Multicomponent density-functional theory for time-dependent systems

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We derive the basic formalism of density functional theory for time-dependent electron-nuclear systems. The basic variables of this theory are the electron density in body-fixed frame coordinates and the diagonal of the nuclear N-body density matrix. The body-fixed frame transformation is carried out in order to achieve an electron density that reflects the internal symmetry of the system. We discuss the implications of this body-fixed frame transformation and establish a Runge-Gross-type theorem and derive Kohn-Sham equations for the electrons and nuclei. We illustrate the formalism by performing calculations on a one-dimensional diatomic molecule for which the many-body Schrödinger equation can be solved numerically. These benchmark results are then compared to the solution of the time-dependent Kohn-Sham equations in the Hartree approximation. Furthermore, we analyze the excitation energies obtained from the linear response formalism in the single pole approximation. We find that there is a clear need for improved functionals that go beyond the simple Hartree approximation.

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I. INTRODUCTION

In the study of the interaction between electrons and nuclei, one often assumes that the electrons adjust their motion adiabatically to the motion of the much heavier nuclei. The decoupling of the electronic and nuclear motion that forms the basis for the Born-Oppenheimer (BO) approximation is only justified if the energy scales of the electronic and nuclear excitations are well separated. When this condition is violated a breakdown of the BO approximation can be expected. In metallic solids, for instance, this is almost certainly the case and the validity of the BO approximation is therefore questionable for these systems. The coupling between electronic and nuclear motion turns out to play an important role in many physical phenomena in solid state physics and chemistry. In metallic solids the electron-phonon coupling is essential in the description of electrical resistivity, Its most dramatic consequence may be that it gives rise to the phenomenon of superconductivity [1]. Recently another important example of a breakdown of the BO approximation was observed in graphene [2]. In molecular systems the coupling between electronic and nuclear motion can also give rise to many interesting phenomena, such as the polaronic motion in long molecular chains. A more difficult case is that of molecules in strong laser fields, where there is a strong coupling between ionization and dissociation dynamics and a severe breakdown of the Born-Oppenheimer approximation. Due to the large number of degrees of freedom a solution of the Schrödinger equation is not possible in general. This applies even to the simplest possible system of the H_2^+ molecule. The latter system has been the subject of many theoretical investigations that go beyond BO [3–6]. In the presence of strong laser fields it is an extremely demanding task to obtain the solution of the time-dependent Schrödinger equation of H_2^+ and larger molecules are inaccessible this way.

Therefore there is a clear need for new methods that can deal with the nonequilibrium dynamics of electrons and nuclei at a full quantum mechanical level. Time-dependent density-functional theory (TDDFT) [7–9] is a strong candidate for such a method. One of the great virtues of TDDFT is that the dynamics of the electrons can, in an exact manner, be described by a set of effective one-particle equations, known as the Kohn-Sham equations, in which the effective Kohn-Sham potential is a functional of the density. This is a great computational advantage. The situation is more complicated if we consider the combined motion of electrons and nuclei, i.e., we need to construct a density-functional theory for different types of particles. Such a multicomponent density-functional theory (MCDFT) has been considered in detail for equilibrium systems by Kalia and Vashishta [10] in the study of electron-hole droplets. Similar versions of multicomponent density-functional theory have been considered by Capitani *et al.* [11] and Gidopoulos [12] to describe stationary non-Born-Oppenheimer ground states of electrons and nuclei. However, these approaches have in common that in the absence of external potentials the densities are constant as a consequence of the fact that in that case the Hamiltonian of the system is translationally and rotationally invariant.

In order to have the electron density display the internal symmetries of the system a body-fixed frame transformation needs to be carried out. This means in practice that the electronic coordinates are referred to a coordinate system attached to the nuclei. Subsequently a density-functional theory can be constructed in terms of intrinsic densities. This has been done for the stationary [13,14] and time-dependent

cases [15–17] by Kreibich and Gross. In this formalism the basic variables are the electron density in body-fixed coordinates and the diagonal of the nuclear density matrix. The latter is a function of all the nuclear coordinates which within a Kohn-Sham scheme is calculated from an equation involving an effective and in general time-dependent potential that depends also on all nuclear coordinates. In this way the formalism can easily be connected to a Born-Oppenheimer picture in the stationary case. However, it should be stressed that the Kohn-Sham scheme goes much beyond BO in that it provides an exact scheme for a full quantum treatment of electrons and nuclei.

This multicomponent density-functional theory has been investigated in detail for the stationary case [13–15]. However, apart from some preliminary work [15–18] this has not been the case for the time-dependent case. It is the aim of the current paper to carry out such an investigation. The paper is set up as follows. In Sec. II we discuss the coordinate transformation that defines our starting Hamiltonian. In Sec. III we give an overview of multicomponent density-functional theory for time-dependent systems. In particular we discuss the Runge-Gross theorems and some important consequences of the body-fixed frame transformation. We then discuss the Kohn-Sham equations and their linearization. In Sec. IV we illustrate the formalism for the case of a diatomic molecule and we carry out some calculations for the case of a one-dimensional model system that can be compared to accurate solutions of the many-body Schrödinger equation. Finally, in Sec. V we present our summary and conclusions.

II. THE BODY-FIXED FRAME

We start out by considering a system of N_e electrons with laboratory frame coordinates $\mathbf{r}_i$ where $i=1\ldots N_e$, and N_n nuclei with laboratory frame coordinates $\mathbf{R}_\alpha$, masses M_α, and charges Z_α where $\alpha=1\ldots N_n$. The corresponding Hamiltonian is then given by

$$\hat{H}(t) = \hat{T}_e(\underline{\mathbf{r}}) + \hat{T}_n(\underline{\mathbf{R}}) + \hat{W}_{ee}(\underline{\mathbf{r}}) + \hat{W}_{nn}(\underline{\mathbf{R}}) + \hat{W}_{en}(\underline{\mathbf{r}},\underline{\mathbf{R}})$$
$$+ \hat{U}_{\text{ext},e}(\underline{\mathbf{r}},t) + \hat{U}_{\text{ext},n}(\underline{\mathbf{R}},t). \tag{1}$$

Here $\underline{\mathbf{r}}$ and $\underline{\mathbf{R}}$ denote the sets of electron and nuclear coordinates. In this expression the electron and nuclear kinetic energy are given by

$$\hat{T}_e(\underline{\mathbf{r}}) = -\sum_{i=1}^{N_e} \frac{\nabla_{\mathbf{r}_i}^2}{2}, \tag{2}$$

$$\hat{T}_n(\underline{\mathbf{R}}) = -\sum_{\alpha=1}^{N_n} \frac{\nabla_{\mathbf{R}_\alpha}^2}{2M_\alpha}. \tag{3}$$

Atomic units ($|e|=m_e=\hbar=4\pi\epsilon_0=1$) are used throughout this article. The electron-electron, nuclear-nuclear, and electron-nuclear Coulomb interactions in the system are represented by

$$\hat{W}_{ee}(\underline{\mathbf{r}}) = \sum_{i<j=1}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{4}$$

$$\hat{W}_{nn}(\underline{\mathbf{R}}) = \sum_{\alpha<\beta=1}^{N_n} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}, \tag{5}$$

$$\hat{W}_{en}(\underline{\mathbf{r}},\underline{\mathbf{R}}) = -\sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}. \tag{6}$$

Finally the potentials due to the time-dependent external field acting on the electrons and nuclei are represented by

$$\hat{U}_{\text{ext},e}(\underline{\mathbf{r}},t) = \sum_{i=1}^{N_e} u(\mathbf{r}_i,t), \tag{7}$$

$$\hat{U}_{\text{ext},n}(\underline{\mathbf{R}},t) = \sum_{\alpha=1}^{N_n} U_\alpha(\mathbf{R}_\alpha,t), \tag{8}$$

where the nuclear potentials may be different for different species of nuclei. In the absence of external fields the Hamiltonian which describes the system in the laboratory frame as given in Eq. (1) is invariant under simultaneous arbitrary translations and rotations of all particles. This implies that all one-body ground-states observables, such as the electronic and nuclear densities, are uniform and isotropic. To describe the internal properties of the system it is therefore convenient to introduce a body-fixed coordinate frame. Following Kreibich and Gross [13] (see also Ref. [19]) we transform the electronic coordinates to a frame attached to the nuclear center of mass (CMN)

$$\mathbf{r}_i' = \mathcal{R}(\mathbf{r}_i - \mathbf{R}_{\text{CMN}}), \tag{9}$$

where $i=1\ldots N_e$. Here

$$\mathbf{R}_{\text{CMN}} = \frac{1}{M_{\text{nuc}}} \sum_{\alpha=1}^{N_n} M_\alpha \mathbf{R}_\alpha \tag{10}$$

denotes the nuclear center of mass, in which the total nuclear mass is given by $M_{\text{nuc}} = \sum_{\alpha=1}^{N_n} M_\alpha$, and the three-dimensional orthogonal matrix $\mathcal{R}$ represents a rotation, which is uniquely determined by three Euler angles [20]. These angles are functions of the nuclear coordinates $\underline{\mathbf{R}}$ and specify the orientation of the body-fixed coordinate frame with respect to the laboratory frame. The dependence of the Euler angles on the nuclear coordinates depends on the way we choose to fix the orientation. This can, for instance, be done by diagonalizing the nuclear inertia tensor [21–23] or by using Eckart-conditions [20,24–30]. The optimal choice will depend on the physical system being studied. A very elegant discussion of the various choices is given in Ref. [31].

The nuclear coordinates themselves are not transformed to a body-fixed frame at this point. Introducing internal nuclear coordinates may, however, also be desirable, but the choice of such coordinates depends strongly on the properties that one wants to study for the electron-nuclear system at hand. For example, to describe vibrations in molecules and solids, introduction of normal coordinates is most appropriate [19,20], while for the description of molecular dissociation the use of Jacobi coordinates [32] is more suitable. To keep the formalism flexible, the nuclear coordinates are left

unchanged for the time being. Transformation to internal nuclear coordinates can be done in the final equations, as we will discuss with the example of the diatomic molecule. The Hamiltonian of Eq. (1) describing the electron-nuclear system in the laboratory frame can now be given in the body-fixed coordinate frame, and reads

$$\hat{H}(t) = \hat{T}_e(\underline{\mathbf{r}}') + \hat{T}_n(\underline{\mathbf{R}}) + \hat{T}_{\text{MPC}}(\underline{\mathbf{r}}',\underline{\mathbf{R}}) + \hat{W}_{ee}(\underline{\mathbf{r}}') + \hat{W}_{nn}(\underline{\mathbf{R}})$$
$$+ \hat{W}_{en}(\underline{\mathbf{r}}',\underline{\mathbf{R}}) + \hat{U}_{\text{ext},e}(\underline{\mathbf{r}}',\underline{\mathbf{R}},t) + \hat{U}_{\text{ext},n}(\underline{\mathbf{R}},t). \quad (11)$$

Since a transformation has been done to a noninertial coordinate frame an additional mass polarization and Coriolis (MPC) term

$$\hat{T}_{\text{MPC}}(\underline{\mathbf{r}}',\underline{\mathbf{R}}) = -\sum_{\alpha=1}^{N_n} \frac{1}{2M_\alpha}\left(\nabla_{\mathbf{R}_\alpha} + \sum_{i=1}^{N_e}\frac{\partial \mathbf{r}'_i}{\partial \mathbf{R}_\alpha}\cdot\nabla_{\mathbf{r}'_i}\right)^2 - \hat{T}_n(\underline{\mathbf{R}}) \quad (12)$$

appears in the Hamiltonian [15,18,19]. The electron-electron interaction $\hat{W}_{ee}$ and electron kinetic energy $\hat{T}_e$ have the same form in the new and the old coordinates. The same is true for the nuclear-nuclear interaction $\hat{W}_{nn}$, the nuclear kinetic energy $\hat{T}_n$, and the external potential $\hat{U}_{\text{ext},n}$ acting on the nuclei. However, the electron-nuclear interaction and the external potential acting on the electrons attain the forms

$$\hat{W}_{en}(\underline{\mathbf{r}}',\underline{\mathbf{R}}) = \sum_{i=1}^{N_e}\sum_{\alpha=1}^{N_n}\frac{-Z_\alpha}{|\mathbf{r}'_i - \mathcal{R}(\mathbf{R}_\alpha - \mathbf{R}_{\text{CMN}})|}, \quad (13)$$

$$\hat{U}_{\text{ext},e}(\underline{\mathbf{r}}',\underline{\mathbf{R}},t) = \sum_{i=1}^{N_e} u(\mathcal{R}^{-1}\mathbf{r}'_i + \mathbf{R}_{\text{CMN}},t). \quad (14)$$

Note that the external potential $\hat{U}_{\text{ext},e}$, while still being a one-body potential with respect to the electronic coordinates $\underline{\mathbf{r}}'$, has turned into an N_n-body interaction with respect to the nuclear coordinates $\underline{\mathbf{R}}$. For notational simplicity we will denote $u(\mathbf{r}',\underline{\mathbf{R}},t) = u(\mathcal{R}^{-1}\mathbf{r}' + \mathbf{R}_{\text{CMN}},t)$. The quantity

$$\mathbf{R}'_\alpha = \mathcal{R}(\mathbf{R}_\alpha - \mathbf{R}_{\text{CMN}}) \quad (15)$$

appearing in Eq. (13) is a so-called shape coordinate [31], as it is invariant under rotations and translations of the nuclear frame work. As a consequence, the potential that the electrons experience from the nuclei is invariant under translation and rotation of the nuclear coordinates, which was, of course, exactly the purpose of our coordinate transformation. This completes our discussion of the transformed Hamiltonian. In the next section we will show how this Hamiltoninian can be used to set up a time-dependent density-functional theory.

III. TIME-DEPENDENT MULTICOMPONENT DENSITY-FUNCTIONAL THEORY

A. Definition of the densities

We now consider a density-functional description of our electron-nuclear system. We start out by defining the basic variables of our formalism [13,15,17]. The electron density is defined in the body-fixed frame as

$$n(\mathbf{r}'_1,t) = N_e \sum_{\underline{\sigma},\underline{s}} \int d\mathbf{r}'_2 \cdots d\mathbf{r}'_{N_e} \int d\underline{\mathbf{R}}|\Psi(\underline{\mathbf{r}}'\,\underline{\sigma},\underline{\mathbf{R}}\,\underline{s},t)|^2, \quad (16)$$

where the wave function $\Psi(\underline{\mathbf{r}}'\,\underline{\sigma},\underline{\mathbf{R}}\,\underline{s},t)$ is the solution of the time-dependent Schrödinger equation for the Hamiltonian of Eq. (11) and where $\underline{\sigma}$ and $\underline{s}$ denote the electron and nuclear spin coordinates. As a second basic variable we introduce the diagonal of the nuclear density matrix

$$\Gamma(\underline{\mathbf{R}},t) = \sum_{\underline{\sigma}\underline{s}} \int d^{N_e}\mathbf{r}'|\Psi(\underline{\mathbf{r}}'\,\underline{\sigma},\underline{\mathbf{R}}\,\underline{s},t)|^2. \quad (17)$$

This is an N_n-body quantity that is symmetric under interchange of space-spin coordinates of nuclei of the same type. By introducing the nuclear density in this way we keep the freedom to choose a transformation to internal coordinates in our final expression that is suitable to the particular system of interest. Furthermore, it turns out that by introducing $\Gamma(\underline{\mathbf{R}},t)$ rather than a single particle density per nuclear type $N_\alpha(\mathbf{R}',t)$ as function of nuclear coordinates in an internal frame, it is much easier to make a connection to the familiar Born-Oppenheimer approach. The latter point is not surprising since, like $\Gamma(\underline{\mathbf{R}},t)$, the Born-Oppenheimer surface is also an N_n-body object. Finally for the quantities n and Γ we can prove a Runge-Gross-type of theorem as we will do in the next section. In the following we will, for the ease of notation, drop the primes on the electronic coordinates. From now on all electronic coordinates are understood to refer to a body-fixed frame unless explicitly stated otherwise.

B. The Runge-Gross theorem

Here we give a brief discussion of the Runge-Gross theorem [33] for multicomponent systems as discussed by Kreibich [15,17]. To this end we define the Hamiltonian

$$\hat{H}(t) = \hat{T}_e(\underline{\mathbf{r}}) + \hat{T}_n(\underline{\mathbf{R}}) + \hat{T}_{\text{MPC}}(\underline{\mathbf{r}},\underline{\mathbf{R}}) + \hat{W}_{ee}(\underline{\mathbf{r}}) + \hat{W}_{en}(\underline{\mathbf{r}},\underline{\mathbf{R}})$$
$$+ \hat{U}_{\text{ext},e}(\underline{\mathbf{r}},\underline{\mathbf{R}},t) + \hat{V}_e(\underline{\mathbf{r}},t) + \hat{V}_n(\underline{\mathbf{R}},t), \quad (18)$$

in which we introduced two potentials $\hat{V}_e(\underline{\mathbf{r}},t)$ and $\hat{V}_n(\underline{\mathbf{R}},t)$ resulting from fields acting on the electrons and nuclei,

$$\hat{V}_e(\underline{\mathbf{r}},t) = \sum_{i=1}^{N_e} v(\mathbf{r}_i,t), \quad (19)$$

$$\hat{V}_n(\underline{\mathbf{R}},t) = V(\underline{\mathbf{R}},t). \quad (20)$$

Note that by setting $V(\underline{\mathbf{R}},t) = W_{nn}(\underline{\mathbf{R}}) + U_{\text{ext}}(\underline{\mathbf{R}},t)$ and $v(\mathbf{r},t) = 0$ we retrieve the Hamiltonian of Eq. (11). The potentials $v(\mathbf{r},t)$ and $V(\underline{\mathbf{R}},t)$ are conjugate to the densities $n(\mathbf{r},t)$ and $\Gamma(\underline{\mathbf{R}},t)$, and are introduced to provide the usual mappings between potentials and densities. We can now apply the Runge-Gross theorem along the lines of Li and Tong [34]. Two sets of densities $\{n(\mathbf{r},t),\Gamma(\underline{\mathbf{R}},t)\}$ and $\{n'(\mathbf{r},t),\Gamma'(\underline{\mathbf{R}},t)\}$,

which evolve from a common initials state $\Psi(\underline{\mathbf{r}}\sigma, \underline{\mathbf{R}}s, t_0)$ under the influence of two sets of potentials $\{v(\mathbf{r},t), V(\underline{\mathbf{R}},t)\}$ and $\{v'(\mathbf{r},t), V'(\underline{\mathbf{R}},t)\}$ always become different infinitesimally later than t_0 provided that at least one component of the potentials differs by more then a purely time-dependent function. Consequently, apart from the usual gauge freedom, a one-to-one mapping between the set of time-dependent densities and the set of potentials is established

$$\{v(\mathbf{r},t), V(\underline{\mathbf{R}},t)\} \leftrightarrow \{n(\mathbf{r},t), \Gamma(\underline{\mathbf{R}},t)\} \qquad (21)$$

for any given initial state. We further note that since the external potential acting on the electrons in the body-fixed frame attains the form of an electron-nuclear interaction $\hat{U}_{\text{ext},e}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t)$, the Runge-Gross mappings is still functionally dependent on $u(\mathbf{r}, \underline{\mathbf{R}}, t)$. Some consequences of this dependence will be discussed later.

C. Consequences of the body-fixed frame transformation

One of the most notable consequences of the body-fixed frame transformation is that some observables which are one-body observables in the laboratory frame can appear as many-body observables when expressed in the body-fixed frame. As an example of this we consider the dipole moment operator for a neutral system, which in the laboratory frame is given by the expression

$$\hat{\mathbf{D}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}) = \sum_{i=1}^{N_e} q_e \mathbf{r}_i + \sum_{\alpha=1}^{N_n} Z_\alpha \mathbf{R}_\alpha, \qquad (22)$$

where $q_e = -1$ is the charge of the electron. This operator has the expectation value

$$\mathbf{D}(t) = \sum_{\sigma, s} \int d\underline{\mathbf{r}} d\underline{\mathbf{R}} \hat{\mathbf{D}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}) |\Psi(\underline{\mathbf{r}}\sigma, \underline{\mathbf{R}}s, t)|^2, \qquad (23)$$

where $\Psi(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t)$ is the solution of the time-dependent Schrödinger equation in the laboratory frame. In the body-fixed frame, on the other hand, the expectation value of the dipole moment is given by

$$\mathbf{D}(t) = \int d\mathbf{r}' d\underline{\mathbf{R}} \hat{\mathbf{D}}(\mathbf{r}', \underline{\mathbf{R}}) \widetilde{\Gamma}(\mathbf{r}', \underline{\mathbf{R}}, t), \qquad (24)$$

where we defined the electron-nuclear density $\widetilde{\Gamma}(\mathbf{r}', \underline{\mathbf{R}}, t)$ and the dipole moment operator $\hat{\mathbf{D}}(\mathbf{r}', \underline{\mathbf{R}})$ as

$$\widetilde{\Gamma}(\mathbf{r}'_1, \underline{\mathbf{R}}, t) = N_e \sum_{\sigma, s} \int d\mathbf{r}'_2 \cdots d\mathbf{r}'_{N_e} |\Psi(\underline{\mathbf{r}}'\sigma, \underline{\mathbf{R}}s, t)|^2, \quad (25)$$

$$\hat{\mathbf{D}}(\mathbf{r}', \underline{\mathbf{R}}) = q_e(\mathcal{R}^{-1}\mathbf{r}' + \mathbf{R}_{\text{CMN}}) + \frac{1}{N_e} \sum_{\alpha=1}^{N_n} Z_\alpha \mathbf{R}_\alpha, \qquad (26)$$

where $\Psi(\underline{\mathbf{r}}', \underline{\mathbf{R}}, t)$ is now the solution of the time-dependent Schrödinger equation in the body-fixed frame. We see that the rotation matrix $\mathcal{R}$ mixes the electronic and nuclear coordinates. Therefore the dipole operator is no longer a simple one-body form with respect to the nuclear coordinates. A

particular consequence for density-functional theory is that $\mathbf{D}[n, \Gamma](t)$ is not a simple functional of n and Γ in the body-fixed frame coordinates. Nevertheless, we can split off a Hartree part and define an exchange-correlation part as follows:

$$\mathbf{D}[n, \Gamma](t) = \int d\mathbf{r}' d\underline{\mathbf{R}} \hat{\mathbf{D}}(\mathbf{r}', \underline{\mathbf{R}}) n(\mathbf{r}', t) \Gamma(\underline{\mathbf{R}}, t) + \mathbf{D}_{\text{xc}}[n, \Gamma](t). \qquad (27)$$

This means in practice, for instance, that in order to calculate the optical absorption of molecules one needs to develop approximations for $\mathbf{D}_{\text{xc}}[n, \Gamma](t)$. However, it seems that just taking the Hartree approximation is a reasonable approximation in the linear response regime.

A second consequence of the body-fixed frame transformation is that the external potential $\hat{U}_{\text{ext},e}(\mathbf{r}', \underline{\mathbf{R}}, t)$ of Eq. (14) acting on the electrons in the body-fixed frame attains the form of an electron-nuclear interaction. For this reason all density-functionals defined through the Runge-Gross mapping are also implicit functionals of $u(\mathbf{r}', \underline{\mathbf{R}}, t)$. Therefore, if we want to calculate the change in the density n and density matrix Γ due to changes in the true external fields by means of solving the Kohn-Sham equations, as we will do later, we also need to specify how the exchange-correlation potentials depend on $u(\mathbf{r}', \underline{\mathbf{R}}, t)$.

D. Multicomponent Kohn-Sham system

On the basis of the Runge-Gross theorem we can set up the Kohn-Sham equations [15–17]. As usual we introduce an auxiliary system with Hamiltonian

$$\hat{H}_{\text{S}}(t) = \hat{T}_e(\underline{\mathbf{r}}) + \hat{T}_n(\underline{\mathbf{R}}) + \hat{V}_{\text{S},e}(\underline{\mathbf{r}}, t) + \hat{V}_{\text{S},n}(\underline{\mathbf{R}}, t) \qquad (28)$$

and effective potentials

$$\hat{V}_{\text{S},e}(\underline{\mathbf{r}}, t) = \sum_{i=1}^{N_e} v_{\text{S}}(\mathbf{r}_i, t), \qquad (29)$$

$$\hat{V}_{\text{S},n}(\underline{\mathbf{R}}, t) = V_{\text{S}}(\underline{\mathbf{R}}, t). \qquad (30)$$

The Kohn-Sham system of Eq. (28) represents a system in which the interelectronic interaction as well as the interaction between electrons and nuclei has been switched off. According to the Runge-Gross theorem there exists for a given initial state at most one set of potentials $\{v_{\text{S}}(\mathbf{r},t), V_{\text{S}}(\underline{\mathbf{R}},t)\}$ determined up to purely time-dependent functions that produces the set of densities $\{n(\mathbf{r},t), \Gamma(\underline{\mathbf{R}},t)\}$. The effective potentials, which henceforth will be denoted as Kohn-Sham potentials, can therefore be regarded as functionals of n, Γ and the initial states of the true and the Kohn-Sham systems. In the Kohn-Sham Hamiltonian the electronic and nuclear motion have become separated. If the initial Kohn-Sham wave function $\Psi_{\text{S}}(\underline{\mathbf{r}}\sigma, \underline{\mathbf{R}}s, t_0)$ is chosen to be a product of a nuclear and an electronic wave function then the time-dependent Kohn-Sham wave function will also be such a product, i.e.,

$$\Psi_{\text{S}}(\underline{\mathbf{r}}\sigma, \underline{\mathbf{R}}s, t) = \Phi(\underline{\mathbf{r}}\sigma, t)\chi(\underline{\mathbf{R}}s, t), \qquad (31)$$

and the corresponding densities are given by

$$\Gamma(\mathbf{R},t) = \sum_{\underline{s}} |\chi(\mathbf{R}\underline{s},t)|^2, \tag{32}$$

$$n(\mathbf{r}_1,t) = N_e \sum_{\underline{\sigma}} \int d\mathbf{r}_2 \dots d\mathbf{r}_{N_e} |\Phi(\underline{\mathbf{r}}\underline{\sigma},t)|^2. \tag{33}$$

The electronic and nuclear Kohn-Sham (KS) wave functions then satisfy

$$0 = [i\partial_t - \hat{T}_n(\mathbf{R}) - \hat{V}_{S,n}(\mathbf{R},t)]\chi(\mathbf{R}\underline{s},t), \tag{34}$$

$$0 = [i\partial_t - \hat{T}_e(\mathbf{r}) - \hat{V}_{S,e}(\mathbf{r},t)]\Phi(\underline{\mathbf{r}}\underline{\sigma},t). \tag{35}$$

Suppose that the initial electron KS wave function is a Slater determinant of spin orbitals with spatial parts $\varphi_i(\mathbf{r},t_0)$. Then the electronic Kohn-Sham equations attain the form

$$i\partial_t\varphi_i(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_S(\mathbf{r},t)\right)\varphi_i(\mathbf{r},t), \tag{36}$$

$$n(\mathbf{r},t) = \sum_{i=1}^{N_e} |\varphi_i(\mathbf{r},t)|^2. \tag{37}$$

The nuclear Kohn-Sham equations (32) and (34) together with the electronic Kohn-Sham equations (36) and (37) provide a self-consistent scheme to calculate the electronic density n and the N_n-body nuclear density Γ. It remains to construct good approximations for the Kohn-Sham potentials for practical applications. More insight into these potentials is obtained from the analysis in the next sections.

E. The action functional for the multicomponent electron-nuclear system

Now we proceed to derive the multicomponent Kohn-Sham equations from an action principle. Action principles in TDDFT have been extensively discussed in the literature [8,9,34,35]. An elegant way to introduce the action functional uses the Keldysh time-contour technique of nonequilibrium Green's function theory [36–39]. For a recent introduction aimed towards application in TDDFT we refer to Ref. [40]. In analogy with the usual electronic time-dependent density-functional theory we define a functional of the external potentials v and V and for later purposes we also indicate the functional dependence on the electron-nuclear interaction u,

$$\widetilde{A}[v,V,u] = i \ln\langle\Psi_0|\hat{U}(t_0,t_0)|\Psi_0\rangle, \tag{38}$$

where the state Ψ_0 is the initial state of the system and the evolution operator $\hat{U}(t_2,t_1)$ is defined as

$$\hat{U}(t_2,t_1) = T_C \exp\left(-i\int_{t_1}^{t_2} dt\hat{H}(t)\right). \tag{39}$$

Here $\hat{H}(t)$ is the Hamiltonian of Eq. (18), and T_C denotes time ordering along the Keldysh contour C. This contour runs from t_0 to the time t at which one wants to evaluate the observables of interest and then back to t_0 [39,40]. One can readily derive [38,40] that

$$\frac{\delta\widetilde{A}}{\delta v(\mathbf{r},t)} = n(\mathbf{r},t), \tag{40}$$

$$\frac{\delta\widetilde{A}}{\delta V(\mathbf{R},t)} = \Gamma(\mathbf{R},t). \tag{41}$$

Note that to obtain this result one needs to consider potential variations that are general functions of the contour variable and therefore in general different on the forward and backward branch of the contour [37]. After differentiation the quantities can be evaluated at a physical potential, i.e., one that is identical on the forward and backward branch. We can now perform a Legendre transformation with respect to the potentials v and V to write the action as a functional of the electron and nuclear densities,

$$A[n,\Gamma,u] = -\widetilde{A}[v,V,u] + \int_C dtd\mathbf{r}n(\mathbf{r},t)v(\mathbf{r},t)$$

$$+ \int_C dtd\mathbf{R}\Gamma(\mathbf{R},t)V(\mathbf{R},t), \tag{42}$$

such that we have

$$\frac{\delta A}{\delta n(\mathbf{r},t)} = v[n,\Gamma,u](\mathbf{r},t), \tag{43}$$

$$\frac{\delta A}{\delta\Gamma(\mathbf{R},t)} = V[n,\Gamma,u](\mathbf{R},t), \tag{44}$$

where the external potentials are now to be regarded as functionals of n and Γ. A similar procedure can be carried out for a noninteracting system with Hamiltonian equation (28), i.e., we can define

$$\widetilde{A}_S[v_S,V_S] = i \ln\langle\Psi_{S,0}|\hat{U}_S(t_0,t_0)|\Psi_{S,0}\rangle \tag{45}$$

where $\Psi_{S,0}$ is the initial state of the noninteracting system with Hamiltonian equation (28). This Hamiltonian has the special feature that it can be written as the sum of a purely electronic and a purely nuclear piece $\hat{H}_S(t) = \hat{H}_{S,e}(t) + \hat{H}_{S,n}(t)$ where

$$\hat{H}_{S,e} = \hat{T}_e + \hat{V}_{S,e}, \tag{46}$$

$$\hat{H}_{S,n} = \hat{T}_n + \hat{V}_{S,n}, \tag{47}$$

where $\hat{H}_{S,e}(t)$ and $\hat{H}_{S,n}(t)$ are commuting. Therefore

$$\hat{U}_S(t_2,t_1) = \hat{U}_{S,e}(t_2,t_1)\hat{U}_{S,n}(t_2,t_1) \tag{48}$$

where

$$\hat{U}_{S,e/n}(t_2,t_1) = T_C \exp\left(-i\int_{t_1}^{t_2} dt\hat{H}_{S,e/n}(t)\right). \tag{49}$$

This equation is readily derived from the equations of motion of the evolution operators and the fact that the nuclear and electronic Hamiltonians commute. This means that *if the initial state is a simple product* $\Psi_{S,0} = \Phi_0\chi_0$ *of an electronic and a nuclear wave function then*

$$\widetilde{A}_S[v_S, V_S] = \widetilde{A}_{S,e}[v_S] + \widetilde{A}_{S,n}[V_S], \qquad (50)$$

where

$$\widetilde{A}_{S,e}[v_S] = i \ln\langle\Phi_0|\hat{U}_{S,e}|\Phi_0\rangle_e, \qquad (51)$$

$$\widetilde{A}_{S,n}[V_S] = i \ln\langle\chi_0|\hat{U}_{S,n}|\chi_0\rangle_n, \qquad (52)$$

where the subindex e/n on the ket denotes integration over electronic and/or nuclear coordinates only. We can now define the Legendre transform of $\widetilde{A}_S[v_S, V_S]$,

$$A_S[n, \Gamma] = -\widetilde{A}_S[v_S, V_S] + \int_C dt d\mathbf{r} \, n(\mathbf{r}, t) v_S(\mathbf{r}, t)$$

$$+ \int_C dt d\underline{\mathbf{R}} \, \Gamma(\underline{\mathbf{R}}, t) V_S(\underline{\mathbf{R}}, t), \qquad (53)$$

with the following properties:

$$\frac{\delta A_S}{\delta n(\mathbf{r}, t)} = v_S[n](\mathbf{r}, t), \qquad (54)$$

$$\frac{\delta A_S}{\delta \Gamma(\underline{\mathbf{R}}, t)} = V_S[\Gamma](\underline{\mathbf{R}}, t). \qquad (55)$$

Note that due to the additive structure of Eq. (50) the potential $v_S[n]$ is a functional of n only and the potential $V_S[\Gamma]$ is a functional of Γ only. Note that this is only true for initial states that are a product of a nuclear and an electronic wave function. Indeed in this case for a given n and Γ Eqs. (34) and (35) can be inverted independently of each other to yield v_S and V_S. Having defined the action functionals $A[n, \Gamma]$ and $A_S[n, \Gamma]$ we can define the exchange-correlation part $A_{xc}[n, \Gamma, u]$ of the action by the equation

$$A[n, \Gamma, u] = A_S[n, \Gamma] - \frac{1}{2} \int_C dt d\mathbf{r} d\mathbf{r}' \, W_{ee}(\mathbf{r}, \mathbf{r}') n(\mathbf{r}, t) n(\mathbf{r}', t)$$

$$- \int_C dt d\mathbf{r} d\underline{\mathbf{R}} \, W_{en}(\mathbf{r}, \underline{\mathbf{R}}) n(\mathbf{r}, t) \Gamma(\underline{\mathbf{R}}, t)$$

$$- \int_C dt d\mathbf{r} d\underline{\mathbf{R}} \, u(\mathbf{r}, \underline{\mathbf{R}}, t) n(\mathbf{r}, t) \Gamma(\underline{\mathbf{R}}, t) - A_{xc}[n, \Gamma, u], \qquad (56)$$

where we separated off a number of Hartree-type terms. Note that, since the external potential acting on the electrons has attained the form of an electron-nuclear interaction $u(\mathbf{r}, \underline{\mathbf{R}}, t)$ in the body-fixed frame, there is also a Hartree-type term involving this potential. We are now ready to discuss in more detail the Kohn-Sham potential and their functional dependencies. This will be done in the next section.

F. The effective potentials of the multicomponent system

The electronic and nuclear time-dependent effective potentials are obtained as derivatives of the action of Eq. (56) with respect to the electron $n(\mathbf{r}, t)$ and nuclear $\Gamma(\underline{\mathbf{R}}, t)$ densi-

ties. This yields expressions with the structure

$$v[n, \Gamma, u] = v_S[n] - v_H[n, \Gamma, u] - v_{xc}[n, \Gamma, u], \qquad (57)$$

$$V[n, \Gamma, u] = V_S[\Gamma] - V_H[n, u] - V_{xc}[n, \Gamma, u], \qquad (58)$$

where we defined the Hartree-type potentials

$$v_H[n, \Gamma, u](\mathbf{r}, t) = \int d\mathbf{r}' W_{ee}(\mathbf{r}, \mathbf{r}') n(\mathbf{r}', t) + \int d\underline{\mathbf{R}}[W_{en}(\mathbf{r}, \underline{\mathbf{R}})$$

$$+ u(\mathbf{r}, \underline{\mathbf{R}}, t)]\Gamma(\underline{\mathbf{R}}, t),$$

$$V_H[n, u](\underline{\mathbf{R}}, t) = \int d\mathbf{r} \, W_{en}(\mathbf{r}, \underline{\mathbf{R}}) n(\mathbf{r}, t) + \int d\mathbf{r} \, u(\mathbf{r}, \underline{\mathbf{R}}, t) n(\mathbf{r}, t),$$

$$(59)$$

and where we have introduced the exchange-correlation (xc) potentials $v_{xc}(\mathbf{r}, t)$ and $V_{xc}(\underline{\mathbf{R}}, t)$ by

$$v_{xc}(\mathbf{r}, t) = \frac{\delta A_{xc}[n, \Gamma, u]}{\delta n(\mathbf{r}, t)}, \qquad (60)$$

$$V_{xc}(\underline{\mathbf{R}}, t) = \frac{\delta A_{xc}[n, \Gamma, u]}{\delta \Gamma(\underline{\mathbf{R}}, t)}. \qquad (61)$$

If we rewrite expressions (57) and (58),

$$v_S[n] = v[n, \Gamma, u] + v_H[n, \Gamma, u] + v_{xc}[n, \Gamma, u], \qquad (62)$$

$$V_S[\Gamma] = V[n, \Gamma, u] + V_H[n, u] + V_{xc}[n, \Gamma, u], \qquad (63)$$

we see that for the electronic Kohn-Sham potential the Hartree and xc terms must compensate the Γ and u dependence of $v[n, \Gamma, u]$, and similarly for the nuclear potentials the Hartree and xc terms must compensate the n and u dependence of $V[n, \Gamma, u]$. This behavior is reflected in the relations

$$\left.\frac{\delta v(\mathbf{r}, t)}{\delta \Gamma(\underline{\mathbf{R}}, t')}\right|_{n, u} = -(W_{en}(\mathbf{r}, \underline{\mathbf{R}}, t) + u(\mathbf{r}, \underline{\mathbf{R}}, t))\delta(t, t')$$

$$- \left.\frac{\delta v_{xc}(\mathbf{r}, t)}{\delta \Gamma(\underline{\mathbf{R}}, t')}\right|_{n, u}, \qquad (64)$$

$$\left.\frac{\delta V(\underline{\mathbf{R}}, t)}{\delta n(\mathbf{r}, t')}\right|_{\Gamma, u} = -[W_{en}(\mathbf{r}, \underline{\mathbf{R}}, t) + u(\mathbf{r}, \underline{\mathbf{R}}, t)]\delta(t, t')$$

$$- \left.\frac{\delta V_{xc}(\underline{\mathbf{R}}, t)}{\delta n(\mathbf{r}, t')}\right|_{\Gamma, u}, \qquad (65)$$

$$\left.\frac{\delta v(\mathbf{r}, t)}{\delta u(\mathbf{r}', \underline{\mathbf{R}}, t')}\right|_{n, \Gamma} = -\Gamma(\underline{\mathbf{R}}, t)\delta(\mathbf{r} - \mathbf{r}')\delta(t, t')$$

$$- \left.\frac{\delta v_{xc}(\mathbf{r}, t)}{\delta u(\mathbf{r}', \underline{\mathbf{R}}, t')}\right|_{n, \Gamma}, \qquad (66)$$

$$\frac{\delta V(\mathbf{\underline{R}},t)}{\delta u(\mathbf{r},\mathbf{\underline{R}}',t')}\bigg|_{n,\Gamma} = -n(\mathbf{r},t)\delta(\mathbf{\underline{R}}-\mathbf{\underline{R}}')\delta(t,t')$$

$$-\frac{\delta V_{\text{xc}}(\mathbf{\underline{R}},t)}{\delta u(\mathbf{r},\mathbf{\underline{R}}',t')}\bigg|_{n,\Gamma}, \quad (67)$$

where $\delta(t,t')$ is a contour δ function [37]. We will use these equations in the next section on linear response theory.

G. Linear response

In this section we will derive the linearized form of the Kohn-Sham equations which will enable us to calculate linear response properties within the multicomponent formalism. To do this we first write the Hamiltonian of the interacting system in the body-fixed frame as

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t). \quad (68)$$

Here $\hat{H}_0$ is the Hamiltonian of the unperturbed time-independent system. Its explicit form is given by

$$\hat{H}_0 = \hat{T}_e(\mathbf{r}) + \hat{T}_n(\mathbf{\underline{R}}) + \hat{T}_{\text{MPC}}(\mathbf{r},\mathbf{\underline{R}}) + \hat{W}_{ee}(\mathbf{r}) + \hat{W}_{nn}(\mathbf{\underline{R}})$$
$$+ \hat{W}_{en}(\mathbf{r},\mathbf{\underline{R}}). \quad (69)$$

The term $\hat{H}_1$ describes the perturbation

$$H_1(t) = \delta\hat{U}_{\text{ext},e}(\mathbf{r},\mathbf{\underline{R}},t) + \delta\hat{V}_e(\mathbf{r},t) + \delta\hat{V}_n(\mathbf{\underline{R}},t). \quad (70)$$

Within linear response the induced electronic and nuclear densities are then given by

$$\delta n(1) = \int d2 \chi_{ee}(1,2)\delta v(2) + \int d\underline{2}\chi_{en}(1,\underline{2})\delta V(\underline{2})$$

$$+ \int d\underline{\underline{2}}\chi_{e,en}(1,\underline{\underline{2}})\delta u(\underline{\underline{2}}), \quad (71)$$

$$\delta\Gamma(\underline{1}) = \int d2\chi_{ne}(\underline{1},2)\delta v(2) + \int d\underline{2}\chi_{nn}(\underline{1},\underline{2})\delta V(\underline{2})$$

$$+ \int d\underline{\underline{2}}\chi_{n,en}(\underline{1},\underline{\underline{2}})\delta u(\underline{\underline{2}}). \quad (72)$$

Here we introduced the notations $i=\mathbf{r}_i t_i$, $\underline{i}=\mathbf{\underline{R}}_i t_i$ and $\underline{\underline{i}}=\mathbf{r}_i\mathbf{\underline{R}}_i t_i$. The response functions are defined as the following set of contour-ordered products:

$$\chi_{ab}(1,2) = -i\theta(t_1,t_2)\langle\Psi_0|T_C[\hat{a}_{\text{H}}(1)\hat{b}_{\text{H}}(2)]|\Psi_0\rangle, \quad (73)$$

where $\theta(t_1,t_2)$ is a contour Heaviside function [37,40] and where $\hat{a}_{\text{H}}$ and $\hat{b}_{\text{H}}$ are the Heisenberg representations (with respect to $\hat{H}_0$) of the operators $\hat{a}$ and $\hat{b}$. In our case $\hat{a}, \hat{b}=\hat{n}, \hat{\Gamma}$ or $\hat{n}\hat{\Gamma}$, corresponding to the indices a, $b=e$, n and en, respectively, which are defined as

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N_e}\delta(\mathbf{r}-\mathbf{r}_i), \quad (74)$$

$$\hat{\Gamma}(\mathbf{\underline{R}}') = \delta(\mathbf{\underline{R}}'-\mathbf{\underline{R}}) \equiv \prod_{\alpha=1}^{N_n}\delta(\mathbf{R}'_\alpha-\mathbf{R}_\alpha) \quad (75)$$

when the equations are subsequently transformed to real time form they attain the usual retarded form

$$\chi_{ab}(1,2) = -i\theta(t_1-t_2)\langle\Psi_0|[\hat{a}_{\text{H}}(1),\hat{b}_{\text{H}}(2)]|\Psi_0\rangle, \quad (76)$$

where $\theta(t)$ is now a real time Heaviside function. In practice all the derivations are always carried out on the Keldysh contour and the transformation to real time is carried out at the end (this can be conveniently done using the conversion table of Ref. [40]). Thus, the multicomponent electron-nuclear system of interacting particles is described by the six response functions which characterize the change of the electron and nuclear densities in the system due to the change of the external potential in the system. The density changes within the Kohn-Sham scheme are given by

$$\delta n(1) = \int d2\chi_{\text{S},ee}(1,2)\delta v_{\text{S}}(2), \quad (77)$$

$$\delta\Gamma(\underline{1}) = \int d\underline{2}\chi_{\text{S},nn}(\underline{1},\underline{2})\delta V_{\text{S}}(\underline{2}). \quad (78)$$

These equations do not contain the mixed response function $\chi_{\text{S},en}$ and $\chi_{\text{S},ne}$ due to the fact that in the multicomponent Kohn-Sham system electrons do not interact with the nuclei. Using the chain rule for differentiation we can now derive relations between the response functions for the interacting and the Kohn-Sham system. We have, for instance,

$$\chi_{ee}(1,2) = \int d3\frac{\delta n(1)}{\delta v_{\text{S}}(3)}\frac{\delta v_{\text{S}}(3)}{\delta v(2)}$$

$$= \frac{\delta n(1)}{\delta v_{\text{S}}(2)} + \int d3\frac{\delta n(1)}{\delta v_{\text{S}}(3)}\frac{\delta v_{\text{Hxc}}(3)}{\delta v(2)}. \quad (79)$$

Using

$$\frac{\delta v_{\text{Hxc}}(3)}{\delta v(2)} = \int d4\frac{\delta v_{\text{Hxc}}(3)}{\delta n(4)}\frac{\delta n(4)}{\delta v(2)} + \int d\underline{4}\frac{\delta v_{\text{Hxc}}(3)}{\delta\Gamma(\underline{4})}\frac{\delta\Gamma(\underline{4})}{\delta v(2)}, \quad (80)$$

where $v_{\text{Hxc}}=v_{\text{H}}+v_{\text{xc}}$, we obtain

$$\chi_{ee}(1,2) = \chi_{\text{S},ee}(1,2) + \int d3d4\chi_{\text{S},ee}(1,3)f_{\text{Hxc},ee}(3,4)\chi_{ee}(4,2)$$

$$+ \int d3d\underline{4}\chi_{\text{S},ee}(1,3)f_{\text{Hxc},en}(3,\underline{4})\chi_{ne}(\underline{4},2), \quad (81)$$

where we defined

$$f_{\text{Hxc},ee}(1,2) = \frac{\delta v_{\text{Hxc}}(1)}{\delta n(2)}, \quad (82)$$

$$f_{\text{Hxc},en}(1,\underline{2}) = \frac{\delta v_{\text{Hxc}}(1)}{\delta \Gamma(\underline{2})}. \tag{83}$$

Similarly, we can derive coupled equations for the other response functions which can be summarized in the following matrix equation:

$$\boldsymbol{\chi} = \boldsymbol{\chi}_{\text{S}} + \boldsymbol{\chi}_{\text{S}} \cdot \mathbf{f}_{\text{Hxc}} \cdot \boldsymbol{\chi}, \tag{84}$$

in which the dot product indicates a matrix product and an integration over the repeated variables. In this equation we defined the matrices

$$\boldsymbol{\chi} = \begin{pmatrix} \chi_{ee} & \chi_{en} \\ \chi_{ne} & \chi_{nn} \end{pmatrix},$$

$$\boldsymbol{\chi}_{\text{S}} = \begin{pmatrix} \chi_{\text{S},ee} & 0 \\ 0 & \chi_{\text{S},nn} \end{pmatrix},$$

$$\mathbf{f}_{\text{Hxc}} = \begin{pmatrix} f_{\text{Hxc},ee} & f_{\text{Hxc},en} \\ f_{\text{Hxc},ne} & f_{\text{Hxc},nn} \end{pmatrix}, \tag{85}$$

where in the matrix $\mathbf{f}_{\text{Hxc}}$ we further defined

$$f_{\text{Hxc},ne}(\underline{1},2) = \frac{\delta V_{\text{Hxc}}(\underline{1})}{\delta n(2)}, \tag{86}$$

$$f_{\text{Hxc},nn}(\underline{1},\underline{2}) = \frac{\delta V_{\text{Hxc}}(\underline{1})}{\delta \Gamma(\underline{2})}. \tag{87}$$

Here $V_{\text{Hxc}} = V_{\text{H}} + V_{\text{xc}}$. We have now demonstrated how to obtain the first-order density response to changes in the potentials $v(\mathbf{r},t)$ and $V(\underline{\mathbf{R}},t)$ acting in the body-fixed frame, while keeping the electron-nuclear interaction $u(\mathbf{r},\underline{\mathbf{R}},t)$ fixed. The response functions involving the electron potential v are not directly accessible in an experiment, however. Let us therefore investigate what happens if we keep the potentials fixed, and change the electron-nuclear interaction, reflecting a change in the external field acting in the laboratory frame. We will need to analyze the response functions,

$$\chi_{e,en}(1,\underline{2}) = \left. \frac{\delta n(1)}{\delta u(\underline{2})} \right|_{v,V}, \tag{88}$$

$$\chi_{n,en}(\underline{1},\underline{2}) = \left. \frac{\delta \Gamma(\underline{1})}{\delta u(\underline{2})} \right|_{v,V}, \tag{89}$$

which describe the changes in n and Γ when we change the electron-nuclear interaction u for fixed potentials v and V. We will now show that we can relate these response functions to the matrix of response functions $\boldsymbol{\chi}$. In order to do this we have to analyze carefully the functional dependence of the various quantities that we have introduced. Let us therefore consider the situation in which we keep the densities n and Γ fixed. Then for each given u there is a unique electron potential v and a unique nuclear potential V that reproduce the fixed densities n and Γ. Hence we can consider these v and V for the given n and Γ to be functionals of u, which we make explicit in the notation $v[u]$ and $V[u]$. By construction we have

$$n[v[u],V[u],u] = \text{const}, \tag{90}$$

$$\Gamma[v[u],V[u],u] = \text{const}. \tag{91}$$

We will assume that the functionals $v[u]$ and $V[u]$ are differentiable for physically reasonable and smooth potentials u. We can then differentiate these expressions with respect to u to obtain

$$\left.\frac{\delta n}{\delta v}\right|_{V,u} \left.\frac{\delta v}{\delta u}\right|_{n,\Gamma} + \left.\frac{\delta n}{\delta V}\right|_{v,u} \left.\frac{\delta V}{\delta u}\right|_{n,\Gamma} + \left.\frac{\delta n}{\delta u}\right|_{v,V} = 0, \tag{92}$$

$$\left.\frac{\delta \Gamma}{\delta v}\right|_{V,u} \left.\frac{\delta v}{\delta u}\right|_{n,\Gamma} + \left.\frac{\delta \Gamma}{\delta V}\right|_{v,u} \left.\frac{\delta V}{\delta u}\right|_{n,\Gamma} + \left.\frac{\delta \Gamma}{\delta u}\right|_{v,V} = 0. \tag{93}$$

Several terms in these equations can be identified with the electronic and nuclear response functions that we defined earlier. In particular the last terms in these equations correspond to the response functions of Eqs. (88) and (89). We thus see that these equations can be rewritten as

$$\begin{pmatrix} \chi_{e,en} \\ \chi_{n,en} \end{pmatrix} = - \boldsymbol{\chi} \left.\begin{pmatrix} \delta v/\delta u \\ \delta V/\delta u \end{pmatrix}\right|_{n,\Gamma}. \tag{94}$$

From Eqs. (66) and (67) we see that the derivatives of the potentials v and V with respect to the potential u are directly expressible in terms of the derivatives of the Hartree-xc potentials, i.e.,

$$\left.\frac{\delta v}{\delta u}\right|_{n,\Gamma} = -\left.\frac{\delta v_{\text{Hxc}}}{\delta u}\right|_{n,\Gamma}, \tag{95}$$

$$\left.\frac{\delta V}{\delta u}\right|_{n,\Gamma} = -\left.\frac{\delta V_{\text{Hxc}}}{\delta u}\right|_{n,\Gamma}. \tag{96}$$

In analogy to the density derivatives of the Hartree-xc potential, we define the u derivatives

$$f_{\text{Hxc},e,en}(1,\underline{2}) = \frac{\delta v_{\text{Hxc}}(1)}{\delta u(\underline{2})}, \tag{97}$$

$$f_{\text{Hxc},n,en}(\underline{1},\underline{2}) = \frac{\delta V_{\text{Hxc}}(\underline{1})}{\delta u(\underline{2})}. \tag{98}$$

Hence our final equation for the $\chi_{e/n,en}$ response functions becomes

$$\begin{pmatrix} \chi_{e,en} \\ \chi_{n,en} \end{pmatrix} = \boldsymbol{\chi} \cdot \begin{pmatrix} f_{\text{Hxc},e,en} \\ f_{\text{Hxc},n,en} \end{pmatrix}. \tag{99}$$

Equations (84) and (99) now completely determine the true response functions of the interacting system in terms of Kohn-Sham response functions and exchange-correlation kernels. The remaining task is to develop approximations for the Hartree-xc kernels f_{Hxc} that appear in our equations. These kernels will be discussed in the next section.

H. Properties of the response equations

We will now give a qualitative discussion of the properties of the response equations. For this purpose it is instructive to transform Eq. (84) to a form which is familiar from the usual electronic density functional theory. We readily obtain the equations

$$\chi_{ee} = \chi_{S,ee} + \chi_{S,ee}(f_{Hxc,ee} + f_{Hxc,en}\bar{\chi}_{nn}f_{Hxc,ne})\chi_{ee}, \quad (100)$$

$$\chi_{ne} = \bar{\chi}_{nn}f_{Hxc,ne}\chi_{ee}, \quad (101)$$

where we defined

$$\bar{\chi}_{nn} = [1 - \chi_{S,nn}f_{Hxc,nn}]^{-1}\chi_{S,nn}. \quad (102)$$

Similar equations for χ_{nn} and χ_{en} are obtained by interchanging the labels e and n in these equations. Equation (100) has an identical form as the equation of the density response function of standard TDDFT [41]. The main difference is that now an additional term $f_{Hxc,en}\bar{\chi}_{nn}f_{Hxc,ne}$ is added to the usual Hartree-xc kernel $f_{Hxc,ee}$ and describes an additional effective electron interaction which is mediated by the nuclei. It resembles the phonon-induced effective electron interaction of diagrammatic many-body perturbation theory where electrons interact with the nuclei through an effective vertex $f_{Hxc,en}$ which is propagated to other nuclei by means of the "propagator" $\bar{\chi}_{nn}$ [19]. The effect of this term is that it introduces extra poles in the response function χ_{ee} with a level spacing corresponding to molecular or phononic vibrations. The response functions $\bar{\chi}_{ee}$ and $\bar{\chi}_{nn}$ can be interpreted as response functions for the separate electronic and nuclear components. This is reflected in the equations

$$\chi_{ee} = \bar{\chi}_{ee} + \bar{\chi}_{ee}(f_{Hxc,en}\bar{\chi}_{nn}f_{Hxc,ne})\chi_{ee}, \quad (103)$$

$$\chi_{nn} = \bar{\chi}_{nn} + \bar{\chi}_{nn}(f_{Hxc,ne}\bar{\chi}_{ee}f_{Hxc,en})\chi_{nn}. \quad (104)$$

From these equations we see that the calculation of the response functions can be performed in a two-step process. The response functions $\bar{\chi}_{nn}$ and $\bar{\chi}_{ee}$ can be obtained separately since they are determined by equations that only involve purely electronic or purely nuclear quantities, although, as discussed later, a dependency on the nuclear motions is still introduced implicitly in the electronic equation through the $f_{Hxc,ee}$ kernel and vice versa. In particular the formal structure of the electronic problem is the one of standard electronic TDDFT. In a second step we can introduce the explicit couplings $f_{Hxc,en}$ and $f_{Hxc,ne}$ in combination with the response functions $\bar{\chi}_{nn}$ and $\bar{\chi}_{ee}$ in order to obtain the response functions χ_{ee} and χ_{nn} for the coupled electron-nuclear system. Then the mixed response functions χ_{ne} and χ_{en} are obtained from Eq. (101) and the one with indices n and e interchanged. Finally the response functions $\chi_{e,en}$ and $\chi_{n,en}$ are then determined from Eq. (99).

We now make a few general remarks about the Hartree-xc kernels. From Eq. (84) we find that they are determined by the equation

$$\begin{pmatrix} f_{Hxc,ee} & f_{Hxc,en} \\ f_{Hxc,ne} & f_{Hxc,nn} \end{pmatrix} = \begin{pmatrix} \chi_{S,ee}^{-1} & 0 \\ 0 & \chi_{S,nn}^{-1} \end{pmatrix} - \begin{pmatrix} \chi_{ee} & \chi_{en} \\ \chi_{ne} & \chi_{nn} \end{pmatrix}^{-1}. \quad (105)$$

We therefore see immediately that the terms $f_{Hxc,en}$ and $f_{Hxc,ne}$ can be expressed solely in terms of the interacting response functions. In contrast, the Hartree-xc kernels $f_{Hxc,ee}$ and $f_{Hxc,nn}$ are determined by both the response functions of the true and the Kohn-Sham system. In particular we see that the expression for $f_{Hxc,ee}$ will also involve the nuclear and mixed electron-nuclear response functions.

Note that we still did not transform the nuclear coordinates to a body-fixed frame. Consequently the Hamiltonian of the system is still invariant under translations and rotations of the nuclear coordinates only. Therefore, in general, the response functions will also describe the continuous spectra associated with the translational motion of the nuclei. In order to have a proper description of rotational and translational motion it is therefore convenient to also transform the nuclear coordinates to an internal coordinate system before solving the response equations. The actual choice of this transformation is, of course, highly dependent on the type of system that will be considered. We will illustrate the procedure in the next section for the case of the diatomic molecule.

IV. EXAMPLE: THE DIATOMIC MOLECULE

A. The Hamiltonian

In this section we apply the formalism introduced above to a diatomic molecule to illustrate the main features of the multicomponent linear response theory. The Hamiltonian of such an electron-nuclear system is given by

$$\begin{aligned} \hat{H}(t) = &-\frac{\nabla_{\mathbf{R}_1}^2}{2M_1} - \frac{\nabla_{\mathbf{R}_2}^2}{2M_2} - \sum_{i=1}^{N_e}\frac{\nabla_i^2}{2} + \sum_{i<j}^{N_e}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z_1 Z_2}{|\mathbf{R}_1 - \mathbf{R}_2|} \\ &- \sum_{i=1}^{N_e}\left(\frac{Z_1}{|\mathbf{r}_i - \mathbf{R}_1|} + \frac{Z_2}{|\mathbf{r}_i - \mathbf{R}_2|}\right)\sum_{i=1}^{N_e}\mathbf{r}_i \cdot \mathbf{E}(t) \\ &- (Z_1\mathbf{R}_1 + Z_2\mathbf{R}_2) \cdot \mathbf{E}(t). \end{aligned} \quad (106)$$

Here $\mathbf{R}_1$ and $\mathbf{R}_2$ are the coordinates of the nuclei with masses M_1 and M_2 and charges Z_1 and Z_2, respectively. The external electromagnetic field is treated here in the dipole approximation where $\mathbf{E}(t)$ is the electric field on the light pulse. We now introduce a convenient transformation: clearly the total center-of-mass position $\mathbf{R}_{CM} = (M_1\mathbf{R}_1 + M_2\mathbf{R}_2 + \Sigma_{i=1}^{N_e}\mathbf{r}_i)/(M_1 + M_2 + N_e)$ of the whole molecule and the internuclear vector $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ represent a favorable choice. We further transform the electronic coordinates to a body-fixed frame attached to the nuclei,

$$\mathbf{r}_i' = \mathcal{R}(\mathbf{r}_i - \mathbf{R}_{CMN}), \quad (107)$$

where the nuclear center of mass is given by

$$\mathbf{R}_{CMN} = \frac{M_1\mathbf{R}_1 + M_2\mathbf{R}_2}{M_{nuc}} \quad (108)$$

and the total nuclear mass is $M_{nuc} = M_1 + M_2$. For the diatomic molecule the natural choice of a nuclear frame is to

define the Euler angles by the requirement to have the internuclear axis parallel to the z axis in the body-fixed frame, i.e., $\mathcal{R}\mathbf{R}=R\mathbf{e}_z$, where $R=|\mathbf{R}|$. Note that for the diatomic molecule the rotation matrix $\mathcal{R}$ only depends on two Euler angles θ and φ as we may put the Euler angle for the final rotation around the z axis to zero. Thus, the complete set of coordinates is $(\mathbf{R}_{CM}, R, \theta, \varphi, \mathbf{r}'_i)$. In terms of these coordinates the Hamiltonian attains the form [18,20]

$$\hat{H}(t) = \hat{H}_{CM}(t) + \hat{H}_{mol}(t) \tag{109}$$

where

$$\hat{H}_{CM}(t) = -\frac{\nabla^2_{\mathbf{R}_{CM}}}{2M_{tot}} - Q_{tot}\mathbf{R}_{CM}\cdot\mathbf{E}(t), \tag{110}$$

$$\hat{H}_{mol}(t) = -\frac{\nabla^2_{\mathbf{R}}}{2\mu_n} - \sum_{i=1}^{N_e}\frac{\nabla'^2_i}{2} + \hat{T}_{MPC}(\mathbf{r}', \mathbf{R}) + \sum_{i<j}^{N_e}\frac{1}{|\mathbf{r}'_i - \mathbf{r}'_j|}$$

$$+ \frac{Z_1 Z_2}{R} - \sum_{i=1}^{N_e}\left(\frac{Z_1}{\left|\mathbf{r}'_i - \frac{M_2}{M_{nuc}}R\mathbf{e}_z\right|} + \frac{Z_2}{\left|\mathbf{r}'_i + \frac{M_1}{M_{nuc}}R\mathbf{e}_z\right|}\right)$$

$$+ \left(q_e\sum_{i=1}^{N_e}\mathcal{R}^{-1}\mathbf{r}'_i - q_n\mathbf{R}\right)\cdot\mathbf{E}(t), \tag{111}$$

where we defined

$$Q_{tot} = Z_1 + Z_2 - N_e, \tag{112}$$

$$q_n = \frac{Z_1 M_2 - Z_2 M_1}{M_1 + M_2}, \tag{113}$$

$$q_e = \frac{Z_1 + Z_2 + M_1 + M_2}{M_{tot}}, \tag{114}$$

$$\mu_n = \frac{M_1 M_2}{M_1 + M_2}. \tag{115}$$

The term $\hat{T}_{MPC} = \hat{T}_{MP} + \hat{T}_C$ is the sum of the mass polarization and Coriolis terms which have the form

$$\hat{T}_{MP} = -\frac{1}{2(M_1 + M_2)}\sum_{i,j=1}^{N_e}\boldsymbol{\nabla}'_i\cdot\boldsymbol{\nabla}'_j, \tag{116}$$

$$\hat{T}_C = -\frac{1}{2\mu_n R^2}\left\{\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta} - i\hat{L}_{e,y}\right)\right.$$

$$\times\sin\theta\left(\frac{\partial}{\partial\theta} - i\hat{L}_{e,y}\right)$$

$$\left. + \frac{1}{\sin^2\theta}\left(\frac{\partial}{\partial\varphi} + i\hat{L}_{e,x}\sin\theta - i\hat{L}_{e,z}\cos\theta\right)^2\right\}$$

$$+ \frac{1}{2\mu_n}\nabla^2_{\mathbf{R}}, \tag{117}$$

where $\hat{L}_e$ denotes the total electronic angular momentum

vector in the body-fixed frame. The mass-polarization term depends only on the electronic coordinates and the Coriolis term depends on the relative vector $\mathbf{R}$ and the transformed electronic coordinates $\mathbf{r}'_i$. If the initial wave function is a product of a center-of-mass wave function and a wave function of the internal coordinates then the time dependence of the wave function of the internal coordinates is completely determined by the Hamiltonian $\hat{H}_{mol}$. We are now ready to derive the Kohn-Sham equations for this system. This will be done in the next section.

B. The Kohn-Sham equations

Let us now apply our multicomponent formalism to the diatomic molecule. We first note that the molecular Hamiltonian $\hat{H}_{mol}(t)$ of Eq. (111) has the same structure of the general transformed Hamiltonian of Eq. (11). The main difference is that the set of nuclear coordinates in Eq. (11) is replaced by the relative internuclear vector $\mathbf{R}$. However, since the structure of both Hamiltonians is identical we can apply the formalism we derived without any problem to the molecular internal Hamiltonian Equation (111). The structure of the terms $\hat{U}_{ext,e}$ and $\hat{U}_{ext,n}$ is given by

$$\hat{U}_{ext,e}(\mathbf{r}', \mathbf{R}, t) = q_e\sum_{i=1}^{N_e}\mathcal{R}^{-1}\mathbf{r}'_i\cdot\mathbf{E}(t), \tag{118}$$

$$\hat{U}_{ext,n}(\mathbf{R}, t) = -q_n\mathbf{R}\cdot\mathbf{E}(t). \tag{119}$$

If $\Psi(\underline{\mathbf{r}}\underline{\sigma}, \mathbf{R}\underline{s}, t)$ is a solution to the time-dependent Schrödinger equation for Hamiltonian $\hat{H}_{mol}(t)$ then in analogy to Eqs. (16) and (17) we define the basic variables

$$n(\mathbf{r}'_1, t) = N_e\sum_{\underline{\sigma}, \underline{s}}\int d\mathbf{r}'_2\cdots d\mathbf{r}'_{N_e}\int d\mathbf{R}|\Psi(\underline{\mathbf{r}}'\underline{\sigma}, \mathbf{R}\underline{s}, t)|^2 \tag{120}$$

where $\underline{\sigma}$ and $\underline{s}$ as before denote the electronic and nuclear spin coordinates. As a second basic variable we introduce the density $N(\mathbf{R}, t)$ of the nuclear relative "particle"

$$N(\mathbf{R}, t) = \sum_{\underline{\sigma}\underline{s}}\int d^{N_e}\mathbf{r}'|\Psi(\underline{\mathbf{r}}'\underline{\sigma}, \mathbf{R}\underline{s}, t)|^2. \tag{121}$$

Corresponding to the Hamiltonian $\hat{H}_{mol}(t)$ there is a Kohn-Sham Hamiltonian in which the nuclear relative particle does not interact with the electrons. If the initial state of this Hamiltonian is a product of an electronic and a nuclear wave function the Kohn-Sham wave function will have the form

$$\Psi_S(\underline{\mathbf{r}}'\underline{\sigma}, \mathbf{R}\underline{s}, t) = \Phi(\underline{\mathbf{r}}'\underline{\sigma}, t)X(\mathbf{R}\underline{s}, t). \tag{122}$$

The nuclear wave function, when it is an eigenstate of the S_z and $\mathbf{S}^2$ operators, will have the general structure

$$X(\mathbf{R}\underline{s}, t) = \chi(\mathbf{R}, t)\theta(s_1, s_2), \tag{123}$$

where θ is the nuclear spin function. For example, for the two protons in the hydrogen molecule the function $\chi(\mathbf{R}, t)$ will behave under interchange of the nuclei similar to

$\chi(\mathbf{R},t) = \pm\chi(-\mathbf{R},t)$, depending on whether the spin function is of singlet or triplet type. The electron density within the Kohn-Sham scheme is calculated according to Eq. (33) where the electronic Kohn-Sham wave function satisfies

$$\{i\partial_t - \hat{T}_e(\underline{\mathbf{r}}') - v_S[n,N](\mathbf{r}',t)\}\Phi(\underline{\mathbf{r}}'\underline{\sigma},t) = 0, \quad (124)$$

where v_S has the explicit form

$$v_S(\mathbf{r},t) = q_e\left(\int d\mathbf{R}\,N(\mathbf{R},t)\mathcal{R}^{-1}\mathbf{r}\right)\cdot\mathbf{E}(t) + \int d\mathbf{R}\,W(\mathbf{r},R)N(\mathbf{R},t)$$

$$+ \int d\mathbf{r}'\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc,U}[n,N](\mathbf{r},t). \quad (125)$$

Assuming as before that the initial electronic wave function has the form of a single Slater determinant then the electronic Kohn-Sham equation leads to the usual orbital equations

$$i\partial_t\varphi_i(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_S[n,N](\mathbf{r},t)\right)\varphi_i(\mathbf{r},t), \quad (126)$$

$$n(\mathbf{r},t) = \sum_{i=1}^{N_e}|\varphi_i(\mathbf{r},t)|^2. \quad (127)$$

In a similar way the nuclear density is calculated from

$$N(\mathbf{R},t) = |\chi(\mathbf{R},t)|^2, \quad (128)$$

where the nuclear Kohn-Sham equation is given by

$$\left(i\partial_t + \frac{1}{2\mu_n}\nabla_{\mathbf{R}}^2 - V_S[n,N](\mathbf{R},t)\right)\chi(\mathbf{R},t) = 0. \quad (129)$$

Here the nuclear Kohn-Sham potential has the explicit form

$$V_S(\mathbf{R},t) = \frac{Z_1Z_2}{R} - q_n\mathbf{R}\cdot\mathbf{E}(t) + q_e\mathcal{R}^{-1}\left(\int d\mathbf{r}\,\mathbf{r}n(\mathbf{r},t)\right)\cdot\mathbf{E}(t)$$

$$+ \int d\mathbf{r}\,W(\mathbf{r},R)n(\mathbf{r},t) + V_{xc,U}[n,N](\mathbf{R},t), \quad (130)$$

with

$$W(\mathbf{r},R) = -\frac{Z_1}{\left|\mathbf{r} - \dfrac{M_2}{M_{\text{nuc}}}R\mathbf{e}_z\right|} - \frac{Z_2}{\left|\mathbf{r} + \dfrac{M_1}{M_{\text{nuc}}}R\mathbf{e}_z\right|}. \quad (131)$$

It only remains to specify how the exchange-correlation potentials dependent on the densities and on the external potential to complete the Kohn-Sham scheme.

Note that in the exchange-correlation potentials introduced in Eqs. (125) and (130) a number of rather complicated interactions are hidden. First of all, as we discussed earlier, there is the u dependence beyond the simple Hartree terms. Secondly, the mass polarization and Coriolis terms are incorporated in the exchange-correlation potentials as well. This leads to the delicate question whether these terms, which act as electron-nuclear interactions by means of differential operators, can be incorporated effectively in a local potential within a Kohn-Sham scheme. This is a fundamental v,V representability question in multicomponent density-

functional theory. At the moment we do not have a clear answer to this question. We finally note that some approximate density functionals for the Coriolis and mass polarization terms were discussed by Kreibich [15].

We will discuss in the next section the one-dimensional diatomic molecules H_2^+ and HD^+ in which only one electron is present. In these systems we can treat the mass polarization and Coriolis terms exactly (the Coriolis terms are zero as there are no rotations in one dimension), and use a simple approximation for the exchange-correlation potentials.

C. Application to a model system

We will now consider a numerical example. For this we use the standard model system of strong laser physics: a one-dimensional molecule with one electron and two nuclei. In recent years such models of reduced dimensionality [42–44] were used successfully to analyze the strong-field dynamics of atoms and molecules. In particular, they provided valuable insight in the influence of electron interactions on strong field atomic dynamics, such as nonsequential double ionization [45–49] and non-BO phenomena such as the generation of even harmonics in intense laser fields [50]. In this section we use the one-dimensional diatomic molecule with a softened electron-nuclear interaction [42] as a benchmark to test approximate density functionals. The Hamiltonian of the model is given by

$$\hat{H}(t) = -\frac{1}{2M_1}\frac{d^2}{dR_1^2} - \frac{1}{2M_2}\frac{d^2}{dR_2^2} - \frac{1}{2}\frac{d^2}{dz^2} + \frac{Z_1Z_2}{|R_1 - R_2|}$$

$$- \left(\frac{Z_1}{\sqrt{(z-R_1)^2 + 1}} + \frac{Z_2}{\sqrt{(z-R_2)^2 + 1}}\right)$$

$$+ zE(t) - (Z_1R_1 + Z_2R_2)E(t). \quad (132)$$

We now carry out a coordinate transformation and introduce new coordinates

$$R_{\text{CM}} = \frac{z + M_1R_1 + M_2R_2}{1 + M_1 + M_2}, \quad (133)$$

$$z' = z - \frac{M_1R_1 + M_2R_2}{M_1 + M_2}, \quad (134)$$

$$R = R_1 - R_2. \quad (135)$$

As in the three-dimensional case this leads to a sum of a center-of-mass Hamiltonian analogous to Eq. (110) and an internal molecular Hamiltonian that has the explicit form

$$H_{\text{mol}}(t) = -\frac{1}{2\mu_n}\frac{d^2}{dR^2} - \frac{1}{2\mu_e}\frac{d^2}{dz'^2} + \frac{Z_1Z_2}{|R|}$$

$$+ W(z',R) + (q_ez' - q_nR)E(t), \quad (136)$$

where $\mu_e = (M_1+M_2)/(M_1+M_2+1)$ and where we defined

$$W(z',R) = -\frac{Z_1}{\sqrt{\left(z' - \dfrac{M_2}{M_1 + M_2}R\right)^2 + 1}}$$

$$-\frac{Z_2}{\sqrt{\left(z' + \dfrac{M_1}{M_1 + M_2}R\right)^2 + 1}}. \quad (137)$$

The Hamiltonian of Eq. (136) is a one-dimensional simplification of the Hamiltonian equation (111) of the diatomic molecule for the case that we have only one electron. In one dimension $T_C = 0$, and T_{MP} simply leads to a reduced effective mass for the electron. In the one-dimensional model the true Coulombic interaction is replaced by soft-Coulomb interaction [42]. The main reason that we study this model system is that for this system the time-dependent Schrödinger equation can be solved numerically, yielding $\Psi(z',R,t)$ to any desired accuracy. We are therefore able to produce benchmark results to which our approximate density functional results can be compared. We obtain the ground state $\Psi_0(z',R)$ that we will use as initial state $\Psi(z',R,t_0)$ using the imaginary time propagation technique. Using the same technique we also obtain the ground state for the Kohn-Sham system $\Psi_{S,0}(z',R) = \varphi_0(z')\chi_0(R)$. By solving the time-dependent Schrödinger and Kohn-Sham equations we obtain the time-dependent densities. In the following we will calculate the induced dipole moment

$$D_{\text{mol}}(t) = \int dR\,dz'\,(q_n R - q_e z')|\Psi(z',R,t)|^2$$

$$= q_n \int dR\,R\,N(R,t) - q_e \int dz'\,z'\,n(z',t) \quad (138)$$

for a weak applied field $E(t) = E\delta(t - t_0)$, i.e., within the linear response regime. In this expression $n(z',t)$ is the electron density and $N(R,t)$ the nuclear density. For this one-dimensional case there are no exchange-correlation contributions to the dipole moment, so we can directly compare the results obtained from the exact solution with the one obtained using the density functional approach. It should be noted that the total dipole moment also involves a term that couples to the total center of mass of the molecule, i.e., $\hat{D}_{\text{CM}} = Q_{\text{tot}}R_{\text{CM}}$. However, for investigating the internal excitations of the molecule this term is not important. From the dipole moment we can obtain the absorption spectrum by taking the Fourier transform of $D_{\text{mol}}(t)$, i.e., $\text{Im}\,\alpha(\omega) = \text{Im}\{D_{\text{mol}}(\omega)/E\}$.

In order to understand which peaks will appear in the spectrum we will analyze the dipole matrix elements

$$D_{i0} = \int dR\,dz'\,(q_n R - q_e z')\Psi_i^*(z',R)\Psi_0(z',R), \quad (139)$$

where $\Psi_i(z',R)$ are the eigenstates of Hamiltonian equation (136) in the absence of the applied field. We will consider the cases of the H_2^+ and HD^+ molecules where we note that for H_2^+ the constant q_n in Eq. (138) is identically zero, whereas for HD^+ we have that $q_n = \pm\frac{1}{3}$ (sign depending on the relative

position of the heavy and light mass with respect to the applied field). Moreover, for the H_2^+ system the unperturbed Hamiltonian is invariant under the transformation $z' \to -z'$ and $R \to -R$. This means that the eigenstates will have either even or odd parity under these transformations, i.e., $\Psi_i(z',R) = \pm\Psi_i(R,-z')$ and $\Psi_i(z',R) = \pm\Psi_i(-z',R)$. Since the ground state has even parity with respect to both inversions, the transition dipole moment

$$d_{i0}^{H_2^+} = -q_e \int dR\,dz'\,z'\,\Psi_i^*(z',R)\Psi_0(z',R) \quad (140)$$

is only nonvanishing for the transitions to states that have even parity with respect to the nuclear coordinate and odd parity with respect to the electronic coordinate. Since in H_2^+ there are no bound states with odd electronic parity up to the dissociation energy, we expect no peaks in the absorption spectrum up to the ionization energy and a broad continuum above this energy. For HD^+ on the other hand, there are no special selection rules and therefore transitions from the ground state to all possible eigenstates can give a contribution to the dipole moment. In particular, we expect that in HD^+ there will be transitions that within a Born-Oppenheimer picture would correspond to vibrational excitations in the lowest Born-Oppenheimer potential (and correspond to transitions between states of even electronic parity). For HD^+ the spectrum will then consist at low energies of a few vibrational peaks below the dissociation threshold. These features are indeed observed in the calculated absorption spectra that we will discuss later. Let us now consider the same system within a density functional approach. The Kohn-Sham equations of the system are then given for the electronic subsystem by (for notational convenience we will replace z' by z from now on)

$$0 = \left(i\partial_t + \frac{1}{2\mu_e}\frac{d^2}{dz^2} - v_S(z,t)\right)\varphi(z,t),$$

$$v_S(z,t) = q_e E(t)z + \int dR\,N(R,t)W(z,R) + v_c[n,N](z,t),$$
$$(141)$$

and similarly for the nuclear subsystem by

$$0 = \left(i\partial_t + \frac{1}{2\mu_n}\frac{d^2}{dR^2} - V_S(R,t)\right)\chi(R,t),$$

$$V_S(R,t) = -q_n E(t)R + \frac{Z_1 Z_2}{|R|} + \int dz\,n(z,t)W(z,R)$$

$$+ V_c[n,N](R,t), \quad (142)$$

where $n(z,t) = |\varphi(z,t)|^2$ and $N(R,t) = |\chi(R,t)|^2$. We used here that in the one-electron system the exchange contribution to the electronic Kohn-Sham potential exactly compensates the Hartree contribution involving the electron density. The main difficulty is now in finding appropriate approximations for the correlation potentials v_c and V_c. As a first step we will take the simplest approximation in which we take $v_c = V_c = 0$. This approximation we will denote as the Hartree ap-

proximation because identical equations are obtained by requiring the wave function action [15,16,18] to be stationary for a Hartree product wave function of the form $\Psi(z',R,t) = \varphi(z',t)\chi(R,t)$ and for arbitrary variations in φ and χ. A discussion of more advanced approximations is deferred to a subsequent paper.

Let us now discuss the features that we expect in the absorption spectrum of H_2^+ and HD^+ within this Hartree approximation. For the case of H_2^+ there is no explicit driving dipole field within the nuclear Kohn-Sham equation. Therefore, for this system, the change in the nuclear potential is only caused by a change of the Hartree potential. If the induced electronic density is odd, i.e., $\delta n(z,t) = -\delta n(-z,t)$, then this first order change is zero since $W(R,z)$ is an even function of z. In that case the first order change $\delta N(R,t)$ is zero. As result the only term first order in the field in the electronic Kohn-Sham potential is the explicit dipole field itself. This field induces an odd density change $\delta n(z,t)$. From these considerations we see that in H_2^+ the Hartree density response $\delta n(z,t)$ to a dipole potential $\delta v(z,t) = zE(t)$ is equal to the bare Kohn-Sham response $\delta n = \chi_{S,ee}\delta v$. Consequently, the peaks in the absorption spectrum of H_2^+ simply correspond to Kohn-Sham eigenvalue differences. Note that this is only true for the response to a field that has odd parity $\delta v(-z,t) = -\delta v(z,t)$. For potentials with even parity the Hartree and bare Kohn-Sham response will in general differ. From this analysis we also see that no vibrational features appear in the Hartree dipole response of H_2^+. In the HD^+ system, such vibrational features will appear in the Hartree dipole response, due to the lack of inversion symmetry. Therefore in HD^+ we will in general observe a shift of the excitation energies with respect to the Kohn-Sham ones. We will investigate these shifts in more detail below using the single-pole approximation (SPA) [41].

We start by investigating the exchange-correlation kernels. Within the Hartree approximation the f_{Hxc} kernels are easily calculated to be

$$f_{Hxc,ee}(zt,z't') = 0, \tag{143}$$

$$f_{Hxc,nn}(Rt,R't') = 0, \tag{144}$$

$$f_{Hxc,en}(zt,R't') = W(z,R')\delta(t,t'), \tag{145}$$

$$f_{Hxc,ne}(Rt,z't') = W(z',R)\delta(t,t'), \tag{146}$$

where $\delta(t,t')$ is a contour δ function [37]. Since $f_{Hxc,ee} = f_{Hxc,nn} = 0$ it immediately follows from Eq. (102) that $\bar{\chi}_{nn} = \chi_{S,nn}$ and similarly that $\bar{\chi}_{ee} = \chi_{S,ee}$. If we further define

$$F_{ee}(zt,z't') = \int dRdR' W(z,R)\chi_{S,nn}(Rt,R't')W(z',R'), \tag{147}$$

$$F_{nn}(Rt,R't') = \int dzdz' W(z,R)\chi_{S,ee}(zt,z't')W(z',R'), \tag{148}$$

then we can write Eq. (100) and Eq. (104) in the form

$$\chi_{ee} = \chi_{S,ee} + \chi_{S,ee}F_{ee}\chi_{ee}, \tag{149}$$

$$\chi_{nn} = \chi_{S,nn} + \chi_{S,nn}F_{nn}\chi_{nn}. \tag{150}$$

These equations have the familiar form of standard electronic density-functional theory. We can therefore directly apply the usual equations of the single-pole approximation (in case they are valid). We start from the Lehmann representation [8,51] of the retarded form of the contour-ordered functions $\chi_{S,ee}(zt,z't')$ and $\chi_{S,nn}(Rt,R't')$ transformed to the frequency domain,

$$\chi_{S,ee}(z,z',\omega) = \sum_{kl} n_{kl} \frac{\Phi_{kl}(z)\Phi_{kl}^*(z')}{\omega_{S,kl} - \omega^+}, \tag{151}$$

$$\chi_{S,nn}(R,R',\omega) = \sum_{ij} n_{ij} \frac{X_{ij}(R)X_{ij}^*(R')}{\Omega_{S,ij} - \omega^+}, \tag{152}$$

where the Kohn-Sham excitation energies $\omega_{S,kl} = \epsilon_k - \epsilon_l$ are defined in terms of the eigenvalues $\epsilon_{k/l}$ of the electronic Kohn-Sham equation of the stationary system, the factors $n_{kl} = n_k - n_l$ in terms of the occupation numbers $n_{k/l}$, with $n_0 = 1$ and $n_{i>0} = 0$, and the excitation functions $\Phi_{kl}(z) = \varphi_k^*(z)\varphi_l(z)$ in terms of the electronic eigenfunctions $\varphi_{k/l}(z)$. Here $\omega^+ = \omega + i\eta$ with η a positive infinitesimal to ensure the causality of the response functions. Similarly we define the Kohn-Sham excitation energies $\Omega_{S,ij} = E_i - E_j$, with $E_{i/j}$ the eigenvalues of the nuclear Kohn-Sham equation, the factors $n_{ij} = n_i - n_j$ with $n_{i/j}$ the occupation numbers with $n_0 = 1$ and $n_{i>0} = 0$, and the excitation functions $X_{ij}(R) = \chi_i^*(R)\chi_j(R)$ with $\chi_{i/j}(R)$ the eigenfunctions of the nuclear Kohn-Sham equation. One readily obtains the single pole approximations for the electronic and nuclear excitation energies ω_{kl} and Ω_{ij},

$$\omega_{kl} = \omega_{S,kl} + \int dzdz' \Phi_{kl}(z)F_{ee}(z,z';\omega_{S,st})\Phi_{kl}^*(z'), \tag{153}$$

$$\Omega_{ij} = \Omega_{S,ij} + \int dRdR' X_{ij}(R)F_{nn}(R,R';\Omega_{S,ij})X_{ij}^*(R'). \tag{154}$$

In these expressions $F_{ee}(z,z';\omega)$ and $F_{nn}(R,R';\omega)$ are the retarded forms of the contour-ordered functions $F_{ee}(zt,z't')$ and $F_{nn}(Rt,R't')$, respectively, transformed to the frequency domain. If we define the coupling strengths,

$$f_{ij,kl} = \int dRdz X_{ij}(R)W(z,R)\Phi_{kl}(z), \tag{155}$$

then the single pole approximations for the excitation energies can also be written as

$$\omega_{kl} = \omega_{S,kl} + \sum_{ij} n_{ij} \frac{|f_{ij,kl}|^2}{\Omega_{S,ij} - \omega_{S,kl}}, \tag{156}$$
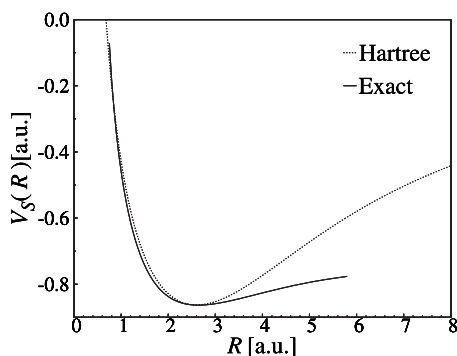
FIG. 1. The exact and Hartree approximation for the nuclear Kohn-Sham ground state potential for the one-dimensional HD⁺ model system.

$$\Omega_{ij} = \Omega_{S,ij} + \sum_{kl} n_{kl} \frac{|f_{ij,kl}|^2}{\omega_{S,kl} - \Omega_{S,ij}}. \qquad (157)$$

As the nuclear excitation energies are small compared to the electronic ones, we expect a downward correction of the lowest Kohn-Sham nuclear vibration energies.

Let us now discuss our numerical results. We start out by comparing the exact nuclear potential to that obtained from the Hartree approximation. Here the exact potential $V_{S,0}(R)$ is readily obtained from the exact ground state nuclear density $N_0(R)$ by inversion of the nuclear Kohn-Sham equation

$$V_{S,0}(R) = \frac{1}{\sqrt{N_0(R)}} \left(E_0 + \frac{1}{2\mu_n} \frac{d^2}{dR^2} \right) \sqrt{N_0(R)}, \qquad (158)$$

where E_0 is the ground state eigenvalue. This potential is depicted for the HD⁺ case in Fig. 1 together with the one obtained from the Hartree approximation. From these figures it becomes clear that the Hartree potential has an incorrect asymptotic value, leading to several bound even and odd electronic states below the dissociation limit. The cause of the wrong dissociation limit is discussed in detail in Refs. [13–15,18]. Within the Hartree approximation the conditional probability distribution $\rho(z,t|R) = |\Psi(z,R,t)|^2/N(R,t)$ of the electrons for a given nuclear separation is independent of the nuclear separation equal to $\rho(z,t|R) = n(z,t)$. When the energy is optimized one then finds a conditional electron distribution that is reasonable for the equilibrium separation but very unrealistic at large nuclear distances. This leads to highly underestimated dissociation probabilities in strong fields [15,16,18]. These deficiencies of the nuclear Hartree potential also affect the linear response properties. The Hartree potential supports more bound states than the exact potential thereby considerably influencing the shape of the absorption spectrum. Moreover the steep rise of the Hartree potential causes the curvature of the nuclear potential to be much too high compared to the exact nuclear potential, thereby causing too large separations between the lowest nuclear energy levels. We will discuss these points in more detail below.
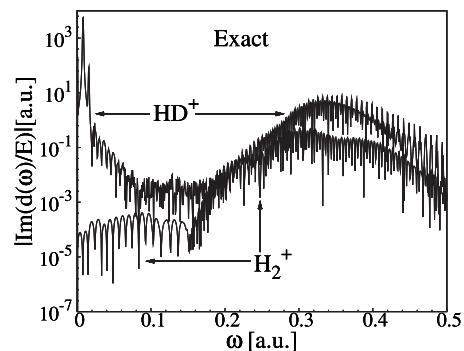

FIG. 2. The exact absorption spectra of the one-dimensional model systems H₂⁺ and HD⁺.

We next discuss the main features of the absorption spectra. We first consider the absorption spectra obtained from an exact solution of the time-dependent many-particle Schrödinger equation. These are displayed in Fig. 2 for the case of H₂⁺ and HD⁺. In the dipole response of the H₂⁺ system no low-lying excitations of vibrational character are excited (nor are they visible) due to their vanishing dipole oscillator strengths. The very low intensity peaks at low frequency are artificial and depend on numerical parameters as box size and grid spacing.

Let us now turn to the electronic excitations. We showed that only odd-parity electronic excitations can have finite oscillator strength and will coincide with the Kohn-Sham excitation energies. In Fig. 2 they form a broad continuum as these excitations lie above the dissociation limit. For the HD⁺ case parity symmetry is broken and therefore energy levels of vibrational character are clearly visible at low frequencies. For the HD⁺ system we also observe a broad continuum at larger frequencies corresponding to excitations of electronic character. As inversion symmetry is broken in this case they cannot be labeled as even and odd and will in general also be shifted as compared to the bare Kohn-Sham excitations.

Let us now see how the Hartree approximation performs. The absorption spectra obtained within the Hartree approximation are displayed in Fig. 3. Regarding the low frequency excitations we obtain a qualitatively similar picture as in the exact case. The HD⁺ system displays vibrational excitations
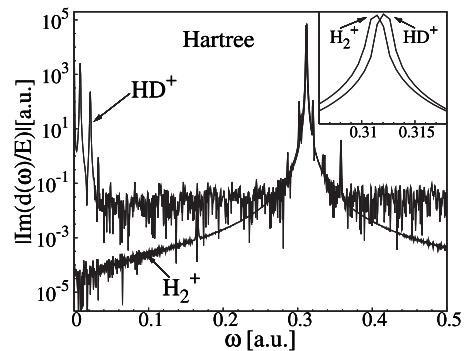

FIG. 3. The absorption spectra of the one-dimensional model systems H₂⁺ and HD⁺ in the Hartree approximation.

TABLE I. The electronic and nuclear excitation energies (in a.u.) within the Hartree approximation for the dipole response of the model H_2^+ and HD^+ molecules in comparison with the Kohn-Sham eigenvalue differences. The electronic and nuclear Kohn-Sham eigenvalues are denoted by ϵ_i and E_i. Excitations with vanishing oscillator strengths are indicated with an "*x*."

i	ϵ_i	$\omega_{S,i0}$	ω_{i0}	E_i	$\Omega_{S,i0}$	Ω_{i0}
			H_2^+ (Hartree)			
0	−1.159910			−0.856120		
1	−0.848653	0.311257	0.3113(6)	−0.843674	0.012446	x
2	−0.490887	0.669023	x	−0.831329	0.024791	x
			HD^+ (Hartree)			
0	−1.160703			−0.857083		
1	−0.848637	0.312066	0.3121(5)	−0.846180	0.010903	0.0081(8)
2	−0.490792	0.669911	0.6700(7)	−0.835375	0.021708	0.0217(3)
3				−0.824672	0.032411	0.0324(9)

whereas they are absent in the H_2^+ case. The spectrum at higher energies is quite different from the exact case. Whereas in the exact case we had a broad continuum we now observe a sharp peak. This peak represents a bound excited state of electronic character in the Hartree system. The appearance of this bound state is, as we discussed before, a consequence of the wrong shape of the nuclear potential within the Hartree approximation.

We finally discuss the excitation energies on the basis of Eqs. (155)–(157). In the H_2^+ case only excitations of odd electronic parity have nonvanishing dipole matrix elements. However, for such excitations we see immediately from Eq. (155) that $f_{ij,kl}=0$ and consequently from Eq. (156) that there will be no shift of the Kohn-Sham excitation. This is consistent with the numerical data. The position of the main peak in the Hartree absorption spectrum (see also the inset in Fig. 3) corresponds to great accuracy with the eigenvalue difference presented in Table I. Furthermore, as we discussed before, the nuclear vibrations are absent in the absorption spectrum of H_2^+.

Let us next consider the case of HD^+. In HD^+ the nuclear vibrational frequencies arises from the coupling of the lowest nuclear and second electronic excitation. We find that for the coefficients $f_{ij,kl}$ of Eq. (155) we obtain the largest contribution for the elements $f=f_{01,02}=f_{01,20}=f_{10,02}=f_{10,20}=0.022\,434$. From this we obtain the following order of magnitude estimates for the shifts

$$\omega_{20} - \omega_{S,20} \approx \frac{2|f|^2\Omega_{S,10}}{\omega_{S,20}^2 - \Omega_{S,10}^2} = 2.4 \times 10^{-5}, \qquad (159)$$

$$\Omega_{10} - \Omega_{S,10} \approx \frac{2|f|^2\omega_{S,20}}{\Omega_{S,10}^2 - \omega_{S,20}^2} = -1.5 \times 10^{-3}. \qquad (160)$$

These shifts are much bigger for the nuclear energies than for the electronic ones, and they are consistent with the numerical results obtained by time propagation of the Kohn-Sham system (see Table I). In the inset of Fig. 3 we see that the

main peak for HD^+ is shifted upward as compared to that of H_2^+. This is due to a higher Kohn-Sham eigenvalue difference in HD^+ plus the additional positive contribution that shifts the bare Kohn-Sham eigenvalue difference upwards.

Let us finally consider the vibrational levels. In Fig. 4 we compare for the HD^+ case these nuclear excitation energies obtained in the Kohn-Sham system using the Hartree approximation with those of the exact system. Only the lowest vibrational excitation energy almost coincides with the exact one, while the higher ones are at much too high energies. As can be seen from Table I, the orbital energy differences are nearly equally spaced, which reflects the nearly harmonic ground-state nuclear potential near its minimum, but with a too high separation as the curvature of this potential well is too high. As mentioned before this is related to the wrong large-R behavior of the nuclear potential in the Hartree approximation. Only the lowest vibrational excitation energy is reduced considerably due to the coupling of the electronic and nuclear subsystems, to an extent that it almost coincides with the exact one. The higher vibrational excitations are however only slightly corrected due to much smaller coupling constants in combination with their higher excitation energies. These small shifts cannot compensate for the large
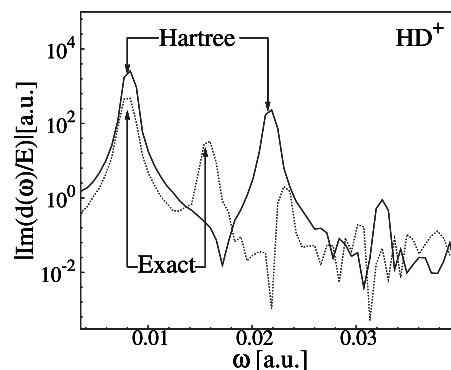

FIG. 4. The exact and Hartree nuclear excitation spectra for the one-dimensional HD^+ model system.

separation of the nuclear orbital energies, resulting in an incorrect vibrational excitation spectrum within the Hartree approximation. There is therefore a clear need to study approximations for the Kohn-Sham potentials that go beyond the simple Hartree approximation. For the ground state case several improvements were proposed [15,14]. However, they are difficult to generalize to the time-dependent situation. For the time-dependent situation an approximate correlated form of the wave function was developed and tested which greatly improved the nuclear potential as well as the dynamics [15,18]. However, the method is not strictly a density-functional scheme and it remains to be investigated if theoretical models within the same spirit can be made to fit within a density-functional approach.

V. SUMMARY AND CONCLUSION

In this paper we developed the time-dependent version of the multicomponent density-functional approach to treat electron-nuclear systems in external time-dependent fields. For this it is important to introduce a body-fixed frame in which the electron density reflects the symmetry of the internal degrees of freedom rather than those of the external potentials in the laboratory frame (which would lead to constant densities in the absence of perturbations). The nuclear particles are described by a diagonal many-body density matrix which depends on all coordinates of the nuclei. In the Kohn-Sham picture this density matrix is calculated from an equation with a time-dependent potential that depends on all nuclear coordinates. For the diatomic molecule in the stationary case this potential turns out to be very close to the familiar Born-Oppenheimer potential. However, the Kohn-Sham scheme goes far beyond the Born-Oppenheimer picture in allowing an exact quantum description of the motion of the nuclei.

As a consequence of the body-fixed frame transformation the external potential acting on the electrons, which is a one-body potential in the laboratory frame, becomes a many-body potential u with respect to the nuclear coordinates in the body-fixed frame. As a consequence the expectation value of the dipole operator, when expressed as a density functional in the terms of the electron density in the body-fixed frame and the nuclear diagonal density matrix, acquires an exchange-correlation part. For a given potential u one can establish a Runge-Gross-type theorem that guarantees the uniqueness of a one-to-one mapping between body-fixed frame densities and potentials. The functional dependence of this mapping on u leads in a linear response formulation to the appearance of two extra response functions that describe the response to potential u. We illustrated the formalism for the example of a diatomic molecule and we performed calculations on a model system for which the many-body Schrödinger equation could be solved numerically. These benchmark results were then compared to the solution of the time-dependent Kohn-Sham equations in the Hartree approximation. Furthermore, we analyzed the excitation energies obtained from the linear response formalism in the single pole approximation. We found that within the Hartree approximation the spacing in the vibrational spectrum is too large. However, the lowest vibrational level was found to be in accordance with the exact result. We found that there is a clear need for improved functionals that go beyond the simple Hartree approximation. This will be the topic of a subsequent publication.

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