon absorption (TPA) by an atom or molecule.  

TPA was theoretically predicted by Goeppert-Mayer  and first observed 30 years later by the generation of a blue fluorescent light upon laser excitation of CaF$_2$:Eu$^{2+}$ crystals with a red light.  The individual photons participating in the TPA process are not necessarily resonant with any of the transitions in the atom or molecule; it is only their sum that is resonant. A simple conceptual model can be employed to explain TPA in terms of a short-lived virtual excited state intermediate between the ground and final excited states. A non-negligible probability of such a process (measured by the TPA cross-section) occurs only when a high-intensity light source is used to assure a quick succession of photons. It is therefore not surprising that TPA was experimentally observed only after the advent of lasers.  

In addition to being of fundamental interest, TPA has numerous important applications, including 3D microscopy, 3D micro- and nano-fabrication, 3D optical storage, optical limiting, and pumped up-conversion lasing. An interesting application of TPA is in photodynamic cancer therapy, a technique that makes use of the high reactivity of singlet oxygen produced by one- or two-photon absorption. The advantage of using TPA in this context is that singlet oxygen formation by TPA occurs only when the incident photon influx is of high intensity, a constraint that allows for precise spatial and temporal control in destroying the cancer-infected tissue as well as an improved possibility of depth penetration in the body.

There are several methods for the computation of linear and nonlinear molecular response properties. Among these, time-dependent density functional theory (TDDFT) presents a balance between accuracy and efficiency. High-level computational methods, such as coupled-cluster (CC), configuration-interaction (CI), and multi-reference (MR) methods provide high accuracy, but they generally have very steep computational scaling with the size of the molecular system. On the other hand, there are simplified approaches such as the few-state models for TPA  using just a limited number of states in the sum-over-states (SOS) approach  that originates from the perturbative treatment of the effect and the finite-field approach. The finite-field approach is valid only for static (hyper-)polarizabilities. The SOS approach and its few-states truncation are sometimes necessary due to the excessive computational cost of the high-level electronic structure methods applied to relatively large molecules. Unfortunately, the simplified methods typically have very low accuracy.

Modern density functionals provide good quality results for many properties and processes, with modest computational cost. However, there are several limitations caused by (1) the TDDFT adiabatic approximation, i.e., the neglect of explicit time-dependence (or frequency-dependence in the Fourier representation) in the TDDFT exchange-correlation term resulting from the use of a time-independent, ground state density functional approximation; (2) the well-known deficiencies of most present-day density functionals, such as...
II. DENSITY-MATRIX BASED LINEAR- AND NONLINEAR-RESPONSE TDDFT

The present work employs the density matrix based approach to nonlinear-response TDDFT. The method of Hirata and Head-Gordon is extended to the second-order response in the applied electric field. A density-matrix approach to second-order-response TDDFT was previously developed by using slightly different formalisms. Although the linear-order response within this formalism recovers the well-known TDDFT matrix equations, it is presented here for consistency of the overall presentation.

The system is initially in the ground state and its reduced one-electron density matrix $\rho(\mathbf{r}, \mathbf{r}')$ can be expanded in the Kohn-Sham spin-orbitals $\phi_p(\mathbf{r})$ as

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{pq} P_{pq} \phi_p(\mathbf{r})\phi_q^*(\mathbf{r}').$$

The expansion coefficients $P_{pr}$ (the discrete-index representation of the density matrix) satisfy the idempotence relation

$$\sum_q P_{pq} P_{qr} = P_{pr}.$$  

A simple derivation of this form of the idempotence relation for closed-shell systems is given in Appendix A.

The electron density $\rho(\mathbf{r})$ can easily be recovered from the density matrix $\rho(\mathbf{r}, \mathbf{r}')$:

$$\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}) = \sum_{pq} P_{pq} \phi_p(\mathbf{r})\phi_q^*(\mathbf{r}).$$

In addition to the idempotence relation, $P_{pr}$ obeys the Heisenberg equation-of-motion (see p. 440 of Ref. 50):

$$\sum_q \{F_{pq} P_{qr} - P_{pq} F_{qr}\} = i \frac{\partial P_{pr}}{\partial t}.$$  

For a non-hybrid density-functional, the Fock-like matrix $\mathbf{F}$ is

$$F_{pq} = \int \phi_p^*(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 + \sum_A -\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \right) \phi_q(\mathbf{r}) d\mathbf{r} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \delta \frac{E^{XC}[\rho]}{\delta \rho(\mathbf{r})} \phi_q(\mathbf{r}) d\mathbf{r}.$$
where \( P(r, r') \) is the permutation operator that creates the exact Hartree-Fock (HF) exchange, and \( c_H \) is a coefficient that mixes in HF exchange. The \( c_H = 0 \) limit recovers the pure DFT expression of Eq. (5). The \( c_H = 1 \) limit recovers the pure HF Fock matrix.

Now, suppose there is an external perturbation, due to a time-dependent electric field, with matrix elements

\[
g_{pq} = \frac{1}{2} \lambda \left[ h_{pq} e^{-i\omega t} + h_{qp}^* e^{i\omega t} \right],
\]

where \( \lambda \) controls the strength of the perturbation and

\[
h_{pq} = \int \phi_p^*(r) (\mathbf{E} \cdot \mathbf{u}) \phi_q(r) \, dr = \sum_{\xi=1}^{3} E_\xi H_{\xi pq},
\]

is a matrix element that couples the dipole-moment operator \( \mu_\xi = -\hat{r}_\xi \) (\( r_1 = x, r_2 = y, r_3 = z \)), to the external electric field \( E_\xi \). For simplicity of notation, only one frequency \( \omega \) is used but it is not difficult to generalize to the case of multiple frequencies.

Both the density matrix and the Fock matrix can be expanded in powers of \( \lambda \), thereby controlling the strength of the external perturbation (Eqs. (9) and (10)):

\[
P_{pq} = P_{pq}^{(0)} + \lambda P_{pq}^{(1)} + \lambda^2 P_{pq}^{(2)} + \lambda^3 P_{pq}^{(3)} + \ldots,
\]

\[
F_{pq} = F_{pq}^{(0)} + \lambda F_{pq}^{(1)} + \lambda^2 F_{pq}^{(2)} + \lambda^3 F_{pq}^{(3)} + \ldots.
\]

In the following, \( \lambda = 1 \) is assumed for simplicity.

The expansions in Eqs. (9) and (10) result in a sequence of idempotence and equation-of-motion relations. In the zeroth order, the idempotence relation

\[
\sum_q P_{pq}^{(0)} P_{qr}^{(0)} = P_{pr}^{(0)}
\]

is trivially satisfied due to

\[
P_{ia}^{(0)} = P_{ai}^{(0)} = P_{ab}^{(0)} = 0
\]

(\( i,j,\ldots \) are used for occupied orbitals, \( a, b, \ldots \) for unoccupied orbitals, and \( q, q', \ldots \) for all orbitals), and

\[
P_{ij}^{(0)} = \delta_{ij}.
\]

The right-hand side of Eq. (13) is the Kronecker delta. The ground state Kohn-Sham equation, Eq. (14), is a special case of the equation of-motion, Eq. (4), such that

\[
\sum_q \{ F_{pq}^{(0)} P_{qr}^{(0)} - P_{pq}^{(0)} F_{qr}^{(0)} \} = 0,
\]

where

\[
F_{pq}^{(0)} = \delta_{pq} \varepsilon_p.
\]

In Eq. (15) \( \varepsilon_p \) are the Kohn-Sham orbital energies. The higher orders of the idempotence relation can also be derived from Eqs. (2) and (8):

\[
\sum_q \{ P_{pq}^{(1)} P_{qr}^{(1)} - P_{pq}^{(0)} P_{qr}^{(1)} \} = P_{pr}^{(1)}
\]

\[
\sum_q \{ P_{pq}^{(2)} P_{qr}^{(2)} + P_{pq}^{(1)} P_{qr}^{(1)} + P_{pq}^{(0)} P_{qr}^{(0)} \} = P_{pr}^{(2)}
\]

\[
\sum_q \{ P_{pq}^{(3)} P_{qr}^{(3)} + P_{pq}^{(2)} P_{qr}^{(2)} + P_{pq}^{(1)} P_{qr}^{(1)} + P_{pq}^{(0)} P_{qr}^{(0)} \} = P_{pr}^{(3)}
\]

and so on. The higher orders of the equations-of-motion are

\[
\sum_q \{ F_{pq}^{(1)} P_{qr}^{(1)} - P_{pq}^{(1)} F_{qr}^{(1)} \} + \sum_q \{ F_{pq}^{(0)} P_{qr}^{(1)} - P_{pq}^{(0)} F_{qr}^{(0)} \} = i \frac{\partial P_{pr}^{(1)}}{\partial t},
\]

\[
\sum_q \{ F_{pq}^{(2)} P_{qr}^{(2)} + P_{pq}^{(1)} P_{qr}^{(1)} + P_{pq}^{(0)} P_{qr}^{(0)} \} + \sum_q \{ F_{pq}^{(0)} P_{qr}^{(1)} - P_{pq}^{(0)} F_{qr}^{(0)} \} = i \frac{\partial P_{pr}^{(2)}}{\partial t},
\]

\[
\sum_q \{ F_{pq}^{(3)} P_{qr}^{(3)} + P_{pq}^{(2)} P_{qr}^{(2)} + P_{pq}^{(1)} P_{qr}^{(1)} + P_{pq}^{(0)} P_{qr}^{(0)} \} + \sum_q \{ F_{pq}^{(0)} P_{qr}^{(1)} - P_{pq}^{(1)} F_{qr}^{(1)} \} = i \frac{\partial P_{pr}^{(3)}}{\partial t},
\]

and so on.

In order to relate the above density-matrix formalism to the molecular (hyper-) polarizabilities, consider the time-dependent induced polarization \( p_\xi(t) \) [for simplicity, assume \( f_{pq} = f_{qp}^* \), i.e., the external perturbation is of the form \( \delta_{pq}(t) = h_{pq}(\omega) \cos(\omega t) \)], where the index \( \xi \in \{x, y, z\} \) specifies the Cartesian component of the vector:

\[
p_\xi(t) = \mu_\xi^P + p_\xi(0) + p_\xi(\omega) \cos(\omega t) + p_\xi(2\omega) \cos(2\omega t) + \ldots,
\]

where \( \mu_\xi^P \) is the permanent ground-state dipole-moment, and the first three Fourier amplitudes of the time-dependent part are

\[
p_\xi(0) = \frac{1}{4} \sum_{\xi,\eta=1}^{3} \beta_{\xi\eta}(0; -\omega, \omega) E_\xi(-\omega) E_\eta(\omega) + \ldots,
\]

\[
p_\xi(\omega) = \sum_{\xi=1}^{3} \alpha_{\xi}( -\omega, \omega) E_\xi(\omega) + \ldots,
\]
\[ p_\xi (2\omega) = \frac{1}{4} \sum_{\zeta, \eta = 1}^{3} \beta_{\xi \zeta \eta} (-2\omega; \omega, \omega) E_\zeta(\omega) E_\eta(\omega) + \ldots \]  
\alpha_{\zeta \xi} \] is the polarizability tensor and \( \beta_{\xi \zeta \eta} \) is the first hyperpolarizability tensor.

The polarizability tensor \( \alpha_{\zeta \xi} (-\omega; \omega) \) has two variables. The frequency \( \omega \) to the right of the semicolon is the frequency of the incoming electric field \( E_\zeta(\omega) \). The outgoing frequency \(-\omega \) to the left of the semicolon is the frequency of the induced polarization \( p_\xi(\omega) \). The sum of all of the variables is taken to be zero. Similarly, the hyperpolarizability tensor \( \beta_{\xi \zeta \eta} (-2\omega; \omega, \omega) \) has two frequencies \( \omega \) to the right of the semicolon that correspond to the two incoming fields \( E_\zeta(\omega) \) and \( E_\eta(\omega) \). There is one “outgoing” frequency \(-2\omega \) to the left of the semicolon that corresponds to the induced polarization \( p_\xi(\omega) \). Once again the sum of all of the variables inside the parentheses is assumed to be zero. \( \beta_{\xi \zeta \eta} (0; -\omega, \omega) \) describes the SHG process and \( \beta_{\xi \zeta \eta} (0; -\omega, \omega) \) describes the OR process. Note that \( p_\xi (0), p_\xi (\omega), p_\xi (2\omega) \), etc. are the Fourier amplitudes of 
\[ p_\xi(t) - \mu_\xi^{(0)} = \sum_{p,q} \mu_{\xi, pq} \left( P_{pq}^{(1)} + P_{pq}^{(2)} + \ldots \right). \]

Based on Eqs. (23)–(25), the components of the (hyper-)polarizability tensors can be obtained by differentiation
\[ \alpha_{\zeta \xi} (-\omega; \omega) = \left. \frac{\partial p_\xi(\omega)}{\partial E_\zeta} \right|_{E=0}, \]
\[ \beta_{\xi \zeta \eta} (-2\omega; \omega, \omega) = \left. \frac{\partial^2 p_\xi(2\omega)}{\partial E_\zeta \partial E_\eta} \right|_{E=0}, \]
\[ \beta_{\xi \zeta \eta} (0; -\omega, \omega) = \left. \frac{\partial^2 p_\xi(0)}{\partial E_\zeta \partial E_\eta} \right|_{E=0}. \]

Only \( P_{pq}^{(1)} \) from the perturbative expansion on the right-hand side of Eq. (26) contributes to \( \alpha_{\zeta \xi} (-\omega; \omega) \), as both are linear terms and only \( P_{pq}^{(2)} \) contributes to \( \beta_{\xi \zeta \eta} (-2\omega; \omega, \omega) \) and \( \beta_{\xi \zeta \eta} (0; -\omega, \omega) \) as these quantities are all quadratic terms, for example,
\[ \alpha_{\zeta \xi} (-\omega; \omega) = \left. \frac{\partial}{\partial E_\zeta} \left( \sum_{p,q} \mu_{\xi, pq} P_{pq}^{(1)} \right) \right|_{E=0} \]
\[ = \sum_{p,q} \mu_{\xi, pq} \left. \left( \frac{\partial P_{pq}^{(1)}}{\partial E_\zeta} \right) \right|_{E=0}. \]

### III. LINEAR-RESPONSE TDDFT

The first-order (linear) response of the density-matrix is expressed as
\[ P_{pq}^{(1)} = \frac{1}{2} \left( d_{pq} e^{-i\omega t} + d_{qp} e^{i\omega t} \right). \]

This form follows from standard time-dependent perturbation theory arguments. The first-order idempotence relation further requires that \( d_{ij} = 0 \) and \( d_{ab} = 0 \), i.e., the Fourier component of the density matrix elements are non-zero only for the occupied-occupied and unoccupied-occupied pairs of indices.

The first-order response of the Fock matrix is due to the original external perturbation, as well as to the dependence of the Fock matrix on the density
\[ F_{pq}^{(1)} = g_{pq} + \sum_{r,s} \frac{\partial F_{pq}}{\partial P_{rs}} P_{rs}^{(1)}. \]

The response of the Fock matrix due to the density matrix response is
\[ \delta F_{pq} = \sum_{r,s} \frac{\partial F_{pq}}{\partial P_{rs}} P_{rs} + \frac{1}{2!} \sum_{r,s} \frac{\partial^2 F_{pq}}{\partial P_{rs} \partial P_{r's'}} P_{rs} P_{r's'} \]
\[ + \frac{1}{3!} \sum_{r,s} \frac{\partial^3 F_{pq}}{\partial P_{rs} \partial P_{r's'} \partial P_{r's''}} P_{rs} P_{r's'} P_{r's''} + \ldots, \]

where \( P_{pq} \) is the full density matrix from the left-hand side of Eq. (9) and \( F_{pq} \) is the full Fock matrix from the left-hand side of Eq. (10). In order to obtain the Fock matrix response to a given order, the density matrix expansion from the right-hand side of Eq. (9) must be inserted into Eq. (33), and the result terminated at the desired order.

Next, the explicit forms of the frequency-dependent density matrix and Fock matrix up to first order, given in Eqs. (31) and (32), respectively, are inserted into the first-order equation-of-motion given in Eq. (19), and all of the terms in front of \( e^{-i\omega t} \) on both sides of the resulting equation are collected. These two steps give
\[ \sum_q \left[ F_{pq}^{(0)} \delta_{qr} - d_{pq} F_{qr}^{(0)} + \left( \hbar_{pq} + \sum_{st} \frac{\partial F_{pq}}{\partial P_{st}} d_{st} \right) P_{qr}^{(0)} \right] - P_{pq}^{(0)} \left( \hbar_{qr} + \sum_{st} \frac{\partial F_{qr}}{\partial P_{st}} d_{st} \right) = \omega d_{pr}. \]

A similar procedure for \( e^{i\omega t} \) will produce the complex conjugate of Eq. (34). Denoting \( \chi_{ai} = d_{ai} \) and \( Y_{ai} = d_{ai} \), the following linear-response matrix equation is obtained
\[ \begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} X(\omega) \\ Y(\omega) \end{bmatrix} = \begin{bmatrix} h \\ \hbar \end{bmatrix}. \]

The solutions \( X \) and \( Y \) are vectors in terms of the index pairs “ai”; and the matrix elements of \( A \) and \( B \) are given by
\[ A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (i a | j b) - c_H (a b | ji) \]
\[ + (1 - c_H) f_{ia,jb}^{XH}. \]

and
\[ B_{ia,jb} = (a i | b j) - c_H (a j | b i) + (1 - c_H) f_{ia,jb}^{XH}. \]
The matrix elements of the exchange-correlation kernel \( f^{XC}_{ai,bj} \) are
\[
f^{XC}_{ai,bj} = \int \int \frac{\delta^2 E^{XC}[\rho]}{\delta \rho(r) \delta \rho(r')} \phi_i^n(r) \phi_j^n(r') \phi_i(r) \phi_j(r') \, dr \, dr'.
\] (38)

The matrix elements of the two-electron integral are
\[
(pq|sr) = \int \frac{\phi_p^n(r) \phi_q^n(r') \phi_s^n(r) \phi_r^n(r')}{|r - r'|} \, dr \, dr'.
\] (39)

The \( \epsilon_p \) are KS orbital energies. The external perturbation \( h_{ai} = \sum_{\xi} E_\xi \mu_{\xi,ai} \) (see Eq. (8)) is also a vector in terms of the index pairs “\( ai \).”

The linear response of the density matrix is
\[
P_{ai}^{(1)} = X_{ai} + Y_{ai}.
\] (40)

The matrix elements of the solution to Eq. (35) are used on the right-hand side of Eq. (40). To obtain the polarizability tensor \( \alpha_{\xi\zeta}(\omega) \) using Eq. (30), one needs \( \frac{\partial P_{ai}^{(1)}}{\partial E_\xi} \bigg|_{E=0} \) instead of \( P_{ai}^{(1)} \) itself. In order to obtain a response equation for \( \frac{\partial P_{ai}^{(1)}}{\partial E_\xi} \bigg|_{E=0} \) the derivative \( \frac{\partial}{\partial E_\xi} \) is taken on both sides of Eq. (35). Referring to Eq. (8), one can see that after the differentiation is carried out, the dipole moment \( \mu_\xi \) becomes the perturbation on the right-hand side of Eq. (35). Since the matrices \( A \) and \( B \) do not depend on the electric field, the differentiation on the left-hand side of Eq. (35) acts only on the \( X \) and \( Y \) tensors that depend implicitly on the electric field. Hence, if a component of the dipole moment \( \mu_\xi \) is used as a perturbation in the linear-response equation, then
\[
\left[ \begin{array}{cc} A & B \\ B & A \end{array} \right] - \omega \left[ \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right] \left[ \begin{array}{c} X_{\xi}(\omega) \\ Y_{\xi}(\omega) \end{array} \right] = - \left( \begin{array}{c} \mu_\xi \\ \mu_\xi \end{array} \right).
\] (41)

In Eq. (41), the dependence of the solution on the frequency \( \omega \) and on the \( \xi \)-component of the dipole moment \( \mu_\xi \) is explicitly noted. The polarizability tensor can be obtained from the solutions \( X_{\xi,ai}(\omega) \) and \( Y_{\xi,ai}(\omega) \):
\[
a_{\xi\zeta}(\omega) = \sum_{ai} \mu_{\xi,ai} (X_{\xi,ai}(\omega) + Y_{\xi,ai}(\omega)).
\] (42)

Equation (42) is a direct consequence of Eqs. (30) and (40). Note that
\[
\frac{\partial P_{pq}^{(1)}}{\partial E_\xi} \bigg|_{E=0} = X_{\xi,ai}(\omega) + Y_{\xi,ai}(\omega).
\] (43)

The polarizability tensor \( \alpha_{\xi\zeta}(\omega) \) diverges at resonances. It is therefore assumed that when \( \omega \) approaches an excitation frequency (resonance) \( \omega_n \), the external perturbation \( f_{ai} \) can be adiabatically removed due to the resonant nature of the excitation. Then, the right-hand side of Eq. (41) is zero, and Eq. (41) becomes
\[
\left[ \begin{array}{cc} A & B \\ B & A \end{array} \right] \left( \begin{array}{c} X_n \\ Y_n \end{array} \right) = \omega_n \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right) \left( \begin{array}{c} X_n \\ Y_n \end{array} \right).
\] (44)

The eigenvalue \( \omega_n \) corresponds to the \( n \)th excitation energy. The eigenvalues of Eq. (44) give the excitation spectrum and the eigenvectors form an orthonormal basis.

The solutions of the inhomogenous matrix equation (44) can be expressed in terms of the eigenvectors and eigenvalues of the homogeneous matrix equation by employing the spectral resolution method (see Appendix C). If the spectral resolution method is used, the averaged polarizability becomes
\[
\bar{\alpha}(-\omega; \omega) = \sum_{\xi=1}^{3} \alpha_{\xi\xi}(-\omega; \omega) = \sum_{n} \frac{f_{0n}}{\omega_n - \omega},
\] (45)

\( f_{0n} \) is an oscillator strength for the \( 0 \to n \) transition. Equation (45) reveals the divergent nature of the averaged polarizability near the excitation frequencies \( \omega_n \). In practice, an eigenvalue matrix equation of half the dimension of Eq. (44) is solved (see Appendix B).

IV. QUADRATIC-RESPONSE TDDFT

The second-order response of the density-matrix is
\[
P_{pq}^{(2)} = \frac{1}{2} (d_{pq}^{(2,2),2} e^{i2\omega t} + d_{pq}^{(2,2),1} e^{2i\omega t}) + d_{pq}^{(2,0)}. \] (46)

The first superscript index of the frequency-independent density matrix elements (Fourier coefficients) \( d_{pq}^{(2,2),2} \) and \( d_{pq}^{(2,0)} \) refers to the order of the response (2 means second order). The second superscript index refers to the frequency in the exponent; for example, \( d_{pq}^{(2,2),2} \) is the second order coefficient multiplying \( e^{i2\omega t} \) and \( d_{pq}^{(2,0)} \) is the coefficient multiplying \( e^{2i\omega t} = 1 \). Also, \( d_{pq}^{(2,2),2} = d_{qp}^{(2,2),2} \) and \( d_{qp}^{(2,0)} = d_{qp}^{(2,0)} \). Since \( d_{pq}^{(2,0)} \) contributes only to the zero-frequency component of the dipole moment and hence to \( \beta_{\xi\zeta}(0; -\omega, \omega) \), it will not be considered here. The second-order idempotence relation determines the exact form of the occupied-occupied and unoccupied-unoccupied blocks of the second order density matrix directly in terms of the first-order density matrix components:
\[
P_{ij}^{(2)} = -\sum_{a} P_{ia}^{(1)} P_{aj}^{(1)}
\] (47)

and
\[
P_{ab}^{(2)} = \sum_{i} P_{ai}^{(1)} P_{ih}^{(1)}
\] (48)

The second-order response of the Fock-matrix is
\[
F_{pq}^{(2)} = \sum_{rs} \frac{\partial F_{pq}}{\partial P_{rs}} P_{rs}^{(2)} + \frac{1}{2!} \sum_{rs} \frac{\partial^2 F_{pq}}{\partial P_{rs} \partial P_{rs}} P_{rs}^{(1)} P_{rs}^{(1)}
\] (49)

where
\[
\frac{\partial^2 F_{pq}}{\partial P_{rs} \partial P_{rs}} = \int \int \frac{\delta^3 E_{XC}[\rho]}{\delta \rho(r) \delta \rho(r') \delta \rho(r''')} \phi_p^*(r) \phi_q(r)
\times \phi_s^*(r') \phi_r^*(r'') \phi_r(r'') \, dr \, dr' \, dr''.
\] (50)

Equation (50) follows from Eqs. (5) and (6).

Using the explicit form of \( F_{pq}^{(2)} \) from Eq. (49) and inserting it into Eq. (20) results in an explicit form of the second-order equation-of-motion:
Compute the polarizability based on Eq. (27) for the polarizability solution gives rise to the SHG hyperpolarizability on just the linear response solution by using the “
\[
\beta_{\xi,\zeta,\eta}(\omega; \omega, \omega) = A + B + C,
\]

where any of the indices \( \xi, \zeta, \eta \) can be x, y, or z and A, B, and C in Eq. (56) are defined as

\[
A = \sum_{\text{perm.} \xi, \zeta, \eta} \left\{ \sum_{aij} X_{\xi,ai}(\omega_k) \left[ -\mu_{\xi,ij} + \sum_{c,k} f^{HXC}_{ij,c,k}(X_{\xi,ck}(\omega_k) \right] + Y_{\xi,ck}(\omega_k) \right\} Y_{\eta,ai}(\omega_k),
\]

\[
B = - \sum_{\text{perm.} \xi, \zeta, \eta} \left\{ \sum_{aij} X_{\xi,ai}(\omega_k) \left[ -\mu_{\xi,ij} + \sum_{c,k} f^{HXC}_{ij,c,k}(X_{\xi,ck}(\omega_k) \right] + Y_{\xi,ck}(\omega_k) \right\} Y_{\eta,ai}(\omega_k),
\]

\[
C = \sum_{\text{perm.} \xi, \zeta, \eta} \left\{ \sum_{aij,bjck} g^{XC}_{ai,bj,c,k}(X_{\xi,ai}(\omega_k) + Y_{\xi,ai}(\omega_k))(X_{\xi,bj}(\omega_k) + Y_{\xi,bj}(\omega_k)) \right\}.
\]

The “permutational sum” (perm. in Eqs. (57)–(59)) of a given quantity \( Q_{\xi,\zeta,\eta} \) is

\[
Q_{\xi,\zeta,\eta} = Q_{\xi,\zeta,\eta} + Q_{\xi,\eta,\zeta} + Q_{\zeta,\xi,\eta} + Q_{\zeta,\eta,\xi} + Q_{\xi,\zeta,\eta} + Q_{\eta,\xi,\zeta} + Q_{\eta,\zeta,\xi},
\]

and

\[
f^{HXC}_{ab,cd} = (ia|jb) - c_H(ab|ji) + (1 - c_H)f^{XC}_{ia,jb}.
\]
are the matrix elements of the combined Hartree-exchange-correlation kernel and
\[
\gamma_{ai,bj,ck}^{XC} = \iint \frac{\delta^3 E^{XC}[\rho]}{\delta \rho(r) \delta \rho(r') \delta \rho(r'')} \phi_i^*(r) \phi_j^*(r') \phi_k(r''') d\mathbf{r} d\mathbf{r'} d\mathbf{r''} 
\]
are the matrix elements of the third functional derivative of the exchange-correlation energy density functional.

The TPA absorption cross-section is proportional to the following residue:
\[
\lim_{\omega \to 0} (2\omega - \omega_0) \tilde{\rho}_{\xi \xi} (2\omega ; \omega, \omega) = \tau_{\xi \xi} (\omega_0) \langle 0 \mid \mathbf{r} \rangle |n\rangle. 
\]

Hence, the TPA cross-section itself is
\[
\sigma_{\xi \xi} (\omega_n) = A + B + C. 
\]

The three terms on the right-hand side of Eq. (64) are
\[
A = - \sum_{\text{perm} \xi,\eta} \sum_{ai} X_{\xi,ai}(\omega_\xi) \left[ - \mu_{\xi,ij}(1 - \delta_{\xi \eta}) + \sum_{ck} f_{ij,ck}^{\text{xc}} (X_{\xi,ck}(\omega_\xi) + Y_{\xi,ck}(\omega_\xi)) Y_{n,aj} \right],
\]
\[
B = \sum_{\text{perm} \xi,\eta} \left[ \sum_{iab} X_{\xi,ai}(\omega_\xi) \left[ - \eta_{\xi,ab}(1 - \delta_{\xi \eta}) + \sum_{ck} f_{iabck}^{\text{xc}} (X_{\xi,ck}(\omega_\xi) + Y_{\xi,ck}(\omega_\xi)) Y_{n,ba} \right] \right],
\]
\[
C = - \sum_{\text{perm} \xi,\eta} \left[ \sum_{ai} \sum_{bj} \gamma_{ai,bj,ck}^{XC} (X_{\xi,ai}(\omega_\xi) + Y_{\xi,ai}(\omega_\xi)) X_{\eta,bj}(\omega_\eta) (X_{\eta,ck}(\omega_\eta) + Y_{\eta,ck}(\omega_\eta)) \right].
\]

The value of the TPA cross section matrix element in Eq. (64) depends on the choice of coordinate system. However, orientationally averaged TPA transition moment quantities can be constructed from the matrix elements of the TPA. For a linear polarization of the light such an orientationally averaged TPA transition moment is
\[
2D_f + 4D_g,
\]
where \(D_f\) and \(D_g\) are defined as
\[
D_f = \frac{1}{30} \sum_{\xi \xi} \sigma_{\xi \xi} \sigma_{\xi \xi} 
\]
and
\[
D_g = \frac{1}{30} \sum_{\xi \xi} \sigma_{\xi \xi} \sigma_{\xi \xi},
\]
while the orientationally averaged TPA transition moment for a circular polarization is
\[
-2D_f + 6D_g.
\]

The polarization ratio is
\[
\frac{(-D_f + 3D_g)}{(D_f + 2D_g)}. 
\]

V. THE EFP METHOD

In the ground-state DFT/EFP1 method, the interaction between the DFT solute and the EFP water molecules is represented by an effective one-body potential that has a Coulomb, polarization, and remainder component. The remainder term, which is fitted to a DFT water dimer potential, contains exchange repulsion, charge transfer, and short-range correlation contributions. The effective potential \(v^{\text{EFP1}}(r)\) is added to the usual Kohn-Sham potential, but since only the EFP polarization term \(v^{\text{POL}}(r)\) depends on the electron density, only the EFP1 polarization term is updated during the SCF cycles.

A key ingredient in the TDDFT linear response equation is the exchange-correlation kernel \(f^{\text{xc}}(r, r') = \frac{\delta f^{\text{xc}}[\rho(r)]}{\delta \rho(r)}\), which is a functional derivative of the exchange-correlation potential \(v^{\text{xc}}[\rho](r)\) with respect to the density. Since only the polarization component of the EFP1 effective potential \(v^{\text{POL}}[\rho](r)\) has a non-zero functional derivative, the EFP1 correction to the linear-response TDDFT matrix equation is given by the following replacement:
\[
f^{\text{xc}}(r, r') \rightarrow f^{\text{xc}}(r, r') + f^{\text{POL}}(r, r').
\]

The last term in Eq. (73) is the EFP polarization kernel \(f^{\text{POL}}(r, r') = \frac{\delta v^{\text{POL}}[\rho(r)]}{\delta \rho(r)}\). The EFP polarization kernel \(f^{\text{POL}}(r, r')\), the derivative of the polarization potential with respect to the density, is expressed through the EFP polarizability tensor. For applications of the combined TDDFT/EFP method, see Refs. 43 and 44.

In order to extend the TDDFT/EFP1 scheme to nonlinear-response TDDFT, the replacement as given in Eq. (73) is performed in the expressions for the first hyperpolarizability and TPA cross-section. Since the EFP polarization potential \(v^{\text{POL}}[\rho](r)\) has only a linear dependence on the density, the EFP polarization kernel \(f^{\text{POL}}(r, r')\) has no effective density dependence and hence \(g^{\text{POL}}(r, r', r'') = \frac{\delta v^{\text{POL}}[\rho(r)]}{\delta \rho(r)} \frac{\delta v^{\text{POL}}[\rho(r')]}{\delta \rho(r')} \) \(= 0\). Therefore, there is no need to correct \(g^{\text{xc}}(r, r', r'') = \frac{\delta f^{\text{xc}}[\rho(r)]}{\delta \rho(r)}\) in Eqs. (59) and (67).

VI. COMPUTATIONAL DETAILS

As an illustration, the difficult to model hyperpolarizability and two-photon absorption of bulk water will be computed with the new nonlinear-response TDDFT/EFP method as implemented in GAMESS.

A system of 400 EFP molecules was equilibrated using a molecular dynamics (MD) simulation in the NVT ensemble. Upon equilibration, a smaller spherical sub-system of 150 EFP waters with a radius of about 9 Å was extracted and one water molecule approximately in the middle of the sub-system was selected to be described by B3LYP/HD(d,p). A harmonic restraint potential with a force field of...
10 kcal/mol/Å², effectively keeping the system in the NPT ensemble, was applied at the spherical boundary in order to prevent the evaporation of the water droplet. The combined DFT/EFP system was equilibrated again for 55 ps and the next 45 ps production run was used to collect and average the optical properties of interest. All of the MD runs were done at 298 K using the velocity-Verlet algorithm with a time step of 0.5 fs.

TDDFT (B3LYP)/EFP linear and nonlinear optical properties of water were computed on snapshots from the production run of the ground state DFT/EFP MD simulation. The d-aug-cc-pVDZ basis set was used for a proper description of the NLO properties. The snapshots from the MD trajectory were chosen with a separation of 250 fs to allow enough time for de-correlation between the snapshots to occur. Figure 1 shows both the running values (blue) and their time-averages (green) for several properties to illustrate the type and magnitude of statistical fluctuations during the MD simulation. All of the gas-phase optical values were computed with TDDFT using B3LYP/d-aug-cc-pVDZ.

The average first excited state (11B₁) excitation energy is computed to be 7.72 eV with a solvent shift of 0.5 eV with respect to the gas phase first excited state energy of 7.22 eV. The corresponding experimental values are 8.2 eV for the liquid phase with a solvent shift of 0.8 eV relative to the 7.4 eV gas phase value.

According to the experimental data, the sign of the SHG hyperpolarizability of liquid water changes relative to that of gas phase water. The average computed SHG hyperpolarizability of liquid water (11.8 a.u.) at the frequency ω = 0.043 a.u. compares reasonably well with the experimental value of 15.5 a.u. at the same frequency. The gas phase TDDFT/B3LYP/d-aug-cc-pVDZ SHG hyperpolarizability of water at ω = 0.0656 is predicted to be −5.9 a.u., again in reasonable agreement with the experimental value of −10.9 a.u. at the same frequency. Importantly, the calculations presented here predict the observed sign change.

The computed average TPA transition moment to the first excited state by two photons of equal energy is 9.9 a.u. with a solvent shift of 4.9 a.u. with respect to the gas phase value of 5.0 a.u. In Ref. 56, the same quantities were computed with a combined coupled cluster/molecular mechanics method to be, respectively, 7.2 a.u., 2.2 a.u., and 5.0 a.u. Reference 56 discusses the favorable qualitative comparison of the computed liquid phase TPA values with experiment but there is no experimental basis to validate the computed TPA solvent shifts.

VII. CONCLUSION

A nonlinear response TDDFT computational scheme has been described that can successfully be combined with the EFP method to account for solvent effects. The combined method is able to correctly predict both gas phase values and aqueous solvent shifts for several important nonlinear properties. More details on the prediction of solvent effects (including non-aqueous solvents) within the presented TDDFT/EFP scheme will be described in subsequent publications.

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APPENDIX A: THE IDEMPOTENCE RELATION OF THE DENSITY MATRIX

Expand the density-matrix in the basis of natural spin-orbitals

$$\rho(r, r') = \sum_{i=1}^{N} \phi_i(r) \phi_i^*(r'). \quad (A1)$$

Using this expansion it is easy to see that

$$\rho(r, r') = \int \rho(r, r'') \rho(r'', r') dr'' \quad (A2)$$

holds. This is the idempotence relation of the density matrix in the coordinate representation. In order to get the form used in the text, insert the expansion of the density matrix in terms of the Kohn-Sham spinorbitals in the above equation.

APPENDIX B: THE MODIFIED LINEAR-RESPONSE TDDFT EQUATION AND THE BIORTHOGONALITY CONDITION

The matrix equation can be simplified by a unitary transformation, which is equivalent to forming new block rows by adding and subtracting the original two block rows and thus forming two matrix equations of half-size, i.e.,

$$(A + B)(X + Y) = \omega (X - Y) \quad (B1)$$
\[ (A - B)(X - Y) = \omega (X + Y). \] (B2)

Multiplying both sides of the first matrix equation on the left by \((A - B)\) and using the second matrix equation results in a matrix eigenvalue equation
\[ (A - B)(A + B)(X + Y) = \omega^2 (X + Y). \] (B3)

Equation (B3) is half the size of the original matrix eigenvalue equation. This is still a non-Hermitian problem through \((X + Y)\) and \((X - Y)\) are the right- and left-eigenvectors of the non-Hermitian matrix \((A - B)(A + B)\) and the usual biorthonormality condition
\[ (X + Y)_i \cdot (X - Y)_j = \delta_{ij}. \] (B4)

is imposed upon them, which condition could be also expressed as
\[ X_i \cdot X_j - Y_i \cdot Y_j = \delta_{ij}. \] (B5)

The matrix equation can further be modified by multiplying both sides on the left by \((A - B)^{-1/2}\) and redefining the eigenvectors
\[ (A - B)^{1/2} (A + B)(A - B)^{-1/2} (\tilde{X} + \tilde{Y}) = \omega^2 (\tilde{X} + \tilde{Y}), \] (B6)

where \((\tilde{X} + \tilde{Y}) = (A - B)^{-1/2} (X + Y).\) This is a Hermitian eigenvalue problem.

The actual linear-response TDDFT implementation in GAMESS uses the Davidson algorithm based on both the Hermitian and non-Hermitian eigenproblem formulations (see Ref. 59 for details).

**APPENDIX C: THE SPECTRAL RESOLUTION METHOD**

The eigenvectors \(\phi_i(r)\) of a Hermitian operator \(L\), i.e.,
\[ L\phi_i(r) = \lambda_i \phi_i(r) \] (C1)
form an orthogonal basis, so any function, say \(u(r)\), can be expanded in it, i.e.,
\[ u(r) = \sum_{i=1}^{\infty} a_i \phi_i(r). \] (C2)

The action of \(L\) on \(u(r)\) becomes
\[ Lu(r) = \sum_{i=1}^{\infty} a_i \lambda_i \phi_i(r). \] (C3)

This representation is convenient for obtaining a function of \(L\), i.e.,
\[ f(L)u(r) = \sum_{i=1}^{\infty} a_i f(\lambda_i) \phi_i(r) \] (C4)
and in the particular case of \(f(L) = (L - \lambda)^{-1}\), it becomes
\[ (L - \lambda)^{-1} u(r) = \sum_{i=1}^{\infty} \frac{a_i \phi_i(r)}{\lambda_i - \lambda}. \] (C5)

For additional information see Ref. 60.

The solutions of the non-homogenous matrix equation in Eq. (41) can be expressed in terms of the eigenvectors and eigenvalues of the homogenous matrix equation in Eq. (44) by employing the spectral resolution method:
\[ X_{\omega}(\omega) = \sum_n [\mu_n \cdot (X_n + Y_n)] \left( \frac{X_n}{\omega_n - \omega} + \frac{Y_n}{\omega_n + \omega} \right) \] (C6)

and
\[ Y_{\omega}(\omega) = \sum_n [\mu_n \cdot (X_n + Y_n)] \left( \frac{Y_n}{\omega_n - \omega} + \frac{X_n}{\omega_n + \omega} \right). \] (C7)

The scalar products on the right-hand side of Eqs. (46) and (47) are expressed in terms of the ai-matrix elements. The above expansions have a formal similarity with the sum-over-state (SOS) method, but the basis of the usual SOS expansion is different.

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