Adiabatic approximation of time-dependent density matrix functional response theory

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Time-dependent density matrix functional theory can be formulated in terms of coupled-perturbed response equations, in which a coupling matrix $\mathbf{K}(\omega)$ features, analogous to the well-known time-dependent density functional theory (TDDFT) case. An adiabatic approximation is needed to solve these equations, but the adiabatic approximation is much more critical since there is not a good "zero order" as in TDDFT, in which the virtual-occupied Kohn-Sham orbital energy differences serve this purpose. We discuss a simple approximation proposed earlier which uses only results from static calculations, called the static approximation (SA), and show that it is deficient, since it leads to zero response of the natural orbital occupation numbers. This leads to wrong behavior in the $\omega \to 0$ limit. An improved adiabatic approximation (AA) is formulated. The two-electron system affords a derivation of exact coupled-perturbed equations for the density matrix response, permitting analytical comparison of the adiabatic approximation with the exact equations. For the two-electron system also, the exact density matrix functional (2-matrix in terms of 1-matrix) is known, enabling testing of the static and adiabatic approximations unobscured by approximations in the functional. The two-electron HeH^+ molecule shows that at the equilibrium distance, SA consistently underestimates the frequency-dependent polarizability $\alpha(\omega)$, the adiabatic TDDFT overestimates $\alpha(\omega)$, while AA improves upon SA and, indeed, AA produces the correct $\alpha(0)$. For stretched HeH^+, adiabatic density matrix functional theory corrects the too low first excitation energy and overpolarization of adiabatic TDDFT methods and exhibits excellent agreement with high-quality CCSD ("exact") results over a large ω range. © *2007 American Institute of Physics.*
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I. INTRODUCTION

In its static variant, density matrix functional theory (DMFT)[1–9] represents a promising many-electron theory, which operates with functionals of the natural orbitals (NOs) ϕ_i and NO occupations n_i. The energy is considered in DMFT as (implicit) functional of the one-particle reduced density matrix (or 1-matrix) γ (Refs. 2 and 10) and the effects of electron correlation are reflected in the functional dependence of the energy on the NOs and the occupation numbers, and of course the shape and values, respectively, of the latter.

For response properties, the time-dependent variant of density matrix functional theory (TDDMFT) is needed, which was formulated in our previous work.[11] The master equation of TDDMFT is the equation of motion (EOM) for the 1-matrix $\gamma(t)$ in the basis of the stationary natural spin-orbitals ϕ_i (atomic units are used throughout the paper),

$$i\frac{\partial \boldsymbol{\gamma}(t)}{\partial t} = [\mathbf{h}(t), \boldsymbol{\gamma}(t)] + \{\mathbf{W}([\boldsymbol{\gamma}];t) - \mathbf{W}^\dagger([\boldsymbol{\gamma}];t)\}, \qquad (1.1)$$

which has been derived in Ref. 11 from the EOM for the Heisenberg field operator.[12] The first term in the right-hand side of Eq. (1.1) is a commutator of the matrix of the time-dependent one-electron operator $\hat{h}(t) = -\frac{1}{2}\nabla^2 + v_{\text{ext}}(t)$ and $\boldsymbol{\gamma}(t)$. The matrix $\mathbf{W}$ in the square brackets is a contraction over three indices of the two-electron integrals $\langle \phi_i \phi_j | \phi_k \phi_l \rangle = \int \phi_i(\mathbf{x}_1)^* \phi_j(\mathbf{x}_2)^* \phi_k(\mathbf{x}_1) \phi_l(\mathbf{x}_2) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\mathbf{x}_1 d\mathbf{x}_2$ ($\mathbf{x}_i \equiv \{\mathbf{r}_i, s_i\}$ denotes spatial and spin electron coordinates) with the time-dependent two-particle reduced density matrix (2-matrix) Γ, which is defined by

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', t)$$

$$= N(N-1) \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N, t)$$

$$\times \Psi^*(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_3, \ldots, \mathbf{x}_N, t) d\mathbf{x}_3 \cdots d\mathbf{x}_N$$

$$= \sum_{jklm} \Gamma_{jklm}(t) \phi_j^*(\mathbf{x}_1') \phi_k^*(\mathbf{x}_2') \phi_l(\mathbf{x}_1) \phi_m(\mathbf{x}_2),$$

and which is considered to be a functional of the 1-matrix,

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$$W_{ij}(t) = \sum_{klm} \Gamma_{jklm}([\boldsymbol{\gamma}];t)\langle \phi_i \phi_k | \phi_l \phi_m \rangle. \tag{1.2}$$

EOM (1.1) represents the full dynamics of $\boldsymbol{\gamma}(t)$ so that it can be partitioned[11] into the EOM for the NOs $\phi_\mu(t)$,

$$\forall_{\mu \neq \nu} \, [n_\nu(t) - n_\mu(t)] \left\{ i \left\langle \phi_\mu(t) \left| \frac{\partial \phi_\nu(t)}{\partial t} \right. \right\rangle \right.$$
$$\left. - h_{\mu\nu}(t) - \frac{W_{\mu\nu}(t) - W_{\nu\mu}^*(t)}{n_\nu(t) - n_\mu(t)} \right\} = 0, \tag{1.3}$$

and the EOM for the NO occupations $n_\mu(t)$,

$$\forall_\mu \, i \frac{\partial n_\mu(t)}{\partial t} = W_{\mu\mu}(t) - W_{\mu\mu}^*(t). \tag{1.4}$$

Here and throughout the paper, we use the Greek indices μ, ν, etc., for the matrices in the basis of the time-dependent NOs $\phi_\mu(t)$ and the Latin indices i, j, etc., for the matrices in the basis of the stationary NOs ϕ_i (the expression of the matrix $\mathbf{W}$ in the time-dependent basis is completely analogous to Eq. (1.2); see Sec. III).

The (linear) response form of TDDMFT (TDDMFRT), which is most useful for chemical applications, was also formulated in Ref. 11. In TDDMFRT, a frequency-dependent response $\delta\gamma_{ij}(\omega)$ of the 1-matrix to an external perturbation $\delta v_{ij}^{\text{ext}}(\omega)$ of frequency ω is produced. Inserting the perturbed 1-matrix $\gamma_{ij}(t) = \delta_{ij} n_i + \delta\gamma_{ij}(t)$ and the matrix elements $v_{ij}^{\text{ext}}(t) = v_{ij}^{\text{ext}} + \delta v_{ij}^{\text{ext}}(t)$ into Eq. (1.1), keeping only the first-order perturbation terms, and taking the Fourier transform of the resultant expression, one obtains the following coupled-perturbed equations:

$$\forall_{ij} \sum_{kl} \left[\omega \delta_{ik} \delta_{jl} - h_{ik} \delta_{jl} + \delta_{ik} h_{lj} - K_{ijkl}(\omega) \right] \delta\gamma_{kl}(\omega)$$
$$= (n_j - n_i) \delta v_{ij}^{\text{ext}}(\omega). \tag{1.5}$$

The 1-matrix changes $\delta\gamma_{ij}(\omega)$ and $\delta\gamma_{kl}(\omega)$ are coupled in Eq. (1.5) with the frequency-dependent coupling matrix $\mathbf{K}(\omega)$ (see the next section for its definition). Note, that in Ref. 11 an alternative to Eq. (1.1) form of EOM was perturbed, which produces slightly different response equations that are entirely equivalent to Eq. (1.5). For electron excitation energies ω_q, the eigenequation

$$\forall_{ij} \sum_{kl} \left[h_{ik} \delta_{jl} - \delta_{ik} h_{lj} + K_{ijkl}(\omega_q) \right] \delta\gamma_{kl} = \omega_q \delta\gamma_{ij} \tag{1.6}$$

follows from Eq. (1.5).

TDDMFRT as given in Eq. (1.6) differs from the popular time-dependent density functional response (TDDFT) theory[13–16] in one crucial aspect. In the latter theory, the leading diagonal terms in the matrix in square brackets are the differences $(\varepsilon_a - \varepsilon_i)$ of the energies of the occupied and virtual Kohn-Sham orbitals (the dimension of the matrix is $n_{\text{occ}} n_{\text{virt}} \times n_{\text{occ}} n_{\text{virt}}$). These differences provide rather accurate zero order approximations to the excitation energies ω_q.[17] The coupling matrix $\mathbf{K}(\omega)$ makes relatively small, though by

no means negligible, modifications to these zero order values. The structure of the total matrix in TDDMFT is more involved. All (fractionally occupied) NOs are involved in the eigenvalue equations (1.6) (the dimension is, in principle, $m^2 \times m^2$, if $m = n_{\text{occ}} + n_{\text{virt}}$ is the total number of basis functions), and the diagonal elements do not have such a clear physical interpretation. The role of the coupling matrix $\mathbf{K}(\omega)$ can be expected to be much more critical. Accurate evaluation of the frequency-dependent coupling matrix, which, in principle, accounts for all dynamical correlation "memory" effects, is at present not feasible in both TDDFT and TDDMFT. Because of this, virtually all applications of TD-DFT use the so-called adiabatic approximation, most often in its simple local density [adiabatic local density approximation (ALDA)] form, with a ω-independent (static) $\mathbf{K}$. In TDDMFT, we are also forced to apply adiabatic approximations.

It is the purpose of this paper to investigate the adiabatic approximation in density matrix functional theory (ADMFT). We use two-electron systems in this work, since the required functional $\boldsymbol{\Gamma}[\boldsymbol{\gamma}]$ [see Eq. (1.2)] is available in that case. We do not have to resort to approximations for the functional[6,8,9,18–21] which would make it difficult to distinguish effects of the adiabatic approximation from deficiencies of the functional. In Sec. II, the matrix form of the coupled-perturbed TDDMFRT equations is presented and a definition of the exact frequency-dependent coupling matrix $\mathbf{K}(\omega)$ is given. In Sec. III, the most straightforward adiabatic approximation to $\mathbf{K}(\omega)$, which was already proposed in Ref. 11 and which we denote static approximation (SA), is analyzed. It is shown that the SA is deficient, since it leads to fixed NO occupations, neglecting the dynamical response of these quantities. This leads to an incorrect static limit $\alpha(\omega \rightarrow 0)$ of the frequency-dependent polarizability, as will be demonstrated by calculations for the prototype two-electron HeH$^+$ molecule. To remedy this deficiency, the SA has to be augmented with response equations for the occupation numbers, which are obtained within the adiabatic approximation (AA) in Sec. IV. In AA, the dynamical change of the NO occupations is considered as an instant response to the perturbation $\delta v = \delta v_{\text{ext}}(t)$ inserted in the variational equations for the n_i of the static DMFT. The physical meaning of the adiabatic approximation can be further assessed by a comparison to exact dynamical equations for the relevant quantities (the density matrix elements, including the diagonal elements which are the occupation numbers in the NO basis). These exact equations can be obtained for two-electron systems, as will be derived in Sec. V. It is well known from the results of Löwdin and Shull[1] that the configuration interaction (CI) expansion of the fully correlated wave function of a singlet two-electron system assumes a simple form in the NO basis. The CI expansion coefficients in that case have a simple relation to one-electron density matrix elements, and the full time-dependent Schrödinger equation can be cast into the form of dynamical equations for the density matrix elements. This affords a comparison of the exact solution for the density matrix dynamics to the various approximations. Comparative DMFT calculations of the HeH$^+$ polarizability are performed in Sec. VI. The SA and

AA $\alpha(\omega)$ values are compared with those calculated with approximate TDDFT methods, employing either the LDA Kohn-Sham potential or the statistical average of (different) orbital potentials (SAOP)[22] and the ALDA for the exchange-correlation kernel throughout. At the equilibrium distance, SA consistently underestimates $\alpha(\omega)$, the adiabatic TDDFT overestimates it, while AA significantly improves upon SA. For the stretched HeH$^+$, both SA and AA DMFT correct the overpolarization and the too low first excitation energies of the LDA-ALDA and SAOP-ALDA.

II. TIME-DEPENDENT DENSITY MATRIX FUNCTIONAL RESPONSE THEORY

Just as all electron-electron interaction terms in the EOMs (1.1), (1.3), and (1.4), the exact frequency-dependent coupling matrix $\mathbf{K}(\omega)$ in the TDDMFRT equation (1.5) is also defined through the matrix $\mathbf{W}$,

$$
\begin{aligned}
&K_{ijkl}(\omega) \\
&= \int e^{-i\omega(t-t')} \frac{\delta[W_{ij}([\gamma];t) - W_{ji}([\gamma];t)^*]}{\delta\gamma_{kl}(t')}\bigg|_{\gamma(t)=\gamma^{(0)}} \\
&\quad \times d(t-t').
\end{aligned}
\tag{2.1}
$$

The functional derivative in Eq. (2.1) is the variation $\delta[W_{ij}([\gamma];t) - W_{ji}([\gamma];t)^*]$ at the time t in response to a variation of the argument $\delta\gamma_{kl}(t')$ at the time t', and the resultant functional is evaluated at the stationary 1-matrix $\gamma(0)$. It can be Fourier transformed on the assumption that it only depends on the time difference $t-t'$. Equation (1.5) with $\mathbf{K}(\omega)$ of Eq. (2.1) can be transformed to a set of "off-diagonal" equations for the Fourier transforms $X_{kl}^R(\omega)$ and $X_{kl}^I(\omega)$ of the real and imaginary (multiplied by i) parts of the changes of off-diagonal elements $\delta\gamma_{kl}(t)$,

$$
\forall_{k>l} \quad X_{kl}^R(\omega) = F\{\mathrm{Re}[\delta\gamma_{kl}]\}(\omega),
\tag{2.2}
$$

$$
\forall_{k>l} \quad X_{kl}^I(\omega) = F\{i\,\mathrm{Im}[\delta\gamma_{kl}]\}(\omega),
\tag{2.3}
$$

where F indicates a Fourier transform, and a "diagonal" equation for the Fourier transformed changes of the diagonal elements $\delta\gamma_{kk}(t)$, which are real since $\boldsymbol{\gamma}$ is a Hermitian matrix,

$$
Z_{kk}^R(\omega) = F\{\delta\gamma_{kk}\}(\omega) = \delta n_k(\omega).
\tag{2.4}
$$

The transformed equations are the off-diagonal equations

$$
\begin{aligned}
\forall_{i>j} \quad &\omega X_{ij}^R(\omega) + \frac{1}{2}\sum_{k>l}(A_{ijkl}(\omega) + A_{ijlk}(\omega) + A_{jikl}(\omega) \\
&+ A_{jilk}(\omega))X_{kl}^R(\omega) + \frac{1}{2}\sum_{k>l}(A_{ijkl}(\omega) - A_{ijlk}(\omega) \\
&+ A_{jikl}(\omega) - A_{jilk}(\omega))X_{kl}^I(\omega) + \frac{1}{2}\sum_k(A_{ijkk}(\omega) \\
&+ A_{jikk}(\omega))Z_{kk}^R(\omega) = V_{ij}^I(\omega),
\end{aligned}
\tag{2.5}
$$

$$
\begin{aligned}
\forall_{i>j} \quad &\omega X_{ij}^I(\omega) + \frac{1}{2}\sum_{k>l}(A_{ijkl}(\omega) + A_{ijlk}(\omega) - A_{jikl}(\omega) \\
&- A_{jilk}(\omega))X_{kl}^R(\omega) + \frac{1}{2}\sum_{k>l}(A_{ijkl}(\omega) - A_{ijlk}(\omega) \\
&- A_{jikl}(\omega) + A_{jilk}(\omega))X_{kl}^I(\omega) + \frac{1}{2}\sum_k(A_{ijkk}(\omega) \\
&- A_{jikk}(\omega))Z_{kk}^R(\omega) = V_{ij}^R(\omega),
\end{aligned}
\tag{2.6}
$$

and the diagonal equation

$$
\begin{aligned}
\forall_i \quad &\omega Z_{ii}^R(\omega) + \sum_{k>l}(A_{iikl}(\omega) + A_{iilk}(\omega))X_{kl}^R(\omega) \\
&+ \sum_{k>l}(A_{iikl}(\omega) - A_{iilk}(\omega))X_{kl}^I(\omega) \\
&+ \sum_k A_{iikk}(\omega)Z_{kk}^R(\omega) \\
&= V_{ii}^I(\omega).
\end{aligned}
\tag{2.7}
$$

$\mathbf{V}^R(\omega)$ and $\mathbf{V}^I(\omega)$ are the Fourier transforms of the real and imaginary (multiplied by i) parts of the external perturbation matrix weighed with occupation number differences

$$
V_{ij}^R(\omega) = (n_j - n_i)\tfrac{1}{2}[\delta v_{ij}^{\mathrm{ext}}(\omega) + \delta v_{ji}^{\mathrm{ext}}(\omega)],
\tag{2.8}
$$

$$
V_{ij}^I(\omega) = (n_j - n_i)\tfrac{1}{2}[\delta v_{ij}^{\mathrm{ext}}(\omega) - \delta v_{ji}^{\mathrm{ext}}(\omega)].
\tag{2.9}
$$

Defining the matrices $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ which include off-diagonal elements of the coupling matrix,

$$
\begin{aligned}
A_{ijkl}(\omega) &= \delta_{ik}h_{lj} - h_{ik}\delta_{jl} - K_{ijkl}(\omega), \\
B_{ijkl}(\omega) &= A_{ijlk}(\omega),
\end{aligned}
\tag{2.10}
$$

we introduce the matrices $\mathbf{A}^+(\omega)$ and $\mathbf{A}^-(\omega)$ as well as $\mathbf{B}^+(\omega)$ and $\mathbf{B}^-(\omega)$,

$$
\begin{aligned}
A_{ijkl}^{\pm}(\omega) &= \tfrac{1}{2}[A_{ijkl}(\omega) \pm A_{jilk}(\omega)], \\
B_{ijkl}^{\pm}(\omega) &= A_{ijlk}^{\pm}(\omega).
\end{aligned}
\tag{2.11}
$$

The set of linear equations (2.5)–(2.7) can be brought to the matrix form

$$
\begin{pmatrix}
\omega + \mathbf{A}^+(\omega) + \mathbf{B}^+(\omega) & \mathbf{A}^-(\omega) - \mathbf{B}^-(\omega) & \mathbf{A}^+(\omega) \\
\mathbf{A}^-(\omega) + \mathbf{B}^-(\omega) & \omega + \mathbf{A}^+(\omega) - \mathbf{B}^+(\omega) & \mathbf{A}^-(\omega) \\
2\mathbf{A}^+(\omega) & 2\mathbf{A}^-(\omega) & \omega + 2\mathbf{A}^+(\omega)
\end{pmatrix}
\begin{pmatrix}
\mathbf{X}^R(\omega) \\
\mathbf{X}^I(\omega) \\
\mathbf{Z}^R(\omega)
\end{pmatrix}
=
\begin{pmatrix}
\mathbf{V}^I(\omega) \\
\mathbf{V}^R(\omega) \\
0
\end{pmatrix}.
\tag{2.12}
$$

Since the functional dependence of the matrix $\mathbf{W}$ in Eq. (2.1) on the time-dependent density matrix is not known, the derivative in the integrand cannot be taken and the Fourier transform to obtain the frequency-dependent coupling matrix $\mathbf{K}(\omega)$ of Eq. (2.1) is not feasible at present. Therefore, for practical TDDMFRT applications, adiabatic approximations are needed and are developed in the following sections.

III. STATIC APPROXIMATION

In conventional adiabatic approximations, the explicit ω dependence of the diagonal terms of matrix equation (2.12) is retained, while the ω-dependent $\mathbf{K}(\omega)$, i.e., the related matrices $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ in Eq. (2.10), are approximated with frequency-independent ones. If we approximate the coupling matrix $\mathbf{K}(\omega)$ by some frequency-independent approximation and choose real basis functions, the general symmetry relation for the $\mathbf{A}(\omega)$ matrix,

$$
A_{ijkl}(\omega) = -A_{jilk}^*(-\omega),
\tag{3.1}
$$

simplifies to

$$
A_{ijkl} = -A_{jilk}.
\tag{3.2}
$$

Using this symmetry relation in the definitions for $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ [Eq. (2.10)] and $\mathbf{A}\pm(\omega)$ and $\mathbf{B}\pm(\omega)$ [Eq. (2.11)], we have

$$
A_{ijkl}^+ = B_{ijkl}^+ = 0,
$$

$$
A_{ijkl}^- = A_{ijkl},
\tag{3.3}
$$

$$
B_{ijkl}^- = B_{ijkl} = A_{ijlk}.
$$

Therefore, matrix equation (2.12) is simplified in adiabatic approximations to

$$
\begin{pmatrix}
\omega & \mathbf{A} - \mathbf{B} & 0 \\
\mathbf{A} + \mathbf{B} & \omega & \mathbf{D} \\
0 & 2\mathbf{G} & \omega
\end{pmatrix}
\begin{pmatrix}
\mathbf{X}^R(\omega) \\
\mathbf{X}^I(\omega) \\
\mathbf{Z}^R(\omega)
\end{pmatrix}
=
\begin{pmatrix}
\mathbf{V}^I(\omega) \\
\mathbf{V}^R(\omega) \\
0
\end{pmatrix},
\tag{3.4}
$$

where we introduced the following matrices:

$$
\forall_{i>j} \quad D_{ijkk} = A_{ijkk},
$$

$$
\forall_{k>l} \quad G_{iikl} = A_{iikl}.
\tag{3.5}
$$

We now start formulation of ADMFT with the partitioning of $\mathbf{K}(\omega)$ of Eq. (2.1) into a static one-electron part $\mathbf{K}^{\text{oe}}$ and a frequency-dependent electron-electron interaction part $\mathbf{K}^{\text{ee}}(\omega)$,

$$
\mathbf{K}(\omega) = \mathbf{K}^{\text{oe}} + \mathbf{K}^{\text{ee}}(\omega).
\tag{3.6}
$$

We accomplish this partitioning by representing W_{ij} in Eq. (2.1) as a unitary transform of the matrix $W_{\mu\nu}$ in the time-dependent basis,

$$
K_{ijkl}(\omega) = \int e^{-i\omega(t-t')} \frac{\delta\left\{ \sum_{\mu\nu} U_{i\mu}([\gamma];t)[\mathbf{W}([\gamma];t) - \mathbf{W}^\dagger([\gamma];t)]_{\mu\nu} U_{j\nu}^*([\gamma];t) \right\}}{\delta\gamma_{kl}(t')} \Bigg|_{\gamma(t)=\gamma(0)} d(t-t'),
\tag{3.7}
$$

with

$$
W_{\mu\nu}(t) = \sum_{\eta\lambda\tau} \Gamma_{\nu\eta\lambda\tau}([\gamma];t) \langle \phi_\mu(t)\phi_\eta(t) | \phi_\lambda(t)\phi_\tau(t) \rangle
\tag{3.8}
$$

and the orbital evolution matrix $\mathbf{U}$,

$$
\phi_\mu(\mathbf{x},t) = \sum_i U_{i\mu}(t)\phi_i(\mathbf{x}),
\tag{3.9}
$$

which connects, by unitary transformation, the time-independent NOs with the time-dependent ones, the latter being conventionally labeled with Greek indices.

Equation (3.7) provides the partitioning in Eq. (3.6) for $\mathbf{K}(\omega)$ with the matrices $\mathbf{K}^{\text{oe}}$,

$$
\begin{aligned}
K_{ijkl}^{\text{oe}} = \int e^{-i\omega(t-t')} &\left\{ \sum_{\mu\nu} [W_{\mu\nu}(t) - W_{\nu\mu}(t)^*] \right. \\
&\left. \times \frac{\partial [U_{i\mu}([\gamma];t) U_{j\nu}^*([\gamma];t)]}{\partial\gamma_{kl}(t')} \right\} \Bigg|_{\gamma(t)=\gamma^{(0)}} \\
&\times d(t-t'),
\end{aligned}
\tag{3.10}
$$

and $\mathbf{K}^{\text{ee}}(\omega)$,

$$K_{ijkl}^{ee}(\omega) = \int e^{-i\omega(t-t')} \left\{ \sum_{\mu\nu} U_{i\mu}(t) U_{j\nu}^{*}(t) \right.$$

$$\left. \times \frac{\partial [W_{\mu\nu}([\gamma];t) - W_{\nu\mu}([\gamma];t)^{*}]}{\partial \gamma_{kl}(t')} \right\} \Bigg|_{\gamma(t)=\gamma^{(0)}}$$

$$\times d(t-t'). \qquad (3.11)$$

Due to the locality in time of the derivative $\partial U_{i\mu}(t)/\partial \gamma_{kl}(t')$ (see the Appendix), matrix (3.10) is evaluated explicitly. Using a variational relation between the one- and two-electron static matrices $\mathbf{h}$ and $\mathbf{W}$, $\mathbf{K}^{oe}$ can be expressed through the elements of the former matrix (see the Appendix for the corresponding formulas).

It is the frequency-dependent matrix $\mathbf{K}^{ee}(\omega)$ for which the adiabatic approximation should be used. This means, in principle, taking the limit $\omega \to 0$ of Eq. (3.11). However, this operation is not feasible, since, as pointed out at the end of the previous section, $\mathbf{K}(\omega)$ cannot be obtained. Because of this, we first take a simpler route, according to which Eq. (3.11) is approximated with the derivative with respect to the static 1-matrix of a static matrix $\mathbf{W}$, which is defined analogous to Eq. (1.2) as functional of the 1-matrix,

$$K_{ijkl}^{ee}(\omega) \approx K_{ijkl}^{ee} = \left. \frac{\partial (W_{ij}[\gamma] - W_{ji}[\gamma]^{*})}{\partial \gamma_{kl}} \right|_{\gamma=\gamma^{(0)}}$$

$$\text{with } W_{ij} = \sum_{klm} \Gamma_{jklm}[\gamma] \langle \phi_i \phi_k | \phi_l \phi_m \rangle. \qquad (3.12)$$

We call this the static approximation. It is, in fact, analogous to the what is usually called the adiabatic approximation in TDDFT, where the static derivative $\delta^2 E_{xc}/\delta\rho^2$ is commonly used.

The sum of Eqs. (3.10) and (3.12) constitutes the coupling matrix $\mathbf{K}$ of SA,

$$\mathbf{K} = \mathbf{K}^{oe} + \mathbf{K}^{ee}. \qquad (3.13)$$

A characteristic feature of the SA is that the subdiagonal elements K_{iikl} of $\mathbf{K}$ vanish in this approximation,

$$K_{iikl}^{ee} = \frac{\partial (W_{ii}[\gamma] - W_{ii}[\gamma]^{*})}{\partial \gamma_{kl}} = 0, \qquad (3.14)$$

due to the vanishing numerator of Eq. (3.12). That the numerator vanishes is evident in the usual case of real static quantities [NOs and $\Gamma(\gamma)$] and therefore real static matrix $\mathbf{W}$. In the general case, one can use the expression for W_{ij} as the orbital derivative of the electron-electron interaction energy functional $E_{ee}[\gamma]$,

$$W_{ij} = \sum_{klm} \Gamma_{jklm}[\gamma] \langle \phi_i \phi_k | \phi_l \phi_m \rangle = \int \frac{\delta E_{ee}[\gamma]}{\delta \phi_j(\mathbf{x}_1)^{*}} \phi_i(\mathbf{x}_1)^{*} d\mathbf{x}_1,$$

$$(3.15)$$

$$E_{ee}[\gamma] = \frac{1}{2} \int \frac{\Gamma([\gamma];\mathbf{x}_1,\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2, \qquad (3.16)$$

which was established in Ref. 23. This leads to a vanishing numerator,

$$W_{ii}[\gamma] - W_{ii}[\gamma]^{*} = \int \frac{\delta E_{ee}[\gamma]}{\delta \phi_i(\mathbf{x}_1)^{*}} \phi_i(\mathbf{x}_1)^{*} d\mathbf{x}_1$$

$$- \int \frac{\delta E_{ee}[\gamma]}{\delta \phi_i(\mathbf{x}_1)} \phi_i(\mathbf{x}_1) d\mathbf{x}_1$$

$$= n_i \int \frac{\delta E_{ee}[\gamma]}{\delta \gamma(\mathbf{x}_1',\mathbf{x}_1)} \phi_i(\mathbf{x}_1') \phi_i(\mathbf{x}_1)^{*} d\mathbf{x}_1 d\mathbf{x}_1'$$

$$- n_i \int \frac{\delta E_{ee}[\gamma]}{\delta \gamma(\mathbf{x}_1,\mathbf{x}_1')} \phi_i(\mathbf{x}_1')^{*} \phi_i(\mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}'$$

$$= 0. \qquad (3.17)$$

With Eq. (3.14), the matrix $\mathbf{G}$ of Eq. (3.5) also vanishes in the SA, $G_{iikl}=0$, since another component of K_{iikl}, the element K_{iikl}^{oe} [see Eq. (A7)] cancels the one-electron terms in $G_{iikl}=A_{iikl}$.

Since Eqs. (3.4) with $\mathbf{G}=0$ lead to $\omega \mathbf{Z}^R = 0$, the SA leads to zero changes of the NO occupations. With $\mathbf{Z}^R=0$, the response SA equations may be reduced to

$$\begin{pmatrix} \omega & \mathbf{A}-\mathbf{B} \\ \mathbf{A}+\mathbf{B} & \omega \end{pmatrix} \begin{pmatrix} \mathbf{X}^R(\omega) \\ \mathbf{X}^I(\omega) \end{pmatrix} = \begin{pmatrix} \mathbf{V}^I(\omega) \\ \mathbf{V}^R(\omega) \end{pmatrix}, \qquad (3.18)$$

where the static matrices $\mathbf{A}$ and $\mathbf{B}$ are obtained according to Eq. (2.10) from SA coupling matrix (3.12). Thus, SA produces a deficient 1-matrix response $\delta\gamma(\omega)$, in which changes of the NO occupations $Z_{ii}^R(\omega)$ are neglected. This deficiency, although not very large, is clearly confirmed numerically with Fig. 1(a), which presents the frequency-dependent polarizability $\alpha(\omega)$ calculated with SA for the prototype two-electron molecule HeH$^+$ (for the details of the calculations, see Sec. VI). One can see in Fig. 1(a), that SA underestimates $\alpha(\omega)$ compared to the full response coupled-cluster singles and doubles (CCSD) calculations. Moreover, SA does not reproduce the accurate static limit $\alpha(0)$, contrary to what one would expect from a correct adiabatic approximation.

An obvious conclusion from the present results is that the dynamic coupling matrix $\mathbf{K}^{ee}(\omega)$ of Eq. (3.11) does not coincide in the limit $\omega \to 0$ with the chosen approximation, the static $\mathbf{K}^{ee}$ of Eq. (3.12). This leads to the wrong $\omega \to 0$ limit for the polarizability. The fact that a similar approximation in "adiabatic" TDDFT does not lead to a wrong limiting behavior is perhaps related to the fact that in the present case, the erroneous behavior has been traced to the wrong behavior (zero response) of the occupation numbers, while in TDDFT the occupation numbers are always fixed according to the Kohn-Sham model.

In the next section, an adiabatic approximation with a nonzero $Z_{ii}^R(\omega)$ will be formulated, which uses the equations of the response DMFT in the case of a static perturbation.

IV. ADIABATIC APPROXIMATION

As was demonstrated in the previous section, the SA is deficient since it leads to zero change of the NO occupations.
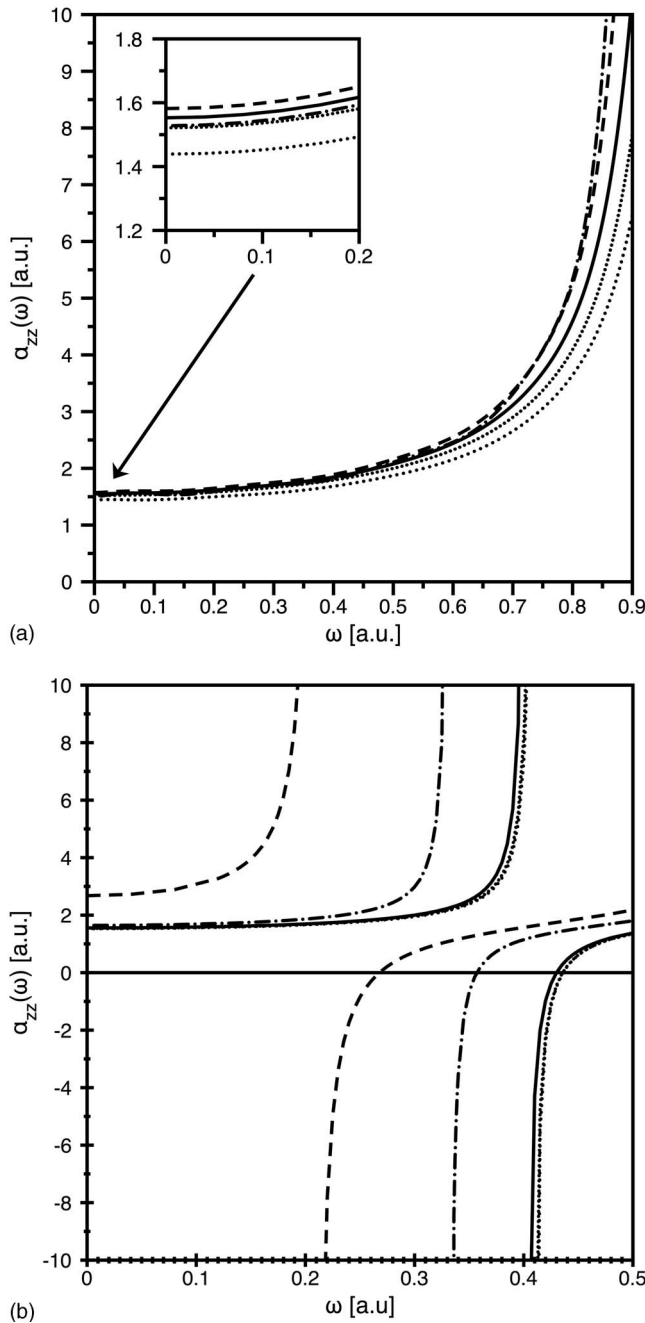
FIG. 1. Comparison of the longitudinal frequency-dependent polarizabilities $\alpha(\omega)$ (a.u.) of the HeH$^+$ molecule calculated with CCSD (solid line), with TDDMFT in the static approximation (SA) (course grained dotted), and with the adiabatic approximation (AA) (fine grained dotted), as well as with TDDFT, in the LDA-ALDA (dashed line) and the SAOP-ALDA (dash-dot line) variants. (a) At the equilibrium bond distance $R_e = 1.43$ bohrs and (b) at $R = 5.0$ Bohr.

In the spirit of adiabatic approximations, we may rather take the opposite view that the occupation numbers should respond instantaneously to a change in the external field. So we take as starting point the static response of the occupation numbers to a perturbation, as derived in Ref. 24, and calculate the responses $\delta n_i(t)$ at time t as the responses in the time-independent theory that would result from a static perturbation $\delta v_{\text{ext}}(\mathbf{r})$ equal to $\delta v_{\text{ext}}(\mathbf{r}, t)$. The equations which determine the static response $\delta n_i \equiv Z_{ii}^R$ of the NO occupations n_i in DMFT have been derived in Ref. 24 from the stationary variational equations for n_i,

$$\forall_i \quad h_{ii} + \frac{\partial E_{\text{ee}}[\gamma]}{\partial n_i} = \mu, \tag{4.1}$$

where μ is the Lagrange multiplier (chemical potential). Inserting the perturbed static quantities $v_{\text{ext}} + \delta v_{\text{ext}}$, $\phi_k + \delta \phi_k$, $n_k + Z_{kk}^R$, $\mu + \delta \mu$ into Eq. (4.1) and keeping only first-order terms, one obtains

$$\forall_i \quad \delta v_{ii}^{\text{ext}} + \langle \delta \phi_i | \hat{h} | \phi_i \rangle + \langle \phi_i | \hat{h} | \delta \phi_i \rangle$$

$$+ \sum_k \frac{\partial \langle (\delta E_{\text{ee}}[\gamma] / \delta \phi_k) \delta \phi_k \rangle}{\partial n_i}$$

$$+ \sum_k \frac{\partial \langle (\delta E_{\text{ee}}[\gamma] / \delta \phi_k^*) \delta \phi_k^* \rangle}{\partial n_i} + \sum_k Q_{ik} Z_{kk}^R = \delta \mu. \tag{4.2}$$

Inserting into Eq. (4.2) the orbital expansion of $\delta \phi_k$, $\delta \phi_k = \sum_{l \neq k} \delta U_{lk} \phi_l$, using relation (A3), and employing definitions (3.5) and (3.12) for the matrices **D**, **K**, and **W**, we obtain from Eq. (4.2) the following equations:

$$\forall_i \quad -2 \sum_{k>l} (n_l - n_k)^{-1} D_{klii} X_{kl}^R + \sum_k Q_{ik} Z_{kk}^R = -\delta v_{ii}^{\text{ext}} + \delta \mu, \tag{4.3}$$

where $\delta \mu$ is the change of the Lagrange multiplier (chemical potential) of the static variational equations for n_i and **Q** is the matrix of the second partial derivatives of the electron-electron interaction energy functional [Eq. (3.16)] with respect to n_i,

$$Q_{ij} = \frac{\partial^2 E_{\text{ee}}[\gamma]}{\partial n_i \partial n_j}. \tag{4.4}$$

So from Eq. (4.3), we obtain the instant response $\mathbf{Z}^R(t)$ to the change of the potential $\delta v^{\text{ext}}(t)$ as well as to the responses $\mathbf{X}^R(t)$ of the off-diagonal 1-matrix elements on the assumption that the potential changes so slowly that these responses adiabatically follow the potential, i.e., are equal to those for a static change of the potential. After Fourier transformation, Eq. (4.3) becomes an equation for the $\mathbf{Z}^R(\omega)$ and $\mathbf{X}^R(\omega)$, which can be used instead of the deficient Eq. (2.7) [or rather its static approximation, the third of Eqs. (3.4)] to complete the set of equations (2.5) and (2.6), i.e., the first two equations of Eqs. (3.4). The resultant set of coupled-perturbed equations,

$$\forall_{i>j} \quad \sum_{k>l} [\omega \delta_{ki} \delta_{lj} X_{kl}^R(\omega) + (A_{ijkl} - B_{ijkl}) X_{kl}^I(\omega)] = V_{ij}^I(\omega), \tag{4.5}$$

$$\forall_{i>j} \quad \sum_{k>l} [\omega \delta_{ki} \delta_{lj} X_{kl}^I(\omega) + (A_{ijkl} + B_{ijkl}) X_{kl}^R(\omega)]$$

$$+ \sum_k D_{ijkk} Z_{kk}^R(\omega) = V_{ij}^R(\omega), \tag{4.6}$$

$$\forall_i \quad -2 \sum_{k>l} (n_l - n_k)^{-1} D_{iikl}^T X_{kl}^R(\omega) + \sum_k Q_{ik} Z_{kk}^R(\omega)$$

$$= -\delta v_{ii}^{\text{ext}}(\omega) + \delta \mu(\omega), \tag{4.7}$$

represents what we call the adiabatic approximation. The

change of the chemical potential $\delta\mu(\omega)$ is determined from the sum-rule condition

$$\sum_k Z^R_{kk}(\omega) = 0. \qquad (4.8)$$

Equations (4.5) and (4.6) are identical to the first two equations of Eq. (3.4). We determine the matrices **A**, **B**, and **D** as in the SA with the static coupling matrix **K** of Eq. (3.12) inserted in the equations for **A**, **B**, and **D**, i.e., they are ω independent. In this way, the AA reproduces the correct static perturbation theory results of TDDMFRT in the limit of $\omega \to 0$, as can be seen as follows. At $\omega=0$, with $\mathbf{V}^I=0$, Eq. (4.5) yields $\mathbf{X}^I=0$, so only the real parts $\mathbf{X}^R$ and $\mathbf{Z}^R$ of the 1-matrix response remain. Equation (4.6) turns to the first equation of the static response DMFT,[24]

$$\forall_{i>j} \quad \sum_{k>l}(A_{ijkl} + B_{ijkl})X^R_{kl} + \sum_k D_{ijkk}Z^R_{kk} = V^R_{ij}, \qquad (4.9)$$

while Eq. (4.7) becomes just Eq. (4.3), which is the second equation of the static perturbation theory[24] from Eq. (4.1). The correct static limiting point $\omega=0$ is therefore obtained.

The matrix form of the AA equations can be written as

$$\begin{pmatrix} \omega & \mathbf{A}-\mathbf{B} & 0 \\ \mathbf{A}+\mathbf{B} & \omega & \mathbf{D} \\ -2\widetilde{\mathbf{D}}^T & 0 & \mathbf{Q} \end{pmatrix} \begin{pmatrix} \mathbf{X}^R(\omega) \\ \mathbf{X}^I(\omega) \\ \mathbf{Z}^R(\omega) \end{pmatrix} = \begin{pmatrix} \mathbf{V}^I(\omega) \\ \mathbf{V}^R(\omega) \\ \widetilde{\mathbf{V}}^R(\omega) \end{pmatrix}, \qquad (4.10)$$

where

$$\widetilde{V}^R_{ij}(\omega) = \delta_{ij}[-\delta v^{\text{ext}}_{ii}(\omega) + \delta\mu(\omega)] \qquad (4.11)$$

and $\widetilde{D}^T_{iikl} = (n_l - n_k)^{-1} D^T_{iikl}$. The quality of the AA will be assessed in Sec. VI.

V. EQUATION OF MOTION FOR THE NO-CI EXPANSION COEFFICIENTS OF THE TWO-ELECTRON WAVE FUNCTION

In order to further assess the adiabatic approximations for the density matrix dynamics, we derive in this section exact dynamical equations for two-electron systems. Two-electron systems play an outstanding role in DMFT. They have been used to develop approximate density matrix functionals.[8,9,20] The basis for these developments has been the finding by Löwdin and Shull[1] that for these systems, the CI expansion of the symmetrical spatial part $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ of the total wave function of a closed-shell system,

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \frac{\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)}{\sqrt{2}}\Psi(\mathbf{r}_1,\mathbf{r}_2), \qquad (5.1)$$

reduces to just a summation over doubly excited configurations when NOs are used as an expansion basis,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_i C_i \phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2). \qquad (5.2)$$

Wave function normalization yields $\sum_i |C_i|^2 = 1$. Note that while in the general N-electron case of the previous sections natural spin-orbitals $\phi_i(\mathbf{x})$ with the occupations $0 \le n_i \le 1$ are used as a basis, in the two-electron case considered in this

section the spatial NOs $\phi_i(\mathbf{r})$ of a closed-shell system ($0 \le n_i \le 2$) are employed. When the wave function is time-dependent, the Löwdin-Shull expansion can be carried out at any time t, using the NOs $\phi_\mu(\mathbf{r},t)$ that diagonalize the density matrix $\boldsymbol{\gamma}(t)$,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = \sum_\mu C_\mu(t)\phi_\mu(\mathbf{r}_1,t)\phi_\mu(\mathbf{r}_2,t)$$

$$= \sum_{kl} C_{kl}(t)\phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2), \quad \sum_{kl}|C_{kl}|^2 = 1, \quad (5.3)$$

where $C_{kl}(t)$ are obtained from the unitary transformation $\phi_\mu(\mathbf{x},t) = \Sigma_i U_{i\mu}(t)\phi_i(\mathbf{x})$ to the time-independent ($t=0$) NOs $\phi_i(\mathbf{x})$, yielding $C_{kl}(t) = \Sigma_\mu U_{k\mu}(t)C_\mu(t)U_{l\mu}(t)$. In keeping with the symmetry of $\Psi(\mathbf{r}_1,\mathbf{r}_2)$, one has $C_{kl}(t) = C_{lk}(t)$.

The spatial part of the two-particle reduced density matrix in the two-electron case reduces to

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2;t) = 2\Psi(\mathbf{r}_1,\mathbf{r}_2,t)\Psi^*(\mathbf{r}'_1,\mathbf{r}'_2,t)$$

$$= 2\sum_{ij,mn} C_{ij}(t)C^*_{mn}(t)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)$$

$$\times \phi^*_m(\mathbf{r}'_1)\phi^*_n(\mathbf{r}'_2), \qquad (5.4)$$

i.e., $\Gamma_{ijmn}(t) = 2C_{ij}(t)C^*_{mn}(t)$, and the spatial part of the 1-matrix is

$$\gamma(\mathbf{r}_1,\mathbf{r}'_1,t) = \int \Gamma(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}_2,t)d\mathbf{r}_2$$

$$= 2\sum_{ij,mn} C_{ij}(t)C^*_{mn}(t)\phi_i(\mathbf{r}_1)\phi^*_m(\mathbf{r}'_1)\delta_{nj}$$

$$= \sum_{im}\left(\sum_j 2C_{ij}(t)C^*_{mj}(t)\right)\phi_i(\mathbf{r}_1)\phi^*_m(\mathbf{r}'_1), \qquad (5.5)$$

i.e., $\gamma_{im}(t) = \Sigma_j 2C_{ij}(t)C^*_{mj}(t)$ or $\boldsymbol{\gamma} = 2\mathbf{CC}^\dagger$.

At $t=0$, the expansions simplify since $C_{ij}(0) = C_i\delta_{ij}$ [cf. Eq. (5.1)], i.e., $\gamma(\mathbf{r}_1,\mathbf{r}'_1) = 2\Sigma_i|C_i|^2\phi_i(\mathbf{r}_1)\phi^*_i(\mathbf{r}'_1)$. Using the natural orbital expansion at $t=0$, $\gamma(\mathbf{r}_1,\mathbf{r}'_1) = \Sigma_i n_i\phi^*_i(\mathbf{r}'_1)\phi_i(\mathbf{r}_1)$, one obtains $C_i = f_i\sqrt{n_i/2}$, with f_i a phase factor, $|f_i|=1$.

Comparing the general expansion of the 2-matrix Γ in the time-independent case in a general orbital basis,

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2) = \sum_{ijkl} \Gamma_{ijkl}\phi^*_i(\mathbf{r}'_1)\phi^*_j(\mathbf{r}'_2)\phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2), \quad (5.6)$$

with the expansion in NOs, which simplifies from Eq. (5.4) to $\Gamma(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1\mathbf{r}'_2) = 2\Sigma_{i,m}C^*_mC_i\phi^*_m(\mathbf{r}'_1)\phi^*_m(\mathbf{r}'_2)\phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2)$, we see that in the two-electron case the elements of the 2-matrix in NO basis become at $t=0$ $\Gamma_{ijkl} = 2C^*_iC_k\delta_{ij}\delta_{kl} = f^*_i f_k\sqrt{n_in_k}\delta_{ij}\delta_{kl}$.

We first obtain the EOM for the coefficients $C_{kl}(t)$ from the time-dependent Schrödinger equation,

$$i\frac{\partial\Psi(\mathbf{r}_1,\mathbf{r}_2,t)}{\partial t} = \hat{H}\Psi(\mathbf{r}_1,\mathbf{r}_2,t), \qquad (5.7)$$

with the time-dependent Hamiltonian $\hat{H} = \hat{h}_1(t) + \hat{h}_2(t) + r^{-1}_{12}$. Substituting the wave function expansion of Eq. (5.2) into Eq. (5.7), we obtain by multiplying with $\phi_k(\mathbf{r}_1)^*\phi_l(\mathbf{r}_2)^*$ and integrating over $\mathbf{r}_1$ and $\mathbf{r}_2$ the EOM for $C_{kl}(t)$,

$$i\frac{\partial C_{kl}(t)}{\partial t} = \sum_i C_{il}(t)h_{ki}(t) + \sum_j C_{kj}(t)h_{lj}(t)$$
$$+ \sum_{ij} C_{ij}(t)\langle\phi_k\phi_l|\phi_i\phi_j\rangle. \tag{5.8}$$

The equations of motion for the $\gamma_{ij}(t)$ can be derived from Eqs. (5.5) and (5.8),

$$i\frac{\partial\gamma_{kl}(t)}{\partial t} = i2\sum_j\left[\frac{\partial C_{kj}(t)}{\partial t}C_{lj}(t)^* + C_{kj}(t)\frac{\partial C_{lj}(t)^*}{\partial t}\right]$$
$$= \sum_j[h_{kj}\gamma_{jl}(t) - \gamma_{kj}(t)h_{jl}] + \sum_{jmn}[2C_{lm}(t)^*C_{nj}(t)$$
$$\times\langle\phi_k\phi_m|\phi_n\phi_j\rangle - 2C_{km}(t)C_{nj}(t)^*\langle\phi_n\phi_j|\phi_l\phi_m\rangle]. \tag{5.9}$$

At this point, we note that there are, in the general N-electron case, many more degrees of freedom for the variables of the full time-dependent wave function than for those of the 1-matrix. Since the latter is Hermitian, the imaginary parts of the diagonal elements are zero, so that there are two variables $\mathrm{Re}(\gamma_{kl})$ and $\mathrm{Im}(\gamma_{kl})$, $k > l$, and one per diagonal element $\gamma_{ii} = \mathrm{Re}(\gamma_{ii})$, m^2 in total where m is the dimension of the basis. In the two-electron case, there are, in contrast to the many-electron case, only a limited number of additional degrees of freedom for the full-CI wave function in a finite basis. There are as many degrees of freedom for the off-diagonal expansion coefficients C_{kl} as there are for the off-diagonal elements γ_{kl}, but for the diagonal C_{ii} the imaginary parts are in general not zero, yielding m additional degrees of freedom.

In order to obtain a set of equations equivalent to the $m^2 + m$ equation (5.8) for the real and imaginary parts of the C_{kl}, i.e., for the full wave function dynamics, we augment the m^2 equation (5.9), which includes the ones for the real diagonal elements $\partial\gamma_{kk}(t)/\partial t = 2\sum_j(\partial C_{kj}(t)/\partial t)C_{kj}(t)^* + 2\sum_j C_{kj}(t)$ $\times(\partial C_{kj}(t)^*/\partial t)$, with the set of m derivatives for the corresponding imaginary quantities

$$2i\left[\sum_j C_{kj}(t)^*\frac{\partial C_{kj}(t)}{\partial t} - \sum_j C_{kj}(t)\frac{\partial C_{kj}(t)^*}{\partial t}\right]$$
$$= \sum_j[\gamma_{jk}(t)h_{kj} + \gamma_{kj}(t)h_{jk}] + 4\sum_{jm}C_{km}(t)^*C_{kj}(t)h_{mj}$$
$$+ 2\sum_{jmn}[C_{km}(t)^*C_{nj}(t)\langle\phi_k\phi_m|\phi_n\phi_j\rangle$$
$$+ C_{km}(t)C_{nj}(t)^*\langle\phi_n\phi_j|\phi_k\phi_m\rangle]. \tag{5.10}$$

We now want to use EOMs (5.9) and (5.10) to derive coupled-perturbed equations for the response of the NO expansion coefficients, or rather the derived quantities, the 1-matrix elements and the imaginary quantity of Eq. (5.10), to a time-dependent perturbation of the external potential. So we consider the coefficient $C_{kl}(t) = C_{kl}^{(0)}(t) + \delta C_{kl}(t)$, which is perturbed with respect to the $C_{kl}^{(0)}(t)$ of the stationary situation (time-independent potential v^{ext}) in response to an external potential variation $\delta v^{\mathrm{ext}}(t)$. The $C_{kl}^{(0)}(t)$ follow from the fact that for a time-independent Hamiltonian, Eq. (5.7) can

be trivially solved by the product of an eigenstate of $\hat{H}$ obeying $\hat{H}\Psi(\mathbf{r}_1,\mathbf{r}_2) = E\Psi(\mathbf{r}_1,\mathbf{r}_2)$ (in particular, for the ground state) and a time-dependent phase factor,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = e^{-iEt}\Psi(\mathbf{r}_1,\mathbf{r}_2). \tag{5.11}$$

So from Eq. (5.2), $\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = e^{-iEt}\Sigma_k C_k\phi_k(\mathbf{r}_1)\phi_k(\mathbf{r}_2)$, and by comparing to the expansion of $\Psi(\mathbf{r}_1,\mathbf{r}_2,t)$ in the general case, $\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = \Sigma_{kl}C_{kl}(t)\phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2)$, we find for $C_{kl}^{(0)}(t)$ in the stationary case

$$C_{kl}^{(0)}(t) = \delta_{kl}e^{-iEt}C_k = \delta_{kl}e^{-iEt}f_k\sqrt{n_k/2}, \tag{5.12}$$

where $|f_k| = 1$. Here, the total energy E is

$$E = \sum_k n_k h_{kk} + E_{\mathrm{ee}}, \tag{5.13}$$

where E_{ee} is the electron-electron repulsion energy,

$$E_{\mathrm{ee}} = \sum_{ij} C_i C_j\langle\phi_i\phi_i|\phi_j\phi_j\rangle$$
$$= \sum_{ij} f_i\sqrt{\frac{n_i}{2}}f_j\sqrt{\frac{n_j}{2}}\langle\phi_i\phi_i|\phi_j\phi_j\rangle. \tag{5.14}$$

In accordance with Eq. (5.11), we slightly redefine $\delta C_{kl}(t)$ so that the phase factor e^{-iEt} is made explicit in both the $C_{kl}^0(t)$ of the stationary case and in the perturbed part of the coefficients,

$$C_{kl}(t) = e^{-iEt}[\delta_{kl}f_k\sqrt{n_k/2} + \delta C_{kl}(t)]. \tag{5.15}$$

The 1-matrix response $\delta\gamma_{kl}(t)$ is

$$\delta\gamma_{kl}(t) = \delta[2\mathbf{C}(t)\mathbf{C}(t)^\dagger]_{kl}$$
$$= 2\delta C_{kl}(t)C_l + 2C_k\delta C_{kl}^\dagger(t)$$
$$= 2\delta C_{kl}(t)f_l\sqrt{n_l/2} + 2f_k\sqrt{n_k/2}\delta C_{kl}^\dagger(t). \tag{5.16}$$

In order to obtain the equations for the real and imaginary parts of the responses $\delta\gamma_{kl}$, to the perturbation $\delta v_{kl}^{\mathrm{ext}}(\omega)$, the perturbed $C_{kl}(t)$ of Eq. (5.15) and the perturbed $v_{kl}^{\mathrm{ext}}(t)$ are inserted into Eqs. (5.9) and (5.10), the first-order terms are collected, and the necessary additions and subtractions are made to obtain the equations for $\delta\gamma_{kl} \pm \delta\gamma_{kl}^*$. A Fourier transformation of the resultant equations is performed, and the 1-matrix responses $X_{kl}^R(\omega)$ and $X_{kl}^I(\omega)$ of Eqs. (2.2) and (2.3) and $Z_{kk}^R(\omega)$ are used which appear in the SA and AA equations, and which follow for two-electron systems from Eq. (5.16),

$$\forall_{k>l} \quad X_{kl}^R(\omega) = 2(f_k\sqrt{n_k/2} + f_l\sqrt{n_l/2})\delta C_{kl}^R(\omega), \tag{5.17}$$

$$\forall_{k>l} \quad X_{kl}^I(\omega) = i2\delta C_{kl}^I(\omega)(f_l\sqrt{n_l/2} - f_k\sqrt{n_k/2}), \tag{5.18}$$

$$\forall_k \quad Z_{kk}^R(\omega) = 2f_k\sqrt{n_k/2}\delta C_{kk}^R(\omega). \tag{5.19}$$

The above mentioned additional m degrees of freedom of the wave function are taken into account with the additional variables

$$\forall_k \quad Z_{kk}^I(\omega) = i\delta C_{kk}^I(\omega). \tag{5.20}$$

The exact coupled-perturbed response equations are now obtained, with off-diagonal equations

$$\forall_{i>j} \quad \sum_{k>l} \left[\omega \delta_{ki} \delta_{lj} X_{kl}^R(\omega) + (A_{ijkl} - B_{ijkl}) X_{kl}^R(\omega) \right]$$
$$- 2 \sum_k M_{ijkk} Z_{kk}^I(\omega) = V_{ij}^I(\omega), \tag{5.21}$$

$$\forall_{i>j} \quad \sum_{k>l} \left[\omega \delta_{ki} \delta_{lj} X_{kl}^I(\omega) + (A_{ijkl} + B_{ijkl}) X_{kl}^R(\omega) \right]$$
$$+ \sum_k D_{ijkk} Z_{kk}^R(\omega) = V_{ij}^R(\omega), \tag{5.22}$$

as well as with diagonal equations

$$\forall_i \quad \omega Z_{ii}^R(\omega) + 2 \sum_{k>l} G_{iikl} X_{kl}^I(\omega) - 2 \sum_k M_{iikk} Z_{kk}^I(\omega) = 0, \tag{5.23}$$

$$\forall_i \quad -2 n_i \sum_{k>l} \tilde{D}_{iikl}^T X_{kl}^R(\omega) + n_i \sum_k Q_{ik} Z_{kk}^R(\omega) - \omega \, 4 f_i \sqrt{n_i/2} Z_{ii}^I(\omega)$$
$$= - 2 n_i \delta v_{ii}^{\text{ext}}(\omega). \tag{5.24}$$

We emphasize that in Eqs. (5.21)–(5.24), the *static* (ω-independent) coupling matrices **A**, **B**, **D**, and **G** enter. They are obtained according to Eqs. (2.10) and (3.5) from the static matrix **K**, which is evaluated according to Eq. (3.12) with

$$K_{ijkl}^{\text{ee}} = \frac{\partial(W_{ij}[\gamma] - W_{ji}[\gamma]^*)}{\partial \gamma_{kl}}. \tag{5.25}$$

The static 2-matrix in the two-electron case has been obtained as [see lines below Eq. (5.6)]

$$\Gamma_{jklm} = f_j^* f_l \sqrt{n_j n_l} \delta_{jk} \delta_{lm}, \tag{5.26}$$

and the matrix **W** is accordingly [cf. Eq. (1.2)]

$$W_{ij} = \sum_{klm} \Gamma_{jklm} \langle \phi_i \phi_k | \phi_l \phi_m \rangle = \sum_l f_j^* f_l \sqrt{n_j n_l} \langle \phi_i \phi_j | \phi_l \phi_l \rangle. \tag{5.27}$$

Differentiation of the **W** elements accoring to Eq. (5.25) leads to the explicit expression of K_{ijkl} in the two-electron case given in the Appendix [Eq. (A9) as well as Eq. (A10) for the matrix **M** in Eq. (5.21)]. In turn, the matrix **Q** in Eq. (5.24) is obtained with the differentiation of the energy E_{ee} of Eq. (5.14) according to Eq. (4.4).

So in the two-electron case, we are able to obtain the exact response equations (5.21)–(5.24) in a form that affords a direct comparison to the SA and AA. It is gratifying indeed that the exact response equations, without any adiabatic approximation, can be cast in a form which resembles in many respects the equations resulting from the static and adiabatic approximations. It is still not straightforward to obtain from the exact equations a physical understanding of these approximations, or deduce alternative (improved) adiabatic approximations. Indeed, the approximations that have to be made to obtain from the exact equations (5.21)–(5.24) the static or adiabatic ones do not appear to be minor. The SA Eqs. (3.18) are seen to arise by removal of the diagonal equations (5.23) and (5.24) and neglecting the last terms in the left-hand sides of Eqs. (5.21) and (5.22). As for the AA equations, they lack the $\mathbf{M} Z^I$ term in the first equation

[Eq. (5.21) → Eq. (4.5)] and the complete third equation [Eq. (5.23)]. As for the comparison of Eq. (5.24) to the third AA equation [Eq. (4.7)], a numerical analysis of the exact equations (5.21)–(5.24) for the prototype two-electron system HeH$^+$ shows that the product $\omega Z_{ii}^I(\omega)$ in Eq. (5.24) tends to a constant in the static limit, $\omega Z_{ii}^I(\omega) \to \alpha_i$ at $\omega \to 0$. With this, Eq. (5.24) becomes equivalent to AA equation (4.7) if $\alpha_i = \delta \mu f_i \sqrt{n_i/2}$. So if we replace $\omega f_i \sqrt{n_i} Z_{ii}^I(\omega)$ in Eq. (5.24) with its static limit $n_i \delta \mu$, remove diagonal equation (5.23), and neglect the term with $Z_{kk}^I(\omega)$ in Eq. (5.21), we transform the exact equations to the AA ones of Eqs. (4.5)–(4.7).

Although we can thus establish the connection between the analytic exact and adiabatic equations, this does not answer the question what deficiencies the adiabatic approximations, in fact, entail. In the following section, a numerical assessment of these approximations is provided for a prototype two-electron system, HeH$^+$.

VI. COMPARATIVE SA, AA, AND TDDFT CALCULATIONS OF THE FREQUENCY-DEPENDENT POLARIZABILITY OF HeH$^+$

Two-electron systems as considered in the previous section offer a unique opportunity to assess the quality of the adiabatic TDDMFT formulated in this paper. In the general N-electron case, the exact functionals $E_{\text{ee}}[\gamma]$, $\mathbf{W}[\gamma]$, and $\mathbf{\Gamma}[\gamma]$ required to obtain the TDDMFT coupling matrix **K** are not known, so that their DMFT approximations are to be introduced. However, in the two-electron case, we do not have to introduce such approximations, since the exact dependence of $\mathbf{\Gamma}$ on γ is known. The coupling matrix **K** of Eq. (A9) is available, obtained from the accurate E_{ee} of Eq. (5.14) and **W** of Eq. (5.27), and we are basically only testing the adiabatic approximations (SA and AA).

This section presents application of the SA and AA to the frequency-dependent polarizability $\alpha(\omega)$ of the prototype two-electron HeH$^+$ molecule. The matrix **K** of Eq. (A9) is used to calculate the SA/AA matrices **A** and **B** and the AA matrix **D**, while the AA matrix **Q** ($Q_{ij} = \partial^2 E_{\text{ee}} / \partial n_i n_j$) is calculated from expression (5.14) for E_{ee}. The NOs, NO occupations, and the phase factors obtained from the full configuration interaction ground-state calculations are used to calculate **K** and **D**. Calculations have been performed with the GAMESS-UK package[25] at the experimental equilibrium bond distance $R(\text{He}-\text{H}^+) = 1.463$ a.u. (Ref. 26) and for the stretched molecule, $R(\text{He}-\text{H}^+) = 5.0$ a.u. The corresponding $\alpha(\omega)$ values are plotted in Figs. 1(a) and 1(b), respectively. The SA and AA curves $\alpha(\omega)$ are compared with the reference curve obtained with the full response CCSD calculations with the DALTON package.[27] All calculations have been performed with the same Gaussian basis sets, which were cc-pVTZ basis sets with specially designed p-type polarization functions for polarizability calculations. The cc-pVTZ basis for H is from Ref. 28 and for He from Ref. 29. The p-type polarization functions are from the work by Chong.[30] These basis sets are able to approach the basis set limit values for the polarizabilities to a few hundredths a.u. Comparison is also made with the TDDFT methods LDA-ALDA and

SAOP-ALDA, which have been obtained in a large basis set of Slater type orbitals.

As was already mentioned in Sec. III, SA consistently underestimates $\alpha(\omega)$ of HeH$^+$ and it is deficient in that it does not reproduce the accurate static limit $\alpha(\omega \to 0)$ [see Fig. 1(a)]. Thus, the SA neglect of the response of the NO occupations established in Sec. III makes the electron distribution of the molecule more rigid (less polarizable). The corresponding error is approximately 7% at $\omega=0$ and increases with ω. In turn, LDA-ALDA somewhat overestimates $\alpha(\omega)$ and this trend was already well documented in the literature for LDA and generalized gradient approximation (GGA) Kohn-Sham potentials, which yield too high occupied orbital energies and have wrong asymptotic behavior.[31,32] As a matter of fact, the overestimation is considerably less than in He,[33] which we attribute to the overall positive charge of HeH$^+$ which makes it "harder" than He. The more advanced Kohn-Sham potential SAOP[22] corrects in SAOP-ALDA calculations this overestimation at low ω, but with increasing ω the SAOP-ALDA polarizability also develops an overestimation.

Addition of the approximate NO occupation response in AA substantially improves the performance of ADMFT [see Fig. 1(a)]. As expected from the formulation of AA, its $\alpha(\omega)$ curve coincides with that of the full response CCSD at small ω. Moreover, AA produces a systematic improvement over SA in the whole range of the frequencies considered, thus providing a good quality approximation to the rigorous response theory, in spite of the adiabatic approximation.

For the stretched HeH$^+$ [Fig. 1(b)], LDA-ALDA considerably overestimates the polarizability at small ω values. The overestimation rapidly increases with increasing ω, since $\alpha(\omega)$ diverges at the first excitation energy. This first excitation energy, which corresponds to the long-range charge transfer (CT) He$\to$H+, is severely underestimated in LDA-ALDA. The first LDA-ALDA excitation energy can be estimated from Fig. 1(b) as the ω value, at which $\alpha(\omega)$ diverges, $\omega \approx 0.2$ a.u. Indeed, while the LDA-ALDA curve diverges at $\omega \approx 0.2$ a.u., the CCSD curve experiences divergence at a twice as high value, $\omega \approx 0.4$ a.u. SAOP-ALDA reduces this underestimation, but still its excitation energy is too low. Note, that HeH$^+$ represents a special type of CT, namely, to the zero-electron system H+, and in this case standard TDDFT does not possess the deficiencies characteristic for a typical CT between donor and acceptor fragments.[34–36] Rather, the present errors of LDA-ALDA and SAOP-ALDA can be traced back to the LDA (much too high) and SAOP (too high) energies of the 1s orbital of He. It is gratifying to see in Fig. 1(b) that the TDDMFT calculations, into which such orbital energies never enter, provide an excellent quality of the response TDDMFT calculations in this case. The static and adiabatic approximations do not worsen the performance appreciably, so that both the overall and near-resonance agreement of the SA and AA curves with the CCSD one are excellent.

In conclusion, we have identified certain deficiencies of the simple SA in TDDMFT, which had been proposed earlier, and we have proposed a remedy in the form of an AA. Numerical results for a simple prototype system (HeH$^+$)

demonstrate the feasibility of the TDDMFT approach, in general, and an encouraging quality of the AA, in particular.

The quality of the AA invites a more extensive investigation, on a larger set of benchmark systems, and not only for the polarizability but notably also for the excitation energies. In particular, the inability of the TDDFT method to provide correct excitation energies along the whole dissociation coordinate for a lengthening electron pair bond (cf. the H$_2$ results in Ref. 37) provides a challenge for TDDMFT. Since approximate DMFT functionals have been proposed that provide much improved ground state E versus R dissociation curves compared to DFT (LDA or GGA),[20] it will be intriguing to investigate their performance for excitation energies along the dissociation coordinate.

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APPENDIX: MATRIX K^{oe} AND THE MATRICES K AND M FOR TWO-ELECTRON SYSTEMS

In this appendix, we present the explicit expressions for the static matrix $\mathbf{K}^{oe}$ of Eq. (3.10) using the relations for the orbital evolution matrix $\mathbf{U}$ of Eq. (3.4) and its response. By its definition, $\mathbf{U}$ connects $\boldsymbol{\gamma}(t)$ with the NO occupations $n_\lambda(t)$ (note that we stick to the convention of labeling the time-dependent NOs with Greek indices),

$$\gamma_{ij}(t) = \sum_\lambda U_{i\lambda}(t) n_\lambda(t) U_{j\lambda}^*(t), \tag{A1}$$

which provides the relation between the linear responses

$$\forall_l \quad \delta\gamma_{ll}(t) = \delta n_\lambda(t), \tag{A2}$$

$$\forall_{m \neq l} \quad \delta\gamma_{ml}(t) = (n_l - n_m)\delta U_{m\lambda}(t), \tag{A3}$$

where of course $\lambda = l$.

From these equations, for the derivatives of the matrix $\mathbf{U}$ follows

$$\left.\frac{\partial U_{i\lambda}^*(t)}{\partial \gamma_{km}(t')}\right|_{\gamma(t)=\gamma^{(0)}} = -\delta(t-t')\frac{(1-\delta_{km})\delta_{im}\delta_{\lambda k}}{n_m - n_k}, \tag{A4}$$

$$\left.\frac{\partial U_{i\lambda}(t)}{\partial \gamma_{km}(t')}\right|_{\gamma(t)=\gamma^{(0)}} = \delta(t-t')\frac{(1-\delta_{km})\delta_{ik}\delta_{\lambda m}}{n_m - n_k}. \tag{A5}$$

Inserting Eqs. (A4) and (A5) into Eq. (3.10) and using in the resultant formula the variational condition for the static one- and two-electron matrices $\mathbf{W}$ and $\mathbf{h}$,[11]

$$\forall_{i \neq j} \quad \frac{W_{ij} - W_{ji}^*}{n_j - n_i} = -h_{ij}, \tag{A6}$$

we obtain the expressions for the matrix elements of $\mathbf{K}^{oe}$,

$$\forall_{i,k>l} \quad K_{iikl}^{oe} = -\delta_{il}h_{ki} + \delta_{ik}h_{il}, \tag{A7}$$

$$\forall_{ij,k>l} \quad K_{ijkl}^{oe} = \frac{h_{jl}(n_l - n_j)}{n_l - n_k}\delta_{ik} - \frac{h_{ki}(n_i - n_k)}{n_l - n_k}\delta_{jl}. \tag{A8}$$

Differentiating the matrix $\mathbf{W}$ of Eq. (5.27) according to Eq. (5.25) and adding the resultant $\mathbf{K}^{ee}$ to the matrix $\mathbf{K}^{oe}$, one obtains the explicit expression of the matrix $\mathbf{K}$ for two-electron systems. For the elements K_{ijkl} $(i>j)$, we have

$$K_{ijkl} = -\frac{1}{2}\delta_{kl}\left[\frac{1}{f_k\sqrt{n_k}}(\delta_{jk} - \delta_{ik})(1 - \delta_{ij})h_{ij}(f_i\sqrt{n_i} + f_j\sqrt{n_j}) + \frac{f_i\sqrt{n_i} - f_j\sqrt{n_j}}{f_k\sqrt{n_k}}\langle\phi_i\phi_j|\phi_k\phi_k\rangle\right] - (f_if_k\sqrt{n_in_k} + f_jf_l\sqrt{n_jn_l})[\langle\phi_k\phi_l|\phi_j\phi_i\rangle$$

$$+ \langle\phi_l\phi_k|\phi_j\phi_i\rangle]\frac{(1 - \delta_{kl})}{n_k - n_l} + \left[f_k\sqrt{n_k}\delta_{jl}\sum_m f_m\sqrt{n_m}\langle\phi_i\phi_k|\phi_m\phi_m\rangle + f_k\sqrt{n_k}\delta_{jk}\sum_m f_m\sqrt{n_m}\langle\phi_m\phi_m|\phi_l\phi_i\rangle\right]\frac{(1 - \delta_{kl})}{n_k - n_l}$$

$$+ \left[f_l\sqrt{n_l}\delta_{il}\sum_m f_m\sqrt{n_m}\langle\phi_k\phi_j|\phi_m\phi_m\rangle + f_l\sqrt{n_l}\delta_{ik}\sum_m f_m\sqrt{n_m}\langle\phi_m\phi_m|\phi_j\phi_l\rangle\right]\frac{(1 - \delta_{kl})}{n_k - n_l}. \tag{A9}$$

In turn, the subdiagonal $(k=l)$ matrix $\mathbf{M}$ in Eq. (5.21) is obtained from $\mathbf{K}$ of Eq. (A9) by a formal (before setting $k=l$) omission of the factor $(1 - \delta_{kl})$, subsequent multiplication of Eq. (A9) by the factor $(f_k\sqrt{n_k}/2 - f_l\sqrt{n_l}/2)$, and, only after those operations, by setting $k=l$,

$$M_{ijkl} = -\delta_{kl}[f_j\sqrt{n_j/2}\langle\phi_k\phi_k|\phi_j\phi_i\rangle + f_i\sqrt{n_i/2}\langle\phi_i\phi_j|\phi_k\phi_k\rangle] + \delta_{kl}\left[\frac{1}{2}\delta_{jk}\sum_m f_m\sqrt{n_m/2}\langle\phi_i\phi_k|\phi_m\phi_m\rangle\right.$$

$$\left. + \frac{1}{2}\delta_{jk}\sum_m f_m\sqrt{n_m/2}\langle\phi_m\phi_m|\phi_k\phi_i\rangle\right] + \delta_{kl}\left[\frac{1}{2}\delta_{ik}\sum_m f_m\sqrt{n_m/2}\langle\phi_k\phi_j|\phi_m\phi_m\rangle + \frac{1}{2}\delta_{ik}\sum_m f_m\sqrt{n_m/2}\langle\phi_m\phi_m|\phi_j\phi_k\rangle\right]. \tag{A10}$$

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