Time-dependent density-matrix-functional theory

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Although good progress has been made in the calculation of correlation energies from total energy expressions which are implicit functionals of the one-particle reduced density matrix, and explicit functionals of the natural orbitals (NOs) and their occupation numbers, a formulation of the calculation of excitation energies in this so-called density-matrix-functional theory (DMFT) is still lacking. In this paper we propose a time-dependent density-matrix-functional theory (TDDMFT). It is based on the equation of motion (EOM) for the 1-matrix $\mathbf{P}_{(s)}(t)$ in the representation of the stationary NOs. In the final form of the EOM, the rate of change of the $\mathbf{P}_{(s)}(t)$, $\partial \mathbf{P}_{(s)}(t)/\partial t$, is determined by the commutator of the generalized time-dependent Fock matrix $\mathbf{F}_{(s)}(t)$ with $\mathbf{P}_{(s)}(t)$ plus an additional term $\mathbf{D}_{(s)}(t)$. The matrix $\mathbf{F}_{(s)}(t)$ determines the evolution of the NOs in the time-dependent one-electron Schrödinger equations, while $\mathbf{D}_{(s)}(t)$ determines the time evolution of the NO occupations. With the neglect of the electron Coulomb correlation, the time-dependent one-electron equations for the NOs reduce to those for the Hartree-Fock (HF) orbitals of time-dependent HF (TDHF) theory. The coupled-perturbed equations of TDDMF response theory (TDDMFRT) are derived for the linear response of the 1-matrix $\delta\mathbf{P}_{(s)}(t)$ to a time-dependent perturbation $\delta v_{\text{ext}}(t)$ of the external potential. The frequency-dependent changes $\delta P_{(s),ij}(\omega)$ and $\delta P_{(s),kl}(\omega)$ are coupled through the coupling matrix $K_{ijkl}(\omega)$, which is produced with the derivatives of $\mathbf{F}_{(s)}(t)$ and $\mathbf{D}_{(s)}(t)$ with respect to $P_{kl}(t')$. Based on the response equations, TDDMFRT eigenvalue equations are derived for the electron excitations ω_q.

I. INTRODUCTION

Density-matrix-functional theory (DMFT) was formulated [1–9] and has been developed [10–17] exclusively as a stationary ground-state theory. In DMFT the ground-state energy is defined as an (implicit) functional $E[\rho_1]$ of the one-particle reduced density matrix (or 1-matrix) $\rho_1(\mathbf{x},\mathbf{x}')$ ($\mathbf{x} \equiv \{\mathbf{r},s\}$ denotes the spatial $\mathbf{r}$ and spin s coordinates). In the rigorous DMFT treatment of two-electron systems [1] and in its many-electron approximations, explicit functionals of the stationary ground-state natural spin-orbitals (NOs) $\phi_i^{(0)}$ and their occupations $n_i^{(0)}$ are considered, with $\phi_i^{(0)}$ and $n_i^{(0)}$ being, respectively, the eigenfunctions and eigenvalues of ρ_1,

$$\rho_1^{(0)}(\mathbf{x},\mathbf{x}') = \sum_i n_i^{(0)} \phi_i^{(0)}(\mathbf{x}')^* \phi_i^{(0)}(\mathbf{x}). \qquad (1.1)$$

Recent DMFT developments include derivation of one-electron equations for NOs [18] with an effective nonlocal potential, $\hat{v}_{ee}^{(0)}$, representing the electron-electron interaction (the atomic units are used throughout the paper)

$$\{\hat{h} + \hat{v}_{ee}^{(0)}\}\phi_i^{(0)}(\mathbf{x}) = \varepsilon_i \phi_i^{(0)}(\mathbf{x}), \qquad (1.2)$$

where $\hat{h} = -\frac{1}{2}\nabla_\mathbf{r}^2 + v_{\text{ext}}(\mathbf{r})$ is the one-electron operator. Based on these equations and on the variational equations for $n_i^{(0)}$, the coupled-perturbed equations were derived in Ref. [19] for the 1-matrix response $\delta\rho_1$ to a static perturbation of v_{ext}. In Ref. [20] corrections to the approximate functional of Buijse and Baerends [9] were made, which improve significantly the quality of the calculated DMFT potential curves for a set of prototype σ-bonded molecules.

Another approximate functional was proposed in Refs. [21,22] and used to calculate bond lengths, vibrational frequencies and ionization potentials (see also Ref. [23]). A variant of open-shell DMFT was proposed in Ref. [24] and in Ref. [25] a rigorous few-orbital functional of $\phi_i^{(0)}$ and $n_i^{(0)}$ was employed to establish the orbital mechanism of van der Waals (vdW) interaction in the "pure" vdW triplet $^3\text{H}_2$ molecule. These and other DMFT functionals can serve as a paradigm for the development of orbital-dependent "fifth-generation" functionals in density functional theory (DFT) [26].

However, while the dynamical time-dependent DFT (TD-DFT) [27–30] enjoys successful development and applications, an analogous time-dependent approach in DMFT is not known. The key function of the stationary ground-state DFT is the diagonal part of $\rho_1^{(0)}(\mathbf{x},\mathbf{x}')$, the electron density $\rho^{(0)}(\mathbf{x})$, which is represented in the Kohn-Sham (KS) theory [31] with the orbitals $\psi_i^{(0)}(\mathbf{x})$ of the auxiliary noninteracting KS system. Then, TDDFT is based on the time-dependent one-electron Schrödinger equations for evolution of $\psi_i(t)$. In the response variant of TDDFT (TDDFRT) the eigenvalue equations for electron excitation energies [32] are an important feature.

In this paper time-dependent density-matrix-functional theory (TDDMFT) is developed. In Sec. II the equation of motion (EOM) is derived for the 1-matrix $\mathbf{P}_{(s)}(t)$ in the representation of the stationary NOs $\phi_i^{(0)}(\mathbf{x})$. According to the EOM, a rate $\partial\mathbf{P}_{(s)}(t)/\partial t$ of the $\mathbf{P}_{(s)}(t)$ change is determined with a matrix, the one-electron part of which is the matrix commutator $[\mathbf{h}_{(s)}(t),\mathbf{P}_{(s)}(t)]$ of $\mathbf{P}_{(s)}(t)$ and the matrix $\mathbf{h}_{(s)}(t)$ of the time-dependent one-electron operator $\hat{h}(t)$. Its two-electron part is the

difference $\{\mathbf{W}_{(s)}(t) - \mathbf{W}_{(s)}^+(t)\}$ for the orbital interaction matrix $W_{(s),ij}(t) = 2\Sigma_{klm}P_{(s),jklm}^{(2)}(t)\langle\phi_i^{(0)}\phi_k^{(0)}|\phi_l^{(0)}\phi_m^{(0)}\rangle$, which involves the time-dependent two-particle reduced density matrix (2-matrix) $\mathbf{P}_{(s)}^{(2)}(t)$. In TDDMFT the time-dependent 2-matrix is considered as a universal functional $\rho_2([\rho_1];t)$ of the time-dependent 1-matrix $\rho_1(\mathbf{x},\mathbf{x}',t)$ by virtue of the Runge-Gross theorem. In Sec. III the EOM matrix is transformed to the commutator $[\mathbf{F}_{(s)}(t),\mathbf{P}_{(s)}(t)]$ of $\mathbf{P}_{(s)}(t)$ and the time-dependent generalized Fock matrix $\mathbf{F}_{(s)}(t)$ plus an additional term $\mathbf{D}_{(s)}(t)$. The two-electron part $\mathbf{F}_{(s)}^{ee}(t)$ of $\mathbf{F}_{(s)}(t)$ is the unitary transformation of the time-dependent generalization $\mathbf{V}_{(t)}^{ee}(t)$ of the electron-electron interaction potential in (1.2) in the representation of the time-dependent NOs $\phi_i(\mathbf{x},t)$. By a unitary transformation, the EOM for $\mathbf{P}_{(s)}(t)$ is split into the time-dependent one-electron Schrödinger equations for evolution of the NOs $\phi_i(\mathbf{x},t)$ and the equations for evolution of the NO occupations $n_i(t)$. In Sec. IV coupled-perturbed equations of response TDDMFT (TDDMFRT) for the linear response of the 1-matrix are derived and, based on these equations, TD-DMFRT eigenvalue equations are derived for the electron excitations ω_q. In Sec. V a compact matrix formulation of the response equations is presented. In Sec. VI the features of the proposed TDDFRT and TDDMFRT are summarized and their place in the dynamical many-electron theory is discussed.

II. EQUATION OF MOTION FOR THE 1-MATRIX

Our strategy in derivation of TDDMFT is to operate with the time-dependent 1-matrix $\rho_1(\mathbf{x},\mathbf{x}',t)$ of the following form:

$$\rho_1(\mathbf{x},\mathbf{x}',t) = \sum_{ij} P_{(s),ij}(t)\phi_i^{(0)}(\mathbf{x})\phi_j^{(0)}(\mathbf{x}')^*, \quad (2.1)$$

where the entire time dependence is accumulated in the 1-matrix $\mathbf{P}_{(s)}(t)$ in the representation of the stationary NOs $\phi_i^{(0)}(\mathbf{x})$ (the subscript s indicates this representation). The matrix elements $P_{(s),ij}(t)$ are obtained from the stationary wave function $\Psi^{(0)}$ with the corresponding second-quantization creation $\hat{c}_i^+(t)_H$ and annihilation $\hat{c}_i(t)_H$ operators in the Heisenberg picture [33]

$$P_{(s),ij}(t) = \langle\Psi^{(0)}|\hat{c}_j^+(t)_H\hat{c}_i(t)_H|\Psi^{(0)}\rangle. \quad (2.2)$$

The operators $\hat{c}_i(t)_H$ form the Heisenberg field operator $\hat{\psi}(\mathbf{x},t)_H$,

$$\hat{\psi}(\mathbf{x},t)_H = \sum_i \hat{c}_i(t)_H\phi_i^{(0)}(\mathbf{x}). \quad (2.3)$$

Then, the equation of motion for the 1-matrix $\mathbf{P}_{(s)}(t)$ can be derived from that for the operator $\hat{\psi}(\mathbf{x},t)_H$ [34]

$$i\frac{\partial\hat{\psi}(\mathbf{x},t)_H}{\partial t} = \hat{h}(\mathbf{x},t)\hat{\psi}(\mathbf{x},t)_H$$

$$+ \int \hat{\psi}(\mathbf{x}'',t)_H^+|\mathbf{r}-\mathbf{r}''|^{-1}\hat{\psi}(\mathbf{x}'',t)_H\hat{\psi}(\mathbf{x},t)_H d\mathbf{x}'', \quad (2.4)$$

where $\hat{h}(\mathbf{x},t)$ is the time-dependent one-particle operator

$$\hat{h}(\mathbf{x},t) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r},t). \quad (2.5)$$

Multiplying (2.4) from the left by $\hat{\psi}(\mathbf{x}',t)_H^+$ and taking the expectation value of both sides for $\Psi^{(0)}$, one obtains

$$i\langle\Psi^{(0)}|\hat{\psi}(\mathbf{x}',t)_H^+\frac{\partial\hat{\psi}(\mathbf{x},t)_H}{\partial t}|\Psi^{(0)}\rangle = \hat{h}(\mathbf{x},t)\langle\Psi^{(0)}|\hat{\psi}(\mathbf{x}',t)_H^+\hat{\psi}(\mathbf{x},t)_H|\Psi^{(0)}\rangle$$

$$+ \int |\mathbf{r}-\mathbf{r}''|^{-1}\langle\Psi^{(0)}|\hat{\psi}(\mathbf{x}',t)_H^+\hat{\psi}(\mathbf{x}'',t)_H^+\hat{\psi}(\mathbf{x}'',t)_H\hat{\psi}(\mathbf{x},t)_H|\Psi^{(0)}\rangle d\mathbf{x}''. \quad (2.6)$$

Insertion of (2.3) in (2.6), multiplication of its both sides by the product $\phi_i^{(0)}(\mathbf{x}')\phi_j^{(0)}(\mathbf{x})^*$ and the subsequent integration over $\mathbf{x}$ and $\mathbf{x}'$ gives

$$i\langle\Psi^{(0)}|\hat{c}_i^+(t)_H\frac{\partial\hat{c}_j(t)_H}{\partial t}|\Psi^{(0)}\rangle$$

$$= \sum_k h_{(s),jk}(t)P_{(s),ki}(t) + \sum_{klm} P_{(s),iklm}^{(2)}(t)\langle\phi_j^{(0)}\phi_k^{(0)}|\phi_l^{(0)}\phi_m^{(0)}\rangle,$$

$$(2.7)$$

where

$$h_{(s),ij}(t) = \langle\phi_i^{(0)}|-\frac{1}{2}\nabla^2 + v_{\text{ext}}(t)|\phi_j^{(0)}\rangle, \quad (2.8)$$

$$\langle\phi_i^{(0)}\phi_j^{(0)}|\phi_k^{(0)}\phi_l^{(0)}\rangle$$

$$= \int \phi_i^{(0)}(\mathbf{x})^*\phi_j^{(0)}(\mathbf{x}')^*\phi_k^{(0)}(\mathbf{x})\phi_l^{(0)}(\mathbf{x}')|\mathbf{r}-\mathbf{r}'|^{-1}d\mathbf{x}d\mathbf{x}'$$

are the integrals of the electron-electron repulsion, and $\mathbf{P}_{(s)}^{(2)}(t)$ is the time-dependent two-particle reduced density matrix (2-matrix) in the representation of $\phi_i^{(0)}(\mathbf{x})$,

$$P^{(2)}_{(s),ijkl}(t) = \frac{1}{2}\langle \Psi^{(0)}|\hat{c}_i^+(t)_H \hat{c}_j^+(t)_H \hat{c}_l(t)_H \hat{c}_k(t)_H|\Psi^{(0)}\rangle. \quad (2.9)$$

Interchanging the indices i and j in (2.7), taking the complex conjugate, using the Hermiticity properties of $\mathbf{h}^{(0)}(t)$, $\mathbf{P}_{(s)}(t)$, $\mathbf{P}^{(2)}_{(s)}(t)$ and subtracting the resultant equation from (2.7), we finally obtain the EOM for $\mathbf{P}_{(s)}(t)$ in the matrix form

$$i\frac{\partial \mathbf{P}_{(s)}(t)}{\partial t} = [\mathbf{h}_{(s)}(t),\mathbf{P}_{(s)}(t)] + \{\mathbf{W}_{(s)}(t) - \mathbf{W}^+_{(s)}(t)\}.$$

$$(2.10)$$

According to (2.10), a rate of the $\mathbf{P}_{(s)}(t)$ change is determined with the matrix, the one-electron part of which in the square brackets is the matrix commutator

$$[\mathbf{h}_{(s)}(t),\mathbf{P}_{(s)}(t)] \equiv \mathbf{h}_{(s)}(t)\mathbf{P}_{(s)}(t) - \mathbf{P}_{(s)}(t)\mathbf{h}_{(s)}(t) \quad (2.11)$$

of $\mathbf{P}_{(s)}(t)$ and the one-electron operator matrix (2.8). Its two-electron part in the curly brackets is the difference between the following orbital interaction matrix $\mathbf{W}_{(s)}(t)$,

$$W_{(s),ij}(t) = 2\sum_{klm} P^{(2)}_{(s),jklm}(t)\langle \phi_i^{(0)}\phi_k^{(0)}|\phi_l^{(0)}\phi_m^{(0)}\rangle \quad (2.12)$$

and its complex conjugate.

In TDDMFT the time-dependent 2-matrix,

$$\rho_2(\mathbf{x}_1,\mathbf{x}_1',\mathbf{x}_2,\mathbf{x}_2',t)$$

$$= \sum_{ijkl} P^{(2)}_{(s),ijkl}(t)\phi_i^{(0)}(\mathbf{x}_1')^*\phi_j^{(0)}(\mathbf{x}_2')^*\phi_k^{(0)}(\mathbf{x}_1)\phi_l^{(0)}(\mathbf{x}_2)$$

$$= \sum_{ijkl} P^{(2)}_{(t),ijkl}(t)\phi_i(\mathbf{x}_1',t)^*\phi_j(\mathbf{x}_2',t)^*\phi_k(\mathbf{x}_1,t)\phi_l(\mathbf{x}_2,t)$$

$$(2.13)$$

will be considered as a universal functional $\rho_2([\rho_1];t)$ of the

time-dependent 1-matrix $\rho_1(\mathbf{x},\mathbf{x}',t)$ by virtue of the Runge-Gross theorem [35] of TDDFT. In (2.13) $P^{(2)}_{(t),ijkl}(t)$ is the 2-matrix in the representation of the time-dependent NOs $\phi_i(\mathbf{x},t)$, which are the eigenfunctions of $\rho_1(t)$ with the eigenvalues $n_i(t)$,

$$\rho_1(\mathbf{x},\mathbf{x}',t) = \sum_i n_i(t)\phi_i(\mathbf{x}',t)^*\phi_i(\mathbf{x},t) \quad (2.14)$$

and which can be obtained from $\{\phi_i^{(0)}(\mathbf{x})\}$ with the unitary orbital evolution matrix $\mathbf{U}(t)$,

$$\phi_i(\mathbf{x},t) = \sum_j U_{ji}(t)\phi_j^{(0)}(\mathbf{x}). \quad (2.15)$$

The map

$$\rho_2(\mathbf{x}_1,\mathbf{x}_1',\mathbf{x}_2,\mathbf{x}_2',t) \rightarrow \rho_1(\mathbf{x}_1,\mathbf{x}_1',t) \quad (2.16)$$

follows trivially from the fact, that the latter function is produced with the incomplete spatial integration of the former one

$$\rho_1(\mathbf{x}_1,\mathbf{x}_1',t) = \frac{2}{N-1}\int \rho_2(\mathbf{x}_1,\mathbf{x}_1',\mathbf{x}_2,\mathbf{x}_2,t)d\mathbf{x}_2. \quad (2.17)$$

On the other hand, the diagonal part of $\rho_1(\mathbf{x}_1,\mathbf{x}_1',t)$ is the electron density, $\rho(\mathbf{x}_1,t) \equiv \rho_1(\mathbf{x}_1,\mathbf{x}_1,t)$, so that $\rho_1(\mathbf{x}_1,\mathbf{x}_1,t) \rightarrow \rho(\mathbf{x}_1,t)$. Then, according to the Runge-Gross theorem, the time-dependent density $\rho(\mathbf{x}_1,t)$ determines the total time-dependent function $\Psi(\mathbf{x}_1,\dots,\mathbf{x}_N,t)$ up to a merely time-dependent phase

$$\rho(\mathbf{x}_1,t) \rightarrow e^{-ic(t)}\Psi(\mathbf{x}_1,\dots,\mathbf{x}_N,t). \quad (2.18)$$

In turn, the right-hand side of (2.18) uniquely determines the time-dependent 2-matrix $\rho_2(\mathbf{x}_1,\mathbf{x}_1',\mathbf{x}_2,\mathbf{x}_2',t)$,

$$\rho_2(\mathbf{x}_1,\mathbf{x}_1',\mathbf{x}_2,\mathbf{x}_2',t) = \frac{N(N-1)}{2}\int [e^{-ic(t)}\Psi(\mathbf{x}_1',\mathbf{x}_2',\dots,\mathbf{x}_N,t)]^*[e^{-ic(t)}\Psi(\mathbf{x}_1,\mathbf{x}_2,\dots,\mathbf{x}_N,t)]d\mathbf{x}_3\cdots d\mathbf{x}_N$$

$$= \frac{N(N-1)}{2}\int \Psi^*(\mathbf{x}_1',\mathbf{x}_2',\dots,\mathbf{x}_N,t)\Psi(\mathbf{x}_1,\mathbf{x}_2,\dots,\mathbf{x}_N,t)d\mathbf{x}_3\cdots d\mathbf{x}_N \quad (2.19)$$

so that the ambiguity in the phase in (2.18) cancels out in (2.19). This provides the map

$$\rho_1(\mathbf{x}_1,\mathbf{x}_1,t) \rightarrow \rho(\mathbf{x}_1,t) \rightarrow e^{-ic(t)}\Psi(\mathbf{x}_1,\dots,\mathbf{x}_N,t)$$

$$\rightarrow \rho_2(\mathbf{x}_1,\mathbf{x}_1',\mathbf{x}_2,\mathbf{x}_2',t). \quad (2.20)$$

The maps (2.16) and (2.20) establish the time-dependent 2-matrix as a universal functional $\rho_2([\rho_1];t)$ of $\rho_1(\mathbf{x}_1,\mathbf{x}_1',t)$. Then, for a fixed initial state $\Psi^{(0)}$ with fixed stationary NOs $\phi_i^{(0)}(\mathbf{x})$ the matrices $\mathbf{U}(t)$, $\mathbf{P}^{(2)}_{(s)}(t)$, and $\mathbf{W}_{(s)}(t)$ are also functionals $\mathbf{U}([\rho_1];t)$, $\mathbf{P}^{(2)}_{(s)}([\rho_1];t)$, and $\mathbf{W}_{(s)}([\rho_1];t)$ of $\rho_1(t)$. This

allows to consider the EOM (2.10), which includes the 2-matrix through (2.12), as the basic equation of TDDMFT.

III. EOM WITH THE GENERALIZED FOCKIAN AND DYNAMICAL EQUATIONS FOR NOS AND NO OCCUPATIONS

The EOM (2.10) for the 1-matrix can be brought to a form with the commutator of a generalized time-dependent Fock matrix. To accomplish this, we consider the orbital interaction matrix of (2.12) in the representation $\mathbf{W}_{(t)}(t)$ of the time-dependent NOs,

$$W_{(t),ij}([\rho_1];t) = 2\sum_{klm} P^{(2)}_{(t),jklm}(t)\langle\phi_i(t)\phi_k(t)|\phi_l(t)\phi_m(t)\rangle, \tag{3.1}$$

$$W_{(t),ij}([\rho_1];t)^* = 2\sum_{klm} P^{(2)}_{(t),klmj}(t)\langle\phi_k(t)\phi_l(t)|\phi_m(t)\phi_i(t)\rangle. \tag{3.2}$$

The representations $\mathbf{W}_{(s)}(t)$ and $\mathbf{W}_{(t)}(t)$ are related via the unitary transformation with the (complex conjugate) orbital evolution matrix $\mathbf{U}^+(t)$ of (2.15),

$$\mathbf{W}_{(s)}(t) = \mathbf{U}(t)\mathbf{W}_{(t)}(t)\mathbf{U}^+(t). \tag{3.3}$$

Inserting (3.3) in (2.10) and combining the resultant equation with (2.11), we obtain the EOM for the 1-matrix in the form

$$i\frac{\partial\mathbf{P}_{(s)}(t)}{\partial t} = [\mathbf{F}_{(s)}(t),\mathbf{P}_{(s)}(t)] + \mathbf{U}(t)\mathbf{D}_{(t)}(t)\mathbf{U}^+(t)$$
$$= [\mathbf{F}_{(s)}(t),\mathbf{P}_{(s)}(t)] + \mathbf{D}_{(s)}(t), \tag{3.4}$$

where $D_{(t),ij}(t) = \delta_{ij}(W_{(t),ii}(t) - W_{(t),ii}(t)^*)$ is the diagonal matrix composed from the diagonal elements of the matrix $\mathbf{W}_{(t)}(t)$.

The important first term of (3.4) is the commutator of the generalized time-dependent Fock matrix $\mathbf{F}_{(s)}(t)$ and $\mathbf{P}_{(s)}(t)$,

$$\mathbf{F}_{(s)}(t) = \mathbf{h}_{(s)}(t) + \mathbf{F}^{ee}_{(s)}(t) = \mathbf{h}_{(s)}(t) + \mathbf{U}(t)\mathbf{V}^{ee}_{(t)}(t)\mathbf{U}^+(t). \tag{3.5}$$

The two-electron part $\mathbf{F}^{ee}_{(s)}(t)$ of the Fockian (3.5) is the unitary transformation with $\mathbf{U}(t)$ of the matrix $\mathbf{V}^{ee}_{(t)}(t)$, which has the zero diagonal, $V^{ee}_{(t),ii}(t)=0$, while its off-diagonal elements are constructed from those of the matrix $\mathbf{W}_{(t)}(t)$ and the occupations $n_i(t)$ of $\phi_i(\mathbf{x},t)$,

$$V^{ee}_{(t),ij}(t) = \frac{[W_{(t)}(t) - W^+_{(t)}(t)]_{ij}}{n_j(t) - n_i(t)}, \quad i \neq j. \tag{3.6}$$

In the stationary case (3.6) turns to the off-diagonal elements

$$V^{(0),ee}_{ij} = \frac{[W^{(0)} - W^{(0)+}]_{ij}}{n_j(t) - n_i(t)} = \langle\phi^{(0)}_i|\hat{v}^{(0)}_{ee}|\phi^{(0)}_j\rangle, \quad i \neq j \tag{3.7}$$

of the time-independent potential $\hat{v}^{(0)}_{ee}$ in the one-electron equations (1.2) for the NOs [18]. In (3.7) $W^{(0)}_{ij}$ is obtained as the integral

$$W^{(0)}_{ij} = \int \frac{\delta E_{ee}[\rho^{(0)}_1]}{\delta\phi^{(0)}_j(\mathbf{x})^*}\phi^{(0)}_i(\mathbf{x})^* d\mathbf{x} \tag{3.8}$$

with the orbital derivative of the electron-electron interaction energy E_{ee} of the stationary state $\Psi^{(0)}$, which is determined with the diagonal part of the stationary 2-matrix $\rho^{(0)}_2$,

$$E_{ee} = \int \frac{\rho^{(0)}_2(\mathbf{x},\mathbf{x}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'$$
$$= \sum_{ijkl} P^{(2)}_{(s),ijkl} \int \frac{\phi^{(0)}_i(\mathbf{x})^*\phi^{(0)}_j(\mathbf{x}')^*\phi^{(0)}_k(\mathbf{x})\phi^{(0)}_l(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'. \tag{3.9}$$

This correspondence in the time-independent case would suggest that the matrix $\mathbf{V}^{ee}_{(t)}(t)$ of (3.6) actually is the time-dependent extension of the potential $\hat{v}^{(0)}_{ee}$, in the sense that it might feature as time-dependent electron-electron interaction operator in time-dependent Schrödinger-type equations for the NOs. As we will see below, this is indeed the case.

With (3.7) and (3.8), the generalized time-dependent Fock matrix $\mathbf{F}_{(s)}(t)$ of (3.5) turns in the stationary case to the generalized time-independent Fock matrix $\mathbf{F}^{(0)}$,

$$F^{(0)}_{ij} = \int \phi^{(0)}_i(\mathbf{x}')^* \frac{\delta E[\rho^{(0)}_1]}{\delta\rho^{(0)}_1(\mathbf{x},\mathbf{x}')}\phi^{(0)}_j(\mathbf{x})d\mathbf{x}d\mathbf{x}'$$
$$= \frac{\partial E[\rho^{(0)}_1]}{\partial P^{(0)}_{ji}} = 0, \quad i \neq j \tag{3.10}$$

that is diagonal for the ground-state 1-matrix. In (3.10) the derivatives of the total energy E,

$$E = \sum_i n^{(0)}_i h^{(0)}_{ii} + E_{ee} \tag{3.11}$$

are taken.

We now turn to the derivation of the equations for the time evolution of the NOs and the NO occupations. These can both be obtained from the EOM (3.4) using a transformation to the basis of time-dependent NOs $\phi_i(\mathbf{x},t)$. Indeed, by the unitary transformation of both sides of (3.4) with the matrix $\mathbf{U}^+$ we obtain the equation

$$i\frac{\partial n_l(t)}{\partial t}\delta_{kl} - in_l(t)\left\langle\frac{\partial\phi_k(t)}{\partial t}\bigg|\phi_l(t)\right\rangle - in_k(t)\left\langle\phi_k(t)\bigg|\frac{\partial\phi_l(t)}{\partial t}\right\rangle$$
$$= [n_l(t) - n_k(t)]h_{(t),kl}(t) + W_{(t),kl}(t) - W_{(t),lk}(t)^*. \tag{3.12}$$

For $k \neq l$ this equation assumes the form

$$[n_l(t) - n_k(t)]\left(i\left\langle\phi_k(t)\bigg|\frac{\partial\phi_l(t)}{\partial t}\right\rangle - F_{(t),kl}(t)\right) = 0, \quad k \neq l, \tag{3.13}$$

where $\mathbf{F}_{(t)}(t)$ is the generalized Fock matrix in the representation of $\phi_i(\mathbf{x},t)$,

$$\mathbf{F}_{(t)}(t) = \mathbf{h}_{(t)}(t) + \mathbf{V}^{ee}_{(t)}(t). \tag{3.14}$$

From (3.13) follow the one-electron time-dependent Schrödinger equations for NOs in the matrix form

$$i\left\langle\phi_k(t)\bigg|\frac{\partial\phi_l(t)}{\partial t}\right\rangle = F_{(t),kl}(t) = h_{(t),kl}(t) + V^{ee}_{(t),kl}(t), \quad k \neq l. \tag{3.15}$$

In turn, for $k=l$ in (3.12) the equations for the time evolution of the NO occupations $n_i(t)$,

$$i\frac{\partial n_k(t)}{\partial t} = D_{(t),kk}(t) \tag{3.16}$$

are obtained. Time-dependent changes of the NO occupations defined in (3.16) correctly conserve the total number of electrons

$$\frac{\partial \sum_k n_k(t)}{\partial t} = 0 \tag{3.17}$$

as follows from (3.1) and (3.2). Thus, the EOM (3.4) for the 1-matrix contains the full dynamics of TDDMFT, with the time evolution of the NOs being governed with the functional in the first term of (3.4), the evolution of the NO occupations being determined with that in the second term of the EOM.

With the neglect of the electron Coulomb correlation, Eq. (3.15) reduces to the one-electron equations of time-dependent Hartree-Fock (TDHF) theory [36]. In TDHF the occupations of the HF orbitals remain constant, $n_i(t)=1$, $1 \leq i \leq N$, and $n_i(t)=0$, $i > N$, so that (3.16) vanishes in this case. Then, it follows from (3.13) that only orbital pairs kl where one orbital is occupied and another orbital is virtual are involved in (3.15). The generalized time-dependent electron-electron interaction potential $\mathbf{V}^{ee}_{(t)}(t)$ turns in this case to the time-dependent HF potential

$$V^{ee}_{(t),kl}(t) = \sum_m^N [\langle \phi_k(t)\phi_m(t)|\phi_l(t)\phi_m(t)\rangle$$
$$- \langle \phi_k(t)\phi_m(t)|\phi_m(t)\phi_l(t)\rangle]. \tag{3.18}$$

IV. LINEAR RESPONSE IN TDDMFT

In time-dependent density-matrix-functional response theory (TDDMFRT) the linear response of the 1-matrix to a time-dependent perturbation $\delta v_{\text{ext}}(\mathbf{x},t)$ of the external potential is evaluated. The initial ground state is characterized with the following matrices:

$$P^{(0)}_{ij} = \delta_{ij} n^{(0)}_i, \tag{4.1}$$

$$U^{(0)}_{ij} = \delta_{ij}, \tag{4.2}$$

$$h^{(0)}_{ij}(n^{(0)}_j - n^{(0)}_i) + W^{(0)}_{ij} - W^{(0)*}_{ji} = 0. \tag{4.3}$$

At $t=t_0$ a Hermitian time-dependent perturbation $\delta v_{\text{ext}}(\mathbf{x},t)$ is switched on that can be represented in the stationary NO basis as

$$\langle \phi^{(0)}_i|\delta v_{\text{ext}}(t)|\phi^{(0)}_j\rangle = \delta v^{\text{ext}}_{(s),ij}(t)\theta(t-t_0) \tag{4.4}$$

and the linear response to this perturbation leads to the 1-matrix

$$P_{(s),ij}(t) = \delta_{ij}n^{(0)}_i + \delta P_{(s),ij}(t). \tag{4.5}$$

Inserting (4.4) and (4.5) in the EOM (3.4), we obtain within first-order perturbation theory

$$i\frac{\partial(\delta P_{(s),ij}(t))}{\partial t} = (n^{(0)}_j - n^{(0)}_i)[\delta v^{\text{ext}}_{(s),ij}(t)\theta(t-t_0) + \delta F^{ee}_{(s),ij}(t)]$$
$$+ (h^{(0)}_{ii} - h^{(0)}_{jj})\delta P_{(s),ij}(t) + \delta D_{(s),ij}(t). \tag{4.6}$$

Linear responses $\delta F^{ee}_{(s),ij}(t)$ and $\delta D_{(s),ij}(t)$ in (4.6) are evaluated as follows:

$$\delta F^{ee}_{(s),ij}(t) = \sum_{kl} \int \left.\frac{\partial F^{ee}_{(s),ij}([\rho_1];t)}{\partial P_{(s),kl}(t')}\right|_{\rho_1(t)=\rho^{(0)}_1} \delta P_{(s),kl}(t')dt', \tag{4.7}$$

$$\delta D^{ee}_{(s),ij}(t) = \sum_{kl} \int \left.\frac{\partial D_{(s),ij}([\rho_1];t)}{\partial P_{(s),kl}(t')}\right|_{\rho_1(t)=\rho^{(0)}_1} \delta P_{(s),kl}(t')dt' \tag{4.8}$$

with the derivatives in (4.7) and (4.8) taken at the ground-state 1-matrix. Inserting (4.7) and (4.8) in (4.6) and taking the Fourier transform of the resultant expression, we obtain the coupled-perturbed equations for the frequency-dependent response $\delta P_{(s),ij}(\omega)$ of the 1-matrix to a perturbation of frequency ω,

$$\omega\delta P_{(s),ij}(\omega) = (n^{(0)}_j - n^{(0)}_i)\delta v^{\text{ext}}_{(s),ij}(\omega) + (h^{(0)}_{ii} - h^{(0)}_{jj})\delta P_{(s),ij}(\omega)$$
$$+ \sum_{kl} K_{(s),ijkl}(\omega)\delta P_{(s),kl}(\omega) \tag{4.9}$$

which can be rewritten as

$$\forall_{ij}\sum_{kl} [(\omega - h^{(0)}_{kk} + h^{(0)}_{ll})\delta_{ki}\delta_{lj} - K_{(s),ijkl}(\omega)]\delta P_{(s),kl}(\omega)$$
$$= (n^{(0)}_j - n^{(0)}_i)\delta v^{\text{ext}}_{(s),ij}(\omega). \tag{4.10}$$

In (4.9) $\delta v^{\text{ext}}_{(s),ij}(\omega)$ is the external perturbation of frequency ω,

$$\delta v^{\text{ext}}_{(s),ij}(\omega) = \int e^{-i\omega t}\delta v^{\text{ext}}_{(s),ij}(t)\theta(t-t_0)dt. \tag{4.11}$$

In (4.9) and (4.10) the 1-matrix changes $\delta P_{(s),ij}(\omega)$ and $\delta P_{(s),kl}(\omega)$ are coupled through the coupling matrix $\mathbf{K}$,

$$K_{(s),ijkl}(\omega) = (n^{(0)}_j - n^{(0)}_i)\int e^{-i\omega(t-t')}$$
$$\times \left.\frac{\partial F^{ee}_{(s),ij}([\rho_1];t)}{\partial P_{(s),kl}(t')}\right|_{\rho_1(t)=\rho^{(0)}_1} d(t-t') + \int e^{-i\omega(t-t')}$$
$$\times \left.\frac{\partial D_{(s),ji}([\rho_1];t)}{\partial P_{(s),kl}(t')}\right|_{\rho_1(t)=\rho^{(0)}_1} d(t-t'). \tag{4.12}$$

From (4.10) and (4.12) follows that the changes of the 1-matrix diagonal elements $\delta P_{(s),ii}(\omega)$ conserve the number of particles

$$\sum_i \delta P_{(s),ii}(\omega) = 0. \tag{4.13}$$

The matrix $\mathbf{K}$ has the following symmetry property:

$$K_{(s),ijkl}(\omega) = -K_{(s),jilk}(-\omega)^* \qquad (4.14)$$

and in the case of real ground-state 1-matrix,

$$K_{(s),ijkl}(\omega) = -K_{(s),jilk}(\omega). \qquad (4.15)$$

In the popular adiabatic approximation [27] the (nonlocal) time dependence of the derivatives in (4.7) and (4.8) is neglected

$$\left.\frac{\partial F^{ee}_{(s),ij}([\rho_1];t)}{\partial P_{(s),kl}(t')}\right|_{\rho_1(t)=\rho_1^{(0)}} \approx \delta(t-t') \left.\frac{\partial F^{ee}_{(s),ij}[\rho_1]}{\partial P_{(s),kl}}\right|_{\rho_1=\rho_1^{(0)}}, \qquad (4.16)$$

$$\left.\frac{\partial D_{(s),ij}([\rho_1];t)}{\partial P_{(s),kl}(t')}\right|_{\rho_1(t)=\rho_1^{(0)}} \approx \delta(t-t') \left.\frac{\partial D_{(s),ij}[\rho_1]}{\partial P_{(s),kl}}\right|_{\rho_1=\rho_1^{(0)}} \qquad (4.17)$$

so that, according to (4.16) and (4.17) and to (3.5)–(3.7), the corresponding frequency-independent coupling matrix **K** has the following form:

$$K_{(s),ijkl} = (n_j^{(0)} - n_i^{(0)}) \left.\frac{\partial F^{ee}_{ij}[\rho_1]}{\partial P_{kl}}\right|_{\rho_1=\rho_1^{(0)}}$$
$$+ \delta_{ij} \left.\frac{\partial (W_{ii}^{(0)} - W_{ii}^{(0)*})}{\partial P_{kl}}\right|_{\rho_1=\rho_1^{(0)}}. \qquad (4.18)$$

Finally, the electron excitation energies ω_q are obtained in TDDMFRT from the eigenequation that follows from (4.10)

$$\forall_{ij} \sum_{kl} [(h_{kk}^{(0)} - h_{ll}^{(0)})\delta_{ki}\delta_{lj} + K_{(s),ijkl}(\omega_q)]\delta P_{(s),kl} = \omega_q \delta P_{(s),ij}. \qquad (4.19)$$

V. MATRIX FORMULATION OF THE RESPONSE EQUATIONS OF TDDFMT

The TDDMFRT equation (4.10) can be recast in matrix form. Considering explicitly in these equations the changes of the diagonal $\delta P_{(s),ii}$ and off-diagonal $\delta P_{(s),ij}$ 1-matrix elements, one obtains for $i > j$,

$$\sum_{k>l} [(\omega - h_{kk}^{(0)} + h_{ll}^{(0)})\delta_{ki}\delta_{lj} - K_{(s),ijkl}(\omega)]\delta P_{(s),kl}(\omega)$$

$$- \sum_{k>l} K_{(s),ijlk}(\omega)\delta P_{(s),lk}(\omega) - \sum_k K_{(s),ijkk}(\omega)\delta P_{(s),kk}(\omega)$$

$$= (n_j^{(0)} - n_i^{(0)})\delta v_{(s),ij}^{ext}(\omega), \qquad (5.1)$$

$$\sum_{k>l} [(\omega - h_{ll}^{(0)} + h_{kk}^{(0)})\delta_{ki}\delta_{lj} - K_{(s),jilk}(\omega)]\delta P_{(s),lk}(\omega)$$

$$- \sum_{k>l} K_{(s),jikl}(\omega)\delta P_{(s),kl}(\omega) - \sum_k K_{(s),jikk}(\omega)\delta P_{(s),kk}(\omega)$$

$$= (n_i^{(0)} - n_j^{(0)})\delta v_{(s),ji}^{ext}(\omega), \qquad (5.2)$$

and for $i = j$,

$$- \sum_{k>l} K_{(s),iikl}(\omega)\delta P_{(s),kl}(\omega) - \sum_{k>l} K_{(s),iilk}(\omega)\delta P_{(s),lk}(\omega)$$

$$- \sum_k \delta P_{(s),kk}(\omega)(K_{(s),iikk}(\omega) - \omega\delta_{ik}) = 0. \qquad (5.3)$$

Denote for $k > l$,

$$\delta P_{(s),kl}(\omega) = X_{kl}(\omega), \qquad (5.4)$$

$$\delta P_{(s),lk}(\omega) = Y_{kl}(\omega), \qquad (5.5)$$

and for $k = l$,

$$Z_{kl}(\omega) = \delta P_{(s),kl}(\omega)\delta_{kl}. \qquad (5.6)$$

For the real ground-state 1-matrix, addition and subtraction of Eqs. (5.1)–(5.3) from each other yields (the ω dependence will be skipped from now on)

$$\forall_{i>j} \sum_{k>l} [\omega\delta_{ki}\delta_{lj}X_{kl}^R + (A_{ijkl} + B_{ijkl})X_{kl}^I] = V_{ij}^I, \qquad (5.7)$$

$$\forall_{i>j} \sum_{k>l} [\omega\delta_{ki}\delta_{lj}X_{kl}^I + (A_{ijkl} - B_{ijkl})X_{kl}^R] - \sum_k C_{ijkk}Z_{kk} = V_{ij}^R, \qquad (5.8)$$

$$\omega Z_{ii} - 2\sum_{k>l} G_{iikl}X_{kl}^I = 0, \qquad (5.9)$$

where for $k > l$,

$$X_{kl}^R = \tfrac{1}{2}(X_{kl} + Y_{kl}) = F\{\text{Re}[\delta P_{kl}]\}, \qquad (5.10)$$

$$X_{kl}^I = \tfrac{1}{2}(X_{kl} - Y_{kl}) = F\{i\,\text{Im}[\delta P_{kl}]\}, \qquad (5.11)$$

where F indicates a Fourier transform.
Also

$$V_{ij}^R = (n_j^{(0)} - n_i^{(0)})\tfrac{1}{2}(\delta v_{(s),ij}^{ext} + \delta v_{(s),ji}^{ext}), \qquad (5.12)$$

$$V_{ij}^I = (n_j^{(0)} - n_i^{(0)})\tfrac{1}{2}(\delta v_{(s),ij}^{ext} - \delta v_{(s),ji}^{ext}). \qquad (5.13)$$

In (5.7)–(5.9) the matrices **A**, **B**, **C**, and **G** are defined as follows:

$$\forall_{i>j,k>l}, \quad A_{ijkl} = (-h_{kk}^{(0)} + h_{ll}^{(0)})\delta_{ki}\delta_{lj} - K_{(s),ijkl}, \qquad (5.14)$$

$$\forall_{i>j,k>l}, \quad B_{ijkl} = K_{(s),ijlk}, \qquad (5.15)$$

$$\forall_{i>j,k,l}, \quad C_{ijkl} = \delta_{kl}K_{(s),ijkl}, \qquad (5.16)$$

$$\forall_{i,j,k>l}, \quad G_{ijkl} = \delta_{ij}K_{(s),ijkl}. \qquad (5.17)$$

With (5.14)–(5.17), the set of linear equations (5.7)–(5.9) can be brought to the matrix form

$$\begin{pmatrix} \omega & \mathbf{A}+\mathbf{B} & 0 \\ \mathbf{A}-\mathbf{B} & \omega & -\mathbf{C} \\ 0 & -2\mathbf{G} & \omega \end{pmatrix} \begin{pmatrix} \mathbf{X}^R \\ \mathbf{X}^I \\ \mathbf{Z} \end{pmatrix} = \begin{pmatrix} \mathbf{V}^I \\ \mathbf{V}^R \\ 0 \end{pmatrix}. \qquad (5.18)$$

Note, that in the static limit $\omega \to 0$ the determinant of main matrix ("3 × 3" supermatrix) vanishes and its inverse di-

verges for finite matrices $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$, and $\mathbf{G}$. As a result, the response diverges at $\omega \to 0$ and that corresponds to an artificial zero-energy excitation $\omega_k \to 0$. In order to suppress this spurious zero excitation, the proper frequency dependence of $\mathbf{K}(\omega)$ should be taken into account. Specifically, the "diagonal" matrices $\mathbf{C}$ and $\mathbf{G}$ should vanish with $\omega \to 0$. In this case (5.18) turns to the 2×2 supermatrix equation for $\mathbf{X}$, which can be considered as the exchange-correlation extension of the corresponding TDHF equations.

VI. CONCLUSIONS

In this paper a time-dependent density-matrix-functional theory is proposed. It is based on the equation of motion for the Heisenberg field operator. From this equation, the EOM is derived for the 1-matrix $\mathbf{P}_{(s)}(t)$ in the representation of the stationary natural orbitals. The two-electron term of the EOM is constructed from the orbital interaction matrix $\mathbf{W}_{(s)}(t)$, which involves the 2-matrix $\mathbf{P}_{(s)}^{(2)}(t)$. The latter matrix is considered in TDDMFT as a functional of $\mathbf{P}_{(s)}(t)$ by virtue of the Runge-Gross theorem.

In the final form of the EOM, the rate of change $\partial \mathbf{P}_{(s)}(t)/\partial t$ of the 1-matrix is expressed as the matrix commutator of the generalized time-dependent Fock matrix $\mathbf{F}_{(s)}(t)$ with $\mathbf{P}_{(s)}(t)$ plus an additional term $\mathbf{D}_{(s)}(t)$. The matrix $\mathbf{F}_{(s)}(t)$ determines the evolution of the NOs $\phi_i(\mathbf{x},t)$ in the time-dependent one-electron Schrödinger equations, while $\mathbf{D}_{(s)}(t)$ determines the time evolution of the NO occupations $n_i(t)$. With the neglect of the electron Coulomb correlation, the time-dependent one-electron equations for the NOs $\phi_i(\mathbf{x},t)$ reduce to those for the Hartree-Fock (HF) orbitals of time-dependent HF (TDHF) theory.

Coupled-perturbed equations of response TDDMFT (TDDMFRT) are derived for the linear response of the 1-matrix $\delta \mathbf{P}_{(s)}(t)$ to a time-dependent perturbation $\delta v_{\text{ext}}(t)$ of the external potential. The frequency-dependent changes $\delta P_{(s),ij}(\omega)$ and $\delta P_{(s),kl}(\omega)$ are coupled through the coupling matrix $K_{ijkl}(\omega)$, which is produced with the derivatives of $\mathbf{F}_{(s)}(t)$ and $\mathbf{D}_{(s)}(t)$ with respect to $P_{kl}(t')$. Based on the response equations, TDDMFRT eigenvalue equations are derived for the electron excitations ω_q.

TDDMFRT equations (4.19) represent an alternative type of eigenvalue equation for excitation energies ω_q. Indeed, the previous one-electron time-dependent response theories, TD-DFT and time-dependent Hartree-Fock (TDHF), are based on independent-particle one-electron equations with different orbital energies ε_i. In these theories, the orbital energy differences provide a zero order of ω_q. Unlike this, TDDMFRT is based on the correlation including one-electron theory of DMFT with fractionally occupied NOs of the same orbital energy μ [2,3,7]. In this case all orbitals, not only pairs ij and kl of one occupied and one virtual orbital (like in TD-DFT and TDHF), are involved in the eigenvalue equations. In these equations, excitation energies ω_q are determined through the diagonal matrix of the differences of the diagonal matrix elements of the one-electron operator $(h_{ll}^{(0)} - h_{kk}^{(0)})$ as well as through the coupling matrix $\mathbf{K}$.

ACKNOWLEDGMENTS

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