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Natural excitation orbitals from linear response theories: Time-dependent density functional theory, time-dependent Hartree-Fock, and time-dependent natural orbital functional theory

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Straightforward interpretation of excitations is possible if they can be described as simple single orbital-to-orbital (or double, etc.) transitions. In linear response time-dependent density functional theory (LR-TDDFT), the (ground state) Kohn-Sham orbitals prove to be such an orbital basis. In contrast, in a basis of natural orbitals (NOs) or Hartree-Fock orbitals, excitations often employ many orbitals and are accordingly hard to characterize. We demonstrate that it is possible in these cases to transform to natural excitation orbitals (NEOs) which resemble very closely the KS orbitals and afford the same simple description of excitations. The desired transformation has been obtained by diagonalization of a submatrix in the equations of linear response time-dependent 1-particle reduced density matrix functional theory (LR-TDDMFT) for the NO transformation, and that of a submatrix in the linear response time-dependent Hartree-Fock (LR-TDHF) equations for the transformation of HF orbitals. The corresponding submatrix is already diagonal in the KS basis in the LR-TDDFT equations. While the orbital shapes of the NEOs afford the characterization of the excitations as (mostly) simple orbital-to-orbital transitions, the orbital energies provide a fair estimate of excitation energies. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4974327>]

I. INTRODUCTION

The development in time of an N -electron system is governed by the N -electron wave function $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t)$, which obeys the time-dependent Schrödinger equation (TDSE). Instead of performing a prohibitively expensive real-time propagation of the wavefunction, approximate information on the electronic dynamics is often obtained from the time-dependence of just one-electron functions, the orbitals $\phi_p(\mathbf{x}t)$, according to one-electron equations of motion (EOMs),

$$\left(\hat{h}(\mathbf{x}t) + \hat{v}_{ee}(\mathbf{x}t)\right) \phi_p(\mathbf{x}t) = i \frac{\partial}{\partial t} \phi_p(\mathbf{x}t), \quad (1)$$

with

$$\hat{h}(\mathbf{x}t) = -\frac{1}{2} \nabla_r^2 + v_{ext}(\mathbf{r}t),$$

where $\mathbf{x} = (\mathbf{r}, s)$ and we restrict ourselves to external potentials that do not depend on the spin variable s . Several of such theories of orbital dynamics are known, which are distinguished by the form taken by the electron-electron potential. The best known is probably the time-dependent Hartree-Fock theory (TDHF), which was first proposed by Dirac.¹ In this case the potential $\hat{v}_{ee}(\mathbf{r}, t)$ of Eq. (1) takes the simple form of the Coulomb and exchange operators of the Hartree-Fock model for stationary wavefunctions, but with the time-dependent HF orbitals substituted,

$$\begin{aligned} \hat{v}_{ee}^{TDHF}(\mathbf{r}_1t) \phi_p(\mathbf{r}_1t) \sigma_p(s_1) &= (\hat{J}(t) - \hat{K}(t)) \phi_p(\mathbf{r}_1t) \sigma_p(s_1) \\ &= \sum_{i=1}^H \int d\mathbf{r}_2 \sum_{s_2} \frac{|\phi_i(\mathbf{r}_2t) \sigma_i(s_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_p(\mathbf{r}_1t) \sigma_p(s_1) \\ &\quad - \sum_i^H \delta_{\sigma_p, \sigma_i} \int d\mathbf{r}_2 \sum_{s_2} \frac{\phi_i^*(\mathbf{r}_2t) \sigma_i(s_2) P_{12} \phi_i(\mathbf{r}_2t) \sigma_i(s_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad \times \phi_p(\mathbf{r}_1t) \sigma_p(s_1), \end{aligned} \quad (2)$$

where H denotes the index of the highest occupied spin orbital (HOMO) and σ_i is the spin function attached to orbital ϕ_i (either α or β). The assumption was that if the time-developing ground state orbitals are put in a single Slater determinant wavefunction, a reasonable approximation to the time-dependent exact wavefunction $\Psi(t)$ is obtained. Dirac showed that Equations (1) and (2) lead to the expression

$$i\dot{\gamma}(t) = [\gamma(t), \mathbf{F}(t)] \quad (3)$$

for the time-dependence of the one-particle density matrix, where \mathbf{F} is the Fock matrix and γ the one-electron reduced density matrix. It is required that the wavefunction is a single determinant of the time-developing orbitals, i.e., the density matrix is idempotent,

$$\gamma(t)^2 = \gamma(t). \quad (4)$$

TDHF has become a very important method in many-particle physics, notably in nuclear physics.²⁻⁴ Often, Equations (3)

and (4) are taken as the basis of TDHF, and the orbital TDSE (1) with the potential (2) can then be derived. Shortly after Dirac's work it was demonstrated by Frenkel⁵ that the TDHF equations can also be derived from a stationarity principle for the time-dependent wavefunction,

$$\delta \left\langle \Psi \left| i \frac{\partial}{\partial t} - \hat{H} \right| \Psi \right\rangle = 0, \quad (5)$$

when one approximates the wavefunction with a (time-dependent) Slater determinant (see for a clear exposition the work of McWeeny⁶). The Frenkel principle (5) has been somewhat controversial,^{7–10} the main criticism being that the obtained stationarity of an approximate wavefunction does not guarantee the proximity of the approximate solution to the exact wavefunction (note the difference with the standard ground state Rayleigh-Ritz variational principle). Least squares methods, which apply minimization of the square of the norm of the error vector $(\hat{H} - i\partial/\partial t)\tilde{\Psi}$ associated with a trial wavefunction $\tilde{\Psi}$, have the advantage of leading to a definite minimum of a positive quantity with a clear lower bound (zero) for the exact solution.^{7,11,12} Nevertheless, the Frenkel principle and in particular the related principle of least action, requiring stationarity of the action integral

$$A = \int_{t_1}^{t_2} \left\langle \Psi \left| i \frac{\partial}{\partial t} - \hat{H} \right| \Psi \right\rangle, \quad (6)$$

have been commonly applied for the derivation of approximate time-dependent theories, not only TDHF^{3,5,13–18} but also time-dependent density functional theory (TDDFT)¹⁹ and time-dependent density matrix functional theory (TDDMFT),^{20–22} the latter also being denoted as natural orbital functional theory (TDNOFT) and extended to phase-including natural orbital functional theory (TDPINOFT).^{23,24} We will follow this route also in this work.

Time-dependent density functional theory in the time-dependent Kohn-Sham orbital form, TDKS,^{19,25–27} differs from TDHF in that it offers a potentially exact scheme: the orbital EOMs (1) with the Hartree-exchange-correlation potential $v^{Hxc}(t)$ of TDKS theory as effective potential provide the time-evolution of the occupied orbitals, which determine the exact time-dependent density, and all properties of the system. In reality, the exact form of the effective potential is not known in this case. $v^{Hxc}(t)$ is in principle a nonlocal functional (in position and time) of the density, $v^{Hxc}[\rho](\mathbf{r}, t)$, where the complete $\rho(\mathbf{r}', t')$ for possibly all values of \mathbf{r}' and for prior times ($t' \leq t$) is in principle involved (“memory effects”). Customarily, the adiabatic approximation is employed in TDKS, in which memory effects ($t' < t$) are neglected, and some approximate ground state functional is used in which nonlocal effects in space are completely neglected (e.g., in the local density approximation (LDA)) or included very approximately via local derivatives of the density (generalized gradient approximation (GGA)). These approximations have severe consequences, such as lack of double excitation character,^{28–30} and serious errors when the excitation energy is not close to the orbital energy difference of the orbitals between which a transition takes place, which happens for bonding \rightarrow antibonding orbital excitations at elongated bond lengths^{31,32} and in the case of charge-transfer transitions.^{33–37}

In time-dependent density matrix functional theory (TDDMFT),^{20,21,38,39} the natural orbitals (NOs) $\phi_p(\mathbf{x}t)$ are propagated together with their fractional occupation numbers (ONs) $n_p(t)$, which together yield the first-order reduced density matrix (1RDM) $\gamma(\mathbf{x}, \mathbf{x}'; t)$,

$$\gamma(\mathbf{x}, \mathbf{x}'; t) = \sum_p n_p(t) \phi_p(\mathbf{x}t) \phi_p^*(\mathbf{x}'t). \quad (7)$$

The NOs obey an orbital EOM (1) while the ONs are propagated according to the additional EOMs,

$$i \frac{\partial n_p(t)}{\partial t} = \langle \phi_p | \hat{v}_{ee}(t) | \phi_p \rangle. \quad (8)$$

In this case, the effective potential is a functional of the 1RDM, i.e., of both NOs and ONs. Strictly speaking, in this paper we are dealing with (time-dependent) phase-including NO functional theory (TDPINOFT), in which additional variables were introduced as the phases of the NOs.^{23,24,38–40} This makes adiabatic TDPINOFT the exact theory in the paradigmatic case of two-electron systems.³⁸

Arguably, the most important application of dynamical orbital theories is the calculation of electronic excitation energies $\{\omega_\alpha\}$ in the linear response approach. With the customary adiabatic approximation the excitation energies then result as eigenvalues of a matrix diagonalization problem which is formally similar in the LR-TDHF, LR-TDKS, and LR-TDDMFT cases,

$$[\sqrt{\mathbf{A}^+ \mathbf{D} \mathbf{A}^+}] \mathbf{F}_\alpha = \omega_\alpha^2 \mathbf{F}_\alpha. \quad (9)$$

The matrices \mathbf{A}^+ and \mathbf{D} will be detailed below. We restrict ourselves to the response to a real (electric field) perturbation and to real orbitals. In that case the equations can be cast into the given simple form with ω_α^2 as eigenvalues. The matrices are very well known in the case of TDHF, where they can be expressed in the standard TDHF matrices \mathbf{A}^{TDHF} and \mathbf{B}^{TDHF} with $\mathbf{A}^+ = \mathbf{A}^{TDHF} - \mathbf{B}^{TDHF}$ and $\mathbf{D} = \mathbf{A}^- = \mathbf{A}^{TDHF} + \mathbf{B}^{TDHF}$. In LR-TDKS \mathbf{A}^+ is particularly simple, and it consists of just the orbital excitation energies, so it assumes the diagonal form

$$A_{ai,jb}^{TDDFT+} = \mathcal{E}_{ai,jb} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i), \quad (10)$$

while the matrix \mathbf{D} contains, besides the orbital energy differences, also a correction coming from the coupling of orbital excitations through the Hxc kernel $f^{Hxc}(\mathbf{x}_1, \mathbf{x}_2)$ (see Section III for the corresponding expression). (Note our convention of using orbital indices i, j for occupied orbitals, a, b for unoccupied orbitals, and $k, l, m, n, p, q, r, s, \dots$ for general orbitals.) In TDHF both matrices \mathbf{A}^{TDHF+} and $\mathbf{D}^{TDHF} = \mathbf{A}^{TDHF-}$ contain, in addition to \mathcal{E} , some corrections, in the form of combinations of two-electron integrals (see Section III). Both in LR-TDHF and LR-TDKS, orbital indices always occur in occupied-unoccupied (ia) pairs, which leads to an interpretation of excitations as exclusively (combinations of) single occupied-to-unoccupied orbital transitions (no doubles). This is a major drawback of LR-TDHF and LR-TDKS, which is remedied in LR-TDDMFT, see below.

A drawback of the LR-TDDMFT approach, which it shares with LR-TDHF, is the unphysical nature of the virtual orbitals (the weakly occupied NOs in case of DMFT). This leads to difficulties in the interpretation of the excitations.^{41,42}

On the other hand, in LR-TDKS an efficient interpretation is provided with the KS orbitals, so that many excitations (not all) are represented as simple single orbital transitions (or short linear combinations of such transitions) in the KS basis.⁴¹ It is the purpose of this paper to present a derivation and further justification of the recently proposed transformation⁴² of the virtual NOs (the weakly occupied NOs) to a set of orbitals that afford a meaningful representation of the excitations calculated in the linear response formalism of TDDMFT. In fact, these “natural excitation orbitals” (NEOs) will prove to almost coincide with the KS orbitals. An extension to the TDHF method will be given, defining a transformation of the virtual HF orbitals to a similar set of improved orbitals for excitations. In the same spirit, similar attempts have been made to obtain more suitable orbitals to describe excitation (and correlation), such as the recent valence virtual orbitals (VVOs) introduced by Schmidt and co-workers,⁴³ and the approximate (local potential derived) IRDM related orbitals for the description of excitations introduced by Lathiotakis, Helbig, and co-workers,^{44,45} and the natural transition orbitals (NTO) of Martin⁴⁶ for the description of excitations as closely as possible as orbital transitions.

In Section II (Eq. (14)) will be derived within TDDMFT, using the stationarity principle for the action integral. The TDSE for the HF orbitals (Eq. (21)) and for the KS orbitals (Eq. (28)) can then easily be derived from the more general TDDMFT formalism. In Section III the linear response equations are obtained in the three cases, using again the more general TDDMFT equation (40) to derive these equations in the TDHF (54) and TDKS (67) cases. When taking the orbital equations of motion (14), (21), and (28), as well as the linear response equations derived from them, (40), (54), and (67), for granted, the reader may take a shortcut to Sections IV and V, where the physical meaning of the matrix elements appearing in the linear response equations is elucidated (Section IV), and on that basis the transformation to NEOs is proposed in Section V and illustrated with a series of examples, the HeH⁺, Li₂, H₂O, and CH₂O molecules. It is demonstrated that the NEOs obtained in TDHF and TDDMFT are close to the KS orbitals and that they restore also in the linear response TDHF and TDDMFT formalisms the single orbital transition structure for excitations, which is an asset of the LR-TDKS method.

II. UNIFIED DERIVATION OF THE TIME-DEPENDENT SCHRÖDINGER EQUATIONS FOR THE NATURAL ORBITALS, THE HARTREE-FOCK ORBITALS, AND THE KOHN-SHAM ORBITALS

The linear response equations of all approaches considered here (TDHF, TDKS and TDDMFT, or NOFT) are derived from time-dependent Schrödinger equations for the one-electron functions (orbitals) that feature in these theories. It has become customary to derive the TDHF orbital equations from stationarity of an action integral,^{2-4,13-16} the TDDFT equations have also been derived from such a stationarity requirement,¹⁹ and the same holds for the time-dependent equations for the natural orbitals.^{23,24,38,39} The time-dependent

Schrödinger equation for the many-electron wavefunction can be derived from stationarity of the action integral,

$$A[\Psi] = \int_0^T dt \langle \Psi(t) | i\partial/\partial t - \hat{H}(t) | \Psi(t) \rangle, \quad (11)$$

where Ψ is the wave function of an interacting N -electron system. As a preliminary step to time-dependent one-electron Schrödinger equations, A is partitioned into a one-electron part A_0 and a two-electron part W ,

$$A = \int_0^T dt \int dx [(i\partial/\partial t - \hat{h}(\mathbf{r}'t))\gamma(\mathbf{x}, \mathbf{x}'; t)]_{\mathbf{x}'=\mathbf{x}} - \int_0^T dt \langle \Psi(t) | \hat{W} | \Psi(t) \rangle = A_0 - W. \quad (12)$$

A. TDDMFT

The matrix element of the electron-electron interaction operator $\langle \Psi(t) | \hat{W} | \Psi(t) \rangle$ depends in principle on the two-particle reduced density matrix (2RDM). However, (one-particle reduced) density matrix functional theory uses the Hohenberg-Kohn type proof given by Gilbert,⁴⁷ which is that the ground state energy and its components are functionals of the ground state one-particle density matrix, to which a time-dependent analogue can be formulated.²⁰ The two-electron part W can then be considered as a functional of the one-matrix, $W[\gamma]$, or of the NOs $\phi_p(\mathbf{x}t)$ and their ONs $n_p(t)$, $W[\{\phi, n\}]$ (note that the ONs assume values in the interval $0 \leq n_p(t) \leq 1$). Stationarity can then be obtained with respect to variation of the orbitals and the occupation numbers, taking proper account of orbital orthonormality and the allowed range $[0,1]$ for the occupation numbers. This of course introduces derivatives of W . The orbital derivatives enter in the form of matrices

$$W_{pq}(t) = \int dx \frac{\delta W}{\delta \phi_p(\mathbf{x}t)} \phi_q(\mathbf{x}t). \quad (13)$$

Analogous to procedures well known in the Hartree-Fock case, elimination of the Lagrange multipliers leads to one-electron equations, in this case the time-dependent Schrödinger equation for the natural orbitals,^{20,21,23,24,38}

$$(\hat{h}(\mathbf{x}t) + \hat{v}^{NO}(\mathbf{x}t))\phi_p(\mathbf{x}t) = i \frac{\partial}{\partial t} \phi_p(\mathbf{x}t). \quad (14)$$

The potential \hat{v}^{NO} introduces the effects of the electron-electron interaction. The off-diagonal matrix elements are obtained from the orbital derivatives of W ,

$$\langle \phi_p(t) | \hat{v}^{NO}(t) | \phi_q(t) \rangle = \frac{W_{pq}^\dagger(t) - W_{pq}(t)}{n_q(t) - n_p(t)}, \quad p \neq q. \quad (15)$$

Stationarity with respect to occupation numbers $n_k(t)$ yields the diagonal matrix elements of the potential \hat{v}^{NO} ,

$$\langle \phi_p(t) | \hat{v}^{NO}(t) | \phi_p(t) \rangle = \frac{\partial W}{\partial n_p}. \quad (16)$$

In TDDMFT we also need the equation of motion for the occupation numbers (the diagonal elements of the IRDM in the NO basis), which is

$$\frac{\partial n_p(t)}{\partial t} = W_{pp}^\dagger(t) - W_{pp}(t). \quad (17)$$

We have glossed over some details of these derivations; refer to Refs. 20, 21, 23, 24, and 38 for a complete discussion. The equations of motion for the NOs and ONs can in principle be solved, but the real time dynamics is time-consuming. Solutions in one-dimensional model systems have been pursued, where stability issues have been addressed using renormalized NOs, RNOs, incorporating the occupation numbers in the NO definition^{48,49} or with semiclassical approximations.⁵⁰ We restrict ourselves to linear response, see Section III.

B. TDHF

The TDHF equations can be obtained straightforwardly from the more general TDDMFT equations. The one-determinant approximation, or equivalently the idempotency condition on the 1RDM, restricts the one-particle density matrix to be diagonal, with 0 and 1 as allowed values for the occupation numbers on the diagonal ($n_p = 1, p \leq N$; $n_p = 0, p > N$). The electron-electron interaction energy is approximated with the well-known Coulomb and exchange energies at time t , consistent with the one-determinant approximation for the wavefunction, with the occupied orbitals at time t , $\{\phi_i^{HF}(\mathbf{x}, t), i \leq N\}$,

$$W^{TDHF}[\{\phi, n\}] = \frac{1}{2} \sum_p \sum_q n_p n_q [\langle \phi_p(t) \phi_q(t) | \phi_p(t) \phi_q(t) \rangle - \langle \phi_p(t) \phi_q(t) | \phi_q(t) \phi_p(t) \rangle]. \quad (18)$$

The elements of the \mathbf{W} matrix, $W_{kl}^{TDHF}(t)$, can be easily evaluated by taking, according to the definition (13), the derivatives with respect to the orbitals (and projecting against an orbital),

$$W_{kl}^{TDHF}(t) = n_k \sum_p n_p [\langle \phi_k(t) \phi_p(t) | \phi_l(t) \phi_p(t) \rangle - \langle \phi_k(t) \phi_p(t) | \phi_p(t) \phi_l(t) \rangle], \quad (19)$$

while the difference ($W_{kl}^{TDHF^\dagger}(t) - W_{kl}^{TDHF}(t)$) is expressed as

$$W_{kl}^{TDHF^\dagger}(t) - W_{kl}^{TDHF}(t) = (n_l - n_k) \sum_p n_p \times [\langle \phi_k(t) \phi_p(t) | \phi_l(t) \phi_p(t) \rangle - \langle \phi_k(t) \phi_p(t) | \phi_p(t) \phi_l(t) \rangle]. \quad (20)$$

This defines the matrix elements of the operator $\hat{v}^{TDHF}(\mathbf{x}t)$ in the TDHF variant of the orbital EOMs (1),

$$(\hat{h}(\mathbf{x}t) + \hat{v}^{TDHF}(\mathbf{x}t))\phi_k(\mathbf{x}t) = i \frac{\partial}{\partial t} \phi_k(\mathbf{x}t) \quad (21)$$

with

$$\hat{v}^{TDHF}(\mathbf{x}t) = \sum_p n_p (\hat{J}^p(\mathbf{x}t) - \hat{K}^p(\mathbf{x}t)),$$

where $\hat{J}^p(\mathbf{x}t)$ and $\hat{K}^p(\mathbf{x}t)$ are defined as

$$\hat{J}^p(\mathbf{x}t)\phi_k(\mathbf{x}t) = \int d\mathbf{x}' \frac{|\phi_p(\mathbf{x}'t)|^2}{|\mathbf{r} - \mathbf{r}'|} \phi_k(\mathbf{x}t)$$

and

$$\hat{K}^p(\mathbf{x}t)\phi_k(\mathbf{x}t) = \int d\mathbf{x}' \frac{\phi_p^*(\mathbf{x}'t)\phi_k(\mathbf{x}'t)}{|\mathbf{r} - \mathbf{r}'|} \phi_p(\mathbf{x}t). \quad (22)$$

Eq. (21) is just the time-dependent variant of the well-known time-independent HF equations. Consistent with the HF model, Eq. (17) for the time-evolution of the occupation numbers yields in this case $\partial n_p / \partial t = 0$, i.e., constant occupation numbers.

C. TDDFT

The TDDFT case¹⁹ is a bit more subtle than TDHF since it introduces a noninteracting system of electrons, but continues to work, in principle, with the exact time-evolution of the density of the system. So in the first place a noninteracting kinetic energy contribution S_0 (which is a functional of the density $\rho(t)$) is distinguished in A_0 , which is characterized by an independent particle 1RDM $\gamma^s(\mathbf{x}, \mathbf{x}', t)$ with integer occupation numbers 0 and 1, but with the exact diagonal density,

$$S_0[\rho] = \int_0^T dt \int d\mathbf{x} [(i\partial/\partial t - \hat{T})\gamma^s(\mathbf{x}, \mathbf{x}'; t)]_{\mathbf{x}'=\mathbf{x}} \gamma^s(\mathbf{x}, \mathbf{x}'; t) = \sum_p n_p \phi_p(\mathbf{x}, t) \phi_p^*(\mathbf{x}', t) \quad (23)$$

with

$$\sum_p n_p |\phi_p(\mathbf{x}, t)|^2 = \rho^{exact}(\mathbf{x}, t) \quad (n_p = 0 \text{ or } 1).$$

Denoting the kinetic energy of the fully interacting system $S_W = \int_0^T dt \int d\mathbf{x} [(i\partial/\partial t - \hat{T})\gamma(\mathbf{x}, \mathbf{x}'; t)]_{\mathbf{x}'=\mathbf{x}}$, this implies that the correction $S_0 - S_W$ has to be absorbed in the electron-electron interaction part, giving $W^{TDDFT} \equiv A_{Hxc} = (S_0 - S_W) + W$ (cf. E_{Hxc} in the time-independent KS theory),

$$A[\rho] = S_0[\rho] - \int d\mathbf{x} v_{ext}(\mathbf{x}t)\rho(\mathbf{x}t) - A_{Hxc}[\rho]. \quad (24)$$

In the adiabatic approximation, the calculation of the potential at time t is simplified by approximating the dependence on the full time-dependent density $\rho(\mathbf{x}, t')$, $t' \leq t$ with dependence on just $\rho(\mathbf{x}, t)$. The necessary orbital derivatives can then be obtained by applying the chain rule since $W^{TDDFT} = A_{Hxc}$ is a functional of ρ , allowing us to identify $\hat{v}^{Hxc}(\mathbf{x}, t)$ with $\delta A_{Hxc}[\rho(\mathbf{x}', t)] / \delta \rho(\mathbf{x}, t)$, cf. Eq. (15),

$$v_{kl}^{Hxc}(\mathbf{x}t) = \frac{W_{kl}^{TDDFT^\dagger} - W_{kl}^{TDDFT}}{n_l - n_k} = \int d\mathbf{x} \phi_k^*(\mathbf{x}t) \frac{\delta A_{Hxc}[\rho]}{\delta \rho(\mathbf{x}t)} \phi_l(\mathbf{x}t) \quad (25)$$

since

$$W_{kl}^{TDDFT}(t) = \int d\mathbf{x} \int d\mathbf{x}' \frac{\delta A_{Hxc}[\rho]}{\delta \rho(\mathbf{x}'t)} \frac{\partial \rho(\mathbf{x}')}{\partial \phi_k(\mathbf{x}t)} \phi_l(\mathbf{x}t) = n_k(t) \int d\mathbf{x} \phi_k^*(\mathbf{x}t) \frac{\delta A_{Hxc}[\rho]}{\delta \rho(\mathbf{x}t)} \phi_l(\mathbf{x}t) = n_k(t) v_{kl}^{Hxc}(t) \quad (26)$$

and similar for $W_{kl}^{TDDFT^\dagger}$. According to Eq. (16), also the diagonal elements of \hat{v}^{Hxc} are obtained with $\hat{v}^{Hxc}(\mathbf{x}, t)$

$$= \delta A_{Hxc}[\rho]/\delta\rho(\mathbf{x}, t),$$

$$\begin{aligned} \frac{\partial A_{Hxc}[\rho]}{\partial n_k} &= \int d\mathbf{x} \frac{\delta A_{Hxc}[\rho(\mathbf{x}t)]}{\delta\rho(\mathbf{x}t)} \frac{\partial\rho(\mathbf{x}t)}{\partial n_k} \\ &= \int d\mathbf{x} \phi_k^*(\mathbf{x}t) \frac{\delta A_{Hxc}[\rho(\mathbf{x}t)]}{\delta\rho(\mathbf{x}t)} \phi_k(\mathbf{x}t) = v_{kk}^{Hxc}. \end{aligned} \quad (27)$$

This then defines the effective potential in the time-dependent equations for the KS orbitals,

$$(\hat{h}(\mathbf{x}t) + \hat{v}^{Hxc}(\mathbf{x}t))\phi_k(\mathbf{x}t) = i \frac{\partial}{\partial t} \phi_k(\mathbf{x}t) \quad (28)$$

with

$$\hat{v}^{Hxc}(\mathbf{x}t) = \frac{\delta A_{Hxc}[\rho]}{\delta\rho(\mathbf{x}t)}.$$

Consistent with our restriction of $\gamma^s(\mathbf{x}, \mathbf{x}'; t)$ to an independent particle 1RDM with fixed integer occupation numbers, we note that Eq. (17) yields in this case, as in the TDHF case, time-independent occupation numbers

$$\frac{\partial n_k(t)}{\partial t} = W_{kk}^{TDDFT^\dagger}(t) - W_{kk}^{TDDFT}(t) = 0. \quad (29)$$

Having obtained the TDSE for the natural orbitals (1), the HF orbitals (21), and the KS orbitals (28), we will proceed in Sec. III to formulate the linear response based equations for the calculation of excitation energies.

III. LINEAR RESPONSE TDDMFT, TDHF, AND TDKS EQUATIONS FOR EXCITATION ENERGIES

Once the TDSE for the orbitals is known, it is in principle straightforward, using linear response (first order perturbation theory) to derive the matrix diagonalisation problem from which the excitation energies can be determined.⁶ However, the derivations are somewhat lengthy and we will only give the essentials for the most general case, the response of the full one-particle density matrix (TDDMFT) (full details can be found in Refs. 20, 21, 23, 24, and 38). The cases of TDHF and TDKS will then be derived using the more general TDDMFT framework.

A. TDDMFT

Starting with the stationary orbitals, we consider a perturbation by a small time-dependent potential $\delta v_{ext}(t)$. The time-dependent perturbations of the orbitals can be expanded in the unperturbed orbitals,

$$\delta\phi_p(\mathbf{x}t) = \sum_q \phi_q(\mathbf{x}) \delta U_{qp}(t), \quad (30)$$

$$\delta\mathbf{U} = -\delta\mathbf{U}^\dagger, \quad (31)$$

where the antihermiticity of the $\delta\mathbf{U}$ matrix is required to ensure orthogonality of the perturbed orbitals. (The stationary $\phi_q(\mathbf{x})$ have the trivial time dependence $e^{-i\epsilon_q t}$, but this plays no role and is not explicitly indicated.)

This leads to a first order change of the 1RDM,

$$\begin{aligned} \gamma(\mathbf{x}, \mathbf{x}') &= \sum_p n_p \phi_p(\mathbf{x}) \phi_p^*(\mathbf{x}'), \\ \delta\gamma(\mathbf{x}, \mathbf{x}'; t) &= \sum_p \delta n_p(t) \phi_p(\mathbf{x}) \phi_p^*(\mathbf{x}') \\ &\quad + \sum_p n_p (\delta\phi_p(\mathbf{x}t) \phi_p^*(\mathbf{x}') + \phi_p(\mathbf{x}) \delta\phi_p^*(\mathbf{x}'t)) \\ &= \sum_p \delta n_p(t) \phi_p(\mathbf{x}) \phi_p^*(\mathbf{x}') \\ &\quad + \sum_{p,q \neq p} (n_p - n_q) \phi_q(\mathbf{x}) \phi_p^*(\mathbf{x}') \delta U_{qp}(t) \end{aligned} \quad (32)$$

from which the first order changes in the density matrix elements follow

$$\delta\gamma_{pr}(t) = \delta n_p(t) \delta_{pr} + (n_r - n_p) \delta U_{pr}(t). \quad (33)$$

According to first order perturbation theory, the δU_{pr} are just (apart from the energy denominator) the matrix elements of the perturbation operator between orbitals ϕ_p and ϕ_r . The perturbation in this case consists of the external perturbation $\delta v_{ext}(rt)$ plus the change in the el.-el. potential (\hat{v}^{NO} in the TDDMFT case) induced by the first order change in the wavefunction (i.e., in the density matrix or natural orbitals and occupation numbers). In order to obtain this induced potential, we need the effect of the changes in orbitals and occupation numbers on the potential, as given in Equations (15) and (16). For this the so-called coupling matrices are required. For instance, in the customary adiabatic approximation

$$\begin{aligned} \delta(W_{kl}^\dagger - W_{kl}) &= \sum_p \int d\mathbf{x} \frac{\delta(W_{kl}^\dagger - W_{kl})}{\delta\phi_p(\mathbf{x})} \delta\phi_p(\mathbf{x}t) \\ &\quad + \sum_p \int d\mathbf{x} \frac{\delta(W_{kl}^\dagger - W_{kl})}{\delta\phi_p^*(\mathbf{x})} \delta\phi_p^*(\mathbf{x}t). \end{aligned} \quad (34)$$

Substituting $\delta\phi_p = \sum_q \phi_q \delta U_{qp}$ and $\delta\phi_p^* = \sum_q \phi_q^* \delta U_{qp}^*$ and using $\delta U_{qp}^* = -\delta U_{pq}$, one obtains

$$\delta(W_{kl}^\dagger - W_{kl}) = \sum_{p,q} K_{kl,pq}^\phi \delta U_{qp} \quad (35)$$

with the coupling matrix $K_{kl,pq}^\phi$ defined as

$$K_{kl,pq}^\phi = \int d\mathbf{x} \left[\frac{\delta(W_{kl}^\dagger - W_{kl})}{\delta\phi_p(\mathbf{x})} \phi_q(\mathbf{x}) - \frac{\delta(W_{kl}^\dagger - W_{kl})}{\delta\phi_q^*(\mathbf{x})} \phi_p^*(\mathbf{x}) \right]. \quad (36)$$

The perturbation of the $\partial W/\partial n_p$ potential in the diagonal v_{pp}^{NO} elements (Eq. (16))

$$\delta \frac{\partial W}{\partial n_k} = \sum_{pq} K_{k,pq}^{n\dagger} \delta U_{qp}(t) + \sum_p \frac{\partial^2 W}{\partial n_k \partial n_p} \delta n_p(t) \quad (37)$$

requires the coupling matrices \mathbf{K}^n (with $K_{k,pq}^{n\dagger} = K_{pq,k}^{n*}$) and $\overline{\mathbf{W}}$, defined as

$$K_{kl,p}^n = \frac{\partial(W_{kl}^\dagger - W_{kl})}{\partial n_p} \quad (38)$$

and

$$\overline{\mathbf{W}}_{k,m} = \frac{\partial^2 W[\{\phi\}, \{n\}]}{\partial n_k \partial n_m}. \quad (39)$$

After considerable manipulation one ends up with the matrix diagonalisation problem for the calculation of excitation energies (remember the restriction to real orbitals and to a real (electric field) perturbation)

$$[\sqrt{\mathbf{A}^+} \mathbf{D} \sqrt{\mathbf{A}^+}] \mathbf{F}_\alpha = \omega_\alpha^2 \mathbf{F}_\alpha. \quad (40)$$

The coupling effects of \mathbf{K}^ϕ are conventionally collected in \mathbf{A} and \mathbf{B} matrices, or equivalently \mathbf{A}^+ and \mathbf{A}^- matrices,

$$\begin{aligned} A_{kl,mn} &= (n_m - n_n)(\delta_{lm} h_{kn} - \delta_{kn} h_{ml}) + K_{kl,mn}^\phi, \\ A_{kl,mn}^\pm &= A_{kl,mn} \pm A_{kl,nm}. \end{aligned} \quad (41)$$

Here we also need, because of the varying occupation number, the matrix \mathbf{C} incorporating the coupling due to \mathbf{K}^n ,

$$C_{kl,m} = h_{kl}(\delta_{lm} - \delta_{km}) + K_{kl,m}^n, \quad (42)$$

and the $\overline{\mathbf{W}}$ matrix. The matrix \mathbf{D} in (40) has the following compound structure:

$$\mathbf{D} = \begin{pmatrix} \mathbf{N}^{-1} \mathbf{A}^- \mathbf{N}^{-1} & \mathbf{N}^{-1} \mathbf{C} \\ \mathbf{C}^T \mathbf{N}^{-1} & \overline{\mathbf{W}} \end{pmatrix}, \quad (43)$$

where the diagonal matrix $N_{kl,mp} = \delta_{kp} \delta_{lm} (n_l - n_k)$ in (43) contains occupation number differences.

Obviously, the detailed form of the coupling matrices \mathbf{K}^ϕ and \mathbf{K}^n , and therefore \mathbf{A}^\pm and \mathbf{C} , as well as $\overline{\mathbf{W}}$, depend on the approximate 1RDM or natural orbital functional used for the electron-electron interaction energy. In spite of the seemingly complicated formalism, the physical meaning proves to be rather simple. This will be demonstrated in Section IV, both for the TDDMFT case and the TDHF and TDDFT cases.

In TDDMFT the solution vector \mathbf{F}_α in principle incorporates the full response (in principle all $\delta\gamma_{pq}$) of the 1RDM

$$\mathbf{F}_\alpha = (\mathbf{A}^+)^{-1/2} \begin{pmatrix} \delta\boldsymbol{\gamma}^R(\omega_\alpha) \\ \delta\mathbf{n}(\omega_\alpha) \end{pmatrix}. \quad (44)$$

Because of the symmetry of the real (in this case) $\boldsymbol{\gamma}$, only the real off-diagonal elements $\delta\gamma_{pq}^R(\omega_\alpha)$ (we choose $p > q$) appear in the \mathbf{F}_α of (9) and (44), together with the changes in the diagonal elements (i.e., in the ONs) $\delta\gamma_{pp}^R(\omega_\alpha) = \delta n_p(\omega_\alpha)$. Because of this structure of its eigenvalue problem, TDDMFT is able to describe not only single excitations but also double excitations. The latter may be of ‘‘diagonal double type’’ (double excitation to a $(\phi_a)^2$ configuration), which is represented by $\delta\gamma_{aa}$, or of off-diagonal type (double excitation to a $(\phi_a)^1(\phi_b)^1$ configuration, represented by $\delta\gamma_{ab}$ ³⁹). Upon incorporation of the NO phases in the functional W , the resulting time-dependent phase-including natural orbital functional theory TDPINOFT is able to exactly reproduce both single and double excitations in the paradigmatic case of two-electron systems.^{23,39}

B. TDHF

In the special case of the linear response TDHF, there is only a limited number of fully occupied orbitals ($n_i = 1$, $i \leq N$; $n_a = 0$, $a > N$), and there are no δn_p terms. Then it follows directly from Eq. (32) that matrix elements $\delta\gamma_{ij}$ (with two occupied orbital indices) and $\delta\gamma_{ab}$ (with two unoccupied orbital indices) drop out in the expression of $\delta\boldsymbol{\gamma}(\mathbf{x}, \mathbf{x}', t)$, see Eqs. (32) and (33). The remaining elements $\delta\gamma_{ai}$, which feature

in the transition density, correspond to single excitations out of a ground state determinantal wavefunction.³⁹ It is a serious limitation of TDHF (and of adiabatic TDDFT as well) that only single excitations can be described.

The expressions for $(W_{ai}^{TDHF\dagger} - W_{ai}^{TDHF})$ in the TDHF case in terms of two-electron integrals (cf. (20)) lead upon taking orbital derivatives to simple expressions in terms of just a few two-electron integrals for the only relevant coupling matrix elements in this case, $K_{ai,jb}^\phi$ and $K_{ai,bj}^\phi$. With

$$W_{ai}^{TDHF\dagger} - W_{ai}^{TDHF} = \sum_p n_p [\langle ap|ip \rangle - \langle ap|pi \rangle], \quad (45)$$

(cf. (20)), one obtains for the derivatives (taken at $t = 0$, i.e., substituting the stationary orbitals)

$$\begin{aligned} \int d\mathbf{x} \frac{\delta (W_{ai}^{TDHF\dagger} - W_{ai}^{TDHF})}{\delta\phi_j(\mathbf{x})} \phi_b(\mathbf{x}) \\ = \delta_{ij} \sum_p n_p [J_{ab}^p - K_{ab}^p] + \langle aj|ib \rangle - \langle aj|bi \rangle, \end{aligned} \quad (46)$$

for the first term of the coupling matrix element $K_{ai,jb}^\phi$ of (36) while its second term is

$$\int d\mathbf{x} \frac{\delta (W_{ai}^{TDHF\dagger} - W_{ai}^{TDHF})}{\delta\phi_b^*(\mathbf{x})} \phi_j^*(\mathbf{x}) = \delta_{ab} \sum_p n_p [J_{ji}^p - K_{ji}^p] \quad (47)$$

so the total $K_{ai,jb}^\phi$ reads

$$\begin{aligned} K_{ai,jb}^\phi &= \delta_{ij} \sum_p n_p [J_{ab}^p - K_{ab}^p] - \delta_{ab} \sum_p n_p [J_{ji}^p - K_{ji}^p] \\ &\quad + \langle aj|ib \rangle - \langle aj|bi \rangle. \end{aligned} \quad (48)$$

Similarly, for the analogous parts of the element $K_{ai,bj}^\phi$ (note the index reversal to bj), we have

$$\int d\mathbf{x} \frac{\delta (W_{ai}^{TDHF\dagger} - W_{ai}^{TDHF})}{\delta\phi_b(\mathbf{x})} \phi_j(\mathbf{x}) = 0 \quad (49)$$

and

$$\int d\mathbf{x} \frac{\delta (W_{ai}^{TDHF\dagger} - W_{ai}^{TDHF})}{\delta\phi_j^*(\mathbf{x})} \phi_b^*(\mathbf{x}) = \langle ab|ij \rangle - \langle ab|ji \rangle, \quad (50)$$

so that

$$K_{ai,bj}^\phi = \langle ab|ji \rangle - \langle ab|ij \rangle. \quad (51)$$

This can be substituted in the equations for \mathbf{A} , leading immediately to the \mathbf{A}^+ and \mathbf{A}^- matrices of TDHF,

$$\begin{aligned} A_{ai,jb}^{TDHF+} &= \delta_{ij} F_{ab} - \delta_{ab} F_{ji} + \langle aj|ib \rangle - \langle aj|bi \rangle \\ &\quad + \langle ab|ji \rangle - \langle ab|ij \rangle \\ &= \delta_{ij} \delta_{ab} (\epsilon_a^{HF} - \epsilon_i^{HF}) + \langle aj|ib \rangle - \langle aj|bi \rangle \\ &\quad + \langle ab|ji \rangle - \langle ab|ij \rangle, \end{aligned} \quad (52)$$

$$\begin{aligned} A_{ai,jb}^{TDHF-} &= \delta_{ij} F_{ab} - \delta_{ab} F_{ji} + \langle aj|ib \rangle - \langle aj|bi \rangle \\ &\quad - \langle ab|ji \rangle + \langle ab|ij \rangle \\ &= \delta_{ij} \delta_{ab} (\epsilon_a^{HF} - \epsilon_i^{HF}) + \langle aj|ib \rangle - \langle aj|bi \rangle \\ &\quad - \langle ab|ji \rangle + \langle ab|ij \rangle. \end{aligned} \quad (53)$$

Since only the occupied-unoccupied index pairs enter, the dimension of the matrix Equation (43) for the excitation energy is considerably reduced, and the \mathbf{D} matrix simplifies to just the \mathbf{A}^- matrix (no \mathbf{C} and \mathbf{W} matrices because no occupation number variation),

$$[\sqrt{\mathbf{A}^{TDHF+}} (\mathbf{A}^{TDHF-}) \sqrt{\mathbf{A}^{TDHF+}}] \mathbf{F}_\alpha = \omega_\alpha^2 \mathbf{F}_\alpha. \quad (54)$$

These are precisely the eigenvalue TDHF linear response equations with the present matrices \mathbf{A}^+ and \mathbf{A}^- being equal to the combinations $\mathbf{A}^+ = \mathbf{A}^{TDHF} - \mathbf{B}^{TDHF}$ and $\mathbf{A}^- = \mathbf{A}^{TDHF} + \mathbf{B}^{TDHF}$ of the familiar TDHF matrices \mathbf{A}^{TDHF} and \mathbf{B}^{TDHF} .⁵¹

C. TDDFT

As in the response TDHF case considered above, in LR-TDKS we only have a fixed number of fully occupied orbitals, $n_i = 1$ for $i \leq N$, $n_a = 0$ for $a > N$. Again, only occupied-unoccupied index pairs $\delta\gamma_{ai}$ need to be used, cf. Eqs. (32) and (33). Only the coupling matrix \mathbf{K}^ϕ , denoted \mathbf{K}^s in this case, is needed and is easily obtained from Eq. (36),

$$K_{ai,jb}^s = (n_i - n_a) \int d\mathbf{x} \left(\frac{\delta v_{ai}^{Hxc}}{\delta \phi_j(\mathbf{x})} \phi_b(\mathbf{x}) - \phi_j^*(\mathbf{x}) \frac{\delta v_{ai}^{Hxc}}{\delta \phi_b^*(\mathbf{x})} \right), \quad (55)$$

which leads to

$$\begin{aligned} K_{ai,jb}^s &= (n_i - n_a) \int d\mathbf{x} \left[\frac{\delta \int \phi_a^*(\mathbf{x}') v^{Hxc}(\mathbf{x}') \phi_i(\mathbf{x}') d\mathbf{x}'}{\delta \phi_j(\mathbf{x})} \phi_b(\mathbf{x}) \right. \\ &\quad \left. - \phi_j^*(\mathbf{x}) \frac{\delta \int \phi_a^*(\mathbf{x}') v^{Hxc}(\mathbf{x}') \phi_i(\mathbf{x}') d\mathbf{x}'}{\delta \phi_b^*(\mathbf{x})} \right] \\ &= (n_i - n_a) (\delta_{ij} v_{ab}^{Hxc} - \delta_{ba} v_{ji}^{Hxc} + (n_j - n_b) f_{ai,jb}^{Hxc}) \\ &= \delta_{ij} v_{ab}^{Hxc} - \delta_{ba} v_{ji}^{Hxc} + f_{ai,jb}^{Hxc}, \end{aligned} \quad (56)$$

where we have applied the chain-rule differentiation as in Eqs. (25) and (26), and have used $n_i = n_j = 1$, $n_a = n_b = 0$ and the standard definition of the exchange-correlation kernel $f_{xc}(\mathbf{x}, \mathbf{x}') = \delta^2 A_{Hxc} / \delta \rho(\mathbf{x}) \delta \rho(\mathbf{x}')$,

$$\begin{aligned} f_{ai,jb}^{Hxc} &= \int \int \phi_a^*(\mathbf{x}') \phi_i(\mathbf{x}') \frac{\delta^2 A_{Hxc}}{\delta \rho(\mathbf{x}) \delta \rho(\mathbf{x}')} \phi_j^*(\mathbf{x}) \phi_b(\mathbf{x}) d\mathbf{x} d\mathbf{x}' \\ &= \int \int \phi_a^*(\mathbf{x}') \phi_i(\mathbf{x}') f^{Hxc}(\mathbf{x}', \mathbf{x}) \phi_j^*(\mathbf{x}) \phi_b(\mathbf{x}) d\mathbf{x} d\mathbf{x}'. \end{aligned} \quad (57)$$

In its turn, the element $K_{ai,bj}^s$ (note the index reversal to bj) reads

$$\begin{aligned} K_{ai,bj}^s &= (n_i - n_a) \int d\mathbf{x} \left[\frac{\delta \int \phi_a^*(\mathbf{x}') v^{Hxc}(\mathbf{x}') \phi_i(\mathbf{x}') d\mathbf{x}'}{\delta \phi_b(\mathbf{x})} \phi_j(\mathbf{x}) \right. \\ &\quad \left. - \phi_b^*(\mathbf{x}) \frac{\delta \int \phi_a^*(\mathbf{x}') v^{Hxc}(\mathbf{x}') \phi_i(\mathbf{x}') d\mathbf{x}'}{\delta \phi_j^*(\mathbf{x})} \right] \\ &= -(n_i - n_a) (n_j - n_b) f_{ai,bj}^{Hxc} = -f_{ai,bj}^{Hxc}. \end{aligned} \quad (58)$$

With the matrix (41) written as \mathbf{A}^s in this case

$$A_{ai,jb}^s = h_{ab} \delta_{ij} - \delta_{ab} h_{ji} + K_{ai,jb}^s, \quad (59)$$

we obtain for the elements $A_{ai,jb}^s$ and $A_{ai,bj}^s$ of the matrix \mathbf{A}^s after inserting (56) and (58)

$$\begin{aligned} A_{ai,jb}^s &= \delta_{ij} (h_{ab} + v_{ab}^{Hxc}) - \delta_{ab} (h_{ji} + v_{ji}^{Hxc}) + f_{ai,jb}^{Hxc} \\ &= \delta_{ij} h_{ab}^s - \delta_{ab} h_{ji}^s + f_{ai,jb}^{Hxc} \end{aligned} \quad (60)$$

and

$$A_{ai,bj}^s = -f_{ai,bj}^{Hxc}, \quad (61)$$

where $\hat{h}^s(\mathbf{x}_1)$ is the one-electron KS operator

$$\hat{h}^s(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) + v^{Hxc}(\mathbf{x}_1). \quad (62)$$

The size of the matrix eigenvalue problem (40) for the excitation energies again (like in TDHF) reduces to just occ.unocc \times occ.unocc (no \mathbf{C} and \mathbf{W} matrices because of constant occupation numbers),

$$[\sqrt{\mathbf{A}^{s+}} (\mathbf{A}^{s-}) \sqrt{\mathbf{A}^{s+}}] \mathbf{F}_\alpha = \omega_\alpha^2 \mathbf{F}_\alpha. \quad (63)$$

Interestingly, as follows from (60) and (61), the matrix \mathbf{A}^{s+} assumes a simple diagonal form in linear response TDKS,

$$A_{ai,jb}^{s+} = \delta_{ij} h_{ab}^s - \delta_{ab} h_{ji}^s = \mathcal{E}_{ai,jb}, \quad (64)$$

where

$$\mathcal{E}_{ai,jb} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i). \quad (65)$$

The matrix \mathbf{A}^{s-} of (63) contains, besides \mathcal{E} , also the contribution from the coupling of the orbital excitations through the Hxc kernel,

$$A_{ai,jb}^{s-} = \delta_{ij} h_{ab}^s - \delta_{ab} h_{ji}^s + 2f_{ai,jb}^{Hxc} = \epsilon_{ai,jb} + 2f_{ai,jb}^{Hxc}. \quad (66)$$

With (64) and (66), the TDFT eigenvalue Equation (63) assume the familiar form⁵²

$$[\sqrt{\mathcal{E}} (\mathcal{E} + 2\mathbf{f}^{Hxc}) \sqrt{\mathcal{E}}] \mathbf{F}^\alpha = [\mathcal{E}^2 + 2\sqrt{\mathcal{E}} \mathbf{f}^{Hxc} \sqrt{\mathcal{E}}] \mathbf{F}^\alpha = \omega_\alpha^2 \mathbf{F}^\alpha. \quad (67)$$

The remarkable diagonal nature of the \mathbf{A}^{s+} matrix in the LR-TDKS case (in the KS orbital basis), and the similar almost diagonal nature of \mathbf{A}^{s-} , with only a relatively small coupling part, leads to a simple structure of the eigenvectors \mathbf{F}^α , many of which are close to unit vectors with a single dominant element $F_{ai}^\alpha \approx 1$ signifying an almost pure single orbital to single orbital excitation. This makes the KS orbitals particularly well suited for a straightforward description of excitations as simple orbital-to-orbital transitions. Many examples are given in Ref. 41. In Sec. IV we discuss the physical origin of this phenomenon and its implications for TDDMFT and TDHF calculations.

IV. PHYSICAL MEANING OF THE MATRIX ELEMENTS (OPERATORS AND ORBITALS) IN THE LINEAR RESPONSE EQUATIONS FOR EXCITATION ENERGIES

The linear response equations for excitation energies for the cases of TDDMFT (40), TDHF (54), and TDKS (63) are formally similar. However, the diagonal nature of the \mathbf{A}^+ matrix only occurs in the TDKS case, with just orbital energy differences on the diagonal $A_{ai,ia}^{s+}$. This raises the question why the \mathbf{A}^+ matrices are so different. It is clear that the strongly non-diagonal nature of the \mathbf{A}^+ matrix in the TDHF and TDDMFT cases causes the solution vectors \mathbf{F}^α in those cases to have many elements, i.e., excitations are described by mixtures of many orbital-to-orbital transitions. There are two possible reasons for the differences: (1) the nature of the effective one-electron hamiltonian that is used in the matrix elements of the $\mathbf{A}_{ai,ia}^{s+}$ matrix may be very different from the KS one, (2) or the

orbitals (virtual HF orbitals and virtual NOs respectively) may be very different from the KS ones, (3) or of course a combination of these two possible causes. We will in this section elucidate the physical meaning of the matrix elements (operators and orbitals) of the $A_{ai,ia}^{s+}$ matrix (and $A_{ai,ia}^{s-}$), which will exhibit the reason for the differences and suggest a remedy for the interpretation difficulty in the TDHF and TDDMFT cases.

A. TDKS

It is clear from Eqs. (64) and (65) that the $A_{ai,ia}^{s+}$ consist of (differences of) matrix elements of the KS one-electron Hamiltonian in the basis of its eigenvectors, the KS orbitals. The fact that these KS orbital energy differences are close to excitation energies has been explained^{35,37,41} by the nature of the potential v^{Hxc} in the KS hamiltonian. This potential is constructed for all orbitals, including the virtual orbitals, as the Coulomb potential of the ground state electron density plus the potential of the exchange-correlation hole surrounding the position where the potential is evaluated. This hole comprises -1 electron, so it mimics the hole that is created upon excitation. The latter hole is approximately $-|\phi_i(\mathbf{r})|^2$ if the excitation is $\phi_i \rightarrow \phi_a$. The exchange-correlation hole is of course not a perfect representation, but arguments can be given³⁷ why the exchange-correlation hole is a good approximation, at least in systems of limited size (molecules). In molecules the largest part of the exchange-correlation hole potential is due to the average potential of the $-|\phi_i(\mathbf{r})|^2$ holes which represent the self-interaction correction part of the exchange potential, and which are responsible for the -1 total charge of the hole. Due to the attractive exchange-correlation hole (the overall $(N-1)$ -electron potential), the lowest virtual KS orbitals have negative orbital energies (are clearly bound) and have realistic (typically valence type or mixed valence-Rydberg type) shapes.^{37,41}

B. TDHF

The TDHF (and TDDMFT) \mathbf{A}^+ matrices are not at all diagonal and do not have orbital energy differences as diagonal elements. Is the nature of the effective one-electron hamiltonian that is implicitly used in the matrix elements of \mathbf{A}^+ in this case maybe not KS-like, in the sense that it does not describe a similar $(N-1)$ -electron field and does not have physically meaningful (virtual) orbital energies? Considering the effective one-electron hamiltonian in the TDHF case, we note that the \mathbf{A}^{TDHF+} matrix elements $A_{ai,jb}^{TDHF+} = \delta_{ij}\delta_{ab}(\epsilon_a^{HF} - \epsilon_i^{HF}) + \langle aj|ib \rangle - \langle aj|bi \rangle + \langle ab|ji \rangle - \langle ab|ij \rangle$ (Eq. (52)) have as leading term on the diagonal ($i = j, a = b$) the HF orbital energy difference. However, the difference $(\epsilon_a^{HF} - \epsilon_i^{HF})$ between the HF orbital energies is not a reasonable estimate of an excitation energy because the virtual orbital energy is much too high. The virtual orbital energy represents in the Koopmans' frozen orbital approximation an electron affinity (the energy of adding an electron), not the energy of exciting an electron. However, the orbital energy difference $(\epsilon_a^{HF} - \epsilon_i^{HF})$ (Eq. (52)) in the diagonal element ($i = j, a = b$) is corrected by the two-electron integral combination $(\langle ai|ia \rangle - \langle ai|ai \rangle + \langle aa|ii \rangle - \langle aa|ii \rangle) \approx -\langle ai|ai \rangle$ (the remaining $\langle aa|ii \rangle$ is much smaller). This

makes a qualitative difference. It is clear that $-\langle ai|ai \rangle = \langle \phi_a | -\hat{J}^i | \phi_a \rangle$ introduces an attractive potential from a "hole" $-|\phi_i|^2$. In the diagonal matrix elements $A_{ai,ia}^{TDHF-}$ of the \mathbf{A}^- matrix (Eq. (53)) the same correction $\langle \phi_a | -\hat{J}^i | \phi_a \rangle$ to the one-electron energy ϵ_a^{HF} appears. If we consider the virt \times virt submatrix $A_{ai,ib}^{TDHF+}$ with fixed occupied orbital index i and a, b running over the unoccupied orbitals, which is denoted \mathbf{A}_i^{TDHF+} , we note that it resembles the matrix in the TDKS case to the extent that its diagonal elements all have the HF virtual orbital energy ϵ_a^{HF} corrected by the hole potential $-\hat{J}^i$. The same hole potential appears in the off-diagonal ($a \neq b$) matrix elements. Just as the KS operator \hat{h}^s of (62), the effective operator in the $A_{ai,ib}^{TDHF+}$ submatrix represents the interaction with $(N-1)$ electrons.

If then the origin of the difference between TDHF and TDKS is not in the nature of the effective one-electron hamiltonian (the effective field it represents), it may be in the nature of the orbitals: the HF virtual orbitals may be too different from the proper bound, KS-type, virtual orbitals, in terms of which excitations can be described as orbital-to-orbital transitions. The HF virtual orbitals are indeed known to be unduly diffuse (often not even bound) due to the lack of an exchange hole in the Fock operator for the virtual orbitals (i.e., the Fock operator has a repulsive N -electron field).⁵³⁻⁵⁷ That is the reason that in the TDHF case the response vectors \mathbf{F}^α have many nonzero elements F_{ai}^α , indicating involvement of many transitions $i \rightarrow a$ in a single excitation.⁴¹ A natural way to improve the orbital character would be to diagonalize the submatrix $A_{ai,ib}^{TDHF+}$ with constant index i . This defines a transformation of the virtual HF orbitals, where from the presence of the attractive operator $-\hat{J}^i$ one may expect the orbitals to get a more realistic (contracted) shape, and the eigenvalues (diagonal elements after transformation) to be a good first approximation to the excitation energies. In fact, one then transforms to KS like orbitals, i.e., eigenfunctions of the same type of one-electron hamiltonian with a hole potential due to -1 electron charge, see Section V. Due to the structure of the linear response equations, the diagonal \mathbf{A}^{TDHF+} matrix will lead to excitation energies ω_α close to the diagonal elements of \mathbf{A}^+ , in the same way we have seen for the diagonal \mathbf{A}^{s+} matrix in TDDFT. Examples will be given in Section V. We note the obvious relation to the so-called improved virtual orbital (IVO) methods, where transformations of the virtual HF orbitals are effected in order to obtain more realistically shaped orbitals for use in excitation and correlation calculations.^{43,54-59}

C. TDDMFT

As was already mentioned previously (TD)HF can be considered as a special simplified case of (TD)DMFT, in which the electron correlation is neglected. If in the exchange-only approximation of TDDMFT (i.e., TDHF) the matrix elements of the \mathbf{A}^+ matrix can be interpreted as arising from an operator with the hole potential included, one may infer that the same remains true when the correlation effects are included. An obvious difference between the TDHF and TDDMFT matrices is that in the former case the effective one-electron hamiltonian (KS-like, i.e., hole potential included) is represented in the basis of the HF orbitals,

while in the latter case it is represented in the NO basis. But first we consider the nature of the effective one-electron hamiltonian.

- (1) The effective hamiltonian of the matrix elements of the TDDMFT \mathbf{A}^+ matrix can be examined exactly for the two-electron case, where the exact 1RDM functional is known and the matrix elements of the \mathbf{A}^+ matrix can be given explicitly. The exact 1RDM functional in the two-electron system is the so-called phase including Löwdin-Shull functional (PILS).^{23,38,60} With the conventional choice of phases (corresponding to one positive CI coefficient for the leading determinant with the doubly occupied natural orbital ϕ_1 with large occupation number, and negative signs for all the remaining CI coefficients) the functional reads

$$W[\{\phi\}, \{n\}] = \sum_k n_k \langle kk|kk \rangle - 2 \sum_{a>1} \sqrt{n_1 n_a} \langle 11|aa \rangle + \sum_{a,b\neq a>1} \sqrt{n_a n_b} \langle aa|bb \rangle, \quad (68)$$

where we use the fact that occupation numbers are equal for α and β spin orbitals ($n_k = n_k^\alpha = n_k^\beta$, occupation numbers are between 0 and 1). The differentiation of (68) according to Eqs. (13), (34), (38), and (39) produces the TDDMFT matrix \mathbf{A}^+ as the sum

$$A_{a1,1b}^+ = (h_{ab} + J_{ab}^1) - \delta_{ab}(h_{11} + J_{11}^1) + A_{a1,1b}^{c+} \quad (69)$$

The leading term is the difference of the expectation values for orbitals ϕ_a and ϕ_1 , respectively, for the KS-type hamiltonian where the hole potential $-\hat{J}^1$ cancels one of the repulsions of $2\hat{J}^1$ (reminiscent of the self-interaction correction of the HF exchange operator for occupied orbitals, but now also applied in matrix elements for the virtual orbitals).

The correlation effects give rise to the part $A_{a1,1b}^{c+}$. These matrix elements are small, at least close to the equilibrium distance where the occupation numbers of the virtual orbitals are small, $n_a \approx 0$, and of orbital ϕ_1 are large, $n_1 \approx 1$, i.e., the hole in ϕ_1 is small, $(1-n_1) \approx 0$. This may be checked from the explicit expressions for $A_{a1,1b}^{c+}$ in this case,

$$A_{a1,1b}^{c+} = (n_1 - 1 - n_b)h_{ab} + \delta_{ab}(1 - n_1 + n_a)h_{11} + (n_1 - 1 - \sqrt{n_1 n_a} - \sqrt{n_1 n_b} + \sqrt{n_a n_b})\langle a1|b1 \rangle + \delta_{ab}(1 - n_1 + \sqrt{n_1 n_a})\langle 11|11 \rangle + (n_1 - \sqrt{n_1 n_a} - \sqrt{n_1 n_b} + \sqrt{n_a n_b})\langle a1|1b \rangle + (\sqrt{n_1 n_a} - n_1) \times \langle 11|ba \rangle + \sum_{c>1} (\sqrt{n_1 n_c} - \sqrt{n_a n_c})\langle ab|cc \rangle + \delta_{ab} \sum_{c>1} (\sqrt{n_1 n_c} - \sqrt{n_a n_b})\langle 11|cc \rangle. \quad (70)$$

- (2) In the second place the orbital basis should be considered. The orbital basis in the TDDMFT calculations is the set of NOs. We will demonstrate in Sec. V that, just as the HF virtual orbitals, the weakly occupied (“virtual”) NOs are not suitable for a description of excitations as simple orbital-to-orbital transitions. A transformation of the set of virtual NOs to a set of physically meaningful orbitals by diagonalization of the \mathbf{A}_i^+ submatrix

is also possible in the TDDMFT case, because of the incorporation of the hole potential $-\hat{J}^i$ in the effective one-electron hamiltonian of these matrix elements.

The analysis in this section reveals the similar physical meaning of the key matrix \mathbf{A}^+ of different linear response theories. The \mathbf{A}^+ matrix of TDKS as well TDHF and TDDMFT can be shown to arise from the same difference between the elements of KS-type operators, but in different basis sets, namely the KS and HF MOs and the NOs, respectively. In Sec. V these findings will be used to provide a unified interpretation of electronic excitations calculated in the considered theories.

V. INTERPRETATION OF ELECTRONIC EXCITATIONS WITH NATURAL EXCITATION ORBITALS

A. The concept of natural excitation orbitals

In TDKS, the matrix \mathbf{A}^{s+} is diagonal in the representation of the KS orbitals, the eigenfunctions of the KS operator \hat{h}^s , cf. Eq. (64). This leads to simple eigenvectors \mathbf{F}^α of the linear response equations, with only one or a few significant elements. This implies that the excitation α with energy ω_α is characterized by just one or only a few large $\delta\gamma_{ia}$ elements since the real parts of the density matrix responses $\delta\gamma_{ai}^R(\omega_\alpha)$ characterizing this excitation are given by the solution vector \mathbf{F}^α ,

$$F_{bj}^\alpha = \sum_{ai} [(\mathbf{A}^+)^{-1/2}]_{bj,ia} \delta\gamma_{ai}^R(\omega_\alpha). \quad (71)$$

In fact, the transition density matrix elements for a $\Psi_0 \rightarrow \Psi_\alpha$ excitation, which are defined by

$$\Delta\gamma_{kl}(\alpha) = \langle \Psi_0 | \hat{\gamma}_{kl} | \Psi_\alpha \rangle, \quad (72)$$

can be shown to be related directly to the eigenvector \mathbf{F}_α of the linear response equations

$$\Delta\gamma^R(\alpha) = \frac{\sqrt{\mathbf{A}^+} \mathbf{F}_\alpha}{2\sqrt{\omega_\alpha}} = \frac{\delta\gamma^R(\omega_\alpha)}{2\sqrt{\omega_\alpha}} \quad (73)$$

(see Ref. 39 for the connection between the 1RDM responses and the transition density matrix elements and for the connection between the $\Delta\gamma_{ia}$ and the nature of the excited state.) The presence in a LR-TDKS calculation of just one or a few large elements F_{ai}^α signifies that the excitation is described by only one or a few single orbital transitions $i \rightarrow a$.³⁹ On the other hand, in TDHF and TDDMFT the \mathbf{A}^+ matrix has a highly non-diagonal form in the basis of the HF orbitals, and the NOs, respectively, resulting in many nonzero elements F_{ia}^α in the \mathbf{F}^α vector. This has been traced in Sec. IV to those orbitals (at least the “virtual” ones) not being eigenfunctions of the effective one-electron hamiltonian that determines the matrix elements of \mathbf{A}^+ , which has a hole potential and is in this sense of KS type. As a result, excitations cannot be described with single orbital-orbital transitions between the HF orbitals or between the NOs.

To demonstrate this, calculations are performed in this paper for the HeH^+ , Li_2 , H_2O , and CH_2O molecules at their equilibrium geometries, which complement those for the H_2 and LiH molecules of our previous work.⁴² In the case

of the two-electron HeH^+ system, the calculations are performed with the exact functional in that case, which is based on the work by Löwdin and Shull⁶⁰ on the natural orbital analysis of two-electron systems. The corresponding phase-including Löwdin-Shull natural orbital functional (PILS, Eq. (68))^{23,24,38–40} yields exact (full-configuration interaction, FCI) results. For general N -electron systems we need approximate 1RDM functionals. For the TDDMFT calculations on the Li_2 molecule the recently developed approximate ELS(1) functional⁶¹ is used. The latter molecule and H_2O and CH_2O are also calculated with linear response TDHF. Table I presents the transition densities $\Delta\gamma_{pq}^\alpha = \delta\gamma_{pq}^\alpha / (2\sqrt{\omega_\alpha})$ ³⁹ for the first 4 $\text{HeH}^+ \ ^1\Sigma^+$ excitations in the NO basis, while Tables II and IV display those for the first 3 $\text{Li}_2 \ ^1\Sigma_g^+$ excitations in the NO and HF basis sets, respectively. Both Tables I and II contain single excitations to the $a\sigma$ ($a\sigma_g$) NOs of Σ (Σ_g) symmetry, which are numbered according to decreasing occupation. These NOs do not have simple character, such as the KS orbitals do have, with valence character and meaningful orbital energies for the lowest virtual orbitals⁴¹ (e.g., $(2p_\sigma + 2p_\sigma)$ and $(3s + 3s)$ for Li_2). As a consequence, as these tables demonstrate, the excitations involve many NOs. They are very far from being simple single orbital to single orbital transitions in the NO basis. NOs are totally unsuitable for the characterization of excitations. Table IV shows that a similar comment, maybe somewhat less extreme, applies to the HF basis:⁴¹ again the transition densities for specific excitations have multiple orbital-to-orbital contributions. Both in the NO basis and the HF basis the

TABLE I. Transition densities for the lowest $^1\Sigma^+$ excitations for HeH^+ at R_e in the natural orbital (NO) basis, calculated with time-dependent density matrix theory (TDPINOPT), yielding the same excitation energies as full CI in the same basis. ψ_1 is the 1σ HOMO. The remaining weakly occupied $a\sigma$ NOs are ordered according to decreasing occupation number. They have mixed character. The transitions have many orbital-to-orbital contributions in the NO basis.

$a\sigma$	$\Delta\gamma_{1a}(\omega_\alpha)$ vectors			
	$2^1\Sigma^+$	$3^1\Sigma^+$	$4^1\Sigma^+$	$5^1\Sigma^+$
2	-0.919	-0.132	-0.366	0.159
3	-0.266	0.553	0.029	0.222
4	-0.539	0.026	-0.092	-0.081
5	-0.164	-0.385	-0.031	0.096
6	0.141	-0.380	-0.087	-0.239
7	0.112	-0.184	0.003	0.197
8	0.427	-0.092	-0.091	0.078
9	-0.145	-0.118	0.088	0.186
10	0.148	0.543	0.037	0.298
11	-0.195	-0.021	0.138	0.151
12	0.172	0.058	-0.111	0.115
13	-0.085	0.392	0.070	-0.289
14	0.125	-0.232	-0.129	0.003
15	0.066	-0.058	-0.052	0.302
16	-0.252	0.194	0.401	0.090
17	-0.105	-0.242	0.043	-0.469
18	0.139	0.369	-0.218	0.085
19	-0.042	-0.405	0.190	0.414
20	0.176	0.027	-0.808	0.737
21	0.019	0.384	-0.719	-0.620
22	0.058	-0.410	-0.505	-0.236

excitations (at R_e) involve $2\sigma_g \rightarrow a\sigma_g$, $a \geq 3$ single excitations. The time-dependent 1RDM response equations have the advantage that they are able to describe double excitation character,^{39,62} in contrast to linear response TDKS or TDHF calculations. Therefore, in Table II also some double excitation character is recorded. However, these entries (at the bottom of the table) show that at R_e double excitation contributions are negligible. This will change, of course, at long bond distances, where notably double excitations describing nondynamic correlation in the ground state and the excited states are known to become important. We show in Table III that in Li_2 at bond distance 9 bohrs there is much more double excitation character (in the NO basis), mostly from “diagonal doubles” such as the expected $(2\sigma_g)^2 \rightarrow (2\sigma_u)^2$ (bonding orbital to antibonding orbital) double excitation. Also the off-diagonal double to $(2\sigma_u)^1(3\sigma_u)^1$ has a nonnegligible contribution. Table IV lists the transition densities for the same three excited states of Li_2 from a LR-TDHF calculation, in the HF MO basis. Again the transition densities show that the excitations in HF basis are difficult to interpret: many single excitations are involved, although slightly fewer than in the NO basis. Similar to LR-TDKS, the LR-TDHF formalism is not able to feature any double excitation character. Obviously, the shapes of the weakly occupied NOs and virtual HF orbitals have little resemblance with the orbitals that characterize the excited states. A simple picture of the excitations is then not possible.

In order to obtain a meaningful interpretation of electronic excitations, in terms of one or only few single orbital-orbital transitions (and possibly a few doubles, notably at long distance) we propose a transformation of the weakly occupied NOs in TDDMFT and the virtual HF orbitals in TDHF to sets

TABLE II. Transition densities for the lowest $^1\Sigma_g^+$ excitations for Li_2 at R_e in the NO basis, calculated with time dependent density matrix functional theory (TDPINOPT) with the ELS(1) functional, see text. ψ_3 is the $2\sigma_g$ HOMO. The weakly occupied NOs ($a\sigma_g$, $a \geq 3$) have mixed (2s, 2p, 3s, ...) character. The excitations have multiple orbital-to-orbital contributions in the NO basis. Diagonal double excitation character (at the bottom end of the table) is small.

$a\sigma_g$	$\Delta\gamma_{3a}(\omega_\alpha)$ vectors		
	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
3	-0.689	-0.251	0.320
4	0.622	-0.181	0.023
5	0.040	0.448	-0.033
6	-0.441	0.180	-0.191
7	-0.168	-0.301	-0.049
8	-0.055	-0.475	-0.146
9	-0.201	0.329	-0.193
10	0.084	-0.104	0.084
11	-0.119	-0.348	-0.131
12	0.275	-0.211	0.388
13	-0.066	-0.469	-0.044
14	-0.071	0.548	-0.300
15	0.167	0.221	0.845
$2\sigma_g \ 2\sigma_g$	-0.001	-0.007	0.025
$1\pi_u(x) \ 1\pi_u(x)$	-0.050	0.007	0.013
$1\pi_u(y) \ 1\pi_u(y)$	-0.050	0.007	0.013
$3\sigma_g \ 3\sigma_g$	0.025	0.036	0.038
$2\sigma_u \ 2\sigma_u$	0.075	-0.043	-0.090

TABLE III. TDPINO transition densities for the lowest $1^1\Sigma_g^+$ excitations for Li_2 at 9 bohrs in the NO basis. Only transition density entries with an absolute value higher than 0.1 for at least one of the three excitations are shown.

a	b	$\Delta\gamma_{ba}(\omega_\alpha)$ vectors		
		$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
$3\sigma_g$	$2\sigma_g$	-0.623	0.490	0.230
$4\sigma_g$	$2\sigma_g$	-0.413	0.202	-0.281
$5\sigma_g$	$2\sigma_g$	-0.054	0.291	0.059
$6\sigma_g$	$2\sigma_g$	0.186	0.428	0.540
$7\sigma_g$	$2\sigma_g$	0.126	-0.059	0.127
$9\sigma_g$	$2\sigma_g$	0.140	-0.150	0.157
$10\sigma_g$	$2\sigma_g$	0.094	-0.157	0.090
$13\sigma_g$	$2\sigma_g$	0.169	0.020	0.646
$14\sigma_g$	$2\sigma_g$	-0.046	0.215	-0.098
$15\sigma_g$	$2\sigma_g$	-0.036	-0.137	-0.239
$2\sigma_g$	$2\sigma_g$	-0.415	-0.351	0.108
$2\sigma_u$	$2\sigma_u$	0.474	0.432	-0.123
$3\sigma_u$	$2\sigma_u$	-0.191	0.087	0.116

of what we call natural excitation orbitals (NEOs). In the case of TDDMFT the NEOs $\theta_a(i)$ have been introduced in our previous work⁴² as the eigenvectors diagonalizing the submatrix \mathbf{A}_i^+ with the elements $A_{ai,ib}^+$ considered in Sec. IV,

$$\mathbf{A}_i^+ \theta_a(i) = \mathcal{E}_a(i) \theta_a(i). \quad (74)$$

We will show that the eigenvalues $\mathcal{E}_a(i)$ of this diagonalization prove to be very good approximations to the excitation energies, while the obtained NEOs $\theta_a(i)$ provide a useful basis, describing the excitations mostly as predominantly single (or few) orbital-orbital transitions. The dependence of the NEOs and the energies $\mathcal{E}_a(i)$ on the occupied orbital index i (the orbital out of which the excitation takes place) turns out to be rather weak, a point that will be discussed below. In this paper the NEO concept is extended to TDHF and the analysis of \mathbf{A}_i^+ carried out in Sec. IV explains and justifies the NEOs for excitations. Indeed, in TDHF and (in the exchange-only approximation) in TDDMFT \mathbf{A}_i^+ is expressed through the elements

TABLE IV. Transition densities for the lowest $1^1\Sigma_g^+$ excitations for Li_2 at R_e from TDHF calculations, in the HF MO basis. The excitations have multiple orbital-to-orbital contributions in the HF basis.

$a\sigma_g$	$\Delta\gamma_{3a}(\omega_\alpha)$ vectors		
	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
3	-0.920	0.709	-0.748
4	-0.145	-1.038	-0.864
5	0.875	0.481	-0.664
6	-0.119	-0.313	-0.084
7	-0.211	-0.179	0.375
8	0.079	0.094	-0.131
9	0.052	0.002	-0.026
10	0.015	0.024	-0.026
11	0.019	0.011	-0.015
12	0.013	-0.002	-0.010
13	0.007	0.000	-0.004
14	0.000	0.000	0.000
15	0.000	0.000	0.000

of a KS-type operator. As a result, the NEOs $\theta_a(i)$ produced with the diagonalization (74) are expected to be close to the KS virtual orbitals. Then, the $\theta_a(i)$ would provide an efficient description of a given electronic excitation as predominantly the transition to a single NEO. In their turn, the eigenvalues $\mathcal{E}_a(i)$, the NEO orbital energies in (74), would resemble the corresponding KS orbital energy differences ($\epsilon_a - \epsilon_i$).

B. NEOs in linear response TDDMFT

In this section we present a number of examples. The basis sets are all aug-cc-pVTZ^{63,64} without the f -functions. This is a sufficiently flexible basis for the illustrations we wish to provide although not sufficiently close to the basis set limit to warrant a detailed comparison to experimental excitation energies. For the small molecules used here as examples, many detailed theoretical studies of the excitation spectra already exist.

1. HeH⁺

We first discuss the transformation to NEOs for the simple two-electron molecule HeH⁺, where, as noted before, we have the exact NO functional available. The nature of the NEOs and their energies obtained from the diagonalization (74) of the TDDMFT submatrix \mathbf{A}_H^+ is elucidated in Table V for the HeH⁺ molecule. H (HOMO) is the NO with smallest occupation number among the strongly occupied ones. We note, first of all, that the shapes of the NEOs $\theta_a(H)$ are, indeed, very close to those of the virtual KS orbitals ϕ_a (we start numbering the NEOs at $a = 2$ to have the numbers corresponding with those of the virtual KS orbitals). With the overlaps $\langle \theta_2(H) | \phi_2 \rangle$ and $\langle \theta_3(H) | \phi_3 \rangle$ exceedingly close to 1, the first two NEOs are in fact coinciding with the first and second virtual KS orbitals. The overlap $\langle \theta_4(H) | \phi_4 \rangle = 0.987$ of the third NEO with the corresponding KS virtual orbital is also close to 1, and only

TABLE V. Energies ω_a of $a^1\Sigma^+$ excitations in HeH⁺ at R_e calculated with various methods (full CI, adiabatic TDDFT with the BP86 functional) and approximated with various one-electron energy differences \mathcal{E} . In the NEO or in the KS virtual orbital basis the excitations are predominantly single orbital-orbital transitions, cf. the transition densities in Table VII. ψ_a denotes the receiving orbital. Top line: Overlap integrals between the NEOs $\theta_a(H)$ and the corresponding virtual KS orbitals ϕ_a . Second line: FCI excitation energies (in eV) of the $1^1\Sigma^+$ excitations. Third line, $\mathcal{E}_a^{\text{NEO}}$: “orbital energies” of the NEOs (eigenvalues of the diagonalization of the $\mathbf{A}_{a1,1b}^+(\Sigma^+)$ matrix), representing the orbital energy difference $\epsilon_a^{\text{NEO}} - \epsilon_H$. Fourth line, exact KS orbital energy differences $\epsilon_a^s - \epsilon_1^s$. Fifth line, same orbital energy differences for BP86 (diagonal elements of the TDDFT matrix $\mathcal{E}_{a1,1a}$). Last line, BP86-TDDFT excitation energies ω_a^{TDDFT} for Σ^+ symmetry.

Excited state	HeH ⁺ $n^1\Sigma^+$ excitations			
	$2^1\Sigma^+$	$3^1\Sigma^+$	$4^1\Sigma^+$	$5^1\Sigma^+$
Orbital character: $1\sigma = H \rightarrow \psi_a$	$\psi_a = 2\sigma$	$\psi_a = 3\sigma$	$\psi_a = 4\sigma$	$\psi_a = 5\sigma$
$\langle \theta_a(H) \phi_a^{\text{KS}} \rangle$	0.999	0.999	0.987	0.896
$\omega_a^{\text{FCI}}(1^1\Sigma^+)$	26.2	33.3	37.6	39.6
$\mathcal{E}_a^{\text{NEO}}(H)$	25.6	33.8	38.2	40.4
$\mathcal{E}_{a1\sigma,1\sigma}^{\text{KS}} = \epsilon_a^s - \epsilon_1^s$	24.0	33.4	38.3	40.2
$\mathcal{E}_{a1\sigma,1\sigma}^{\text{BP86}} = \epsilon_a^{\text{BP86}} - \epsilon_1^{\text{BP86}}$	23.0	30.1	32.8	35.3
$\omega_a(1^1\Sigma^+)(\text{TDDFT-BP86})$	25.6	30.4	33.1	35.7

the overlap $\langle \theta_5(H) | \phi_5 \rangle = 0.896$ is a little smaller. The reference KS orbitals have been obtained from the rather accurate KS solution constructed from the reference electron density $\rho(x)$ of the FCI method with the reverse engineering scheme of van Leeuwen and Baerends (LB).⁶⁵

In their turn, the NEO orbital energies $\mathcal{E}_a^{\text{NEO}}(H)$ resemble the FCI excitation energies $\omega_a(\text{FCI})$. The orbital energies $\mathcal{E}_a^{\text{NEO}}(H)$ differ from the FCI excitation energies $\omega_a(\text{FCI})$ with an absolute average error of 0.6 eV (only a few percent). In fact, the $\mathcal{E}_a^{\text{NEO}}(H)$ are very close to the “exact” KS orbital energy differences ($\epsilon_a - \epsilon_H$). We also compare in Table V to TDDFT-BP86 excitation energies and TDDFT-BP86 orbital energy differences. One can see that standard TDDFT-BP86 substantially underestimates the considered excitation energies except for the lowest one, and the average error amounts to 3 eV. This is related to the fact that the excitations to $3^1\Sigma^+$ and higher states are to high-lying, fairly diffuse orbitals, for which the good agreement of GGA KS occupied-unoccupied orbital energy differences with excitation energies (and with exact KS orbital energy differences) that holds for low-lying unoccupied valence orbitals, breaks down. That break-down is due to deficiencies of the GGA potential.^{41,66} Compared to the exact KS potential, the GGA potentials are considerably upshifted in the bulk atomic (or molecular) region, resulting in a similar upshift of the occupied orbitals and of the low-lying valence-type (not diffuse) virtuals, if present. The orbital energy differences are then good approximations to the excitation energies. High lying diffuse orbitals are less upshifted by the GGA potential compared to the exact KS potential (they are already close to the energy zero anyway), so the orbital energy difference becomes considerably smaller than the exact KS orbital energy difference, with poor excitation energy as a consequence.⁴¹

2. Li_2

As our next example of the NO to NEO transformation we take Li_2 . The results for the $1^1\Sigma_g^+$ excitations at R_e in the Li_2 molecule are shown in Table VI. Note that, unlike in the previous case of HeH^+ , the electrons in Li_2 are excited to low-lying unoccupied valence orbitals, so that the energies of the lowest excitations in Li_2 are much smaller and are indeed more representative of “normal” molecular valence excitations. The overlaps $\langle \theta_a(H) | \phi_a \rangle$ are larger than 0.95, indicating that the NEOs and KS orbitals are again very similar. For these excitations the $\mathcal{E}_a^{\text{NEO}}(H)$ provide a close estimate of the reference FCI excitation energies. The “exact” Kohn-Sham orbital energy differences ($\epsilon_a - \epsilon_H$) approach $\omega_a(\text{FCI})$ from below. For the third excitation $\mathcal{E}_a^{\text{NEO}}(H)$ and ($\epsilon_a^{\text{KS}} - \epsilon_H^{\text{KS}}$) coincide. For these excitations TDDFT-BP86 also provides a good estimate of the excitation energies (see Table VI), in keeping with the valence character of the excitations, the excitation energies being typically a bit too low.⁴¹

3. Interpretation of excitations of HeH^+ and Li_2 using NEOs

The demonstrated proximity of the NEOs and the exact KS virtual orbitals suggests that, similar to the KS case, the excitations should be described by predominantly single orbital-orbital excitations in the NEO case. This is shown in

TABLE VI. Orbital character and energies of the NEOs $\{\theta_a(H)\}$ of Li_2 at R_e for the lowest $n^1\Sigma_g^+$ excitations. The FCI excitation energies ω_a^{FCI} , equal to the TDPINOFT excitation energies, are compared to adiabatic TDDFT with the BP86 functional and to one-electron energy differences \mathcal{E} for NEOs and for KS orbitals. In the NEO or in the KS virtual orbital basis the excitations are predominantly single orbital-orbital transitions, cf. the transition densities in Table VIII. ψ_a denotes the receiving orbital. Top line: Overlap integrals between the NEOs and the corresponding virtual KS orbitals. Second line: FCI excitation energies (in eV) of the related $1^1\Sigma_g^+$ excitations. Third line, $\mathcal{E}_a^{\text{NEO}}(H)$: “orbital energies” of the NEOs (eigenvalues of the diagonalization of the $A_{aH,Hb}^+(\Sigma_g^+)$ matrix). Fourth line, exact KS orbital energy differences $\mathcal{E}_{a2\sigma_g,2\sigma_g}^{\text{KS}} = \epsilon_a^s - \epsilon_H^s$. Fifth line ($\epsilon_a^s - \epsilon_{2\sigma_g}^s$) (BP86): same orbital energy differences for BP86. Last line, BP86-TDDFT excitation energies for Σ_g^+ symmetry.

Excited state	Li_2 $n^1\Sigma_g^+$ excitations		
	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
Orbital character: $2\sigma_g = H \rightarrow \psi_a$	$\psi_a = 3\sigma_g$	$\psi_a = 4\sigma_g$	$\psi_a = 5\sigma_g$
$\langle \theta_a(H) \phi_a^{\text{KS}} \rangle$	0.996	0.982	0.956
$\omega_a^{\text{FCI}}(1^1\Sigma_g^+)$	2.7	3.5	4.0
$\mathcal{E}_a^{\text{NEO}}(H)$	2.9	3.8	4.1
$\mathcal{E}_{a2\sigma_g,2\sigma_g}^{\text{KS}} = \epsilon_a^s - \epsilon_{2\sigma_g}^s$	2.4	3.2	4.1
$(\epsilon_a^{\text{BP86}} - \epsilon_{2\sigma_g}^{\text{BP86}})$	2.4	3.4	3.7
$\omega_a^{\text{TDDFT-BP86}}(1^1\Sigma_g^+)$	2.6	3.3	3.7

Tables VII and VIII for HeH^+ and Li_2 respectively, which present the transition densities in the NEO basis instead of the NO basis (same transitions as in Tables I and II). Note that the transition density of an excitation from a

TABLE VII. TDPINO transition densities for the lowest $1^1\Sigma^+$ excitations for HeH^+ at R_e in the NEO basis. ψ_1 is the HOMO 1σ orbital, and a labels the virtual σ orbitals starting with the LUMO $\psi_2 = 2\sigma$. The doubles (omitted) contribute negligibly also in the NEO basis at R_e .

$a\sigma$	$\Delta\gamma_{1a}(\omega_a)$ vectors			
	$2^1\Sigma^+$	$3^1\Sigma^+$	$4^1\Sigma^+$	$5^1\Sigma^+$
2	1.292	0.048	0.067	-0.051
3	-0.069	1.367	0.094	0.019
4	-0.130	-0.108	1.363	-0.078
5	0.060	-0.036	0.078	1.327
6	0.013	0.029	0.052	0.379
7	-0.058	-0.080	-0.093	0.003
8	-0.102	-0.024	-0.076	0.035
9	-0.019	0.017	-0.004	0.012
10	0.002	0.012	0.007	0.015
11	-0.006	0.040	0.005	0.015
12	-0.073	-0.024	-0.043	0.014
13	0.002	-0.010	-0.002	-0.002
14	0.022	-0.015	0.007	-0.013
15	0.013	-0.013	0.004	-0.008
16	0.007	0.005	0.004	0.001
17	-0.018	-0.002	-0.009	0.004
18	0.025	0.009	0.014	-0.004
19	0.003	0.007	0.003	0.000
20	-0.002	0.006	0.000	0.003
21	0.005	-0.001	0.002	-0.002
22	-0.002	-0.001	-0.001	0.001

TABLE VIII. TDPINO transition densities for the lowest $^1\Sigma_g^+$ excitations of Li_2 at R_e in the NEO basis. Transitions out of the $\psi_3 = 2\sigma_g$ HOMO to NEOs $3\sigma_g$ ($2^1\Sigma_g^+$), etc.

$a\sigma_g$	$\Delta\gamma_{3a}(\omega_\alpha)$ vectors		
	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
3	1.019	0.376	-0.018
4	-0.380	1.109	-0.399
5	0.125	0.322	0.995
6	0.224	0.060	-0.088
7	-0.048	0.128	0.146
8	0.012	0.042	0.038
9	-0.105	-0.030	0.041
10	0.019	0.027	0.018
11	-0.007	-0.004	0.001
12	-0.026	-0.009	0.013
13	0.015	0.008	0.000
14	0.000	0.000	0.001
15	0.000	0.000	0.000
$2\sigma_g 2\sigma_g$	-0.001	-0.007	0.025
$2\sigma_u 2\sigma_u$	0.072	-0.037	-0.085
$1\pi_u(x) 1\pi_u(x)$	-0.041	0.013	0.008
$1\pi_u(y) 1\pi_u(y)$	-0.041	0.013	0.008
$3\sigma_g 3\sigma_g$	0.033	0.036	0.046

closed shell single determinantal wavefunction to the singlet of the open shell configuration resulting from a single $i \rightarrow a$ orbital transition is $\Delta\gamma_{ia} = \sqrt{2}$ (and all other $\Delta\gamma_{jb}$ and $\Delta\gamma_{pp}$ equal to zero).³⁹ Contrary to what we saw in the case of the NOs in Tables I and II, these excitations can be assigned to predominantly single orbital-to-orbital transitions $\phi_H \rightarrow \theta_a(H)$. For HeH^+ , Table VII, there is one dominant $\Delta\gamma_{1a}$ element for each excited state, approaching $\sqrt{2}$. For Li_2 , Table VIII, this is also true, although the dominant $\Delta\gamma_{1a}$ element is not as close to $\sqrt{2}$ as in HeH^+ and there are a few other sizable elements. Nevertheless, the transformation to NEOs solves the problem of lack of clear orbital character of the excitations that exists with the NO basis.

At stretched bond length the change from NO basis to NEO basis is less striking, cf. Table IX, to be compared to Table III. The occupied $2\sigma_g$ ($2s + 2s$ bonding) orbital and its

TABLE IX. TDPINO transition densities for the lowest $^1\Sigma_g^+$ excitations for Li_2 at 9 bohrs in the NEO basis. Only transition density entries with an absolute value higher than 0.1 for at least one of the excitations are shown.

a	b	$\Delta\gamma_{ba}(\omega_\alpha)$ vectors		
		$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
$3\sigma_g$	$2\sigma_g$	-0.713	0.681	0.148
$4\sigma_g$	$2\sigma_g$	-0.349	-0.198	-0.971
$5\sigma_g$	$2\sigma_g$	0.105	0.314	0.001
$6\sigma_g$	$2\sigma_g$	-0.137	0.047	-0.087
$7\sigma_g$	$2\sigma_g$	0.121	0.206	0.006
$2\sigma_g$	$2\sigma_g$	-0.415	-0.351	0.108
$2\sigma_u$	$2\sigma_u$	0.486	0.421	-0.142
$3\sigma_u$	$2\sigma_u$	-0.026	0.120	0.113

antibonding partner $2\sigma_u$ are practically identical in the NO and NEO bases, and the expected strong double excitation $(2\sigma_g)^2 \rightarrow (2\sigma_u)^2$ at this long bond length shows up in both bases. The single excitations are reduced in the NEO basis, excitations with transition densities > 0.1 go up to $15\sigma_g$ in the NO basis, but only up to $7\sigma_g$ in the NEO basis. We emphasize that the (adiabatic) TDDMFT method affords double excitations, in contrast to TDDFT (in the adiabatic approximation) and TDHF. Therefore it is able to describe potential energy curves along the complete dissociation coordinate, which TDDFT cannot do.³⁹ The double excitation character of excited states shows up in the diagonal elements $\Delta\gamma_{pp}$ in the bottom lines of the table (with p referring to both the HOMO $2\sigma_g$ and LUMO $2\sigma_u$) and the off-diagonal double element $\Delta\gamma_{3\sigma_u, 2\sigma_u}$. See also the SI at Ref. 42 for other examples of TDDMFT at stretched bond lengths.

C. NEOs in linear response TDHF

1. Li_2

Table X demonstrates the extension of the NEO concept to LR-TDHF with the same Li_2 example. The NEOs obtained from the diagonalization of the TDHF submatrix \mathbf{A}_H^+ (denoted TDHF-NEOs, $\theta_a(H)$) are compared with the virtual KS orbitals ϕ_a obtained with the LB scheme^{67,68} from the density $\rho^{HF}(\mathbf{x})$ of the HF method (denoted $\text{KS}(\rho^{HF})$ orbitals). In their turn, the eigenvalues from the \mathbf{A}_H^+ diagonalization, the TDHF-NEO orbital energies $\mathcal{E}_a^{\text{TDHF-NEO}}(H)$, are compared with the $\text{KS}(\rho^{HF})$ orbital energy differences ($\epsilon_a - \epsilon_H$). The TDHF excitation energies $\omega_\alpha(\text{TDHF})$ obtained with the LR-TDHF calculations according to Eq. (54) are given as a reference. Comparison is also made with the excitation energies $\omega_\alpha(\text{CIS})$ of the CI-singles (CIS) method,^{51,69} which are often very similar to the TDHF ones.

We note, first of all, that for the considered Li_2 molecule the CIS excitation energies are close to the FCI ones, and the TDHF ones are even closer. (In general the TDHF energies are not so good.) The TDHF-NEO energies

TABLE X. Li_2 : TDHF $n^1\Sigma_g^+$ excitation energies at R_e compared to TDHF-NEO orbital energy differences and $\text{KS}(\rho^{HF})$ orbital energy differences. Top line: Overlap integrals between the TDHF-NEOs $\theta_a(2\sigma_g)$ and the corresponding virtual KS orbitals ϕ_a^{KS} obtained with the HF density (denoted $\text{KS}(\rho^{HF})$). Second line: CIS excitation energies (in eV) of the $^1\Sigma_g^+$ excitations. Third line: TDHF excitation energies $\omega(a^1\Sigma_g^+)$ (in eV) of the $^1\Sigma_g^+$ excitations. Fourth line, $\mathcal{E}_a^{\text{TDHF-NEO}}(H)$: “orbital energies” of the TDHF-NEOs (eigenvalues of the diagonalization of the $\mathbf{A}_{a3,3b}^+(2\sigma_g)$ matrix). Last line, $\text{KS}(\rho^{HF})$ orbital energy differences $\Delta\epsilon_a(\text{KS}(\rho^{HF})) = \epsilon_a - \epsilon(2\sigma_g)$.

Excited state	Li_2 $n^1\Sigma_g^+$ excitations		
	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
Orbital character: $2\sigma_g = H \rightarrow \psi_a$	$\psi_a = 3\sigma_g$	$\psi_a = 4\sigma_g$	$\psi_a = 5\sigma_g$
$\langle \theta_a(2\sigma_g) \phi_a^{KS}(\rho^{HF}) \rangle$	0.995	0.968	0.962
$\omega_{n^1\Sigma_g^+}(\text{FCI})$	2.7	3.5	4.0
$\omega_{n^1\Sigma_g^+}(\text{CIS})$	3.0	3.4	3.9
$\omega_{n^1\Sigma_g^+}(\text{TDHF})$	2.9	3.4	3.9
$\mathcal{E}_a^{\text{TDHF-NEO}}(H)$	2.4	3.3	3.8
$\Delta\epsilon_a(\text{KS}(\rho^{HF})) = \epsilon_a - \epsilon(2\sigma_g)$	2.3	3.1	3.9

TABLE XI. TDHF transition densities for the lowest $1^1\Sigma_g^+$ excitations for Li_2 at R_e in the HF-NEO basis.

$a\sigma_g$	$\Delta\gamma_{2\sigma_g,a}(\omega_\alpha)$ vectors		
	$2^1\Sigma_g^+$	$3^1\Sigma_g^+$	$4^1\Sigma_g^+$
3	1.020	0.136	-0.477
4	-0.096	1.297	0.008
5	-0.749	-0.007	-1.118
6	0.146	-0.445	-0.336
7	-0.249	-0.201	0.554
8	-0.031	-0.033	0.074
9	0.070	-0.080	-0.084
10	-0.042	-0.060	0.055
11	0.024	0.013	-0.025
12	0.009	-0.023	-0.010
13	0.000	-0.007	0.002
14	0.001	-0.008	-0.001
15	0.000	0.001	0.000

\mathcal{E}_a^H (TDHF-NEO) are close to the KS(ρ^{HF}) orbital energy differences ($\epsilon_a - \epsilon_H$) and they both provide a fair estimate of the excitation energies (in this case both the full CI ones and the TDHF ones). The TDHF-NEOs very much resemble the virtual KS(ρ^{HF}) orbitals with the overlaps $\langle\theta_a(H)|\phi_a\rangle$ larger than 0.96. Because of this, the transformation from the HF MOs to HF-NEOs leads to a more compact representation of the considered TDHF excitations as predominantly single orbital-to-orbital transitions $\phi_H \rightarrow \theta_a(H)$. This can be seen from the comparison of Tables IV and XI, which display the composition of the TDHF transition densities of the same excited states

in the basis of the HF MOs and TDHF-NEOs, respectively. The transition densities in the TDHF-NEO basis are characterized by fewer large elements, although obviously these transitions do not purely consist of a single orbital-to-orbital transition. Since the TDHF submatrix \mathbf{A}_H^+ can be easily constructed and diagonalized, it is obviously straightforward (in *ab initio* calculations) to construct an orbital basis, the TDHF-NEOs, which approximates the NEO and the (exact) Kohn-Sham basis sufficiently closely so that a simple orbital description of excitations can be given. Transformation to the same basis would also improve the interpretation of CI calculations.

2. H_2O

An important issue with the proposed NEO concept is the extent to which the NEOs depend on the choice of the orbital index i of the submatrix \mathbf{A}_i^+ in the diagonalization (74). This dependence is analyzed with TDHF calculations of the 14 lowest excited states of the water molecule, 9 of which are excitations out of the HOMO ($1b_1 = \psi_5$) (see upper part of Table XII) and 5 are out of the HOMO-1 ($3a_1 = \psi_4$) (lower part of the table). The HOMO of H_2O of B_1 symmetry represents the π lone pair of the O atom oriented perpendicular to the molecular plane, while the HOMO-1 of A_1 symmetry describes the O atom σ lone pair in the molecular plane and, in addition, it has some O-H bonding character. Excitations to 9 TDHF-NEOs $\theta_a(H)$ obtained from the diagonalization of the TDHF submatrix \mathbf{A}_H^+ are shown in Table XII. The table displays the overlaps $\langle\theta_a(H)|\phi_a\rangle$ of these TDHF-NEOs with the corresponding virtual KS(ρ^{HF}) orbitals (the KS orbitals that reproduce the HF density). Excitations out of the HOMO-1

TABLE XII. Lowest calculated singlet excitations in H_2O at R_e : The first 9 excitations out of HOMO $\psi_H = \psi_5 = 1b_1$ in the upper half of the table, and 5 excitations out of HOMO-1 $\psi_4 = 3a_1$ in the lower half of the table. ω_{CIS} : CIS excitation energy. ω_{TDHF} : TDHF excitation energy. $\Delta\epsilon^{KS}(\rho^{HF})$: KS orbital energy difference $\epsilon_a - \epsilon_i$ of the involved KS(ρ^{HF}) orbitals. $\mathcal{E}_a^{\text{NEO}}(i)$ "orbital energies" of the NEOs $\theta_a(i)$, i.e., eigenvalues of the diagonalization of the $\mathbf{A}_{ai,ib}^+$ matrix with $i = 5 = \text{HOMO}$ for excitations out of HOMO $1b_1$ and with $i = 4 = \text{HOMO-1}$ for excitations out of HOMO-1 $= 3a_1$. $\langle\theta_a(i)|\phi_a\rangle$: Overlap integrals of the two different sets of NEOs $\theta_a(i)$ with $i = H$ and $i = H - 1$ respectively, resulting from the two diagonalizations, with the single set of corresponding virtual KS orbitals ϕ_a .

State	Description	ω_{CIS}	ω_{TDHF}	$\Delta\epsilon^{KS}(\rho^{HF})$	$\mathcal{E}_a^{\text{NEO}}(H)$	$\langle\theta_a(H) \phi_a\rangle$
	$\psi_H \rightarrow \psi_a$			$\epsilon_a - \epsilon_H$		
1^1B_1	$1b_1 \rightarrow 4a_1$	8.68	8.63	8.56	8.40	0.997
1^1A_2	$1b_1 \rightarrow 2b_2$	10.35	10.30	10.67	10.21	0.998
2^1B_1	$1b_1 \rightarrow 5a_1$	11.71	11.69	11.99	11.64	0.955
3^1A_1	$1b_1 \rightarrow 2b_1$	12.43	12.36	12.18	12.27	0.995
3^1B_1	$1b_1 \rightarrow 6a_1$	12.66	12.64	12.77	12.54	0.932
2^1A_2	$1b_1 \rightarrow 3b_2$	12.74	12.71	12.91	12.64	0.927
3^1A_2	$1b_1 \rightarrow 4b_2$	13.80	13.79	14.07	13.78	0.928
4^1B_1	$1b_1 \rightarrow 7a_1$	14.30	14.29	13.95	14.21	0.971
2^1B_2	$1b_1 \rightarrow 1a_2$	14.88	14.87	14.84	14.91	0.997
	$\psi_{H-1} \rightarrow \psi_a$			$\epsilon_a - \epsilon_{H-1}$	$\mathcal{E}_a^{\text{NEO}}(H-1)$	$\langle\theta_a(H-1) \phi_a\rangle$
2^1A_1	$3a_1 \rightarrow 4a_1$	10.97	10.94	10.46	10.82	0.995
1^1B_2	$3a_1 \rightarrow 2b_2$	12.62	12.58	12.58	12.46	0.994
4^1A_1	$3a_1 \rightarrow 5a_1$	14.15	14.08	13.90	14.02	0.981
5^1B_1	$3a_1 \rightarrow 2b_1$	13.99	13.95	14.09	13.93	0.999
5^1A_1	$3a_1 \rightarrow 6a_1$	14.75	14.74	14.67	14.63	0.960

to 5 TDHF-NEOs $\theta_a(H-1)$ obtained from the diagonalization of \mathbf{A}_{H-1}^+ are given. The overlaps $\langle \theta_a(H-1) | \phi_a \rangle$ of these slightly different TDHF-NEOs with the same virtual KS(ρ^{HF}) orbitals are in the lower part of the table. The dependence of $\theta_a(i)$ on i is found to be very weak in the considered case, and the NEOs $\theta_a(H)$ and $\theta_a(H-1)$ with the same index a produce very similar overlaps with the common virtual KS orbital ϕ_a (see Table XIII). In all cases $\theta_a(H)$ and $\theta_a(H-1)$ both resemble very much the virtual KS orbital $\phi_a^{KS}(\rho^{HF})$, with overlaps varying from 0.999 to 0.927. In their turn, the TDHF-NEO energies $\mathcal{E}_a^{\text{TDHF-NEO}}(H)$ and $\mathcal{E}_a^{\text{TDHF-NEO}}(H-1)$ are very close to the TDHF excitation energies $\omega_a(\text{TDHF})$. Also the KS(ρ^{HF}) orbital energy differences $(\epsilon_a - \epsilon_H)$ and $(\epsilon_a - \epsilon_{H-1})$ are close to the TDHF excitation energies.

The transition density vectors of the considered 14 excited states in the basis set of the virtual HF MOs ψ_a are characterized in Table XIII. Tables XIV and XV present the transition densities for the same excitations in the NEO basis sets $\theta_a(H)$ and $\theta_a(H-1)$, respectively. For each $\Delta\gamma$ vector its largest and the second largest (in absolute value) elements in the particular basis are presented as well as the number of remaining elements, which are larger than the threshold value 0.1. These data show that the NEOs yield a more compact representation of $\Delta\gamma^\alpha$ compared to the HF MOs. Indeed, when going from the HF MOs to $\theta_a(H)$, the average value (for the first 9 excitations) of the largest $|\Delta\gamma_{ja}^\alpha|$ increases from 1.12 to 1.39, the average second largest $|\Delta\gamma_{ja}^\alpha|$ decreases from 0.63 to 0.13, and the average number of the remaining elements $|\Delta\gamma_{ja}^\alpha| > 0.1$ reduces from 4 to 0.44 (compare Tables XIII and XIV). The data also show the proximity of the NEOs $\theta_a(H)$ and $\theta_a(H-1)$ obtained from the diagonalization of the submatrices \mathbf{A}_H^+ and \mathbf{A}_{H-1}^+ . Indeed, in the basis of the NEOs $\theta_a(H-1)$ (Table XV) the average largest and second largest $|\Delta\gamma_{ja}^\alpha|$ amount to 1.37 and 0.18, respectively, while the average number of the remaining $|\Delta\gamma_{ja}^\alpha| > 0.1$ is 0.56, which is close to the corresponding quantities of the $\theta_a(H)$ basis (Compare Tables XIV and XV).

TABLE XIII. TDHF transition densities for the lowest excitations of H₂O at R_e in HF basis. Second to fourth column: Largest absolute transition density element. Next 3 columns: Second largest absolute transition density element. Last column: Number of remaining “large” transition density elements ($|\Delta\gamma| > 0.1$).

Excitation to	i_1	a_1	$\Delta\gamma_{i_1 a_1}$	i_2	a_2	$\Delta\gamma_{i_2 a_2}$	$N_{\Delta\gamma}^L$
1^1B_1	$1b_1$	$4a_1$	-1.093	$1b_1$	$6a_1$	0.615	3
1^1A_2	$1b_1$	$2b_2$	-1.040	$1b_1$	$3b_2$	-0.673	4
2^1B_1	$1b_1$	$5a_1$	1.191	$1b_1$	$4a_1$	0.501	4
3^1A_1	$1b_1$	$2b_1$	1.286	$3a_1$	$4a_1$	0.346	6
3^1B_1	$1b_1$	$6a_1$	1.139	$1b_1$	$4a_1$	0.717	3
2^1A_2	$1b_1$	$3b_2$	-0.973	$1b_1$	$2b_2$	0.849	4
3^1A_2	$1b_1$	$3b_2$	-1.115	$1b_1$	$4b_2$	0.679	4
4^1B_1	$1b_1$	$7a_1$	1.332	$3a_1$	$2b_1$	0.299	4
2^1B_2	$1b_1$	$1a_2$	1.145	$3a_1$	$4b_2$	-0.567	4
2^1A_1	$3a_1$	$4a_1$	-1.113	$3a_1$	$6a_1$	0.616	5
1^1B_2	$3a_1$	$2b_2$	-1.118	$3a_1$	$3b_2$	-0.672	3
4^1A_1	$3a_1$	$5a_1$	-1.228	$3a_1$	$6a_1$	0.304	9
5^1B_1	$3a_1$	$2b_1$	1.318	$3a_1$	$3b_1$	-0.344	1
5^1A_1	$3a_1$	$6a_1$	1.117	$3a_1$	$4a_1$	0.740	4

TABLE XIV. TDHF transition densities for the lowest couple of excitations of H₂O at R_e in NEO(5) basis from diagonalization of $\mathbf{A}^+(H)$. Second to fourth column: Largest absolute transition density element. Next 3 columns: Second largest absolute transition density element. Last column: Number of remaining “large” transition density elements ($|\Delta\gamma| > 0.1$).

Excitation to	i_1	a_1	$\Delta\gamma_{i_1 a_1}$	i_2	a_2	$\Delta\gamma_{i_2 a_2}$	$N_{\Delta\gamma}^L$
1^1B_1	$1b_1$	$4a_1$	-1.391	$1b_1$	$6a_1$	-0.059	0
1^1A_2	$1b_1$	$2b_2$	1.403	$1b_1$	$3b_2$	-0.050	0
2^1B_1	$1b_1$	$5a_1$	1.410	$3a_1$	$2b_1$	-0.044	0
3^1A_1	$1b_1$	$2b_1$	1.319	$3a_1$	$5a_1$	0.387	2
3^1B_1	$1b_1$	$6a_1$	1.407	$1b_1$	$4a_1$	-0.038	0
2^1A_2	$1b_1$	$3b_2$	1.408	$1b_1$	$2b_2$	0.036	0
3^1A_2	$1b_1$	$4b_2$	1.413	$1b_2$	$2b_1$	-0.014	0
4^1B_1	$1b_1$	$7a_1$	-1.369	$3a_1$	$2b_1$	0.309	1
2^1B_2	$1b_1$	$1a_2$	1.158	$3a_1$	$3b_2$	0.813	0
2^1A_1	$3a_1$	$4a_1$	-1.350	$1b_1$	$2b_1$	0.359	1
1^1B_2	$3a_1$	$2b_2$	1.382	$3a_1$	$3b_2$	-0.219	1
4^1A_1	$3a_1$	$5a_1$	-1.293	$1b_2$	$2b_2$	0.316	4
5^1B_1	$3a_1$	$2b_1$	1.370	$1b_1$	$7a_1$	0.325	0
5^1A_1	$3a_1$	$6a_1$	1.390	$3a_1$	$5a_1$	0.153	1

3. CH₂O

Table XVI shows the results of the response TDHF calculations of the 7 lowest states of the formaldehyde molecule. For 5 states representing transitions from the HOMO of B_2 symmetry the characteristics of the corresponding NEOs $\theta_a(H)$ are displayed. Once again, with the overlaps $\langle \theta_a(H) | \phi_a \rangle$ ranging from 0.958 to 0.997, the NEOs resemble very much the virtual KS orbitals. The TDHF-NEO energies $\mathcal{E}_a^{\text{NEO}}(H)$ are exceedingly close to the TDHF and the CIS excitation energies. These energies differ somewhat from the KS(ρ^{HF}) orbital energy differences $(\epsilon_a - \epsilon_H)$ (from 0.2 to 0.7 eV). For the 3^1A_1 state representing the transition from the (HOMO-2) $1b_1$ to the next orbital of B_1 symmetry the deviation of the KS ($\epsilon_{2b_1} - \epsilon_{1b_1}$) from $\omega(3^1A_1)(\text{TDHF})$ is exceptionally large (1.1 eV),

TABLE XV. TDHF transition densities for the lowest excitations of H₂O at R_e in NEO(4) basis from diagonalization of $\mathbf{A}^+(H-1)$. Second to fourth column: Largest absolute transition density element. Next 3 columns: Second largest absolute transition density element. Last column: Number of remaining “large” transition density elements ($|\Delta\gamma| > 0.1$).

State	i_1	a_1	$\Delta\gamma_{i_1 a_1}$	i_2	a_2	$\Delta\gamma_{i_2 a_2}$	$N_{\Delta\gamma}^L$
1^1B_1	$1b_1$	$4a_1$	1.380	$1b_1$	$5a_1$	0.169	0
1^1A_2	$1b_1$	$2b_2$	-1.402	$1b_1$	$3b_2$	0.067	0
2^1B_1	$1b_1$	$5a_1$	1.371	$1b_1$	$6a_1$	-0.236	2
3^1A_1	$1b_1$	$2b_1$	-1.316	$3a_1$	$5a_1$	0.332	2
3^1B_1	$1b_1$	$6a_1$	-1.386	$1b_1$	$5a_1$	-0.237	0
2^1A_2	$1b_1$	$3b_2$	1.405	$1b_1$	$2b_2$	0.081	0
3^1A_2	$1b_1$	$4b_2$	-1.412	$3a_1$	$1a_2$	0.028	0
4^1B_1	$1b_1$	$7a_1$	-1.373	$3a_1$	$2b_1$	-0.309	0
2^1B_2	$1b_1$	$1a_2$	1.159	$3a_1$	$3b_2$	0.814	0
2^1A_1	$3a_1$	$4a_1$	1.358	$1b_1$	$2b_1$	-0.364	0
1^1B_2	$3a_1$	$2b_2$	-1.397	$1b_1$	$1a_2$	0.104	1
4^1A_1	$3a_1$	$5a_1$	-1.329	$1b_2$	$2b_2$	-0.308	3
5^1B_1	$3a_1$	$2b_1$	-1.373	$1b_1$	$7a_1$	0.320	1
5^1A_1	$3a_1$	$6a_1$	-1.399	$1b_1$	$3b_1$	-0.134	0

TABLE XVI. Lowest singlet excitations in CH₂O at R_e . ω_{CIS} : CIS excitation energy. ω_{TDHF} : TDHF excitation energy. $\Delta\epsilon^{\text{KS}}$: KS orbital energy difference of involved orbitals $\epsilon_a - \epsilon_i$. $\mathcal{E}_a^{\text{NEO}}(H)$ “orbital energies” of the NEOs(H) (eigenvalues of the diagonalization of the $A_{aH,Hb}^+$ matrix). $\langle\theta_a(H)|\phi_a\rangle$: Overlap integrals between the NEOs(H) and the corresponding virtual KS orbitals.

State	Description	ω_{CIS}	ω_{TDHF}	$\Delta\epsilon^{\text{KS}}(\rho^{\text{HF}})$	$\mathcal{E}_a^{\text{NEO}}(H)$	$\langle\theta_a(H) \phi_a\rangle$
1^1A_2	$2b_2 \rightarrow 2b_1$	4.57	4.39	5.11	4.43	0.997
1^1B_2	$2b_2 \rightarrow 6a_1$	8.54	8.53	7.92	8.55	0.958
2^1B_2	$2b_2 \rightarrow 7a_1$	9.36	9.34	8.80	9.37	0.960
2^1A_1	$2b_2 \rightarrow 3b_2$	9.50	9.53	9.16	9.51	0.969
3^1A_1	$1b_1 \rightarrow 2b_1$	9.71	9.23	8.08
1^1B_1	$5a_1 \rightarrow 2b_1$	9.87	9.62	9.80
2^1A_2	$2b_2 \rightarrow 3b_1$	9.99	9.99	9.65	10.02	0.995

while for the 1^1B_1 state (orbital transition out of HOMO-1, $5a_1 \rightarrow 2b_1$) the corresponding deviation is small (0.2 eV) (see Table XVI).

The transition density vectors of the considered 7 excited states of CH₂O in the basis sets of the virtual HF MOs ψ_a^{HF} and NEOs $\theta_a(H)$ are characterized in Tables XVII and XVIII, respectively. Again, the NEOs yield an efficient interpretation of the excitations with one dominant $|\Delta\gamma_{ja}^\alpha|$. Indeed, when going from ψ_a^{HF} to $\theta_a(H)$, the average largest $|\Delta\gamma_{ja}^\alpha|$ increases from 1.08 to 1.37, close to the maximum of $\sqrt{2}$; the average second largest $|\Delta\gamma_{ja}^\alpha|$ decreases from 0.72 to 0.15, while the average number of remaining $|\Delta\gamma_{ja}^\alpha| > 0.1$ reduces from 4.4 to 1 (compare Tables XVII and XVIII). In fact, only the transition density vector of the 3^1A_1 state has 7 remaining elements $|\Delta\gamma_{ja}^\alpha| > 0.1$ in the NEO basis, while for all other states there are only two elements $|\Delta\gamma_{ja}^\alpha| > 0.1$, with the largest element $|\Delta\gamma_{ib}^\alpha|$ being about an order of magnitude larger than any other element (See Table XVI). Then, the corresponding excitations can be safely considered as just the single orbital-to-orbital transitions $\phi_i \rightarrow \theta_a(H)$, so that the shape of the NEO $\theta_a(H)$ represents the density distribution of the excited electron.

VI. SUMMARY

We have introduced a transformation of the (virtual) NO basis to a set of natural excitation orbitals (NEOs). The primary purpose is to get a good characterization of excitations that are calculated with TDDMFT, which employ NOs. We have

TABLE XVII. TDHF transition densities for the lowest couple of excitations of CH₂O at R_e in HF basis. Second to fourth column: Largest absolute transition density element. Next 3 columns: Second largest absolute transition density element. Last column: Number of remaining “large” transition density elements ($|\Delta\gamma| > 0.1$).

State	i_1	a_1	$\Delta\gamma_{i_1a_1}$	i_2	a_2	$\Delta\gamma_{i_2a_2}$	$N_{\Delta\gamma}^L$
1^1A_2	$2b_2$	$3b_1$	0.968 34	$2b_2$	$2b_1$	0.823 69	4
1^1B_2	$2b_2$	$6a_1$	-1.189 2	$2b_2$	$8a_1$	-0.614 39	4
2^1B_2	$2b_2$	$7a_1$	-1.249 82	$2b_2$	$11a_1$	-0.453 47	3
2^1A_1	$2b_2$	$3b_2$	-1.216 48	$2b_2$	$4b_2$	-0.606 86	4
3^1A_1	$1b_1$	$3b_1$	-0.902 44	$1b_1$	$2b_1$	-0.873 32	9
1^1B_1	$5a_1$	$3b_1$	-0.999 14	$5a_1$	$2b_1$	-0.807 58	4
2^1A_2	$2b_2$	$2b_1$	-1.040 29	$2b_2$	$3b_1$	0.887 83	3

TABLE XVIII. TDHF transition densities for the lowest couple of excitations of CH₂O at R_e in NEO(8) basis from diagonalization of $\mathbf{A}^+(H)$. Second to fourth column: Largest absolute transition density element. Next 3 columns: Second largest absolute transition density element. Last column: Number of remaining “large” transition density elements ($|\Delta\gamma| > 0.1$).

State	i_1	a_1	$\Delta\gamma_{i_1a_1}$	i_2	a_2	$\Delta\gamma_{i_2a_2}$	$N_{\Delta\gamma}^L$
1^1A_2	$2b_2$	$2b_1$	-1.346	$1b_2$	$2b_1$	0.162	0
1^1B_2	$2b_2$	$6a_1$	-1.399	$1b_2$	$7a_1$	0.094	0
2^1B_2	$2b_2$	$7a_1$	-1.397	$1b_2$	$6a_1$	0.110	0
2^1A_1	$2b_2$	$3b_2$	1.384	$1b_1$	$2b_1$	-0.232	0
3^1A_1	$1b_1$	$2b_1$	1.285	$2b_2$	$5b_2$	0.267	7
1^1B_1	$5a_1$	$2b_1$	1.372	$3a_1$	$2b_1$	-0.124	0
2^1A_2	$2b_2$	$3b_1$	-1.410	$1b_2$	$4b_1$	0.059	0

demonstrated NOs to be totally unsuitable for characterizing excitations, any excitation being expressed in terms of many orbital-to-orbital transitions. The proposed method produces orbitals which are very close to virtual KS orbitals, which are known to be very suitable for describing excitations (if calculated accurately). In principle just KS orbitals could be used, or very good approximations to KS orbitals such as are provided with special functionals for the KS potential like SAOP⁴¹ and B-GLLB.⁶⁶ However, the present method offers a consistent method completely within the TDDMFT formalism.

We have demonstrated that the linear response equations for the calculation of excitation energies in the cases of time-dependent density matrix functional theory, time-dependent Hartree-Fock theory, and time-dependent Kohn-Sham DFT are formally very similar. Indeed, a unified derivation has been given where the latter two are derived as special cases of the more general density matrix functional case. However, in these three response theories, the bases in which the relevant matrices are being expressed are different. In the LR-TDKS equations we have noted that the matrix \mathbf{A}^{s+} is diagonal, and \mathbf{A}^{s-} almost diagonal in the Kohn-Sham MO basis, and therefore the compound matrix $(\sqrt{\mathbf{A}^{s+}}\mathbf{A}^{s-}\sqrt{\mathbf{A}^{s+}})$ is so too. This can be understood from the fact that the elements of these matrices are exactly differences of matrix elements of the KS hamiltonian in the \mathbf{A}^{s+} matrix and for a large part in \mathbf{A}^{s-} . This makes them (almost) diagonal in the KS orbital basis. Diagonal elements of the LR matrix describe $i \rightarrow a$ orbital-to-orbital excitations, while the off-diagonal elements cause mixing of $i \rightarrow a$ and $j \rightarrow b$ transitions. Diagonalization does not mix the orbital-to-orbital transitions very much, so excitations are mostly represented as single orbital transitions in the KS MO basis. This makes the KS orbitals a very suitable basis to describe excitations.⁴¹ We have stressed that there is a good physical reason for this. The KS hamiltonian incorporates, also for the virtual orbitals, a hole charge potential. It is due to the exchange-correlation hole, which comprises -1 electron and mimics the hole left behind by the excited electron. This gives the virtual orbital KS orbitals a realistic shape and energy.

As an aside we note that there are cases of course in TDKS calculations where there is genuine mixing of single orbital transitions, and indeed the TDKS method can fully account for such mixing. An example is provided by the porphyrin molecule and the derived porphyrins. These are characterized by an aromatic ring system, that can be D_{4h} symmetric, unless

substituents destroy the symmetry. In the symmetric systems mixing of orbital-to-orbital transitions (between the so-called Gouterman orbitals^{70,71}) is dictated by symmetry, yielding the well-known Q and B bands in the spectrum. This mixing is described by TDKS calculations in which symmetry is fully exploited in the LR equations.^{72,73} However, when the symmetry is lowered, still strong mixing will occur and it has been demonstrated that TDKS is fully capable of rendering such mixing.⁷⁴

The analogous matrices \mathbf{A}^+ and \mathbf{A}^- are by no means diagonal in the TDHF and TDDMFT cases. We have shown that this is not due to the difference in the one-electron hamiltonian that is implicitly used in these matrix elements. This one-electron hamiltonian is actually KS-like in that it incorporates for $i \rightarrow a$ excitations the potential due to a hole charge $-|\phi_i(\mathbf{r})|^2$, describing the hole left behind by the excited electron. Since neither the unoccupied HF orbitals nor the weakly occupied NOs (which we both call “virtual” orbitals) are solutions to a Schrödinger equation with such a hole potential, they do not diagonalize such a hamiltonian. This explains the strongly nondiagonal character of the \mathbf{A}^+ and \mathbf{A}^- matrices in these bases. We have proposed to diagonalize the submatrix \mathbf{A}_i^+ , which is a virt \times virt matrix with elements $A_{ai,ib}^+$ (constant i , a and b run over the virtual orbitals). This defines a transformation of the set of virtual orbitals to a set that are eigenfunctions of the hamiltonian with the hole potential due to $-|\phi_i(\mathbf{r})|^2$. We have demonstrated that these orbitals are very close to KS orbitals (they have overlaps with the KS orbitals very close to 1.0). The excitations again reduce (in most cases) to predominantly a single orbital-to-orbital transition. We have therefore called these new orbitals natural excitation orbitals (NEOs). Since the NOs have proven to be totally unsuitable for an interpretation of excitations,^{42,75} this defines in the TDDMFT case a much desired transformation to a set of orbitals in which the excitations can be meaningfully expressed. In the TDHF case a transformation can be carried out in exactly the same way with diagonalization of the $\mathbf{A}_i^{\text{TDHF}+}$ matrix. These natural excitation orbitals in the HF case are easily obtained and would also constitute a much better basis for correlation calculations, see, e.g., Refs. 43 and 54–59. A difference with the natural transition orbitals of Martin⁴⁶ is that the latter constitute a pair of optimal orbitals for each excitation, while the NEOs come from a single transformation of the set of virtual orbitals, i.e., they are a single set of virtual orbitals that are in principle used for all transitions.

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