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Efficient exact-exchange time-dependent density-functional theory methods and their relation to time-dependent Hartree–Fock

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A recently introduced time-dependent exact-exchange (TDEXX) method, i.e., a response method based on time-dependent density-functional theory that treats the frequency-dependent exchange kernel exactly, is reformulated. In the reformulated version of the TDEXX method electronic excitation energies can be calculated by solving a linear generalized eigenvalue problem while in the original version of the TDEXX method a laborious frequency iteration is required in the calculation of each excitation energy. The lowest eigenvalues of the new TDEXX eigenvalue equation corresponding to the lowest excitation energies can be efficiently obtained by, e.g., a version of the Davidson algorithm appropriate for generalized eigenvalue problems. Alternatively, with the help of a series expansion of the new TDEXX eigenvalue equation, standard eigensolvers for large regular eigenvalue problems, e.g., the standard Davidson algorithm, can be used to efficiently calculate the lowest excitation energies. With the help of the series expansion as well, the relation between the TDEXX method and time-dependent Hartree–Fock is analyzed. Several ways to take into account correlation in addition to the exact treatment of exchange in the TDEXX method are discussed, e.g., a scaling of the Kohn–Sham eigenvalues, the inclusion of (semi)local approximate correlation potentials, or hybrids of the exact-exchange kernel with kernels within the adiabatic local density approximation. The lowest lying excitations of the molecules ethylene, acetaldehyde, and pyridine are considered as examples.

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I. INTRODUCTION

Methods based on time-dependent density-functional theory (TDDFT), more precisely time-dependent density-functional response methods,^{1,2} at present, are probably the most widely used methods to describe electronically excited states of molecules. Despite their widespread usage conventional TDDFT response methods, i.e., TDDFT response methods based on approximate exchange-correlation functionals employing the local density approximation (LDA) or generalized gradient approximations (GGAs), suffer from a whole list of severe shortcomings.

(i) Excitations with charge-transfer character cannot be described correctly.^{3–10} Charge-transfer excitations are calculated at much too low energies and therefore appear in the wrong region of the excitation spectrum. In case of charge transfer excitations between two fragments the behavior of the charge-transfer excitation energy with the distance of the fragments is qualitatively wrong. This not only makes the calculation of charge-transfer excitations impossible with conventional TDDFT response methods but also can impair the description of simple valence-valence excitations because the charge-transfer excitations erroneously occur in the same energy region and may even interact with the former or with excitations of some charge-transfer character.

(ii) Excitations into states with Rydberg character cannot be described by conventional TDDFT response methods.¹¹ This problem arises from the fact that the orbital and

eigenvalue spectrum of conventional Kohn–Sham (KS) methods is qualitatively wrong and does not contain Rydberg orbitals. Because KS orbitals and eigenvalues are the input data of density-functional response methods it is not surprising that conventional TDDFT response methods cannot describe Rydberg excitations. Indeed, excitation energies from density-functional response methods in many cases, including the case of Rydberg excitations, can be considered as KS eigenvalue differences plus a correction given by the density-functional response method.

(iii) Excitation energies of long chain-like aromatic molecules^{12–16} are systematically underestimated by conventional TDDFT response methods.

(iv) Excitation energies that, in a one-electron picture, can be characterized as two-electron excitations, cannot be treated in conventional TDDFT response methods. It has, however, been reported that standard TDDFT methods, to some extent, are capable to describe double excited states in contrast to the configuration interaction singles method.¹⁷ Nevertheless, there has been quite some effort in recent years to extend TDDFT methods to multielectron excitations.^{18–20}

(v) Even for simple valence-valence excitation energies the accuracy of conventional TDDFT response methods is quite limited, deviations from experiment of up to half an electron volt are not uncommon if nonhybrid functionals are used.²¹ With hybrid functionals this problem is often less severe, however, even with hybrid functionals the high lying core excitations are considerably underestimated due to self-interaction errors.²²

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One way to overcome some of the problems of conventional TDDFT response methods is to go beyond LDA and GGA exchange-correlation functionals^{23–25} and to turn to density-functional methods with orbital-dependent functionals,²⁶ in particular to methods that treat the exchange exactly.^{27–39} Such exact-exchange (EXX) KS and TDDFT response methods must not be confused with Hartree–Fock (HF) and time-dependent Hartree–Fock (TDHF) methods. In HF as well as EXX methods exchange is treated exactly according to the respective definitions. However, these definitions are different. This most obviously shows up in the exchange potential which is a nonlocal potential in the case of HF and a local multiplicative potential in the case of EXX. A recently introduced time-dependent exact-exchange (TDEXX) response method,^{37–39} i.e., a density-functional response method that is based on EXX orbitals and eigenvalues and employs the exact frequency-dependent exchange kernel,^{40–44} solves the problems (i), (ii), and (iii) of the above list. The exchange-correlation kernel is the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density and is the density-functional occurring in linear density-functional response methods. In conventional density-functional response methods the frequency dependence of the kernel is neglected (an approximation called the adiabatic approximation) and the kernel is obtained simply as the derivative of LDA and GGA exchange-correlation potentials with respect to the electron density.

The problem of treating two-electron excitations, problem (iv) of the above list, is not solved by the recently introduced TDEXX response methods. However, in many cases this problem does not show up and an efficient TDDFT response method that solves all the other listed shortcomings would be a great step forward. In the recently introduced TDEXX response method³⁷ electron correlation was completely neglected, although it is straightforward to include correlation at the LDA or GGA level. Excitation energies from an exchange-only TDEXX response method are similar to those from TDHF. TDHF like TDEXX does not suffer from shortcomings (i), (ii), and (iii). However, both TDHF and exchange-only TDEXX excitations energies are not very accurate, indeed, for valence-valence excitations they are often less accurate than conventional TDDFT excitations energies. A further disadvantage of the recently presented TDEXX procedure is that it is computationally much more demanding than TDHF and conventional TDDFT methods because it does not only require the determination of the lowest eigenvalues of a linear eigenvalue problem. Instead, due to the frequency dependence of the exact-exchange kernel, separately for each excitation, a nonlinear eigenvalue problem has to be iteratively solved.

In order to turn the TDEXX procedure of Refs. 37–39 into an efficient, generally applicable, and sufficiently accurate approach, two tasks have to be tackled. The efficiency has to be increased and the accuracy has to be improved. In this work we focus, for the most part, on the first task and introduce a linear TDEXX procedure that requires similar computational effort than conventional TDDFT or TDHF response methods. To this end, firstly, we convert the basic nonlinear

TDEXX eigenvalue problem into a linear generalized eigenvalue problem. Then, in a second step, we present strategies to solve this generalized eigenvalue problem by efficient procedures like the Davidson algorithm, which is frequently employed in conventional TDDFT and TDHF methods. Indeed, the presented TDEXX procedure can be straightforwardly implemented in any computer code containing a TDHF module. With the TDEXX procedure presented here, one of the two above tasks on the way to an efficient, generally applicable, and accurate TDDFT method has been solved. Some information concerning the second task, the improvement of accuracy, is given in this work by considering how modifications of the KS eigenvalue spectrum and the inclusion of correlation at the LDA and GGA level in the KS potential and in the kernel of the actual TDDFT calculation influences the performance of TDEXX response methods.

The reformulation of the TDEXX equation introduced here facilitates a comparison of TDEXX and TDHF methods. We therefore discuss the relations between the two methods.

The article is organized as follows. In Sec. II on formalism, we first briefly review the derivation of a response equation for the effective KS potential that is better suited to deal with orbital-dependent exchange-correlation kernels than the standard TDDFT response equation for the electron density. Then the TDEXX equation underlying the TDEXX procedure of Ref. 37 is reconsidered. Next, the original TDEXX equation is reformulated, efficient methods to solve it are presented, and the relation to the basic equation of TDHF is discussed. Section III describes the computational details. In Sec. IV results for the test molecules ethylene, acetaldehyde, and pyridine are presented and the influence of modifications of the KS eigenvalue spectrum and the inclusion of LDA and GGA correlation is briefly investigated. In Sec. V concluding remarks are made.

II. FORMALISM

A. Response equation for the effective Kohn–Sham potential, TDEXX

We consider the linear response $\rho^{(1)}(\omega, \mathbf{r})$ of the electron density of an electronic system that is initially in its ground state to a time-dependent external perturbation $v^{(1)}(\omega, \mathbf{r})$ of frequency ω . The perturbation $v^{(1)}(\omega, \mathbf{r})$ has to be a local multiplicative potential in order to stay within the formal framework of density-functional theory. Within the time-dependent KS formalism this linear response of the electron density is determined with the help of the KS model system and is given by

$$\rho^{(1)}(\omega, \mathbf{r}) = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') v_s^{(1)}(\omega, \mathbf{r}'). \quad (1)$$

In Eq. (1) χ_s is the KS response function

$$\chi_s(\omega, \mathbf{r}, \mathbf{r}') = \sum_i^{\text{occ.}} \sum_a^{\text{unocc.}} \varphi_{ia}(\mathbf{r}) \lambda_{ia}(\omega) \varphi_{ia}(\mathbf{r}') \quad (2)$$

containing products $\varphi_{ia}(\mathbf{r}) = \varphi_i(\mathbf{r})\varphi_a(\mathbf{r})$ of occupied times unoccupied KS orbitals φ_i and φ_a , respectively. Throughout the manuscript we consider non-spin-polarized electronic

systems with real-valued KS orbitals. The factors $\lambda_{ia}(\omega)$ in the KS response function χ_s , Eq. (2), are given by

$$\lambda_{ia}(\omega) = 4\varepsilon_{ia}/(\omega^2 - \varepsilon_{ia}^2), \quad (3)$$

with $\varepsilon_{ia} = \varepsilon_a - \varepsilon_i$ denoting differences of the KS eigenvalues ε_a and ε_i of unoccupied and occupied KS orbitals, respectively. Throughout, indices i, j denote occupied and indices a, b denote unoccupied orbitals.

The first order change $v_s^{(1)}(\omega, \mathbf{r}')$ of the effective KS potential occurring in Eq. (1) corresponds to the applied external perturbation $v^{(1)}(\omega, \mathbf{r}')$. This first order change of the effective KS potential is given by

$$v_s^{(1)}(\omega, \mathbf{r}') = v^{(1)}(\omega, \mathbf{r}') + \int d\mathbf{r}'' f_{\text{Hxc}}(\omega, \mathbf{r}', \mathbf{r}'') \rho^{(1)}(\omega, \mathbf{r}''), \quad (4)$$

with f_{Hxc} denoting the sum of the Coulomb (Hartree) kernel

$$f_{\text{H}}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

and the exchange-correlation kernel f_{xc} , which is the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density. By inserting Eq. (4) into Eq. (1) and rearranging terms, the basic equation of time-dependent density-functional response theory is obtained,^{1,2}

$$\int d\mathbf{r}'' \left[\delta(\mathbf{r} - \mathbf{r}'') - \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') f_{\text{Hxc}}(\omega, \mathbf{r}', \mathbf{r}'') \right] \times \rho^{(1)}(\omega, \mathbf{r}'') = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') v^{(1)}(\omega, \mathbf{r}'). \quad (5)$$

Equation (5) can be directly derived⁴⁵ from the Runge–Gross theorem,⁴⁶ the basic theorem underlying TDDFT, without recourse to the action formalism, which requires great caution from a formal point of view^{47,48} in the context of density-functional response theory.

From now on, we will concentrate on the exchange contribution f_{x} of the exchange-correlation kernel and neglect the correlation contribution. However, including the latter contribution at the LDA or GGA level is straightforward. The exact frequency-dependent exchange kernel obeys the integral equation

$$f_{\text{x}}(\omega, \mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' d\mathbf{r}''' \chi_s^{-1}(\omega, \mathbf{r}, \mathbf{r}'') \times h_{\text{x}}(\omega, \mathbf{r}'', \mathbf{r}''') \chi_s^{-1}(\omega, \mathbf{r}''', \mathbf{r}'). \quad (6)$$

The function h_{x} in Eq. (6) (see Appendix A or Refs. 38 and 40–43) can be decomposed into two contributions. The dominant one is given by

$$h_{\text{x}}(\omega, \mathbf{r}, \mathbf{r}') = \sum_{ia,jb} \varphi_{ia}(\mathbf{r}) \lambda_{ia}(\omega) X_{ia,jb}(\omega) \lambda_{jb}(\omega) \varphi_{jb}(\mathbf{r}'), \quad (7)$$

with

$$X_{ia,jb}(\omega) = \frac{1}{4}(A_{ia,jb} + B_{ia,jb} + \Delta_{ia,jb}) + \omega^2 \frac{1}{4} \varepsilon_{ia}^{-1} \times (A_{ia,jb} - B_{ia,jb} + \Delta_{ia,jb}) \varepsilon_{jb}^{-1} - C_{ia,jb} \quad (8)$$

and

$$A_{ia,jb} = 2(ai|jb) - (ab|ji), \quad (9)$$

$$B_{ia,jb} = 2(ai|bj) - (aj|bi), \quad (10)$$

$$\Delta_{ia,jb} = \delta_{ij} \langle \varphi_a | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_b \rangle - \delta_{ab} \langle \varphi_i | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_j \rangle, \quad (11)$$

$$C_{ia,jb} = (ai|jb) = (ai|bj), \quad (12)$$

with integrals of the type $(ai|jb)$ being defined according to $\int d\mathbf{r} d\mathbf{r}' \varphi_a(\mathbf{r}) \varphi_i(\mathbf{r}) \varphi_b(\mathbf{r}') \varphi_j(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$ and $\hat{v}_{\text{x}}^{\text{NL}}$ being the non-local exchange operator defined by $\sum_i \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$. The second contribution to the function h_{x} (see Eq. (A5) in Appendix A), in a previous work,³⁷ turned out to have a negligible effect on the considered excitation energies because it contains the matrix elements $\langle \varphi_i | \hat{v}_{\text{x}}^{\text{NL}} - \hat{v}_{\text{x}} | \varphi_a \rangle$ between occupied and unoccupied EXX orbitals that are very small due to the similarity of the HF and EXX determinants⁴⁹ and therefore shall not be taken into account any further. The specific form of Eqs. (7) and (8) to express the dominant contribution to the function h_{x} was chosen because this form facilitates a reformulation of the TDEXX equation of Refs. 37–39, which is the crucial point of this work (see Sec. II B). The complete function h_{x} can be found in Appendix A and Refs. 38, 40–43.

If Eq. (6) is inserted into the basic Eq. (5), and if Eq. (1) is taken into account, then a frequency-dependent response equation³⁷

$$\int d\mathbf{r}' \left[\chi_s(\omega, \mathbf{r}, \mathbf{r}') - \int d\mathbf{r}'' d\mathbf{r}''' \frac{\chi_s(\omega, \mathbf{r}, \mathbf{r}'') \chi_s(\omega, \mathbf{r}''', \mathbf{r}')}{|\mathbf{r}'' - \mathbf{r}'''|} - h_{\text{x}}(\omega, \mathbf{r}, \mathbf{r}') \right] v_s^{(1)}(\omega, \mathbf{r}') = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') v^{(1)}(\omega, \mathbf{r}') \quad (13)$$

for the change $v_s^{(1)}$ of the effective KS potential is obtained. The crucial advantage of Eq. (13) compared to Eq. (5) is that it contains the function h_{x} instead of the kernel f_{x} . The function h_{x} is explicitly known in terms of the KS orbitals and its eigenvalues whereas the kernel f_{x} can only be obtained by solving the integral Eq. (6). Attempts to solve this equation, however, suffered from severe numerical instabilities even in the adiabatic, i.e., zero frequency, limit.^{44,50}

Equation (13) can be written in the form

$$\mathbf{W}^T(\mathbf{r}) \frac{1}{4} [\omega^2 \mathbf{1} - \boldsymbol{\varepsilon}^2 - 4 \boldsymbol{\varepsilon}^{1/2} [\mathbf{C} + \mathbf{X}(\omega)] \boldsymbol{\varepsilon}^{1/2}] \mathbf{z}(\omega) = \mathbf{W}^T(\mathbf{r}) \boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega) \quad (14)$$

with the matrix elements of the diagonal matrix $\boldsymbol{\varepsilon}$ given by $\varepsilon_{ia,jb} = \delta_{ia,jb} \varepsilon_{ia} = \delta_{ia,jb} (\varepsilon_a - \varepsilon_i)$, the matrix elements of

the diagonal matrix $\lambda(\omega)$ given by $\lambda_{ia,jb}(\omega) = \delta_{ia,jb} \lambda_{ia}(\omega)$ with $\lambda_{ia}(\omega)$ defined in Eq. (3), the elements $W_{ia}(\mathbf{r})$ of the vector $\mathbf{W}(\mathbf{r})$ given by $W_{ia}(\mathbf{r}) = \varepsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \varphi_{ia}(\mathbf{r})$, the elements $\mathbf{v}_s^{(1)}(\omega)$ of the vector $\mathbf{v}^{(1)}(\omega)$ given by $\langle \varphi_a | \mathbf{v}^{(1)}(\omega) | \varphi_i \rangle$, and the elements of the matrices $\mathbf{C}$ and $\mathbf{X}(\omega)$ defined in Eqs. (12) and (8), respectively. The vector $\mathbf{z}(\omega)$ is related by

$$\mathbf{z}(\omega) = \boldsymbol{\varepsilon}^{-1/2} \lambda(\omega) \mathbf{v}_s^{(1)}(\omega) \quad (15)$$

to the vector $\mathbf{v}_s^{(1)}(\omega)$ with vector elements $\mathbf{v}_{s,ia}^{(1)}(\omega)$ given by $\langle \varphi_a | \mathbf{v}_s^{(1)}(\omega) | \varphi_i \rangle$. The dimension of the above matrices and vectors equals the number of products of occupied times unoccupied orbitals, the index ia represents a superindex labeling the products. If the products of occupied times unoccupied orbitals, or more precisely the products $W_{ia}(\mathbf{r}) = \varepsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \varphi_{ia}(\mathbf{r})$ were linear independent then Eq. (14) would imply the matrix equation

$$[\omega^2 \mathbf{1} - \boldsymbol{\varepsilon}^2 - 4\boldsymbol{\varepsilon}^{1/2} [\mathbf{C} + \mathbf{X}(\omega)] \boldsymbol{\varepsilon}^{1/2}] \mathbf{z}(\omega) = 4\boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega). \quad (16)$$

The products $\varepsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \varphi_{ia}(\mathbf{r})$ actually are not linear independent. Therefore, from a formal point of view, Eq. (16) should be projected onto the space spanned by the products $\varepsilon_{ia}^{-1/2} \lambda_{ia}(\omega) \varphi_{ia}(\mathbf{r})$. It turned out that such a projection has only a negligible effect on low-lying excitations.³⁷ Moreover, we show below, how it can be checked that a solution of Eq. (16) is not affected by the linear dependence of the products of occupied times unoccupied orbitals.

By solving Eq. (16) the vector $\mathbf{z}(\omega)$ can be obtained, which determines the linear response $\rho^{(1)}(\omega, \mathbf{r})$ of the electron density to a frequency-dependent external perturbation $\mathbf{v}^{(1)}(\omega, \mathbf{r})$ according to

$$\begin{aligned} \rho^{(1)}(\omega, \mathbf{r}) &= \sum_i^{\text{occ.}} \sum_a^{\text{unocc.}} \varphi_{ia}(\mathbf{r}) \lambda_{ia}^{1/2} \langle \varphi_a | \mathbf{v}_s^{(1)}(\omega) | \varphi_i \rangle \\ &= \sum_i^{\text{occ.}} \sum_a^{\text{unocc.}} z_{ia}(\omega) \varepsilon_{ia}^{1/2} \varphi_{ia}(\mathbf{r}). \end{aligned} \quad (17)$$

The first line of Eq. (17) directly follows from Eqs. (1) and (2), the second line with Eq. (15). More important than calculating the frequency-dependent linear response of the electron density is to determine excitation energies. To that end, those frequencies are determined for which the linear response of the electron density becomes infinite. For these frequencies Eq. (16) becomes singular, i.e., for these frequencies the matrix in the square parenthesis on the left hand side of Eq. (16) has eigenvalues equal to zero. These frequencies and thus the excitation energies can be obtained by solving the nonlinear eigenvalue problem

$$[\boldsymbol{\varepsilon}^2 + 4\boldsymbol{\varepsilon}^{1/2} [\mathbf{C} + \mathbf{X}(\omega)] \boldsymbol{\varepsilon}^{1/2}] \mathbf{z}_n(\omega) = \Omega_n^2(\omega) \mathbf{z}_n(\omega) \quad (18)$$

in order to obtain eigenvalues Ω_n and eigenvectors $\mathbf{z}_n$.³⁷ If the frequency ω equals an eigenvalue Ω_n , then Eq. (16) becomes singular and this frequency $\omega = \Omega_n$ is an excitation frequency of the considered electronic system. This means, in order to calculate the n th excitation energy with Eq. (18), the frequency ω has to be adjusted such that it equals the n th eigenvalue Ω_n (see Sec. II.B.). The eigenvectors $\mathbf{z}_n(\omega = \Omega_n)$

characterize the excitations and, if properly normalized (see Appendix B), yield the corresponding oscillator strength f_n according to

$$f_n = \frac{4}{3} \sum_{\mu=x,y,z} (\mathbf{d}_\mu^T \boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n)^2, \quad (19)$$

with the elements $d_{\mu,ia}$ of the vectors $\mathbf{d}_\mu$ with $\mu = x, y, z$ given by $\langle \varphi_i | x | \varphi_a \rangle$, $\langle \varphi_i | y | \varphi_a \rangle$, and $\langle \varphi_i | z | \varphi_a \rangle$, respectively. Equation (18) is the equation that underlies the work on the TDEXX response methods of Refs. 37 and 38.

In order to check if solutions $\mathbf{z}(\omega)$ of Eq. (16) or the eigenvectors $\mathbf{z}_n(\omega)$ of Eq. (18) are affected by linear dependencies of products φ_{ia} of occupied times unoccupied orbitals, we consider a singular-value decomposition

$$\mathbf{S} = (\mathbf{U} \quad \mathbf{U}^0) \begin{pmatrix} \mathbf{s} & \mathbf{0} \\ \mathbf{0} & \mathbf{s}^0 \end{pmatrix} \begin{pmatrix} \mathbf{U}^T \\ \mathbf{U}^{0T} \end{pmatrix} \quad (20)$$

of the overlap matrix $\mathbf{S}$ of pairs φ_{ia} with φ_{jb} of products of occupied times unoccupied orbitals with matrix elements $S_{ia,jb} = \int d\mathbf{r} \varphi_{ia}(\mathbf{r}) \varphi_{jb}(\mathbf{r})$. The diagonal matrix $\mathbf{s}$ shall contain those eigenvalues of the overlap matrix $\mathbf{S}$ that are greater than zero. The corresponding eigenvectors, the columns of the matrix $\mathbf{U}$, define the space spanned by the products of occupied times unoccupied orbitals φ_{ia} . The diagonal matrix $\mathbf{s}^0$ contains the eigenvalues of $\mathbf{S}$ that are zero or, in practice, below a given numerical threshold. The corresponding eigenvectors, the columns $\mathbf{u}_\ell^0$ of the matrix $\mathbf{U}^0$, contain the coefficients of linear combinations of products φ_{ia} that are identical to zero or, in practice, are close to zero,

$$\sum_{ia} u_{\ell,ia}^0 \varphi_{ia}(\mathbf{r}) = 0. \quad (21)$$

A solution $\mathbf{z}(\omega)$ of Eq. (16) is related by Eq. (15) with the vector $\mathbf{v}_s^{(1)}(\omega)$ with vector elements $\mathbf{v}_{s,ia}^{(1)}(\omega) = \langle \varphi_a | \mathbf{v}_s^{(1)}(\omega) | \varphi_i \rangle = \int d\mathbf{r} \mathbf{v}_s^{(1)}(\omega, \mathbf{r}) \varphi_{ia}(\mathbf{r})$. We now consider a vector $\mathbf{t}^0$ given by

$$\mathbf{t}^0 = \mathbf{U}^{0T} \mathbf{v}_s^{(1)}(\omega) = \mathbf{U}^{0T} \lambda^{-1}(\omega) \boldsymbol{\varepsilon}^{1/2} \mathbf{z}(\omega). \quad (22)$$

If the vector $\mathbf{t}^0$ does not equal the zero vector, i.e., if it contains elements $t_\ell^0 \neq 0$, then the solution $\mathbf{z}(\omega)$ of Eq. (16) is not physically meaningful because the elements t_ℓ^0 equal

$$\begin{aligned} t_\ell^0 &= \mathbf{u}_\ell^{0T} \mathbf{v}_s^{(1)}(\omega) \\ &= \sum_{ia} u_{\ell,ia}^0 \int d\mathbf{r} \mathbf{v}_s^{(1)}(\omega, \mathbf{r}) \varphi_{ia}(\mathbf{r}) \\ &= \int d\mathbf{r} \left[\sum_{ia} u_{\ell,ia}^0 \varphi_{ia}(\mathbf{r}) \right] \mathbf{v}_s^{(1)}(\omega, \mathbf{r}) \\ &= 0, \end{aligned} \quad (23)$$

i.e., equal integrals that must be zero, because it is integrated over the local multiplicative potential $\mathbf{v}_s^{(1)}(\omega, \mathbf{r})$ times linear combinations of products φ_{ia} that are zero according to Eq. (21). This means physical meaningful solutions of Eq. (16) must obey the criterion

$$\sum_\ell t_\ell^{02} = 0 \quad (24)$$

or, in practice, the left-hand side of Eq. (24) must lie below a given threshold. Because the vectors $\mathbf{v}_s^{(1)}(\omega) = \lambda^{-1}(\Omega) \boldsymbol{\varepsilon}^{1/2} \mathbf{z}(\omega)$ are not normalized, a threshold defined relative to the norm of the vectors seems reasonable. We, therefore, besides the vector $\mathbf{t}^0$ of Eq. (22), calculate a vector $\mathbf{t}$ according to

$$\mathbf{t} = \begin{pmatrix} \mathbf{U}^T \\ \mathbf{U}^{0T} \end{pmatrix} \lambda^{-1}(\omega) \boldsymbol{\varepsilon}^{1/2} \mathbf{z}(\omega) \quad (25)$$

and take the measure

$$\frac{\sum_{\ell} (t_{\ell}^0)^2}{\sum_m (t_m)^2} \quad (26)$$

as criterion to judge whether solutions $\mathbf{z}(\omega)$ are affected by linear dependencies of products of occupied times unoccupied orbitals. Similarly, eigenvectors of $\mathbf{z}_n(\omega = \Omega_n)$ of Eq. (18) can be analyzed with the help of vectors

$$\mathbf{t}_n^0 = \mathbf{U}^{0T} \lambda^{-1}(\Omega_n) \boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n(\Omega_n) \quad (27)$$

and

$$\mathbf{t} = \begin{pmatrix} \mathbf{U}^T \\ \mathbf{U}^{0T} \end{pmatrix} \lambda^{-1}(\Omega_n) \boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n(\Omega_n). \quad (28)$$

In order to avoid that products φ_{ia} that have a small norm fall below the threshold identifying products as being close to zero, we renormalize the overlap matrix according to

$$\tilde{\mathbf{S}} = \boldsymbol{\sigma} \mathbf{S} \boldsymbol{\sigma}^T, \quad (29)$$

with the diagonal matrix $\boldsymbol{\sigma}$ containing matrix elements $\sigma_{ia,ia} = 1/\sqrt{S_{ia,ia}}$. In this case, Eq. (27) assumes the form

$$\mathbf{t}_{0,n} = \mathbf{U}^{0T} \boldsymbol{\sigma} \lambda^{-1}(\Omega_n) \boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n(\Omega_n) \quad (30)$$

and Eqs. (22), (25), and (28) need to be analogously modified. It will be shown in Sec. IV that the eigenvectors $\mathbf{z}_n(\Omega_n)$ of all excitations studied in this work are only very slightly affected by linear dependencies of products of occupied times unoccupied orbitals according to the measure (26) evaluated on the basis of the overlap matrix $\tilde{\mathbf{S}}$. Therefore, the use of the unprojected Eq. (18) seems to be justified.

B. Reformulation of TDEXX equation

The lowest eigenvalues of Eq. (18) for a given frequency ω can be efficiently obtained by iteratively solving Eq. (18) by a Davidson algorithm (see, e.g., Ref. 51). However, due to the nonlinearity of Eq. (18), i.e., the frequency dependence of the matrix $\mathbf{X}(\omega)$, this, in general, does not lead to eigenvalues Ω_n corresponding to excitation energies. Only if the frequency ω in Eq. (18) equals one of the eigenvalues Ω_n , i.e., if $\omega = \Omega_n$ then this eigenvalue corresponds to an excitation energy. This means that for each excitation energy, the frequency ω needs to be adjusted to the corresponding eigenvalue, which in turn depends on the frequency. This adjustment can be straightforwardly done in an iterative manner, it requires, however, in each iteration step a solution of Eq. (18). Usually, only a few (three to five) iteration steps are necessary. Nevertheless, this

means that instead of obtaining all excitation energies of interest by carrying out the Davidson algorithm once, it has to be carried out for each excitation several times. This amounts to a drastic increase in computational effort compared to a conventional TDDFT response approach within the adiabatic approximation. Alternatively, the excitation energies of interest can also be obtained by interpolation from excitation energy data generated, e.g., on a regular frequency grid. This, however, also requires at least four or more (depending on the range of excitation energies to be computed) diagonalization steps in comparison to just one as in standard TDDFT.

If the matrix $\mathbf{X}(\omega)$ in Eq. (18) is decomposed according to Eq. (8) into matrices $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{\Delta}$ with matrix elements given by Eqs. (9)–(11), then, after rearrangement of terms, Eq. (18) assumes the form

$$\begin{aligned} & [\boldsymbol{\varepsilon}^2 + \boldsymbol{\varepsilon}^{1/2} [\mathbf{A} + \mathbf{B} + \mathbf{\Delta}] \boldsymbol{\varepsilon}^{1/2}] \mathbf{z}_n \\ &= \Omega_n^2 [\mathbf{1} - \boldsymbol{\varepsilon}^{-1/2} [\mathbf{A} - \mathbf{B} + \mathbf{\Delta}] \boldsymbol{\varepsilon}^{-1/2}] \mathbf{z}_n. \end{aligned} \quad (31)$$

Indeed, the way the matrix elements $X_{ia}(\omega)$ are written in Eq. (8) was chosen because then the TDEXX Eq. (18) assumes the form of Eq. (31). This is crucial because Eq. (31), in contrast to the original Eq. (18), is linear. More precisely, the fact that the TDEXX problem is a linear one is hidden if it is formulated according to Eq. (18) while it becomes obvious in Eq. (31). This means the linear generalized eigenvalue problem (31) directly yields the squares of all excitation energies and no frequency iteration is required. However, it cannot be solved by a standard Davidson algorithm. Instead, special versions of the Davidson algorithm for generalized eigenvalue problems are required. This means the advantage of having at hand a linear formulation the TDEXX response problem is accompanied by having to deal with a generalized instead of a simple eigenvalue problem.

The fact that Eq. (31) is a linear generalized eigenvalue equation means that frequency-dependent TDEXX response methods, like conventional TDDFT response methods, yield as many excitation energies as there are products of occupied times unoccupied orbitals. (Note that we have neglected terms in the function h_x of Eq. (6) for the exchange kernel. We have no indications that these terms could lead to additional excitation energies, indeed we have no indication that these terms have any non-negligible effect at all. However, we did not investigate any further potential implications of these terms on the number of excitations.) Because an exact TDDFT response method has to yield all excitations that are accompanied by a linear response of the electron density including excitations that, within an independent electron picture, are described as two-electron excitations, the unknown frequency-dependent correlation kernel has to introduce a nonlinearity leading to additional excitations, which are neither present in conventional adiabatic TDDFT methods nor in the frequency-dependent TDEXX method considered here.

Formally, we can convert Eq. (31) into a regular eigenvalue equation. To this end, we first introduce the abbreviation

$$\mathbf{D} = \boldsymbol{\varepsilon}^{-1/2} [\mathbf{A} - \mathbf{B} + \mathbf{\Delta}] \boldsymbol{\varepsilon}^{-1/2} \quad (32)$$

and rewrite Eq. (31) as

$$[\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B} + \mathbf{\Delta}] \epsilon^{1/2}] \mathbf{z}_n = \Omega_n^2 [\mathbf{1} - \mathbf{D}] \mathbf{z}_n. \quad (33)$$

Provided the matrix $\mathbf{1} - \mathbf{D}$ is positive definite, the generalized eigenvalue Eq. (32) is equivalent to the regular Hermitian eigenvalue equation

$$\begin{aligned} (\mathbf{1} - \mathbf{D})^{-1/2} [\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B} + \mathbf{\Delta}] \epsilon^{1/2}] (\mathbf{1} - \mathbf{D})^{-1/2} \mathbf{p}_n \\ = \Omega_n^2 \mathbf{p}_n \end{aligned} \quad (34)$$

with

$$\mathbf{p}_n = (\mathbf{1} - \mathbf{D})^{1/2} \mathbf{z}_n. \quad (35)$$

Construction of the matrix $(\mathbf{1} - \mathbf{D})^{-1/2}$, like the explicit construction of any of the involved matrices, except those that are diagonal, has to be avoided in a computationally efficient algorithm. Therefore, Eq. (34) is of no help directly. We now expand the matrix $(\mathbf{1} - \mathbf{D})^{-1/2}$ into a Taylor expansion, according to

$$(\mathbf{1} - \mathbf{D})^{-1/2} \approx \mathbf{1} + \frac{1}{2} \mathbf{D} + \frac{3}{8} \mathbf{D}^2 + \dots \quad (36)$$

and substitute this Taylor expansion into the eigenvalue Eq. (34) to convert it into the form

$$\begin{aligned} (\mathbf{1} + \frac{1}{2} \mathbf{D} + \frac{3}{8} \mathbf{D}^2 + \dots) [\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B} + \mathbf{\Delta}] \epsilon^{1/2}] \\ \times (\mathbf{1} + \frac{1}{2} \mathbf{D} + \frac{3}{8} \mathbf{D}^2 + \dots) \mathbf{p}_n = \Omega_n^2 \mathbf{p}_n, \end{aligned} \quad (37)$$

with

$$\mathbf{z}_n = (\mathbf{1} + \frac{1}{2} \mathbf{D} + \frac{3}{8} \mathbf{D}^2 + \dots) \mathbf{p}_n. \quad (38)$$

Equation (37) lends itself for an iterative solution with a regular Davidson algorithm provided the Taylor expansion (37) converges fast enough. If only the leading term of the Taylor expansion is taken into account, then the frequency dependence in the adiabatic TDEXX response equation is neglected, i.e., the adiabatic approximation is made, resulting in an adiabatic TDEXX (termed as ATDEXX in the following) response method with the simplified eigenvalue equation

$$[\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B} + \mathbf{\Delta}] \epsilon^{1/2}] \mathbf{p}_n = \Omega_n^2 \mathbf{p}_n. \quad (39)$$

Vector matrix multiplications as they are required in a Davidson algorithm now consist of $2n + 1$ instead of one individual vector matrix multiplication compared to adiabatic TDDFT response methods with n being the order up to which the Taylor expansion needs to be taken into account. The vector matrix multiplications with the matrix $\mathbf{D}$ like those with the matrix $[\mathbf{A} + \mathbf{B} + \mathbf{\Delta}]$ can be carried out efficiently without explicitly constructing the matrices. For a value of $n = 2$ that is shown later on to be sufficient to closely approach the full frequency-dependent results the number of individual vector matrix multiplication increases by a factor of five. The resulting computational effort should still be of the same order of magnitude as that for conventional TDDFT methods, in particular as that of conventional TDDFT methods with hybrid functionals like B3LYP that require the solution of a TDHF-like problem, which has twice the dimension of the eigenvalue problem considered here. The scaling with system size of a

TDEXX method based on Eq. (37) is identical to that of other TDDFT response methods or the TDHF method. In summary, on the basis of Eq. (37) TDEXX response methods can be implemented that are competitive to TDHF or conventional TDDFT response methods with respect to the computational effort.

C. Relation between TDEXX and TDHF

The basic equation of TDHF,^{51–54}

$$\left[\begin{pmatrix} \epsilon & 0 \\ 0 & \epsilon \end{pmatrix} + \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \right] \begin{pmatrix} \mathbf{x}_n \\ \mathbf{y}_n \end{pmatrix} = \Omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{x}_n \\ \mathbf{y}_n \end{pmatrix}, \quad (40)$$

has twice the dimension of the eigenvalue equations occurring in TDDFT response methods. The matrices ϵ , $\mathbf{A}$, and $\mathbf{B}$ are defined as above, however, with respect to HF eigenvalues and orbitals instead of EXX eigenvalues and orbitals. This means for matrices that differ only because they refer to different types of orbitals or eigenvalues, i.e., EXX or HF orbitals or eigenvalues, the same symbol is used and the context determines what is exactly meant. Equation (40) can be alternatively written in the form of two coupled matrix equations with half the original dimension, i.e., with the same dimension as the eigenvalue equations occurring in TDDFT response methods,

$$[\epsilon + \mathbf{A}] \mathbf{x}_n + \mathbf{B} \mathbf{y}_n = \Omega_n \mathbf{x}_n, \quad (41)$$

$$\mathbf{B} \mathbf{x}_n + [\epsilon + \mathbf{A}] \mathbf{y}_n = -\Omega_n \mathbf{y}_n. \quad (42)$$

By inserting the two above equations into each other and by using the definition

$$\mathbf{z}_n = \epsilon^{-1/2} (\mathbf{x}_n + \mathbf{y}_n), \quad (43)$$

the generalized eigenvalue equation

$$\begin{aligned} [\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B}] \epsilon^{1/2}] \mathbf{z}_n \\ = \Omega_n^2 [\mathbf{1} + \epsilon^{-1/2} [\mathbf{A} - \mathbf{B}] \epsilon^{-1/2}]^{-1} \mathbf{z}_n \end{aligned} \quad (44)$$

is obtained, which is equivalent to the original TDHF Eq. (40).

In order to relate TDEXX and TDHF methods, we exploit the fact that the exact exchange-only KS determinant, the EXX determinant, and the HF determinant are almost identical.^{38,39,55} If the small differences between the two determinants are neglected, then the occupied HF and EXX orbitals can be transformed into each other by a unitary transformation and the same holds true for the unoccupied HF and EXX orbitals. The transformation matrices that transform the occupied and unoccupied HF orbitals into EXX orbitals shall be denoted by $\mathbf{U}^{\text{occ}}$ and $\mathbf{U}^{\text{unocc}}$. The direct product $\mathbf{U} = \mathbf{U}^{\text{occ}} \otimes \mathbf{U}^{\text{unocc}}$ of these matrices is a unitary matrix transforming products of occupied times unoccupied HF orbitals into products of occupied times unoccupied EXX orbitals. If we carry out a similarity transformation of the matrices $\mathbf{A}$ and $\mathbf{B}$ constructed from HF orbitals with the matrix $\mathbf{U}$ and

its transposed, then the matrices **A** and **B** turn into the corresponding matrices constructed with EXX orbitals. A diagonal matrix **ϵ** containing differences of HF eigenvalues turns into the matrix **$\epsilon + \Delta$** , which is a sum of a matrix **ϵ** containing differences of KS eigenvalues and the matrix **Δ** with matrix elements that are given by expectation values of KS orbitals according to Eq. (11).³⁹ If we now carry out a similarity transformation of the TDHF Eq. (40) with a block diagonal matrix containing on the diagonal twice the matrix **U**, then we obtain the equation

$$\left[\begin{pmatrix} \epsilon & 0 \\ 0 & \epsilon \end{pmatrix} + \begin{pmatrix} \mathbf{A} + \Delta & \mathbf{B} \\ \mathbf{B} & \mathbf{A} + \Delta \end{pmatrix} \right] \begin{pmatrix} \mathbf{x}_n \\ \mathbf{y}_n \end{pmatrix} = \Omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{x}_n \\ \mathbf{y}_n \end{pmatrix}. \quad (45)$$

If the HF and EXX determinants were exactly identical, then Eq. (45) would be exactly equivalent to the original TDHF Eq. (40). It would be a TDHF equation represented in products of EXX orbitals. Because HF and EXX determinants are very close but not exactly identical, Eq. (45) will yield results not identical but very close to TDHF. The differences will reflect the differences of HF and EXX determinants.

Like the original TDHF Eq. (40), we can transform Eq. (45) into a generalized eigenvalue equation of half the dimension

$$[\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B} + \Delta] \epsilon^{1/2}] \mathbf{z}_n = \Omega_n^2 [\mathbf{1} + \mathbf{D}]^{-1} \mathbf{z}_n. \quad (46)$$

It is instructive to compare Eq. (46) with the generalized TDEXX Eq. (33). The two equations only differ by the matrix in front of the eigenvectors **$\mathbf{z}_n$** on the right-hand side of the equation. The meaning of this difference becomes clearer if we first turn Eq. (46) into the regular eigenvalue equation

$$(\mathbf{1} + \mathbf{D})^{+1/2} [\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B} + \Delta] \epsilon^{1/2}] \times (\mathbf{1} + \mathbf{D})^{+1/2} \mathbf{p}_n = \Omega_n^2 \mathbf{p}_n \quad (47)$$

with

$$\mathbf{p}_n = (\mathbf{1} + \mathbf{D})^{-1/2} \mathbf{z}_n, \quad (48)$$

and then insert the Taylor expansion

$$(\mathbf{1} + \mathbf{D})^{1/2} \approx \mathbf{1} + \frac{1}{2}\mathbf{D} - \frac{1}{8}\mathbf{D}^2 + \dots \quad (49)$$

to obtain

$$(\mathbf{1} + \frac{1}{2}\mathbf{D} - \frac{1}{8}\mathbf{D}^2 + \dots) [\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{B} + \Delta] \epsilon^{1/2}] \times (\mathbf{1} + \frac{1}{2}\mathbf{D} - \frac{1}{8}\mathbf{D}^2 + \dots) \mathbf{p}_n = \Omega_n^2 \mathbf{p}_n \quad (50)$$

with

$$\mathbf{z}_n = (\mathbf{1} + \frac{1}{2}\mathbf{D} - \frac{1}{8}\mathbf{D}^2 + \dots) \mathbf{p}_n. \quad (51)$$

Comparison of Eq. (50) and Eq. (37) shows that the TDEXX and TDHF equations differ only in terms of second order in the Taylor expansions (36) and (49). In addition, the differences caused by the small differences in EXX and HF

determinants have to be taken into account. These differences, however, are also small. In summary, the comparison of Eq. (50) and Eq. (37) together with the similarity of HF and EXX determinants explains why TDEXX response methods yield quite similar results as TDHF methods. A consequence of this similarity is that TDEXX response methods like TDHF can treat charge transfer excitations and excitations into states with Rydberg character and that excitations in long chain-like aromatic molecules should not be a problem for TDEXX response methods. On the other hand, TDEXX response methods exhibit the same low accuracy for valence-valence excitations as TDHF methods.

TDEXX response methods have two important advantages over TDHF methods. First, within the TDDFT framework correlation functionals can be included. This might give the chance to improve the accuracy of TDEXX methods. Second, the EXX method yields meaningful occupied and, in contrast to HF methods, also meaningful unoccupied orbitals. Therefore it is usually easy to determine the nature of an electronic excitation by simply inspecting the corresponding eigenvector **$\mathbf{z}_n$** . In TDHF this is often not possible in such a simple way. For example, the eigenvectors **$\mathbf{z}_n$** corresponding to excitations into states with Rydberg character, in TDHF, contain a very large number of small entries that do not help in characterizing the excitations, whereas in TDEXX response methods, in these cases the eigenvectors **$\mathbf{z}_n$** are dominated by one entry that corresponds to an excitation from the involved occupied to the involved unoccupied Rydberg orbital. This happens because the EXX method yields well defined, bound, physical meaningful Rydberg orbitals with negative eigenvalues, whereas HF yields unoccupied orbitals that usually exhibit positive eigenvalues and therefore do not correspond to bound, physically meaningful orbitals.

D. Tamm–Dancoff approximation

The Tamm–Dancoff (TD) approximation to the TDHF Eq. (40) neglects the matrix **B** that couples the contributions **$\mathbf{x}_n$** and **$\mathbf{y}_n$** to the TDHF eigenvectors. By this, the TDHF Eq. (40) is decoupled into two separate eigenvalue equations for **$\mathbf{x}_n$** and **$\mathbf{y}_n$** with eigenvalues Ω_n and $-\Omega_n$. If we apply the TD approximation to Eq. (45), i.e., to the TDHF equation expressed in EXX orbitals (if differences between the HF and EXX determinants are neglected), then we obtain the two equations

$$(\epsilon + \mathbf{A} + \Delta) \mathbf{x}_n = \Omega_n \mathbf{x}_n \quad (52)$$

and

$$(\epsilon + \mathbf{A} + \Delta) \mathbf{y}_n = -\Omega_n \mathbf{y}_n, \quad (53)$$

which imply

$$\mathbf{x}_n = \mathbf{y}_n. \quad (54)$$

Because Eq. (52) and (53) are equivalent, only one of them needs to actually be solved. Note that the TD approximation yields a qualitatively correct description of charge-transfer excitations like the fully coupled Eq. (45).

As discussed in Sec. II.C., the TDHF Eq. (40) is equivalent to the generalized eigenvalue Eq. (44), which has half the

dimension as the original TDHF Eq. (40). Similarly Eq. (45), the TDHF equation expressed in EXX orbitals, is related to the generalized eigenvalue Eq. (46). If the TD approximation is applied to Eq. (46), then we obtain

$$\begin{aligned} [\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{\Delta}] \epsilon^{1/2}] \mathbf{z}_n \\ = \Omega_n^2 [\mathbf{1} + \epsilon^{-1/2} [\mathbf{A} + \mathbf{\Delta}] \epsilon^{-1/2}]^{-1} \mathbf{z}_n. \end{aligned} \quad (55)$$

By multiplying from the left by $(1/2)\epsilon^{-1/2}$, by inserting the relation

$$\mathbf{z}_n = \epsilon^{-1/2} 2 \mathbf{x}_n = \epsilon^{-1/2} 2 \mathbf{y}_n, \quad (56)$$

which follows from Eq. (43) with Eq. (54), and by rearranging, we obtain the equation

$$(\epsilon + \mathbf{A} + \mathbf{\Delta})^2 \mathbf{x}_n = \Omega_n^2 \mathbf{x}_n, \quad (57)$$

which is equivalent to Eqs. (52) and (53).

If we apply a TD approximation, that is the approximation $\mathbf{B} = 0$, to the TDEXX Eq. (31), then the equation

$$\begin{aligned} [\epsilon^2 + \epsilon^{1/2} [\mathbf{A} + \mathbf{\Delta}] \epsilon^{1/2}] \mathbf{z}_n \\ = \Omega_n^2 [\mathbf{1} - \epsilon^{-1/2} [\mathbf{A} + \mathbf{\Delta}] \epsilon^{-1/2}] \mathbf{z}_n \end{aligned} \quad (58)$$

results. This equation cannot be turned into the form of a simple eigenvalue problem analogous to Eqs. (52) and (57). This means the TD approximation does not lead to a simple eigenvalue problem in the TDEXX case.

For the systems considered later on (see Sec. IV), the matrix $[\mathbf{1} - \epsilon^{-1/2} [\mathbf{A} + \mathbf{\Delta}] \epsilon^{-1/2}]$ turned out to be not positive definite and consequently Eq. (58) did not yield physically reasonable, i.e., real-valued positive, eigenvalues Ω_n^2 . The approximation to set $\mathbf{B} = 0$, therefore, seems not to be a reasonable approximation in the case of TDEXX in contrast to the TDHF case, despite the fact that the full TDEXX and TDHF methods are closely related as discussed in Sec. II.C. This may be explained by considering the Taylor expansions (37) and (50) of the TDEXX and TDHF equations with respect to the matrix $\mathbf{D} = \epsilon^{-1/2} [\mathbf{A} - \mathbf{B} + \mathbf{\Delta}] \epsilon^{-1/2}$. If differences between the HF and the EXX determinants are negligible, then the similarity of the TDEXX and TDHF method can be explained by the fact that the Taylor series Eqs. (36) and (49) and thus the TDEXX and TDHF Eq. (37) and (50) differ only in terms of second order in $\mathbf{D}$. Because the matrix $\mathbf{D}$ is small compared to the unit matrix these terms have only a small effect. The matrix $\mathbf{D}$ contains small matrix elements because the matrices $\mathbf{A}$ and $\mathbf{B}$ partially cancel each other. If, however, the matrix $\mathbf{B}$ is neglected, then this cancellation no longer exists, the Taylor series no longer converges that rapidly, and terms of quadratic and higher order in $\mathbf{D}$ may be significant.

III. COMPUTATIONAL DETAILS

Excitation energies were calculated for the three organic molecules ethylene, acetaldehyde, and pyridine. The geometries of the molecules were taken from Ref. 56.

The ground-state EXX calculations were performed in two steps. First the exact-exchange potentials were calculated

with the OEP (optimized effective potential) method and the balanced orbital and auxiliary triple-zeta basis sets from Ref. 35. The choice of the basis sets in OEP calculations has to be made carefully since OEP calculations with standard contracted orbital basis sets yield wrong exchange-correlation potentials and thus wrong KS orbitals and eigenvalues.^{35,49,57} In the second step, the thus obtained EXX potentials, represented in the auxiliary basis set, were used in a subsequent ground-state density-functional theory (DFT) calculation using a smaller orbital basis set. In this second ground-state DFT calculation only the Coulomb potential was optimized self-consistently. All results shown in this work were obtained with the 6-311(3+,3+)** orbital basis set from Refs. 56 and 58 that, in addition to the 6-311++G** standard basis set,⁵⁹ is augmented with the following diffuse functions with exponents: carbon/s+p: 0.0131928,0.00440, oxygen/s+p: 0.0254518,0.00848, nitrogen/s+p: 0.0192470,0.00642, and hydrogen/s: 0.0108434,0.00361.

In order to analyze the impact of the Kohn–Sham orbitals and/or the Kohn–Sham eigenvalue spectrum on the excitation energies, we have also done calculations with various other approximations for the ground-state. By comparison of the EXX single-particle spectrum with more accurate KS eigenvalues obtained with the localized and asymptotically corrected Perdew–Burke–Ernzerhof hybrid (LPBE0AC) exchange-correlation potential,^{60,61} it was found that the main differences (due to electron correlation) occur close to the highest occupied (HOMO) and the lowest unoccupied (LUMO) KS orbital eigenvalues, while the low lying occupied and higher unoccupied EXX and LPBE0AC KS orbital energies are closer to each other and thus do not seem to be affected as much by electron correlation effects.

The LPBE0AC exchange-correlation potential has been chosen here as a reference since it has been proven to yield accurate electron densities, molecular electric properties, and first- and second-order intermolecular interaction energies.^{60,62–64} The 25% exact exchange contribution in this xc potential, however, has been replaced by a modified model exact-exchange potential developed by Becke and Johnson.⁶⁵ In this modified exchange potential the Slater potential contribution was approximated using the Becke–Roussel exchange model⁶⁶ with an optimized γ value of 1.15 (see Ref. 67). The asymptotic correction for the total xc potential was done using the gradient regulated asymptotic correction scheme by Grüning *et al.*⁶⁸ with the derivative discontinuity shifts (ethylene: 0.0820 Hartree, acetaldehyde: 0.0895 Hartree, and pyridine: 0.0727 Hartree) calculated as the difference of the negative LPBE0 HOMO energies and the PBE0 ionization potentials (see below).

Therefore, in one set of calculations, we have used the following correction method for obtaining more accurate KS eigenvalues from the EXX orbital eigenvalue spectrum

$$\epsilon_i = \epsilon_i^{\text{EXX}} + \alpha \frac{\beta}{\beta + (\epsilon_i^{\text{EXX}} - \epsilon_N^{\text{EXX}})^2}, \quad (59)$$

where α and β are parameters and ϵ_N^{EXX} is the EXX HOMO eigenvalue. Since for $i = N$ Eq. (59) reduces to $\epsilon_N = \epsilon_N^{\text{EXX}}$

+ α , the parameter α was set to the difference between the EXX HOMO energy and the negative ionization potential of the molecule in the calculations, i.e.,

$$\alpha = -(\epsilon_N^{\text{EXX}} - (-E_{\text{IP}})), \quad (60)$$

such that the corrected HOMO orbital energy is identical to the ionization potential as in exact KS theory.⁶⁹ The ionization potentials for the systems studied in this work have been determined by unrestricted DFT calculations using the PBE0 functional with the aug-cc-pVTZ basis set⁷⁰ (ethylene: 10.441 eV, acetaldehyde: 10.079 eV, and pyridine 9.555 eV). The corresponding HOMO energies from the EXX method were ethylene: -10.216 eV, acetaldehyde: -11.548 eV, and pyridine -9.446 eV. The parameter β in Eq. (59) has been set to values of 0.02 and 0.03 in the calculations [Eq. (59) was evaluated in atomic units]. TDEXX calculations were then performed using unmodified EXX orbitals and modified KS eigenvalues as obtained with Eq. (59).

Furthermore, correlated ground-state DFT calculations were performed by adding local and semi-local correlation functionals to EXX, namely VWN (Vosko–Wilk–Nusair)⁷¹ and PBEC (Perdew–Burke–Ernzerhof correlation).⁷² The calculations have been done in the same way as described above for pure EXX calculations except that the employed semi-local correlation potential was added to the exact-exchange potential. In the second step, in the calculations with the small basis set, the local KS correlation potential was optimized, too, and not held fixed as the exact-exchange potential. Note that the matrix elements of the Δ matrix defined in Eq. (11) have been evaluated with the corresponding matrix elements of the exact-exchange potential only and not with the total xc (exchange-correlation) potential matrix elements.

We have also tested a hybrid approach in which the adiabatic or nonadiabatic exact exchange kernel is combined with the adiabatic local density approximation (ALDA) kernel. This was done by modifying Eq. (31) in the following way

$$\begin{aligned} & [\epsilon^2 + \epsilon^{1/2} [\alpha(\mathbf{A} + \mathbf{B} + \mathbf{\Delta})] + (1 - \alpha)(4\mathbf{C} + \mathbf{K}_{\text{xc}}^{\text{ALDA}}) \epsilon^{1/2}] \mathbf{z}_n \\ &= \Omega_n^2 [1 - \epsilon^{-1/2} [\alpha(\mathbf{A} - \mathbf{B} + \mathbf{\Delta})] \epsilon^{-1/2}] \mathbf{z}_n, \end{aligned} \quad (61)$$

where α is a switching parameter that can have values between 0 (full ALDA kernel) and 1 (full TDEXX kernel). $\mathbf{K}_{\text{xc}}^{\text{ALDA}}$ is the ALDA xc kernel matrix with the matrix elements $(K_{\text{xc}}^{\text{ALDA}})_{ia,jb} = \int \varphi_{ia}(\mathbf{r}) f_{\text{xc}}^{\text{ALDA}}(\mathbf{r}) \varphi_{jb}(\mathbf{r}) d\mathbf{r}$ and $f_{\text{xc}}^{\text{ALDA}}(\mathbf{r})$ is the second functional derivative of the LDA xc functional. In the calculations done in this work the scaling parameter α was set to values of 0.25 and 0.5.

The calculations with the hybrid time-dependent EXX-ALDA kernel were done in conjunction with the localized and asymptotically corrected LPBE0AC xc potential^{60,61} (see above). Since in this model potential, not such a clear separation of exact exchange and correlation is possible, the matrix elements of Δ given in Eq. (11) were calculated with the matrix elements of the full LPBE0AC xc potential.

All calculations were performed with the developers version of the Molpro quantum chemistry program.⁷³

TABLE I. Percentage of unphysical contributions due to linear dependencies of products of occupied times unoccupied orbitals to the eigenvectors $\mathbf{z}_n$ measured by the ratio $\mathbf{t}_{0,n}^0 \mathbf{t}_n^0 / (\mathbf{t}_n^T \mathbf{t}_n)$, Eq. (26), of the squared norm of the vector $\mathbf{t}_0$ defined in Eq. (27) and the squared norm of the unprojected vector $\mathbf{t}$ corresponding to Eq. (28). Linear dependencies are determined with respect to the overlap matrix $\tilde{\mathbf{S}}$ of Eq. (29). The ratio $\mathbf{t}_{0,n}^0 \mathbf{t}_n^0 / (\mathbf{t}_n^T \mathbf{t}_n)$ is shown for three different cutoff values used in the singular value decomposition (SVD) of $\tilde{\mathbf{S}}$.

Molecule	Excitation	Threshold in SVD		
		10^{-8}	10^{-10}	10^{-12}
Acetaldehyde	A''	0.1	0.0	0.0
	2A'	2.6	0.1	0.0
	3A'	2.4	0.1	0.0
	4A'	4.4	0.3	0.0
	6A'	7.0	1.0	0.0
	7A'	8.6	0.8	0.0
Pyridine	B ₁	4.5	0.1	0.0
	B ₂	7.6	0.4	0.0
	A ₂	9.4	0.6	0.0
	A ₁	7.9	0.6	0.0

IV. RESULTS AND DISCUSSION

Table I displays the percentage of unphysical contributions of linear combinations of products of occupied times unoccupied orbitals with zero norm to the eigenvectors $\mathbf{z}_n$ according to the measure $\mathbf{t}_{0,n}^T \mathbf{t}_{0,n} / (\mathbf{t}_n^T \mathbf{t}_n)$, Eq. (26). The linear combinations of products of occupied times unoccupied orbitals with zero norm are determined with respect to the overlap matrix (norm matrix) $\tilde{\mathbf{S}}$ of Eq. (27) and form the Null space of the overlap matrix. As described in Sec. II A, large contributions of $\mathbf{t}_{0,n}^T \mathbf{t}_{0,n} / (\mathbf{t}_n^T \mathbf{t}_n)$ for a given excitation indicate that this excitation does not correspond to a physically meaningful TDDFT excitation on the basis of the linear response Eq. (13). If a threshold of 10^{-12} is used to define the Null space of $\tilde{\mathbf{S}}$, then Table I shows that all excitations are virtually free of unphysical contributions. For a threshold of 10^{-10} the percentage of unphysical contributions still lies below one percent in all cases. For a threshold of 10^{-8} the percentage of contribution with a norm below this threshold can rise to 10 %. However, a norm in the order of 10^{-8} can no longer be considered as zero. In summary, we conclude that all excitations in Table I are proper TDDFT excitations and that the eigenvalue Eq. (16) is valid for these excitations without requiring a projection as described in Ref. 37. Therefore, the following discussion will only refer to the solutions of the unprojected eigenvalue Eq. (16).

Tables II–IV show the lowest singlet excitation energies for ethylene, acetaldehyde, and pyridine calculated using time-dependent Hartree–Fock (TDHF) based on TDHF orbitals and eigenvalues and by methods based on EXX orbitals combined with various approximations for the exchange-correlation kernel as described in Sec. II. (In the tables, the acronym of the method, the orbitals and eigenvalues were calculated with, is given in parenthesis after the acronym of the response method.) Furthermore, EXX eigenvalue differences corresponding to the excitations are displayed. The energetically lowest excitations in ethylene and

TABLE II. Experimental and calculated transition energies for ethylene from TDHF based on HF orbitals and eigenvalues [TDHF, Eqs. (40), and (44)] and from methods based on EXX orbitals combined with various approximations for the exchange-correlation kernel: TDHF with EXX orbitals [TDHF(EXX), Eqs. (45) and (46)], ATDEXX [Eq. (39)], full TDEXX, [Eq. (33)], ALDA(EXX) [Eq. (61) with $\alpha = 0$], and TDHF in the Tamm–Dancoff approximation [TDHF(TD)(EXX), Eq. (52)]. Also shown are first and second order Taylor expansion approximations to TDEXX and TDHF(EXX) denoted by TDEXX[n] and TDHF(EXX)[n], where n denotes the order of the expansion in Eqs. (37) and (50). Note that TDEXX[1] equals TDHF(EXX)[1]. Furthermore, EXX eigenvalue differences $\Delta\epsilon(\text{EXX})$ corresponding to the considered excitations are displayed. Energies are in eV.

	1B _{3u} Ryd	1B _{1u} $\pi \rightarrow \pi^*$	1B _{1g} Ryd	1B _{2g} Ryd	2A _g Ryd	2B _{3u} Ryd	3B _{3u} Ryd	4B _{3u} Ryd	3B _{1g} Ryd	2B _{1u} Ryd	5B _{3u} Ryd
TDHF	7.08	7.36	7.67	7.83	8.04	8.57	8.81	8.90	9.23	8.95	9.35
$\Delta\epsilon(\text{EXX})$	7.07	6.00	7.88	7.81	7.94	8.58	8.69	8.90	8.17	8.87	9.33
ATDEXX	7.13	7.07	7.80	7.84	8.01	8.59	8.77	8.91	8.73	8.92	9.35
TDEXX[1]	7.09	7.34	7.68	7.83	8.05	8.57	8.81	8.90	9.16	8.95	9.35
TDEXX[2]	7.10	7.38	7.69	7.84	8.05	8.57	8.82	8.90	9.23	8.95	9.35
TDEXX	7.10	7.38	7.69	7.83	8.05	8.57	8.82	8.90	9.25	8.95	9.35
TDHF(EXX)[2]	7.08	7.33	7.68	7.82	8.05	8.57	8.81	8.90	9.13	8.95	9.35
TDHF(EXX)	7.08	7.33	7.68	7.83	8.05	8.57	8.81	8.90	9.13	8.95	9.35
ALDA(EXX)	7.07	7.78	7.86	7.81	7.98	8.57	8.68	8.91	8.42	8.98	9.33
TDHF(TD)(EXX)	7.09	7.69	7.69	7.83	8.07	8.57	8.82	8.91	9.19	8.98	9.35
Exp.	7.11	7.65	7.80	7.90	8.28	8.62	8.90	9.08	9.20	9.33	9.51

acetaldehyde are mostly of Rydberg character, while in the case of pyridine the four considered excitations are the lowest valence-valence excitations. In case of ethylene, it can be seen that all methods yield almost identical results for the Rydberg transitions (see Table II). This also holds true if the TDEXX and ALDA(EXX) results are compared with each other. It can therefore be concluded that in this case, the xc kernel has only a very small effect on the excitation energy and that the Rydberg excitations are close to the corresponding EXX single-particle energy differences. It can be observed in Table II that this is true with the exception of the 3B_{1g} excitation, where the $\Delta\epsilon(\text{EXX})$ excitation energy underestimates the TDEXX excitation energy by about 1 eV. In contrast to the Rydberg excitations, for the $\pi \rightarrow \pi^*$ excitation energies shown in the third column of Table II a different behavior is found: a significant difference of about 0.3 eV is observed between the adiabatic TDEXX and nonadiabatic TDEXX result, on the one hand, and another shift of 0.4 eV between TDEXX and ALDA(EXX) is observed on the other hand. TDEXX and also the TDHF method with EXX orbitals [TDHF(EXX), Eqs. (45) and (46)] yield $\pi \rightarrow \pi^*$ excitation energies that

are very close to TDHF based on HF orbitals. Furthermore the Taylor expansion approximations to TDEXX and TDHF(EXX), denoted as TDEXX[n] and TDHF(EXX)[n], respectively [n : order of expansion, see Eqs. (37) and (50)] are close to their infinite order counterparts already at first order. This underlines the usefulness of approaches based on the expansions described in Sec. II.B. and II.C. A comparison of the calculated excitation energies with the experimental ones displayed in the last line of Table II shows a good agreement for all Rydberg excitations. In case of the $\pi \rightarrow \pi^*$ excitation, however, the TDEXX excitation energy is about 0.3 eV too low. This, interestingly, is corrected if the Tamm–Dancoff approximation to TDHF(EXX), denoted as TDHF(TD)(EXX) [Eq. (52)], is made. Then the experimental $\pi \rightarrow \pi^*$ excitation energy is reproduced up to +0.04 eV. All methods considered in Table II except ATDEXX reproduce the experimental values for the excitation energies of ethylene with mean absolute deviations of less than 0.2 eV.

This is clearly different for acetaldehyde where all methods (based on EXX orbitals) overestimate the experimental excitations depicted in Table III in all cases except of

TABLE III. Experimental and calculated transition energies for acetaldehyde. See Table II for details. Energies are in eV.

	A'' $n \rightarrow \pi^*$	2A' Ryd	3A' Ryd	4A' Ryd	6A' Ryd	7A' Ryd
TDHF	4.75	8.45	9.10	9.19	10.04	10.12
$\Delta\epsilon(\text{EXX})$	5.26	7.13	8.04	8.47	8.84	9.10
ATDEXX	5.11	7.87	8.55	8.70	9.54	9.62
TDEXX[1]	4.70	8.35	9.01	9.09	9.93	10.01
TDEXX[2]	4.90	8.42	9.09	9.13	9.97	10.06
TDEXX	4.87	8.45	9.12	9.15	9.98	10.07
TDHF(EXX)[2]	4.63	8.32	8.98	9.07	9.92	10.00
TDHF(EXX)	4.62	8.33	8.98	9.07	9.92	10.00
ALDA(EXX)	5.54	7.19	8.07	8.46	8.87	9.09
TDHF(TD)(EXX)	4.80	8.34	9.06	9.14	9.92	10.05
Exp.	4.28	6.82	7.46	7.75	8.43	8.69

TABLE IV. Experimental and calculated transition energies for pyridine. See Table II for details. Energies are in eV.

	B ₁ $n \rightarrow \pi^*$	B ₂ $\pi \rightarrow \pi^*$	A ₂ $n \rightarrow \pi^*$	A ₁ $\pi \rightarrow \pi^*$
TDHF	5.95	5.85	7.33	6.09
$\Delta\epsilon(\text{EXX})$	5.05	4.92	5.46	5.33
ATDEXX	5.66	5.00	6.34	5.36
TDEXX[1]	5.88	5.88	7.30	6.12
TDEXX[2]	6.11	6.14	7.64	6.31
TDEXX	6.19	6.29	7.86	6.43
TDHF(EXX)[2]	5.80	5.80	7.18	6.05
TDHF(EXX)	5.81	5.82	7.20	6.07
ALDA(EXX)	5.34	5.51	5.50	6.31
TDHF(TD)(EXX)	5.99	6.07	7.29	6.41
Exp.	4.59	4.99	5.43	6.38

ALDA(EXX), by about 1–1.3 eV on average and in the case of ALDA(EXX) by about 0.6 eV on average. Table III also shows that in this case, the xc kernel has a significant effect on both the $n \rightarrow \pi^*$ valence and on the Rydberg excitations. For example, the comparison between ATDEXX and TDEXX shows a difference of -0.24 eV for the $n \rightarrow \pi^*$ excitation and up to $+0.46$ eV for the Rydberg excitation. This shows that the use of the nonadiabatic terms in the kernel has a nonuniform effect on the excitation energies and does not always lead to improvements of the ATDEXX method if compared with experimental results. In case of acetaldehyde, see Table III, the TDEXX performs notably better than ATDEXX for the $n \rightarrow \pi^*$ excitation energy, while in case of the five Rydberg excitations considered this is reversed. The Tamm–Dancoff approximation to TDHF(EXX), i.e., TDHF[TD](EXX), yields excitation energies of acetaldehyde that are very close to the TDEXX and TDHF values, which are also close to each other. The excitation energies from the ALDA(EXX) approach, on the other hand, are clearly different to those from TDEXX: for the $n \rightarrow \pi^*$ transition an excitation energy that is $+0.64$ eV higher is found while the Rydberg excitation energies are constantly smaller by as much as 1.26 eV. In fact, the ALDA(EXX) Rydberg excitation energies are fairly close to the experimental values while the corresponding $n \rightarrow \pi^*$ excitation energy lies 1.26 eV too high (see Table III). Another notable difference to the ethylene results from Table II is that the first order Taylor expansion approximation to TDEXX (TDEXX[1]) deviates more from the infinite order solutions. This is even more so in case of pyridine where one also finds a larger deviation between the TDEXX and the TDHF(EXX) excitation energies (see Table IV). Here it is found that even the second order terms in the expansion of Eq. (37) are not yet sufficient to obtain converged results, deviations of up to 0.22 eV between TDEXX[2] and TDEXX are observed for the four lowest valence excitations as can be seen in Table IV. Table IV also shows relative strong deviations for all approaches with respect to the experimental reference energies with relative errors of up to 30%. Notable exceptions are the first $\pi \rightarrow \pi^*$ excitation energy which is nicely reproduced by ATDEXX and the second $\pi \rightarrow \pi^*$ excitation energy which is well described by TDEXX. It is also interesting to see that the EXX eigenvalue differences reproduce the first three experimental excitation energies much better than the TDEXX method while with the adiabatic TDEXX kernel only the $n \rightarrow \pi^*$ excitations are changed in comparison to $\Delta\epsilon(\text{EXX})$. A similar trend is also found for acetaldehyde where all Rydberg type excitations are better described by $\Delta\epsilon(\text{EXX})$ than with ATDEXX or TDEXX (see Table III). Among the systems studied in this work, the neglect of the nonadiabatic contributions to the EXX kernel has the largest effect for the excitation energies of pyridine, e.g., a large difference of about -1.5 eV between ATDEXX and TDEXX is found for the second $n \rightarrow \pi^*$ excitation energy. Nevertheless, the ATDEXX method still overestimates the experimental $n \rightarrow \pi^*$ excitation energy of 5.43 eV by almost 1 eV.

These results show that it is important to account for electron correlation effects in order to obtain a better agreement with the experiment. In the TDEXX method correlation

is neglected while exchange is treated exactly. Correlation enters at two points: (i) in the calculation of the KS orbitals and eigenvalues via the correlation potential and (ii) in the actual TDDFT response calculation via correlation contributions to the xc kernel. In order to get a certain estimate of the first effect, we have considered the impact of modifications of the orbital eigenvalues on the excitation energies using the correction scheme of Eq. (59) in conjunction with unmodified EXX orbitals. The corresponding results for the excitation energies for the three considered molecules for the approaches ATDEXX, ALDA(EXX), and TDHF[TD](EXX) are listed in Tables V–VII under the labels ATDEXX(β), ALDA(EXX)(β), and TDEXX[TD](EXX)(β) [with $\beta = 0.02, 0.03$ corresponding to the parameter from Eq. (59)]. A comparison with the standard results for ethylene and pyridine from Tables II and IV shows that the ATDEXX(β) approaches yield only marginal improvements over ATDEXX. In fact, in case of pyridine the ATDEXX(β) excitation energies are even slightly worse than the ATDEXX values on average. This can be explained with the rather small differences between the EXX HOMO energies and the negative ionization energies obtained with the PBE0 method, (see Sec. III), so that the correction of Eq. (59) did not have a large effect on the KS energy levels. This is verified by the small differences of the uncoupled eigenvalue spectra $\Delta\epsilon$ in Tables II, V and IV, VII, respectively. This indicates that the larger deviations between the TDEXX excitation energies and the experimental ones for pyridine are not due to errors in the KS eigenvalue spectrum but are mainly due to approximations in the xc kernel. For example, it can be seen in Table VII that with the exception of the B₂ excitation the results for ALDA(EXX)(β) are notably better than the ATDEXX(β) ones. The use of the Tamm–Dancoff approximation (TDHF[TD](EXX)(β) in Table VII) or the full nonadiabatic EXX kernel (not shown) did not lead to an improvement here with exception of the A₁ excitation (see Table VII). For acetaldehyde the effect of a correction of the EXX eigenvalues in contrast to the situation for ethylene and pyridine is dramatically different. As described in Sec. III, a strong difference of 1.5 eV between the EXX HOMO energy and the calculated negative ionization potential is found and therefore the KS eigenvalues are largely effected by the correction scheme of Eq. (59). As can be seen in Table VI, strong improvements are obtained for excitations calculated for acetaldehyde using the ATDEXX(β) approach. For example, with $\beta = 0.03$ the average absolute deviation to the experimental values amounts to only 0.06 eV compared to ATDEXX where an average deviation of about 1 eV is found. A similar improvement is also found for TDHF[TD](EXX)(β) compared to the uncorrected TDEXX[TD](EXX) approach. The TDEXX[TD](β) and also the ALDA(EXX)(β) results are, however, not as good as the ATDEXX(β) excitation energies.

In order to test whether such improvements can also be obtained if the EXX functional is combined with a standard local or semilocal correlation functional, instead of applying the explicit correction scheme of Eq. (59), we have also performed ground-state calculations with a combination of the EXX potential with VWN (Vosko–Wilk–Nusair local correlation functional) and PBEC (Perdew–Burke–Ernzerhof GGA

TABLE V. Experimental and calculated transition energies for ethylene calculated by combining the adiabatic EXX kernel, the HF kernel in the Tamm-Dancoff approximation according to Eq. (52), and the ALDA kernel with a modified EXX eigenvalue spectrum [ATDEXX(β), TDHF[TD](EXX)(β), ALDA(EXX)(β) with $\beta = 0.02, 0.03$ corresponding to the parameter from Eq. (59)] and by combining the full and adiabatic EXX kernel with a KS eigenvalue spectrum obtained with the EXX exchange potential supplemented by (semi)local correlation functionals [TDEXX(EXX+VWN), ATDEXX(EXX+VWN), TDEXX(EXX+PBEC), ATDEXX(EXX+PBEC)]. Also shown are results obtained by combining EXX/ALDA hybrid kernels defined in Eq. (61) with KS orbitals and eigenvalues from the LPBE0AC potential [TDEXX-ALDA(α)(LPBE0AC), ATDEXX-ALDA(α)(LPBE0AC), with the corresponding scaling factor α from Eq. (61)]. Furthermore, KS eigenvalue differences $\Delta\epsilon$ corresponding to the excitations are displayed for EXX, EXX(β), EXX+VWN, EXX+PBEC, and LPBE0AC orbitals. The standard TDPBE and TDPBE0 results and the experimental data are taken from Ref. 56. Energies are in eV.

	1B _{3u} Ryd	1B _{1u} $\pi \rightarrow \pi^*$	1B _{1g} Ryd	1B _{2g} Ryd	2A _g Ryd	2B _{3u} Ryd	3B _{3u} Ryd	4B _{3u} Ryd	3B _{1g} Ryd	2B _{1u} Ryd	5B _{3u} Ryd
$\Delta\epsilon(\text{EXX}(0.02))$	7.25	6.16	8.06	7.99	8.13	8.76	8.87	9.09	8.28	9.06	9.52
$\Delta\epsilon(\text{EXX}(0.03))$	7.23	6.14	8.04	7.97	8.11	8.75	8.86	9.08	8.27	9.04	9.51
$\Delta\epsilon(\text{EXX}+\text{VWN})$	7.81	6.09	8.66	8.60	8.96	9.43	9.62	10.04	8.36	10.07	10.50
$\Delta\epsilon(\text{EXX}+\text{PBEC})$	7.92	6.12	8.73	8.68	8.93	9.45	9.63	9.90	8.16	9.86	10.32
$\Delta\epsilon(\text{LPBE0AC})$	7.08	5.69	7.75	7.30	8.80	7.92	9.17	8.90	7.58	10.35	9.92
ATDEXX(0.02)	7.30	7.24	7.98	8.03	8.20	8.78	8.96	9.10	8.84	9.11	9.54
ATDEXX(0.03)	7.28	7.22	7.96	8.01	8.18	8.76	8.95	9.09	8.83	9.09	9.53
ALDA(EXX)(0.02)	7.25	7.95	8.04	7.99	8.16	8.76	8.87	9.10	8.52	9.17	9.53
TDHF[TD](EXX)	7.09	7.69	7.69	7.83	8.07	8.57	8.82	8.91	9.19	8.98	9.35
TDHF[TD](EXX)(0.02)	7.27	7.84	7.87	8.01	8.25	8.76	9.00	9.10	9.30	9.17	9.54
ATDEXX(EXX+VWN)	7.89	7.24	8.61	8.70	9.04	9.52	9.73	10.04	8.93	10.11	10.52
TDEXX(EXX+VWN)	7.88	7.59	8.52	8.71	9.08	9.52	9.80	10.03	9.45	10.13	10.52
ATDEXX(EXX+PBEC)	7.99	7.28	8.68	8.76	8.99	9.51	9.73	9.90	8.72	9.90	10.34
TDEXX(EXX+PBEC)	7.99	7.64	8.59	8.78	9.03	9.52	9.79	9.89	9.20	9.92	10.34
TDEXX-ALDA(0.5)(LPBE0AC)	6.98	7.48	7.61	7.67	8.21	8.61	8.93	9.11	8.54	9.31	9.56
TDEXX-ALDA(0.25)(LPBE0AC)	7.06	7.58	7.69	7.71	8.41	8.73	9.10	9.37	8.19	9.57	9.80
ATDEXX-ALDA(0.5)(LPBE0AC)	7.07	7.29	7.70	7.72	8.40	8.74	9.12	9.36	8.13	9.52	9.80
ATDEXX-ALDA(0.25)(LPBE0AC)	7.10	7.49	7.73	7.72	8.51	8.79	9.20	9.50	7.99	9.67	9.93
LPBE0AC/TDEXX-ALDA(0.5)	6.98	7.51	7.58	7.55	8.37	8.15	8.89	8.73	8.54	9.74	9.48
LPBE0AC/TDEXX-ALDA(0.25)	7.05	7.61	7.66	7.45	8.63	8.03	9.05	8.81	8.19	10.04	9.69
LPBE0AC/ATDEXX-ALDA(0.5)	7.06	7.32	7.68	7.45	8.61	8.04	9.05	8.83	8.14	10.01	9.69
LPBE0AC/ATDEXX-ALDA(0.25)	7.08	7.52	7.71	7.39	8.74	7.97	9.12	8.86	8.00	9.88	9.80
TDPBE(PBE)	6.38	7.07	6.79	6.77	6.92	6.86	7.08	7.29	7.41	7.33	7.78
TDPBE0(PBE0)	6.80	7.46	7.32	7.33	7.54	7.66	7.83	7.98	8.06	7.88	8.35
Exp.	7.11	7.65	7.80	7.90	8.28	8.62	8.90	9.08	9.20	9.33	9.51

TABLE VI. Experimental and calculated transition energies for acetaldehyde. See Table V for details. Energies are in eV.

	A'' $n \rightarrow \pi^*$	2A' Ryd	3A' Ryd	4A' Ryd	6A' Ryd	7A' Ryd
$\Delta\epsilon(\text{EXX}(0.02))$	4.30	5.99	6.84	7.26	7.61	7.85
$\Delta\epsilon(\text{EXX}(0.03))$	4.45	6.11	6.94	7.35	7.70	7.94
$\Delta\epsilon(\text{EXX}+\text{VWN})$	5.35	7.80	7.91	8.80	9.47	10.01
$\Delta\epsilon(\text{EXX}+\text{PBEC})$	5.23	7.78	7.89	8.73	9.39	9.84
$\Delta\epsilon(\text{LPBE0AC})$	4.00	6.29	6.99	7.64	8.28	8.49
ATDEXX(0.02)	4.15	6.73	7.42	7.61	8.32	8.43
ATDEXX(0.03)	4.29	6.85	7.52	7.70	8.41	8.51
ALDA(EXX)(0.02)	4.58	6.06	6.88	7.25	7.63	7.85
TDHF[TD](EXX)	4.80	8.34	9.06	9.14	9.92	10.05
TDHF[TD](EXX)(0.02)	3.85	7.19	8.00	7.87	8.68	8.65
ATDEXX(EXX+VWN)	4.75	8.45	9.10	9.19	10.04	10.12
TDEXX(EXX+VWN)	4.96	9.31	9.46	10.17	11.13	11.23
ATDEXX(EXX+PBEC)	5.07	8.52	8.91	9.42	10.26	10.42
TDEXX(EXX+PBEC)	4.82	9.25	9.42	10.00	10.86	10.93
TDEXX-ALDA(0.5)(LPBE0AC)	4.61	7.60	8.25	8.45	9.22	9.38
TDEXX-ALDA(0.25)(LPBE0AC)	4.46	7.03	7.65	8.03	8.73	8.96
ATDEXX-ALDA(0.5)(LPBE0AC)	4.42	6.93	7.60	7.98	8.60	8.84
ATDEXX-ALDA(0.25)(LPBE0AC)	4.37	6.67	7.32	7.73	8.31	8.71
TDPBE(PBE)	4.11	5.43	5.88	6.05	6.12	6.22
TDPBE0(PBE0)	4.24	6.45	6.95	7.17	7.45	7.49
Exp.	4.28	6.82	7.46	7.75	8.43	8.69

TABLE VII. Experimental and calculated transition energies for pyridine. See Table V for details. Energies are in eV.

	B ₁ $n \rightarrow \pi^*$	B ₂ $\pi \rightarrow \pi^*$	A ₂ $n \rightarrow \pi^*$	A ₁ $\pi \rightarrow \pi^*$
$\Delta\epsilon(\text{EXX}(0.02))$	5.12	4.99	5.54	5.40
$\Delta\epsilon(\text{EXX}(0.03))$	5.11	4.98	5.53	5.39
$\Delta\epsilon(\text{EXX}+\text{VWN})$	5.15	4.94	5.57	5.36
$\Delta\epsilon(\text{EXX}+\text{PBEC})$	5.03	4.97	5.45	5.39
$\Delta\epsilon(\text{LPBE0AC})$	4.15	4.80	4.52	5.17
ATDEXX(0.02)	5.73	5.07	6.41	5.43
ATDEXX(0.03)	5.72	5.06	6.40	5.42
ALDA(EXX)(0.02)	5.41	5.58	5.58	6.38
TDHF[TD](EXX)	5.99	6.07	7.29	6.41
TDHF[TD](EXX)(0.02)	6.06	6.13	7.36	6.47
ATDEXX(EXX+VWN)	5.76	5.02	6.47	5.40
TDEXX(EXX+VWN)	6.29	6.33	8.01	6.49
ATDEXX(EXX+PBEC)	5.63	5.06	6.31	5.44
TDEXX(EXX+PBEC)	6.15	6.36	7.81	6.54
TDEXX-ALDA(0.5)(LPBE0AC)	5.51	5.79	6.42	6.49
TDEXX-ALDA(0.25)(LPBE0AC)	5.02	5.57	5.42	6.41
ATDEXX-ALDA(0.5)(LPBE0AC)	4.87	5.15	5.25	5.88
ATDEXX-ALDA(0.25)(LPBE0AC)	4.70	5.26	4.94	6.10
TDPBE(PBE)	4.34	5.31	4.44	6.17
TDPBE0(PBE0)	4.85	5.53	5.21	6.33
Exp.	4.59	4.99	5.43	6.38

correlation functional) correlation potential. The results for the excitation energies using EXX+VWN and EXX+PBEC orbitals and eigenvalues with ATDEXX and TDEXX kernels are displayed in the Tables V–VII and labeled ATDEXX(EXX+VWN), ATDEXX(EXX+PBEC), TDEXX(EXX+VWN), TDEXX(EXX+PBEC). It can be clearly seen in case of ethylene (Table V) and acetaldehyde (Table VI) that the use of the standard correlation potentials do not lead to improvements over ATDEXX or TDEXX results, while for pyridine only slight improvements are obtained by ATDEXX(EXX+VWN), ATDEXX(EXX+PBEC). For acetaldehyde the scheme of Eq. (59) leads to a smaller HOMO–LUMO gap compared to the uncorrected EXX eigenvalue differences, while the additional LDA or GGA correlation potential increases the HOMO–LUMO gap and therefore cannot improve the exchange-only results for acetaldehyde. This finding shows that standard (semi)local correlation potentials are not good candidates to be used in conjunction with the EXX functional.

Often good results are obtained by hybrid approaches that mix a certain amount of exact (HF or EXX) exchange (conventionally 20–25%) with a standard GGA exchange functional. We have tested such a hybrid functional termed as LPBE0AC that is based on the standard Perdew-Burke-Ernzerhof hybrid (PBE0) hybrid functional⁷⁴ but is asymptotically corrected (see Sec. III). The resulting orbitals have been combined with the TDEXX-ALDA and ATDEXX-ALDA hybrid method of Eq. (61) where a scaling parameter of $\alpha = 0.25$ and 0.5 has been used. The results for this approach are shown in Tables V–VII [labeled TDEXX-ALDA(α)(LPBE0AC) and ATDEXX-ALDA(α)(LPBE0AC) with $\alpha = 0.25$ and 0.5] together with the standard time-

dependent PBE and PBE0 excitation energies (labeled TDPBE and TDPBE0). In case of ethylene (Table V), it can be observed that the TDEXX-ALDA(α)(LPBE0AC) and ATDEXX-ALDA(α)(LPBE0AC) hybrid methods perform rather well for the lower excitations but deviate stronger from experiment for some of the higher lying excitation energies. Altogether it can be seen in Table V that the hybrid approach yields excitations that are worse than the excitation energies from ATDEXX(β), but that are clearly better than both the TDPBE and TDPBE0 results. This finding is certainly due to the incorrect asymptotic behavior of the xc potentials of the PBE and the PBE0 functional and the subsequently wrong description of Rydberg states. The same holds true for the Rydberg excitations of acetaldehyde shown in Table VI, where deviations of up to 30% are found for TDPBE and 14% for TDPBE0 with respect the experiment. In contrast to this, the TDEXX-ALDA(α)(LPBE0AC) and ATDEXX-ALDA(α)(LPBE0AC) hybrid methods yield Rydberg excitation energies for acetaldehyde that are rather close to the experiment if a scaling factor of $\alpha = 0.25$ is used. Furthermore the $n \rightarrow \pi^*$ excitation in acetaldehyde is relatively well described by the hybrid method, the experimental value of 4.28 eV is overestimated by only 0.1–0.2 eV. The average absolute deviation from the experimental transition energies of acetaldehyde for the ATDEXX-ALDA(0.25)(LPBE0AC) approach of 0.09 eV is almost as small as for ATDEXX(0.03), where a deviation of 0.06 eV is found. A clear improvement, over both standard TDEXX and the TDEXX results with modified KS eigenvalue spectra is observed for pyridine (see Table VII). Here, all hybrid methods shown in the Table, with exception of TDEXX-ALDA(0.5)(LPBE0AC), deviate on average only by 0.3 eV from the experimental values for the four excitations. This is also clearly better than standard TDDFT based on the PBE functional, i.e., TDPBE, but of a similar accuracy as it is found for TDPBE0 (see Table VII). In summary, the TDEXX-ALDA(α)(LPBE0AC) and ATDEXX-ALDA(α)(LPBE0AC) hybrid methods give a rather balanced description of both Rydberg-type and valence excitations, while the ATDEXX(β) approach and related methods perform better for Rydberg excitations whereas standard TDDFT better describes valence excitations.

V. CONCLUDING REMARKS

The recently introduced frequency-dependent time-dependent density-functional response method based on the exact-exchange kernel, TDEXX,³⁷ has been transformed into a practical and efficient computational scheme. The new generalized eigenvalue equation for the TDEXX method, Eq. (33), is not much more difficult to solve than the standard TDDFT response eigenvalue equation due to Casida,⁷⁵ see also Ref. 45 and 76, and can be used in conjunction with iterative Davidson solvers for generalized eigenvalue equations or, if the Taylor expansion approximation of Eq. (37) is employed, in conjunction with standard Davidson solvers for eigenvalue problems. When deriving the new eigenvalue Eq. (33) underlying the present TDEXX implementation, the basic TDDFT response Eq. (14) is replaced by a

matrix response equation, Eq. (16), by making the assumption that linear dependencies of products of occupied times unoccupied KS orbitals have no significant effect. To check whether this assumption is justified, a diagnosis scheme for eigenvectors of the TDEXX eigenvalue equation was developed and applied. In all cases it was found that unphysical contributions from linear combinations of products of occupied times unoccupied orbitals with zero norm are very small. Therefore, the above assumption seems to be justified and a projection of the eigenvalue Eq. (33) on the linearly independent occupied-virtual orbital product space was not necessary.

The excitation energies obtained with the new TDEXX method were found to be very similar to those obtained with TDHF. This finding can be explained by an analytical comparison of the underlying eigenvalue equations of the TDHF and TDEXX method. If differences between HF and EXX determinants, which are known to be small, are disregarded, then with the help of unitary transformations between occupied HF and EXX orbitals as well as unoccupied HF and EXX orbitals it was shown that the TDHF and TDEXX method differ only in terms of second order in a Taylor expansion given in Eqs. (36) and (49). Notable differences between TDHF and TDEXX excitation energies were, e.g., found for the pyridine molecule with differences of up to 0.3 eV.

A comparison between TDEXX excitation energies and experimental excitation energies for ethylene, acetaldehyde, and pyridine has shown a good agreement only in case of ethylene, while for acetaldehyde and pyridine stronger differences of 1.3 eV on average were found. Here it has been found that the adiabatic approximation to TDEXX, termed as ATDEXX, performs better, however, still yields deviations of in average about 1 eV compared to the experiment.

In order to improve the results for the excitation energies of TDEXX we have also tried to account for electron correlation effects in various ways. The modification of the EXX single-particle spectrum as described in Sec. III has lead to clear improvements for the description of the excitation energies of acetaldehyde, but for ethylene and pyridine this approach was less successful. Also the combination of the EXX potential with two standard (semi)local correlation potentials in order to improve the KS orbitals and eigenvalues as input quantities to TDEXX did not perform very well or partially even worse than TDEXX with EXX orbitals. These findings indicate that for an accurate description of excitation energies, depending on the considered system, both a combination of the EXX potential with an adequate correlation potential may be needed in order to improve the KS eigenvalues and also a combination of the EXX kernel with a suitable correlation kernel may be required. Conventional (semi)local correlation potentials and kernels, however, did not show convincing results. A hybrid approach where the TDEXX exchange kernel is mixed with the ALDA xc kernel combined with a proper xc potential for the ground-state calculation has yielded quite accurate excitation energies for the molecules considered in this work. Certainly a more natural way to include electron correlation in the TDEXX method would be to use orbital-dependent correlation potentials and

kernels. Orbital-dependent correlation functionals that are derived from perturbation theory, e.g., according to Refs. 77 and 78, however, would lead to significantly higher computational costs while it seems unclear whether this would lead to a clearly better agreement with the experiment considering the results of Ref. 78. More economical solutions to the electron correlation problem in our orbital-dependent time-dependent density-functional method will be investigated in a future study.

APPENDIX A: FUNCTION DETERMINING THE EXCHANGE KERNEL

In contrast to the main text, in Appendix A we consider the somewhat more general case that the molecular orbitals may be complex. The function $h_x(\mathbf{r}, \mathbf{r}', \omega)$ defining the exchange kernel of Eq. (6) can be decomposed into four terms $h_x^{[p]}(\mathbf{r}, \mathbf{r}', \omega)$ with $p = 1, 2, 3, 4$

$$h_x(\mathbf{r}, \mathbf{r}', \omega) = \sum_{p=1,4} h_x^{[p]}(\mathbf{r}, \mathbf{r}', \omega). \quad (\text{A1})$$

The four terms are given by

$$\begin{aligned} h_x^{[1]}(\mathbf{r}, \mathbf{r}', \omega) &= -2 \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{unocc}} \left[\frac{\varphi_i^*(\mathbf{r})\varphi_a(\mathbf{r})\langle aj|bi\rangle\varphi_b^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a + \omega + i\eta)(\varepsilon_j - \varepsilon_b + \omega + i\eta)} \right. \\ &\quad \left. + \frac{\varphi_a^*(\mathbf{r})\varphi_i(\mathbf{r})\langle ib|ja\rangle\varphi_j^*(\mathbf{r}')\varphi_b(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a - \omega - i\eta)(\varepsilon_j - \varepsilon_b - \omega - i\eta)} \right], \quad (\text{A2}) \end{aligned}$$

$$\begin{aligned} h_x^{[2]}(\mathbf{r}, \mathbf{r}', \omega) &= -2 \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{unocc}} \left[\frac{\varphi_i^*(\mathbf{r})\varphi_a(\mathbf{r})\langle ab|ji\rangle\varphi_j^*(\mathbf{r}')\varphi_b(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a + \omega + i\eta)(\varepsilon_j - \varepsilon_b - \omega - i\eta)} \right. \\ &\quad \left. + \frac{\varphi_a^*(\mathbf{r})\varphi_i(\mathbf{r})\langle ij|ba\rangle\varphi_b^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a - \omega - i\eta)(\varepsilon_j - \varepsilon_b + \omega + i\eta)} \right], \quad (\text{A3}) \end{aligned}$$

$$\begin{aligned} h_x^{[3]}(\mathbf{r}, \mathbf{r}', \omega) &= -2 \sum_{ij}^{\text{occ}} \sum_a^{\text{unocc}} \left[\frac{\varphi_i^*(\mathbf{r})\varphi_a(\mathbf{r})\langle j|\hat{v}_x^{\text{NL}} - \hat{v}_x|i\rangle\varphi_a^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a + \omega + i\eta)(\varepsilon_j - \varepsilon_a + \omega + i\eta)} \right. \\ &\quad \left. + \frac{\varphi_a^*(\mathbf{r})\varphi_i(\mathbf{r})\langle i|\hat{v}_x^{\text{NL}} - \hat{v}_x|j\rangle\varphi_j^*(\mathbf{r}')\varphi_a(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a - \omega - i\eta)(\varepsilon_j - \varepsilon_a - \omega - i\eta)} \right] \\ &\quad + 2 \sum_i^{\text{occ}} \sum_{ab}^{\text{unocc}} \left[\frac{\varphi_i^*(\mathbf{r})\varphi_a(\mathbf{r})\langle a|\hat{v}_x^{\text{NL}} - \hat{v}_x|b\rangle\varphi_b^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a + \omega + i\eta)(\varepsilon_i - \varepsilon_b + \omega + i\eta)} \right. \\ &\quad \left. + \frac{\varphi_a^*(\mathbf{r})\varphi_i(\mathbf{r})\langle b|\hat{v}_x^{\text{NL}} - \hat{v}_x|a\rangle\varphi_i^*(\mathbf{r}')\varphi_b(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a - \omega - i\eta)(\varepsilon_i - \varepsilon_b - \omega - i\eta)} \right], \quad (\text{A4}) \end{aligned}$$

and

$$\begin{aligned}
 h_x^{[4]}(\mathbf{r}, \mathbf{r}', \omega) = & -2 \sum_{ij}^{\text{occ}} \sum_a^{\text{unocc}} \left[\frac{\varphi_j^*(\mathbf{r}) \varphi_a(\mathbf{r}) \langle a | \hat{v}_x^{\text{NL}} - \hat{v}_x | i \rangle \varphi_i^*(\mathbf{r}') \varphi_j(\mathbf{r}')}{(\varepsilon_j - \varepsilon_a + \omega + i\eta)(\varepsilon_i - \varepsilon_a)} + \frac{\varphi_j^*(\mathbf{r}) \varphi_i(\mathbf{r}) \langle i | \hat{v}_x^{\text{NL}} - \hat{v}_x | a \rangle \varphi_a^*(\mathbf{r}') \varphi_j(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a + \omega + i\eta)} \right. \\
 & + \frac{\varphi_a^*(\mathbf{r}) \varphi_j(\mathbf{r}) \langle i | \hat{v}_x^{\text{NL}} - \hat{v}_x | a \rangle \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{(\varepsilon_j - \varepsilon_a - \omega - i\eta)(\varepsilon_i - \varepsilon_a)} + \left. \frac{\varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \langle a | \hat{v}_x^{\text{NL}} - \hat{v}_x | i \rangle \varphi_j^*(\mathbf{r}') \varphi_a(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a - \omega - i\eta)} \right] \\
 & + 2 \sum_i^{\text{occ}} \sum_{ab}^{\text{unocc}} \left[\frac{\varphi_i^*(\mathbf{r}) \varphi_b(\mathbf{r}) \langle a | \hat{v}_x^{\text{NL}} - \hat{v}_x | i \rangle \varphi_b^*(\mathbf{r}') \varphi_a(\mathbf{r}')}{(\varepsilon_i - \varepsilon_b + \omega + i\eta)(\varepsilon_i - \varepsilon_a)} + \frac{\varphi_a^*(\mathbf{r}) \varphi_b(\mathbf{r}) \langle i | \hat{v}_x^{\text{NL}} - \hat{v}_x | a \rangle \varphi_b^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b + \omega + i\eta)} \right. \\
 & + \left. \frac{\varphi_b^*(\mathbf{r}) \varphi_i(\mathbf{r}) \langle i | \hat{v}_x^{\text{NL}} - \hat{v}_x | a \rangle \varphi_a^*(\mathbf{r}') \varphi_b(\mathbf{r}')}{(\varepsilon_i - \varepsilon_b - \omega - i\eta)(\varepsilon_i - \varepsilon_a)} + \frac{\varphi_b^*(\mathbf{r}) \varphi_a(\mathbf{r}) \langle a | \hat{v}_x^{\text{NL}} - \hat{v}_x | i \rangle \varphi_i^*(\mathbf{r}') \varphi_b(\mathbf{r}')}{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b - \omega - i\eta)} \right]. \quad (\text{A5})
 \end{aligned}$$

Matrix elements of the type $\langle aj | bi \rangle$ are defined by

$$\langle aj | bi \rangle = \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi_a^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_b(\mathbf{r}) \varphi_i(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|. \quad (\text{A6})$$

The parameter η in the denominators guarantees that perturbations are switched on adiabatically. In applications the limit $\eta \rightarrow 0$ is considered.

The contributions due to $h_x^{[4]}$ in earlier work³⁷ had only negligible effect and therefore are neglected in this work.

APPENDIX B: RESPONSE FUNCTION IN TERMS OF EXX EIGENVALUES AND EIGENVECTORS

In Appendix B we derive a sum over states expression for the response function of an electronic system in terms of the excitation energies Ω_n and the corresponding eigenvectors $\mathbf{z}_n$ resulting from solving the TDEXX Eq. (31). From this expression for the response function follows expression (19) for the oscillator strengths in terms of eigenvectors $\mathbf{z}_n$.

Starting point is Eq. (14) for the response of the electron density due to an external perturbation. A sufficient condition for Eq. (14) to be obeyed is that Eq. (16) holds true, which can be reformulated as

$$\begin{aligned}
 & \left[\omega^2 [\mathbf{1} - \boldsymbol{\varepsilon}^{-1/2} [\mathbf{A} - \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\varepsilon}^{-1/2}] - \boldsymbol{\varepsilon}^2 \right. \\
 & \left. - \boldsymbol{\varepsilon}^{1/2} [\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\varepsilon}^{1/2} \right] \mathbf{z}(\omega) = 4\boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega) \quad (\text{B1})
 \end{aligned}$$

if the matrices $\mathbf{C}$ and $\mathbf{X}(\omega)$ are expressed by the matrices $\mathbf{A}$, $\mathbf{B}$, and $\boldsymbol{\Delta}$ according to Eqs. (8) to (12).

Next we introduce a matrix $\mathbf{Z}$ that shall contain in its columns the eigenvectors $\mathbf{z}_n$ of the TDEXX Eq. (31) and a diagonal matrix $\boldsymbol{\Omega}$ that shall contain the eigenvalues Ω_n of the TDEXX Eq. (31). With the matrices $\mathbf{Z}$ and $\boldsymbol{\Omega}$ the TDEXX

Eq. (31) can be rewritten according to

$$\begin{aligned}
 & \left[\boldsymbol{\varepsilon}^2 + \boldsymbol{\varepsilon}^{1/2} [\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\varepsilon}^{1/2} \right] \mathbf{Z} \\
 & = \left[\mathbf{1} - \boldsymbol{\varepsilon}^{-1/2} [\mathbf{A} - \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\varepsilon}^{-1/2} \right] \mathbf{Z} \boldsymbol{\Omega}^2. \quad (\text{B2})
 \end{aligned}$$

Because the TDEXX Eq. (B2) is a generalized eigenvalue equation, its eigenvalues can and shall be chosen orthonormal with respect to the norm of the overlap matrix

$$\mathbf{S} = [\mathbf{1} - \boldsymbol{\varepsilon}^{-1/2} [\mathbf{A} - \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\varepsilon}^{-1/2}] \quad (\text{B3})$$

occurring on its right-hand side, i.e.,

$$\mathbf{Z}^T \mathbf{S} \mathbf{Z} = \mathbf{1}, \quad (\text{B4})$$

which implies

$$\mathbf{Z} \mathbf{Z}^T = \mathbf{S}^{-1} \quad (\text{B5})$$

and

$$\mathbf{S} \mathbf{Z} \mathbf{Z}^T \mathbf{S} = \mathbf{S}. \quad (\text{B6})$$

Next, we multiply the TDEXX Eq. (B2) from the right by $\mathbf{Z}^T \mathbf{S}$, insert Eqs. (B3) and (B5), and obtain

$$\boldsymbol{\varepsilon}^2 + \boldsymbol{\varepsilon}^{1/2} [\mathbf{A} + \mathbf{B} + \boldsymbol{\Delta}] \boldsymbol{\varepsilon}^{1/2} = \mathbf{S} \mathbf{Z} \boldsymbol{\Omega}^2 \mathbf{Z}^T \mathbf{S}. \quad (\text{B7})$$

If we insert this equation together with Eq. (B6) into Eq. (B1), then we obtain

$$[\omega^2 \mathbf{S} \mathbf{Z} \mathbf{Z}^T \mathbf{S} - \mathbf{S} \mathbf{Z} \boldsymbol{\Omega}^2 \mathbf{Z}^T \mathbf{S}] \mathbf{z}(\omega) = 4\boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega) \quad (\text{B8})$$

or

$$[\mathbf{S} \mathbf{Z} (\omega^2 \mathbf{1} - \boldsymbol{\Omega}^2) \mathbf{Z}^T \mathbf{S}] \mathbf{z}(\omega) = 4\boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega). \quad (\text{B9})$$

With Eqs. (B4) and (B5), it follows that the inverse of the matrix $[\mathbf{S} \mathbf{Z} (\omega^2 \mathbf{1} - \boldsymbol{\Omega}^2) \mathbf{Z}^T \mathbf{S}]$ on the left-hand side of Eq. (B9) is the matrix $[\mathbf{Z} (\omega^2 \mathbf{1} - \boldsymbol{\Omega}^2)^{-1} \mathbf{Z}^T]$. Multiplication

of Eq. (B9) from the left with this inverse yields the vector $\mathbf{z}(\omega)$ as

$$\begin{aligned}\mathbf{z}(\omega) &= 4 [\mathbf{Z}(\omega^2 \mathbf{1} - \Omega_n^2)^{-1} \mathbf{Z}^T] \boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega) \\ &= 4 \sum_n \mathbf{z}_n (\omega^2 \mathbf{1} - \Omega_n^2)^{-1} \mathbf{z}_n^T \boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega).\end{aligned}\quad (\text{B10})$$

Insertion of expression (B10) for $\mathbf{z}(\omega)$ into Eq. (17) for the linear response $\rho^{(1)}(\omega, \mathbf{r})$ of the electron density to a frequency-dependent perturbation $v^{(1)}(\omega, \mathbf{r})$ yields

$$\begin{aligned}\rho^{(1)}(\omega, \mathbf{r}) &= 4 \sum_n \sum_{ia} \varphi_{ia}(\mathbf{r}) \left[\boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n (\omega^2 \mathbf{1} - \Omega_n^2)^{-1} \mathbf{z}_n^T \boldsymbol{\varepsilon}^{1/2} \mathbf{v}^{(1)}(\omega) \right]_{ia} \\ &= 4 \sum_n \sum_{ia} \sum_{jb} \varphi_{ia}(\mathbf{r}) \left[\boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n (\omega^2 \mathbf{1} - \Omega_n^2)^{-1} \mathbf{z}_n^T \boldsymbol{\varepsilon}^{1/2} \right]_{ia,jb} \\ &\quad \times \langle \varphi_b | v^{(1)}(\omega) | \varphi_j \rangle \\ &= \int d\mathbf{r}' 4 \sum_n \sum_{ia} \sum_{jb} \varphi_{ia}(\mathbf{r}) \left[\boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n (\omega^2 \mathbf{1} - \Omega_n^2)^{-1} \right. \\ &\quad \times \left. \mathbf{z}_n^T \boldsymbol{\varepsilon}^{1/2} \right]_{ia,jb} \varphi_{jb}(\mathbf{r}') v^{(1)}(\omega, \mathbf{r}') \\ &= \int d\mathbf{r}' \chi(\omega, \mathbf{r}, \mathbf{r}') v^{(1)}(\omega, \mathbf{r}').\end{aligned}\quad (\text{B11})$$

Equation (B11) implies that the response function $\chi(\omega, \mathbf{r}, \mathbf{r}')$ of an electronic system within the TDEXX approach is given by

$$\begin{aligned}\chi(\omega, \mathbf{r}, \mathbf{r}') &= 4 \sum_n \sum_{ia} \sum_{jb} \varphi_{ia}(\mathbf{r}) \left[\boldsymbol{\varepsilon}^{1/2} \mathbf{z}_n (\omega^2 \mathbf{1} - \Omega_n^2)^{-1} \mathbf{z}_n^T \boldsymbol{\varepsilon}^{1/2} \right]_{ia,jb} \\ &\quad \times \varphi_{jb}(\mathbf{r}') \\ &= 4 \sum_n \sum_{ia} \sum_{jb} \varphi_{ia}(\mathbf{r}) \left[\mathbf{U}_n \frac{\Omega_n}{\omega^2 - \Omega_n^2} \mathbf{U}_n^T \right] \varphi_{jb}(\mathbf{r}'),\end{aligned}\quad (\text{B12})$$

with $\mathbf{U}_n$ defined as $\mathbf{U}_n = \mathbf{z}_n \boldsymbol{\varepsilon}^{1/2} \Omega_n^{-1/2}$, see Ref. 79. From this expression of the response function, the frequency-dependent polarizability tensor can be obtained by integrating over components of the dipole operator with respect to both $\mathbf{r}$ and $\mathbf{r}'$ and expression (19) for the oscillator strengths follows.

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