6 Multicomponent Density-Functional Theory

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6.1 Introduction

The coupling between electronic and nuclear motion plays an essential role in a wide range of physical phenomena. A few important research fields in which this is the case are superconductivity in solids, quantum transport where one needs to take into account couplings between electrons and phonons, the polaronic motion in polymer chains, and the ionization-dissociation dynamics of molecules in strong laser fields. Our goal is to set up a time-dependent multicomponent density-functional theory (TDMCDFT) to provide a general framework to describe these diverse phenomena. In TDMCDFT the electrons and nuclei are treated completely quantum mechanically from the outset. The basic variables of the theory are the electron density n, which will be defined in a body-fixed frame attached to the nuclear framework, and the diagonal of the nuclear N-body density matrix Γ, which will depend on all the nuclear coordinates. The chapter is organized as follows: We start out by defining the coordinate transformations to obtain a suitable Hamiltonian for defining our densities to be used as basic variables in the theory. We then discuss the basic one-to-one correspondence between TD potentials and TD densities, and subsequently, the resulting TD Kohn-Sham equations, the action functional, and linear response theory. As an example we discuss a diatomic molecule in a strong laser field.

6.2 Fundamentals

We consider a system composed of N_e electrons with coordinates $\{r\}$ and N_n nuclei with masses $M_1 \ldots M_{N_n}$, charges $Z_1 \ldots Z_{N_n}$, and coordinates denoted by $\{R\}$. By convention, the subscripts "e" and "n" refer to electrons and nuclei, respectively, and atomic units are employed throughout this chapter. In non-relativistic quantum mechanics, the system described above is characterized by the Hamiltonian

$$\hat{H}(t) = \hat{T}_n(\{R\}) + \hat{V}_{nn}(\{R\}) + \hat{U}_{ext,\,n}(\{R\},t) + \hat{T}_e(\{r\}) + \hat{V}_{ee}(\{r\})$$
$$+ \hat{U}_{ext,\,e}(\{r\},t) + \hat{V}_{en}(\{r\},\{R\}), \quad (6.1)$$

where

$$\hat{T}_{\mathrm{n}} = -\frac{1}{2} \sum_{\alpha=1}^{N_{\mathrm{n}}} \frac{\nabla_{\alpha}^2}{M_{\alpha}} \qquad \text{and} \qquad \hat{T}_{\mathrm{e}} = -\frac{1}{2} \sum_{j=1}^{N_{\mathrm{e}}} \nabla_j^2 \tag{6.2}$$

denote the kinetic-energy operators of the nuclei and electrons, respectively,

$$\hat{V}_{\mathrm{nn}} = \frac{1}{2} \sum_{\substack{\alpha,\beta=1 \\ \alpha \neq \beta}}^{N_{\mathrm{n}}} \frac{Z_{\alpha} Z_{\beta}}{|\boldsymbol{R}_{\alpha} - \boldsymbol{R}_{\beta}|} \,, \qquad \hat{V}_{\mathrm{ee}} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N_{\mathrm{e}}} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \,, \tag{6.3}$$

and

$$\hat{V}_{\mathrm{en}} = -\sum_{j=1}^{N_{\mathrm{e}}} \sum_{\alpha=1}^{N_{\mathrm{n}}} \frac{Z_{\alpha}}{|\boldsymbol{r}_j - \boldsymbol{R}_{\alpha}|} \tag{6.4}$$

represent the interparticle Coulomb interactions. Truly external potentials representing, e.g., a laser pulse applied to the system, are contained in

$$\hat{U}_{\mathrm{ext,\,n}}(t) = \sum_{\alpha=1}^{N_{\mathrm{n}}} u_{\mathrm{ext,\,n}}(\boldsymbol{R}_{\alpha}, t) \tag{6.5a}$$

$$\hat{U}_{\mathrm{ext,\,e}}(t) = \sum_{j=1}^{N_{\mathrm{e}}} u_{\mathrm{ext,\,e}}(\boldsymbol{r}_j, t) \,. \tag{6.5b}$$

Defining electronic and nuclear single-particle densities conjugated to the true external potentials (6.5a) and (6.5b), a multicomponent density-functional theory (MCDFT) formalism can readily be formulated on the basis of the above Hamiltonian [Capitani 1982, Gidopoulos 1998]. However, as discussed in [Kreibich 2000, Kreibich 2001a, Kreibich 2005], such a MCDFT is not useful in practice because the single-particle densities necessarily reflect the symmetry of the true external potentials and are therefore not characteristic of the internal properties of the system. In particular, for all isolated systems where the external potentials (6.5a) and (6.5b) vanish, these densities are constant, as a consequence of the translational invariance of the respective Hamiltonian. A suitable MCDFT is obtained by defining the densities with respect to internal coordinates of the system [Kreibich 2001a, van Leeuwen 2004b]. To this end, new electronic coordinates are introduced according to

$$\boldsymbol{r}_j' = \mathcal{R}(\alpha, \beta, \gamma) \ (\boldsymbol{r}_j - \boldsymbol{R}_{\mathrm{CMN}}) \qquad j = 1 \ldots N_{\mathrm{e}} \,, \tag{6.6}$$

where the nuclear center-of-mass is defined as

$$\boldsymbol{R}_{\mathrm{CMN}} := \frac{1}{M_{\mathrm{nuc}}} \sum_{\alpha=1}^{N_{\mathrm{n}}} M_{\alpha} \boldsymbol{R}_{\alpha} \,, \quad \text{where} \quad M_{\mathrm{nuc}} = \sum_{\alpha=1}^{N_{\mathrm{n}}} M_{\alpha} \,. \tag{6.7}$$

The quantity $\mathcal{R}$ is a three-dimensional orthogonal matrix representing the Euler rotations. The Euler angles (α, β, γ) are functions of the nuclear coordinates $\{\boldsymbol{R}\}$ and specify the orientation of the body-fixed coordinate frame.

They can be determined in various ways. One way is by requiring the inertial tensor of the nuclei to be diagonal in the body-fixed frame. The conditions that the off-diagonal elements of the inertia tensor are zero in terms of the rotated coordinates $\mathcal{R}(\boldsymbol{R}_\alpha - \boldsymbol{R}_{\mathrm{CMN}})$ then give three determining equations for the three Euler angles in terms of the nuclear coordinates $\{\boldsymbol{R}\}$ [Villars 1970]. A common alternative to determine the orientation of the body-fixed system is provided by the so-called Eckart conditions [Eckart 1935, Louck 1976, Bunker 1998] (for recent reviews see [Sutcliffe 2000, Meyer 2002]) which are suitable to describe small vibrations in molecules and phonons in solids [van Leeuwen 2004b]. A general and very elegant discussion on the various ways the body-fixed frame can be chosen is given in reference [Littlejohn 1997] . In this work we will not make a specific choice, as our derivations are independent of such choice. The most important point is that, by virtue of (6.6), the electronic coordinates are defined with respect to a coordinate frame that is attached to the nuclear framework and rotates as the nuclear framework rotates. The nuclear coordinates themselves are not transformed any further at this point, i.e.,

$$\boldsymbol{R}'_\alpha = \boldsymbol{R}_\alpha \qquad \alpha = 1 \dots N_{\mathrm{n}}. \tag{6.8}$$

Of course, introducing internal nuclear coordinates is also desirable. However, the choice of such coordinates depends strongly on the specific situation to be described: If near-equilibrium situations in systems with well-defined geometries are considered, normal or – for a solid – phonon coordinates are most appropriate, whereas fragmentation processes of molecules are better described in terms of Jacobi coordinates [Meyer 2002, Schinke 1993]. Therefore, to keep a high degree of flexibility, the nuclear coordinates are left unchanged for the time being and are transformed to internal coordinates only prior to actual applications of the final equations that we will derive.

As a result of the coordinate changes of (6.6), the Hamiltonian (6.1) transforms into

$$\hat{H}(t) = \hat{T}_{\mathrm{n}}(\{\boldsymbol{R}\}) + \hat{V}_{\mathrm{nn}}(\{\boldsymbol{R}\}) + \hat{U}_{\mathrm{ext,\,n}}(\{\boldsymbol{R}\}, t) + \hat{T}_{\mathrm{e}}(\{\boldsymbol{r}'\}) + \hat{V}_{\mathrm{ee}}(\{\boldsymbol{r}'\})$$
$$+ \hat{T}_{\mathrm{MPC}}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}) + \hat{V}_{\mathrm{en}}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}) + \hat{U}_{\mathrm{ext,\,e}}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}, t). \tag{6.9}$$

Since we transformed to a noninertial coordinate frame a mass-polarization and Coriolis (MPC) term

$$\hat{T}_{\mathrm{MPC}} := \sum_{\alpha=1}^{N_{\mathrm{n}}} -\frac{1}{2M_\alpha} \left[\nabla_{\boldsymbol{R}_\alpha} + \sum_{j=1}^{N_{\mathrm{e}}} \frac{\partial \boldsymbol{r}'_j}{\partial \boldsymbol{R}_\alpha} \nabla_{\boldsymbol{r}'_j} \right]^2 - \hat{T}_{\mathrm{n}}(\{\boldsymbol{R}\}) \tag{6.10}$$

appears. Obviously, this MPC term is not symmetric in the electronic and nuclear coordinates. However, this was not expected since only the electrons refer to a noninertial coordinate frame, whereas the nuclei are still defined

with respect to the inertial frame. Therefore, all MPC terms arise solely from the electronic coordinates, representing fictious forces due to the electronic motion in noninertial systems (for a detailed form of these terms within the current coordinate transformation see [van Leeuwen 2004b]). The kinetic-energy operators $\hat{T}_n$ and $\hat{T}_e$, the electron-electron and nuclear-nuclear interactions, as well as the true external potential $\hat{U}_{ext,\,n}$ acting on the nuclei are formally unchanged in (6.9) and therefore given by (6.2) and (6.3) with the new coordinates replacing the old ones, whereas the electron-nuclear interaction now reads

$$\hat{V}_{en}(\{r'\}, \{R\}) = -\sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|r'_j - \mathcal{R}(\alpha, \beta, \gamma)(R_\alpha - R_{CMN})|} \,. \qquad (6.11)$$

The quantity

$$R''_\alpha = \mathcal{R}(\alpha, \beta, \gamma)(R_\alpha - R_{CMN}) \qquad (6.12)$$

that appears in (6.11) is a so-called shape coordinate [Littlejohn 1997, van Leeuwen 2004b], i.e., it is invariant under rotations and translations of the nuclear framework. This is, of course, precisely the purpose of introducing a body-fixed frame: The attractive nuclear Coulomb potential (6.11) that the electrons in the body-fixed frame experience is invariant under rotations or translations of the nuclear framework. As a further consequence of the coordinate transformation (6.6), the true external potential acting on the electrons now not only depends on the electronic coordinates, but also on all the nuclear coordinates:

$$\hat{U}_{ext,\,e}(\{r'\}, \{R\}, t) = \sum_{j=1}^{N_e} u_{ext,\,e}(\mathcal{R}^{-1} r'_j + R_{CMN}, t) \,. \qquad (6.13)$$

Therefore, in the chosen coordinate system, the electronic external potential is not a one-body operator anymore, but acts as an effective interaction. Consequences of this fact are discussed later.

6.2.1 Definition of the Densities

As already mentioned above, it is not useful to define electronic and nuclear single-particle densities in terms of the inertial coordinates r and R, since such densities necessarily reflect the symmetry of the corresponding true external potentials, e.g., they are constant for vanishing external potentials. Instead, we use the diagonal of the nuclear N_n-body density matrix

$$\Gamma(\{R\}, t) = \sum_{\{s\}, \{\sigma\}} \int d^3 r'_1 \cdots \int d^3 r'_{N_e} \left| \Psi_{\{s\}\{\sigma\}}(\{R\}, \{r'\}, t) \right|^2 , \qquad (6.14)$$

and the electronic single-particle density referring to the body-fixed frame:

$$n(\boldsymbol{r}',t) = N_\mathrm{e} \sum_{\{s\},\{\sigma\}} \int \mathrm{d}^3 R_1' \cdots \int \mathrm{d}^3 R_{N_\mathrm{n}}' \int \mathrm{d}^3 r_1' \cdots \int \mathrm{d}^3 r_{N_\mathrm{e}-1}'$$

$$\left| \Psi_{\{s\}\{\sigma\}}(\{\boldsymbol{R}\}, \{\boldsymbol{r}'\}, t) \right|^2 . \quad (6.15)$$

Here $\Psi_{\{s\}\{\sigma\}}(\{\boldsymbol{R}\}, \{\boldsymbol{r}'\}, t)$ represents the full solution of the TD Schrödinger equation with the Hamiltonian (6.9). The quantities $\{s\}$ and $\{\sigma\}$ denote the nuclear and electronic spin coordinates. The electronic density (6.15) represents a conditional density. It is proportional to the probability density of finding an electron at postion $\boldsymbol{r}'$ as measured from the nuclear center-of-mass, given a certain orientation of the nuclear framework. Therefore the electronic density calculated through (6.15) reflects the internal symmetries of the system, e.g., the cylindrical symmetry of a diatomic molecule, instead of the Galilean symmetry of the underlying space.

6.3 The Runge-Gross Theorem for Multicomponent Systems

In order to set up a density-functional framework, our next task is to prove the analogue of the Runge-Gross theorem [Runge 1984] for multicomponent systems. To this end, we slightly modify the Hamiltonian (6.9) to take the form

$$\hat{H}(t) = \hat{T}_\mathrm{n}(\{\boldsymbol{R}\}) + \hat{V}_\mathrm{nn}(\{\boldsymbol{R}\}) + \hat{T}_\mathrm{e}(\{\boldsymbol{r}'\}) + \hat{V}_\mathrm{ee}(\{\boldsymbol{r}'\}) + \hat{T}_\mathrm{MPC}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\})$$
$$+ \hat{V}_\mathrm{en}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}) + \hat{U}_\mathrm{ext,\,e}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}, t) + \hat{V}_\mathrm{ext,\,n}(\{\boldsymbol{R}\}, t) + \hat{V}_\mathrm{ext,\,e}(\{\boldsymbol{r}'\}, t).$$
$$(6.16)$$

The potentials $\hat{V}_\mathrm{ext,\,n}(\{\boldsymbol{R}\}, t)$ and $\hat{V}_\mathrm{ext,\,e}(\{\boldsymbol{r}'\}, t)$, given by

$$\hat{V}_\mathrm{ext,\,n}(\{\boldsymbol{R}\}, t) = v_\mathrm{ext,\,n}(\{\boldsymbol{R}\}, t) \quad \text{and} \quad \hat{V}_\mathrm{ext,\,e}(\{\boldsymbol{r}'\}, t) = \sum_{j=1}^{N_\mathrm{e}} v_\mathrm{ext,\,e}(\boldsymbol{r}_j', t) ,$$
$$(6.17)$$

are potentials conjugate to the densities $\Gamma(\{\boldsymbol{R}\}, t)$ and $n(\{\boldsymbol{r}'\}, t)$ and are introduced to provide the necessary mappings between potentials and densities. In the special case $\hat{V}_\mathrm{ext,\,n}(\{\boldsymbol{R}\}, t) = \hat{U}_\mathrm{ext,\,n}(\{\boldsymbol{R}\}, t)$ and $\hat{V}_\mathrm{ext,\,e}(\{\boldsymbol{r}'\}, t) = 0$, the external potentials reduce to those of the Hamiltonian (6.9). It is important to note that the potential $\hat{U}_\mathrm{ext,\,e}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}, t)$ depends on both the electronic and nuclear coordinates and is therefore treated as a fixed many-body term in Hamiltonian (6.16). The mass-polarization and Coriolis terms in $\hat{T}_\mathrm{MPC}$ are complicated many-body operators. They are treated here as additional electron-nuclear interactions which ultimately enter the exchange-correlation functional. For Hamiltonians of the form (6.16) we can apply the proof of the basic $1-1$ correspondence along the same lines as Li and Tong [Li 1986]. Two

sets of densities $\{\Gamma(\{\boldsymbol{R}\}, t), n(\boldsymbol{r}', t)\}$ and $\{\Gamma'(\{\boldsymbol{R}\}, t), n'(\boldsymbol{r}', t)\}$, which evolve from a common initial state Ψ_0 at $t = t_0$ under the influence of two sets of potentials $\{v_{\text{ext, n}}(\{\boldsymbol{R}\}, t), v_{\text{ext, e}}(\boldsymbol{r}', t)\}$ and $\{v'_{\text{ext, n}}(\{\boldsymbol{R}\}, t), v'_{\text{ext, e}}(\boldsymbol{r}', t)\}$ always become different infinitesimally after t_0 provided that at least one component of the potentials differs by more than a purely time-dependent function:

$$v_{\text{ext, n}}(\{\boldsymbol{R}\}, t) \neq v'_{\text{ext, n}}(\{\boldsymbol{R}\}, t) + C(t) \quad \text{or} \quad v_{\text{ext, e}}(\boldsymbol{r}', t) \neq v'_{\text{ext, e}}(\boldsymbol{r}', t) + C(t) \tag{6.18}$$

Consequently a one-to-one mapping between time-dependent densities and external potentials,

$$\{v_{\text{ext, n}}(\{\boldsymbol{R}\}, t), v_{\text{ext, e}}(\boldsymbol{r}', t)\} \leftrightarrow \{\Gamma(\{\boldsymbol{R}\}, t), n(\boldsymbol{r}', t)\} \tag{6.19}$$

is established for a given initial state Ψ_0. We again stress that since the external potential acting on the electrons $\hat{U}_{\text{ext, e}}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}, t)$ in the body-fixed frame attains the form of an electron-nuclear interaction, the $1 - 1$ mapping is still functionally dependent on $u_{\text{ext, e}}(\boldsymbol{r}', \{\boldsymbol{R}\}, t)$.

6.4 The Kohn-Sham Scheme for Multicomponent Systems

On the basis of the multi-component Runge-Gross (MCRG) theorem we can set up the Kohn-Sham equations. For this we consider an auxiliary system with Hamiltonian

$$\hat{H}_{\text{KS}}(t) = \hat{T}_{\text{n}}(\{\boldsymbol{R}\}) + \hat{T}_{\text{e}}(\{\boldsymbol{r}'\}) + \hat{V}_{\text{KS, n}}(\{\boldsymbol{R}\}, t) + \hat{V}_{\text{KS, e}}(\{\boldsymbol{r}'\}, t) , \tag{6.20}$$

where we introduced the potentials

$$\hat{V}_{\text{KS, n}}(\{\boldsymbol{R}\}, t) = v_{\text{KS, n}}(\{\boldsymbol{R}\}, t) \quad \text{and} \quad \hat{V}_{\text{KS, e}}(\{\boldsymbol{r}'\}, t) = \sum_{j=1}^{N_{\text{e}}} v_{\text{KS, e}}(\boldsymbol{r}'_j, t) . \tag{6.21}$$

This represents a system in which the interelectronic interaction as well as the interaction between the nuclei and the electrons has been switched off. According to the MCRG theorem there is at most one set of potentials $\{\hat{V}_{\text{KS, n}}(\{\boldsymbol{R}\}, t), \hat{V}_{\text{KS, e}}(\{\boldsymbol{r}'\}, t)\}$ (up to a purely time-dependent function) that reproduces a given set of densities $\{\Gamma(\{\boldsymbol{R}\}, t), n(\boldsymbol{r}', t)\}$. The potentials determined in this way are therefore functionals of the densities n and Γ and will henceforth be denoted as the Kohn-Sham potentials for the multicomponent system. The corresponding Hamiltonian of (6.20) will be denoted as the multicomponent Kohn-Sham Hamiltonian. In the Kohn-Sham Hamiltonian the electronic and nuclear motion have become separated. If we therefore choose the initial Kohn-Sham wavefunction $\Phi_{\text{KS, 0}}$ to be a product

of a nuclear and an electronic wavefunction then the time-dependent Kohn-Sham wavefunction will also be such a product, i.e.,

$$\Phi_{KS,\,\{s\}\{\sigma\}}(\{\boldsymbol{R}\},\{\boldsymbol{r}'\},t) = \Phi_{\mathrm{e},\,\{\sigma\}}(\{\boldsymbol{r}'\},t)\,\Phi_{\mathrm{n},\,\{s\}}(\{\boldsymbol{R}\},t) \tag{6.22}$$

and the corresponding densities are given by

$$\Gamma(\{\boldsymbol{R}\},t) = \sum_{\{s\}} \left|\Phi_{\mathrm{n},\,\{s\}}(\{\boldsymbol{R}\},t)\right|^2 \tag{6.23a}$$

$$n(\boldsymbol{r}',t) = N_{\mathrm{e}} \sum_{\{\sigma\}} \int \mathrm{d}^3 r_1' \cdots \int \mathrm{d}^3 r_{N_{\mathrm{e}}-1}' \left|\Phi_{\mathrm{e},\,\{\sigma\}}(\{\boldsymbol{r}'\},t)\right|^2. \tag{6.23b}$$

The electronic and nuclear Kohn-Sham wavefunctions satisfy the equations

$$\left\{ \mathrm{i}\frac{\partial}{\partial t} - \hat{T}_{\mathrm{n}}(\{\boldsymbol{R}\}) - \hat{V}_{\mathrm{KS,\,n}}[n,\Gamma](\{\boldsymbol{R}\},t) \right\} \Phi_{\mathrm{n},\,\{s\}}(\{\boldsymbol{R}\},t) = 0 \tag{6.24a}$$

$$\left\{ \mathrm{i}\frac{\partial}{\partial t} - \hat{T}_{\mathrm{e}}(\{\boldsymbol{r}'\}) - \hat{V}_{\mathrm{KS,\,e}}[n,\Gamma](\{\boldsymbol{r}'\},t) \right\} \Phi_{\mathrm{e},\,\{\sigma\}}(\{\boldsymbol{r}'\},t) = 0\,. \tag{6.24b}$$

Note that the potential $\hat{V}_{\mathrm{KS,\,n}}$ in the nuclear Kohn-Sham equation (6.24a) is an N_{n}-body interaction, whereas the electronic Kohn-Sham potential $\hat{V}_{\mathrm{KS,\,e}}$ is a one-body operator. Hence, by choosing the initial electronic Kohn-Sham wavefunction as a Slater determinant consisting of orbitals φ_j , the electronic Kohn-Sham (6.24b) attains the usual form

$$\left\{ \mathrm{i}\frac{\partial}{\partial t} - \left[-\frac{1}{2}\nabla'^2 + v_{\mathrm{KS,\,e}}[n,\Gamma](\boldsymbol{r}',t) \right] \right\} \varphi_j(\boldsymbol{r}',t) = 0 \tag{6.25a}$$

$$n(\boldsymbol{r}',t) = \sum_{j}^{N_{\mathrm{e}}} |\varphi_j(\boldsymbol{r}',t)|^2\,. \tag{6.25b}$$

The nuclear (6.23a) and (6.24a), together with the electronic (6.25a) and (6.25b), provide a formally exact scheme to calculate the electronic density n and N_{n}-body nuclear density Γ. For practical applications it remains to obtain good approximations for the potentials $v_{\mathrm{KS,\,n}}[n,\Gamma]$ and $v_{\mathrm{KS,\,e}}[n,\Gamma]$. More insight into this question is obtained from the multicomponent action functional to be discussed in the next paragraph.

6.5 The Multicomponent Action

We start by defining a multicomponent action functional

$$\tilde{A}[v_{\mathrm{ext,\,e}}, v_{\mathrm{ext,\,n}}] = \mathrm{i}\ln\langle\Psi_0|\hat{\mathcal{T}}_{\mathrm{C}}\exp\left\{-\mathrm{i}\int_C \mathrm{d}t\,\hat{H}(t)\right\}|\Psi_0\rangle \tag{6.26}$$

The Hamiltonian in this expression is the one of (6.16). Furthermore Ψ_0 is the initial state of the system and $\hat{\mathcal{T}}_C$ denotes time-ordering along the Keldysh time contour C running along the real time-axis from t_0 to t and back to t_0. The time-dependent potentials $v_{\mathrm{ext,\,e}}$ and $v_{\mathrm{ext,\,n}}$ are correspondingly defined on this contour. The case discussed here is for an initial pure state. In case the initial system is in thermodynamic equilibrium the expectation value with respect to Ψ_0 can be replaced by a thermodynamic trace and the contour can be extended to include a final vertical stretch running from t_0 to $t_0 - \mathrm{i}\beta$, where β is the inverse temperature of the initial ensemble. In that case the functional is closely related to the grand potential as is extensively discussed in Chap. 3. The main property of the action (6.26) which is important for multicomponent density-functional theory is that

$$\frac{\delta\tilde{A}}{\delta v_{\mathrm{ext,\,e}}(\boldsymbol{r},t)} = n(\boldsymbol{r},t) \quad \text{and} \quad \frac{\delta\tilde{A}}{\delta v_{\mathrm{ext,\,n}}(\{\boldsymbol{R}\},t)} = \Gamma(\{\boldsymbol{R}\},t)\,. \qquad (6.27)$$

(From now on, for ease of notation, we will remove the prime from the electronic coordinate.) We now do a Legendre transform to obtain a functional of n and Γ and we define

$$A[n,\Gamma] = -\tilde{A}[v_{\mathrm{ext,\,e}},v_{\mathrm{ext,\,n}}] + \int_C \mathrm{d}t \int \mathrm{d}^3r\, n(\boldsymbol{r},t)\, v_{\mathrm{ext,\,e}}(\boldsymbol{r},t)$$
$$+ \int_C \mathrm{d}t \int \mathrm{d}^3R_1 \cdots \int \mathrm{d}^3R_{N_\mathrm{n}}\, \Gamma(\{\boldsymbol{R}\},t)\, v_{\mathrm{ext,\,n}}(\{\boldsymbol{R}\},t)\,, \quad (6.28)$$

where in this equation $v_{\mathrm{ext,\,e}}$ and $v_{\mathrm{ext,\,n}}$ (by virtue of the MCRG theorem) are now regarded as functionals of n and Γ. From the chain rule of differentiation we then easily obtain

$$\frac{\delta A}{\delta n(\boldsymbol{r},t)} = v_{\mathrm{ext,\,e}}(\boldsymbol{r},t) \quad \text{and} \quad \frac{\delta A}{\delta\Gamma(\{\boldsymbol{R}\},t)} = v_{\mathrm{ext,\,n}}(\{\boldsymbol{R}\},t)\,. \qquad (6.29)$$

For the Hamiltonian $\hat{H}_{\mathrm{KS}}(t)$ of (6.20) we can now further define an action functional analogous to (6.26)

$$\tilde{A}_{\mathrm{KS}}[v_{\mathrm{KS,\,e}},v_{\mathrm{KS,\,n}}] = \mathrm{i}\ln\langle\Phi_0|\hat{\mathcal{T}}_C \exp\left\{-\mathrm{i}\int_C \mathrm{d}t\,\hat{H}_{\mathrm{KS}}(t)\right\}|\Phi_0\rangle \qquad (6.30)$$

where Φ_0 is the initial state of the auxiliary system. By a Legendre transform we then obtain the functional $A_{\mathrm{KS}}[n,\Gamma]$. With $A[n,\Gamma]$ and $A_{\mathrm{KS}}[n,\Gamma]$ well-defined we now can define the exchange-correlation part $A_{\mathrm{xc}}[n,\Gamma]$ of the action through the equation

$$A[n, \Gamma] = A_{\mathrm{KS}}[n, \Gamma] - \frac{1}{2} \int_C \mathrm{d}t \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, v_{\mathrm{ee}}(\boldsymbol{r}_1, \boldsymbol{r}_2) n(\boldsymbol{r}_1, t) n(\boldsymbol{r}_2, t)$$

$$- \int_C \mathrm{d}t \int \mathrm{d}^3 r \int \mathrm{d}^3 R_1 \cdots \int \mathrm{d}^3 R_{N_{\mathrm{n}}} \, [v_{\mathrm{en}}(\boldsymbol{r}, \{\boldsymbol{R}\})$$

$$+ \, u_{\mathrm{ext, \, e}}(\boldsymbol{r}, \{\boldsymbol{R}\}, t)] \, n(\boldsymbol{r}, t) \Gamma(\{\boldsymbol{R}\}, t)$$

$$- \int_C \mathrm{d}t \int \mathrm{d}^3 R_1 \cdots \int \mathrm{d}^3 R_{N_{\mathrm{n}}} \, v_{\mathrm{nn}}(\{\boldsymbol{R}\}) \Gamma(\{\boldsymbol{R}\}, t) - A_{\mathrm{xc}}[n, \Gamma] \,, \quad (6.31)$$

where we subtracted the Hartree-like parts of the electron-electron and electron-nuclear interaction and the internuclear repulsion, using the definitions

$$v_{\mathrm{en}}(\boldsymbol{r}, \{\boldsymbol{R}\}) = - \sum_{\alpha=1}^{N_{\mathrm{n}}} \frac{Z_\alpha}{|\boldsymbol{r} - \mathcal{R}(\boldsymbol{R} - \boldsymbol{R}_{\mathrm{CMN}})|} \tag{6.32a}$$

$$u_{\mathrm{ext, \, e}}(\boldsymbol{r}, \{\boldsymbol{R}\}, t) = u_{\mathrm{ext, \, e}}(\mathcal{R}^{-1}\boldsymbol{r} + \boldsymbol{R}_{\mathrm{CMN}}, t) \,. \tag{6.32b}$$

These Hartree terms are treated separately because they are expected to be the dominant potential-energy contributions whereas the remainder, $A_{\mathrm{xc}}[n, \Gamma]$, is expected to be smaller. No such dominant contributions arise from the mass-polarization and Coriolis terms which are usually rather small. The contributions coming from $\hat{T}_{\mathrm{MPC}}$ are therefore completely retained in $A_{\mathrm{xc}}[n, \Gamma]$. Differentiation of (6.31) with respect to n and Γ then yields

$$v_{\mathrm{KS, \, e}}(\boldsymbol{r}, t) = v_{\mathrm{ext, \, e}}(\boldsymbol{r}, t) + \int \mathrm{d}^3 r' \, v_{\mathrm{ee}}(\boldsymbol{r}, \boldsymbol{r}') n(\boldsymbol{r}', t)$$

$$+ \int \mathrm{d}^3 R_1 \cdots \int \mathrm{d}^3 R_{N_{\mathrm{n}}} \, [v_{\mathrm{en}}(\boldsymbol{r}, \{\boldsymbol{R}\})$$

$$+ \, u_{\mathrm{ext, \, e}}(\boldsymbol{r}, \{\boldsymbol{R}\}, t)] \, \Gamma(\{\boldsymbol{R}\}, t) + v_{\mathrm{xc, \, e}}(\boldsymbol{r}, t) \,, \quad (6.33)$$

and

$$v_{\mathrm{KS, \, n}}(\{\boldsymbol{R}\}, t) = v_{\mathrm{ext, \, n}}(\{\boldsymbol{R}\}, t) + v_{\mathrm{nn}}(\{\boldsymbol{R}\})$$

$$+ \int \mathrm{d}^3 r \, [v_{\mathrm{en}}(\boldsymbol{r}, \{\boldsymbol{R}\}) + u_{\mathrm{ext, \, e}}(\boldsymbol{r}, \{\boldsymbol{R}\}, t)] \, n(\boldsymbol{r}, t) + v_{\mathrm{xc, \, n}}(\{\boldsymbol{R}\}, t) \,, \quad (6.34)$$

where we have defined the electronic and nuclear exchange-correlation potentials as

$$v_{\mathrm{xc, \, e}}(\boldsymbol{r}, t) = \frac{\delta A_{\mathrm{xc}}[n, \Gamma]}{\delta n(\boldsymbol{r}, t)} \quad \text{and} \quad v_{\mathrm{xc, \, n}}(\{\boldsymbol{R}\}, t) = \frac{\delta A_{\mathrm{xc}}[n, \Gamma]}{\delta \Gamma(\{\boldsymbol{R}\}, t)} \,. \tag{6.35}$$

The main question is now how to obtain explicit functionals for the exchange-correlation potentials. One of the most promising ways of obtaining these may be the development of orbital functionals as in the OEP approach. Such functionals can be deduced by a diagrammatic expansion of the action functionals.

6.6 Linear Response and Multicomponent Systems

We will now consider the important case of linear response in the multicomponent formalism. Such approach will, for instance, be very useful in the weak field problems such as the electron-phonon coupling in solids. For convenience we first introduce the notation $i = (\boldsymbol{r}_i, t_i)$ and $\underline{i} = (\{\boldsymbol{R}\}, t_i)$. Let us then define the set of response functions:

$$\boldsymbol{\chi}_{12} = \begin{pmatrix} \chi_{\mathrm{ee}}(1,2) & \chi_{\mathrm{en}}(1,\underline{2}) \\ \chi_{\mathrm{ne}}(\underline{1},2) & \chi_{\mathrm{nn}}(\underline{1},\underline{2}) \end{pmatrix} = \begin{pmatrix} \frac{\delta n(1)}{\delta v_{\mathrm{e}}(2)} & \frac{\delta n(1)}{\delta v_{\mathrm{n}}(\underline{2})} \\ \frac{\delta \Gamma(\underline{1})}{\delta v_{\mathrm{e}}(2)} & \frac{\delta \Gamma(\underline{1})}{\delta v_{\mathrm{n}}(\underline{2})} \end{pmatrix} . \tag{6.36}$$

Similarly for the Kohn-Sham system we have

$$\boldsymbol{\chi}_{\mathrm{KS},\,12} = \begin{pmatrix} \chi_{\mathrm{KS},\,\mathrm{ee}}(1,2) & 0 \\ 0 & \chi_{\mathrm{KS},\,\mathrm{nn}}(\underline{1},\underline{2}) \end{pmatrix} = \begin{pmatrix} \frac{\delta n(1)}{\delta v_{\mathrm{KS},\,\mathrm{e}}(2)} & \frac{\delta n(1)}{\delta v_{\mathrm{KS},\,\mathrm{n}}(\underline{2})} \\ \frac{\delta \Gamma(\underline{1})}{\delta v_{\mathrm{KS},\,\mathrm{e}}(2)} & \frac{\delta \Gamma(\underline{1})}{\delta v_{\mathrm{KS},\,\mathrm{n}}(\underline{2})} \end{pmatrix} , \tag{6.37}$$

in which the mixed response functions $\chi_{\mathrm{KS},\,\mathrm{en}} = \chi_{\mathrm{KS},\,\mathrm{ne}} = 0$ since in the Kohn-Sham system the nuclear and electronic systems are decoupled. The two sets of response functions are related by an equation that is very similar to that of ordinary TDDFT

$$\boldsymbol{\chi}_{12} = \boldsymbol{\chi}_{\mathrm{KS},\,12} + \boldsymbol{\chi}_{\mathrm{KS},\,13} \cdot (\boldsymbol{v}_{34} + \boldsymbol{f}_{\mathrm{xc},\,34}) \cdot \boldsymbol{\chi}_{42} \tag{6.38}$$

where "·" denotes a matrix product and integration over the variables 3 and 4, respectively. The matrices $\boldsymbol{f}_{\mathrm{xc}}$ and $\boldsymbol{v}$ are defined as

$$\boldsymbol{f}_{\mathrm{xc},\,12} = \begin{pmatrix} f_{\mathrm{xc},\,\mathrm{ee}}(1,2) & f_{\mathrm{xc},\,\mathrm{en}}(1,\underline{2}) \\ f_{\mathrm{xc},\,\mathrm{ne}}(\underline{1},2) & f_{\mathrm{xc},\,\mathrm{nn}}(\underline{1},\underline{2}) \end{pmatrix} = \begin{pmatrix} \frac{\delta v_{\mathrm{xc},\,\mathrm{e}}(1)}{\delta n(2)} & \frac{\delta v_{\mathrm{xc},\,\mathrm{e}}(1)}{\delta \Gamma(\underline{2})} \\ \frac{\delta v_{\mathrm{xc},\,\mathrm{n}}(\underline{1})}{\delta n(2)} & \frac{\delta v_{\mathrm{xc},\,\mathrm{n}}(\underline{1})}{\delta \Gamma(\underline{2})} \end{pmatrix} \tag{6.39a}$$

$$\boldsymbol{v}_{12} = \begin{pmatrix} v_{\mathrm{ee}}(1,2) & v_{\mathrm{en}}(1,\underline{2}) + u_{\mathrm{ext},\,\mathrm{e}}(1,\underline{2}) \\ v_{\mathrm{en}}(2,\underline{1}) + u_{\mathrm{ext},\,\mathrm{e}}(2,\underline{1}) & 0 \end{pmatrix} . \tag{6.39b}$$

The (6.38) is the central equation of the multicomponent response theory and is readily derived by application of the chain rule of differentiation. As an example we calculate

$$\begin{aligned}
\chi_{\mathrm{ee}}(1,2) &= \frac{\delta n(1)}{\delta v_{\mathrm{e}}(2)} \\
&= \int \mathrm{d}3 \, \frac{\delta n(1)}{\delta v_{\mathrm{KS},\,\mathrm{e}}(3)} \frac{\delta v_{\mathrm{KS},\,\mathrm{e}}(3)}{\delta v_{\mathrm{ext},\,\mathrm{e}}(2)} + \int \mathrm{d}\underline{3} \, \frac{\delta n(1)}{\delta v_{\mathrm{KS},\,\mathrm{n}}(\underline{3})} \frac{\delta v_{\mathrm{KS},\,\mathrm{n}}(\underline{3})}{\delta v_{\mathrm{ext},\,\mathrm{e}}(2)} \\
&= \frac{\delta n(1)}{\delta v_{\mathrm{KS},\,\mathrm{e}}(2)} + \int \mathrm{d}3 \, \frac{\delta n(1)}{\delta v_{\mathrm{KS},\,\mathrm{e}}(3)} \frac{\delta v_{\mathrm{Hxc},\,\mathrm{e}}(3)}{\delta v_{\mathrm{ext},\,\mathrm{e}}(2)} ,
\end{aligned} \tag{6.40}$$

From which readily follows

$$\chi_{\text{ee}}(1,2) = \chi_{\text{KS, ee}}(1,2) + \int d3 \, \chi_{\text{KS, ee}}(1,3)$$

$$\times \left\{ \int d4 \, \frac{\delta v_{\text{Hxc, e}}(3)}{\delta n(4)} \chi_{\text{ee}}(4,2) + \int d\underline{4} \, \frac{\delta v_{\text{Hxc, e}}(3)}{\delta \Gamma(\underline{4})} \chi_{\text{ne}}(\underline{4},2) \right\}, \quad (6.41)$$

where $v_{\text{Hxc, e}} = v_{\text{KS, e}} - v_{\text{e}}$. We further have

$$\frac{\delta v_{\text{Hxc, e}}(3)}{\delta n(4)} = v_{\text{ee}}(3,4) + f_{\text{xc, ee}}(1,2) \qquad (6.42a)$$

$$\frac{\delta v_{\text{Hxc, e}}(3)}{\delta \Gamma(\underline{4})} = v_{\text{en}}(3,\underline{4}) + u_{\text{ext, e}}(3,\underline{4}) + f_{\text{xc, en}}(3,\underline{4}) . \qquad (6.42b)$$

Inserting these expressions into (6.41) we have established one entry in the matrix (6.38). The other entries can be verified analogously. We finally note that (6.39b) still contains the term $u_{\text{ext, e}}$, which is inconvenient in practice. However, to calculate the linear response to the true external field we anyway need to expand further in powers of $u_{\text{ext, e}}$. If we do this we obtain (6.38) with $u_{\text{ext, e}} = 0$ in (6.39b) and two additional equations for the response functions $\delta n / \delta u_{\text{ext, e}}$ and $\delta \Gamma / \delta u_{\text{ext, e}}$ which will not be discussed here [Butriy 2005]. From the structure of the linear response equation (6.38) it is readily seen that electronic Kohn-Sham excitations (poles of $\chi_{\text{ee, KS}}$) and nuclear vibrational Kohn-Sham excitations (poles of $\chi_{\text{nn, KS}}$) will in general mix. The exchange-correlation kernels in $\boldsymbol{f}_{\text{xc}}$ will then have to provide the additional shift such that the true response functions in $\boldsymbol{\chi}$ will contain the true excitations of the coupled electron-nuclear system.

6.7 Example

As an application of the formalism we discuss the case of a diatomic molecule in a strong laser field. The Hamiltonian of this system in laboratory frame coordinates is given by

$$\hat{H}(t) = -\frac{1}{2M_1}\nabla^2_{\boldsymbol{R}_1} - \frac{1}{2M_2}\nabla^2_{\boldsymbol{R}_2} - \frac{1}{2}\sum_{i=1}^{N_{\text{e}}} \nabla_i^2 + v_{\text{en}} + v_{\text{ee}} + v_{\text{nn}} + v_{\text{laser}}(t) \quad (6.43)$$

where

$$v_{\text{nn}}(\{\boldsymbol{R}\}) = \frac{Z_1 Z_2}{|\boldsymbol{R}_1 - \boldsymbol{R}_2|} \qquad (6.44a)$$

$$v_{\text{en}}(\{\boldsymbol{r}\}, \{\boldsymbol{R}\}) = -\sum_{i=1}^{N_{\text{e}}} \left\{ \frac{Z_1}{|\boldsymbol{r}_i - \boldsymbol{R}_1|} + \frac{Z_2}{|\boldsymbol{r}_i - \boldsymbol{R}_2|} \right\} \qquad (6.44b)$$

$$v_{\text{laser}}(\{\boldsymbol{r}\}, \{\boldsymbol{R}\}, t) = \left\{ \sum_{i=1}^{N_{\text{e}}} \boldsymbol{r}_i - Z_1 \boldsymbol{R}_1 - Z_2 \boldsymbol{R}_2 \right\} \cdot \boldsymbol{E}(t) \qquad (6.44c)$$

and where $\boldsymbol{E}(t)$ represents the electric field of the laser.

We now have to perform a suitable body-fixed frame transformation to refer the electron coordinates to a nuclear frame. For the diatomic molecule a natural choice presents itself: We determine the Euler angles by the requirement that the internuclear axis be parallel to the z-axis in the body-fixed frame, i.e., $\mathcal{R}(\boldsymbol{R}) = R\boldsymbol{e}_z$, where $\boldsymbol{R} = \boldsymbol{R}_1 - \boldsymbol{R}_2$ and $R = |\boldsymbol{R}|$. For the special case of the diatomic molecule only two Euler angles are needed to specify the rotation matrix $\mathcal{R}$. From (6.6) and (6.7) we see that the electron-nuclear interaction and the external laser field transform to

$$v_{\text{en}}(\{\boldsymbol{r}'\}, \{\boldsymbol{R}\}) = -\sum_{i=1}^{N_e} \left\{ \frac{Z_1}{|\boldsymbol{r}'_i - \frac{M_2}{M_1+M_2} R\boldsymbol{e}_z|} + \frac{Z_2}{|\boldsymbol{r}'_i + \frac{M_1}{M_1+M_2} R\boldsymbol{e}_z|} \right\} \quad (6.45a)$$

$$v_{\text{laser}}(t) = \left\{ N_e \boldsymbol{R}_{\text{CMN}} - Z_1 \boldsymbol{R}_1 - Z_2 \boldsymbol{R}_2 + \sum_{i=1}^{N_e} \mathcal{R}^{-1} \boldsymbol{r}'_i \right\} \cdot \boldsymbol{E}(t) \,.$$
$$(6.45b)$$

With these expressions the Kohn-Sham potentials of (6.33) and (6.34) attain the form

$$v_{\text{KS, e}}(\boldsymbol{r}, t) = \int \mathrm{d}^3 r' \, v_{\text{ee}}(\boldsymbol{r}, \boldsymbol{r}') n(\boldsymbol{r}', t)$$
$$+ \int \mathrm{d}^3 R_1 \cdots \int \mathrm{d}^3 R_{N_n} \left[v_{\text{en}}(\boldsymbol{r}, \{\boldsymbol{R}\}) + \mathcal{R}^{-1} \boldsymbol{r} \cdot \boldsymbol{E}(t) \right] \Gamma(\{\boldsymbol{R}\}, t) + v_{\text{xc, e}}(\boldsymbol{r}, t)$$
$$(6.46)$$

and

$$v_{\text{KS, n}}(\{\boldsymbol{R}\}, t) = [N_e \boldsymbol{R}_{\text{CMN}} - Z_1 \boldsymbol{R}_1 - Z_2 \boldsymbol{R}_2] \cdot \boldsymbol{E}(t) + v_{\text{nn}}(\{\boldsymbol{R}\})$$
$$+ \int \mathrm{d}^3 r \left[v_{\text{en}}(\boldsymbol{r}, \{\boldsymbol{R}\}) + \mathcal{R}^{-1} \boldsymbol{r} \cdot \boldsymbol{E}(t) \right] n(\boldsymbol{r}, t) + v_{\text{xc, n}}(\{\boldsymbol{R}\}, t) \,. \quad (6.47)$$

Since the rotation matrix $\mathcal{R}$ only depends on $\boldsymbol{R}$ the nuclear Kohn-Sham potential is readily seen to be separable in terms of the coordinates $\boldsymbol{R}$ and $\boldsymbol{R}_{\text{CMN}}$. The nuclear Kohn-Sham wavefunction can then be written as

$$\Phi_{\text{n}, s_1, s_2}(\boldsymbol{R}_1, \boldsymbol{R}_2, t) = \Upsilon(\boldsymbol{R}_{\text{CMN}}, t) \xi(\boldsymbol{R}, t) \theta(s_1, s_2) \quad (6.48)$$

where θ is a nuclear spin function of the nuclear spin coordinates s_1 and s_2 and Υ and ξ satisfy the equations

$$\left\{ i\partial_t - \left[-\frac{1}{M_{\text{nuc}}} \nabla^2_{\boldsymbol{R}_{\text{CMN}}} + Q_{\text{tot}} \boldsymbol{R}_{\text{CMN}} \cdot \boldsymbol{E}(t) \right] \right\} \Upsilon(\boldsymbol{R}_{\text{CMN}}, t) = 0 \quad (6.49a)$$

$$\left\{ i\partial_t - \left[-\frac{1}{2\mu} \nabla^2_{\boldsymbol{R}} + \bar{v}_{\text{KS, n}}[n, \Gamma](\boldsymbol{R}, t) \right] \right\} \xi(\boldsymbol{R}, t) = 0 \,, \quad (6.49b)$$

where we defined the total nuclear mass $M_{\text{nuc}} = M_1 + M_2$, the total charge $Q_{\text{tot}} = N_e - Z_1 - Z_2$ and the reduced mass $\mu = M_1 M_2/(M_1 + M_2)$. The potential $\bar{v}_{\text{KS, n}}$ has the form

$$\bar{v}_{\text{KS, n}}(\boldsymbol{R}, t) = [-q_{\text{n}}\boldsymbol{R} + \boldsymbol{d}(\boldsymbol{R}, t)] \cdot \boldsymbol{E}(t) + \frac{Z_1 Z_2}{R}$$

$$- \int d^3 r \, n(\boldsymbol{r}, t) \left\{ \frac{Z_1}{|\boldsymbol{r} - \frac{M_2}{M_1 + M_2} R \boldsymbol{e}_z|} + \frac{Z_2}{|\boldsymbol{r} + \frac{M_1}{M_1 + M_2} R \boldsymbol{e}_z|} \right\} + v_{\text{xc, n}}(\boldsymbol{R}, t) \,,$$

$$(6.50)$$

where we have defined

$$q_{\text{n}} = \frac{M_2 Z_1 - M_1 Z_2}{M_1 + M_2} \tag{6.51a}$$

$$\boldsymbol{d}(\boldsymbol{R}, t) = \mathcal{R}^{-1} \int d^3 r \, n(\boldsymbol{r}, t) \boldsymbol{r} \,. \tag{6.51b}$$

We see that the nuclear center-of-mass motion has been decoupled from the nuclear relative motion. The nuclear center-of-mass wavefunction corresponds to a so-called Volkov plane wave. If it is normalized to a volume $\mathcal{V}$ then the nuclear density matrix can be written as

$$\Gamma(\boldsymbol{R}_1, \boldsymbol{R}_2, t) = \frac{1}{\mathcal{V}} N(\boldsymbol{R}, t) \,, \tag{6.52}$$

where we defined the density of the relative nuclear "particle" as

$$N(\boldsymbol{R}, t) = |\xi(\boldsymbol{R}, t)|^2 \,. \tag{6.53}$$

In terms of this quantity, the electronic Kohn-Sham potential (6.46) attains the form

$$v_{\text{KS, e}}(\boldsymbol{r}, t) = \mathcal{D}^{-1}\boldsymbol{r} \cdot \boldsymbol{E}(t) + \int d^3 r' \frac{n(\boldsymbol{r}', t)}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

$$- \int d^3 R \, N(\boldsymbol{R}, t) \left\{ \frac{Z_1}{|\boldsymbol{r} - \frac{M_2}{M_1 + M_2} R \boldsymbol{e}_z|} + \frac{Z_2}{|\boldsymbol{r} + \frac{M_1}{M_1 + M_2} R \boldsymbol{e}_z|} \right\} + v_{\text{xc, e}}(\boldsymbol{R}, t) \,,$$

$$(6.54)$$

where

$$\mathcal{D}^{-1} = \int d^3 R \, N(\boldsymbol{R}, t) \mathcal{R}^{-1} \,. \tag{6.55}$$

We have now completely defined the multicomponent Kohn-Sham equations for a diatomic molecule in a laser field in the dipole approximation. The next task is to develop appropriate functionals for the exchange-correlaton potentials, particularly for the electron-nuclear correlation. The simplest approach is to treat the electron-nuclear correlation in the Hartree approach where we put $v_{\text{xc, n}} = 0$ in (6.50). This approach has been tested [Kreibich 2004] in a one-dimensional model system for H_2^+ which is a suitable testcase since (i) it can be compared to the exact solution of the Schrödinger equation and, (ii) there are no electron-electron correlations.
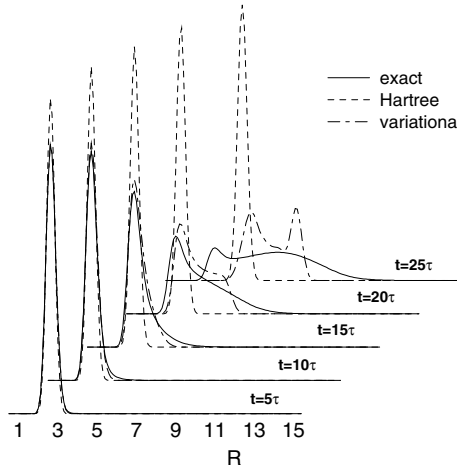
Fig. 6.1. Time-evolution (in units of optical cycles τ) of the nuclear density $N(R,t)$ obtained for a one-dimensional model H_2^+-molecule in a $\lambda = 228\,\mathrm{nm}$, $I = 5 \times 10^{13}\,\mathrm{W/cm^2}$ laser field from the exact solution, the time-dependent Hartree approximation and a time-dependent correlated variational approach

When the model molecule is exposed to a strong laser field, the nuclear density $N(R,t)$ shows a time-dependence as shown in Fig. 6.1. In this plot we can clearly see that the exact nuclear wavepacket splits, and part of the nuclear wavepacket moves away and decribes a dissociating molecule. However, within the Hartree approach to the electron-nuclear correlation, the nuclear wavepacket remains sharply peaked around the molecular equilibrium bond distance. This means that electron-nuclear correlation beyond the Hartree approximation is very important (for a more extensive discussion see [Kreibich 2001a, Kreibich 2004]). This is corroborated by the fact that a variational ansatz for the time-dependent wavefunction in terms of correlated orbitals (denoted as "variational" in Fig. 6.1) does yield the qualitatively correct splitting of the nuclear wavepacket.

6.8 Conclusions

We showed how to set up a multicomponent density-functional scheme for general systems of electrons and nuclei in time-dependent external fields. The basic quantities in this theory are the electron density referred to a body-fixed frame and the nuclear density matrix. Important for future applications will be the development of functionals for electron-nuclear correlations. The first steps in this direction have already been taken in the MCDFT for stationary systems [Kreibich 2001a, Kreibich 2004]. The development of such functionals for the time-dependent case is an important goal for the future.