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# Density functional theory of time-dependent phenomena

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## 1 Introduction

The basic idea of density functional theory (DFT) is to describe an interacting many-particle system exclusively and completely in terms of its density. The formalism rests on two basic theorems:

- I. Every observable quantity can be calculated, at least in principle, from the density alone, i. e. each quantum mechanical observable can be written as a functional of the density.
- II. The density of the interacting system of interest can be obtained as the density of an auxiliary system of non-interacting particles moving in an effective *local* single-particle potential, the so-called Kohn Sham potential.

In the original work of Hohenberg and Kohn (HK) [1] and Kohn and Sham (KS) [2] these theorems were proven for the ground-state density of *static* many-body systems. On the basis of these theorems, DFT has provided an extremely successful description of ground-state properties of atoms, molecules and solids [3, 4, 5]. The quality of approximations for the Kohn-Sham potential has steadily improved over the years and the currently best functionals yield ground-state properties in very close agreement with configuration interaction results [6]. Excited-state properties, however, are notoriously difficult to calculate within the traditional density functional framework and time-dependent phenomena are not accessible at all.

Time-dependent density functional theory (TDDFT) as a complete formalism [7] is a more recent development, although the historical roots date back to the time-dependent Thomas-Fermi model proposed by Bloch [8] as early as 1933. The first and rather successful steps towards a time-dependent Kohn-Sham (TDKS) scheme were taken by Peuckert [9] and by Zangwill and Soven [10]. These authors treated the linear density response of rare-gas atoms to a time-dependent external potential as the response of non-interacting electrons to an effective time-dependent potential. In analogy to stationary KS theory, this effective potential was assumed to contain an exchange-correlation (xc) part,  $v_{xc}(\mathbf{r}, t)$ , in addition to the time-dependent external and Hartree terms:

$$v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}, t) \quad . \quad (1)$$

Peuckert suggested an iterative scheme for the calculation of  $v_{xc}$ , while Zangwill and Soven adopted the functional form of the static exchange-correlation potential in local density approximation. Significant steps towards a rigorous foundation of time-dependent density functional theory were taken by Deb and Ghosh [11]–[14] and by Bartolotti [15]–[18] who formulated and explored HK and KS type theorems for the time-dependent density. Each of these derivations, however, was restricted to a rather narrow set of allowable time-dependent potentials (to potentials periodic in time in the theorems of Deb and Ghosh, and to adiabatic processes in the work of Bartolotti). A general proof of statements I and II above for the time-dependent density was given by Runge and Gross [7]. A novel feature of this formalism, not present in ground-state density functional theory, is the dependence of the respective density functionals on the initial (many-particle) state. A detailed description of the time-dependent density functional formalism will be presented in section 2. The central result is a set of TDKS equations which are structurally similar to the time-dependent Hartree equations but include (in principle exactly) all many-body effects through a *local* time-dependent exchange-correlation potential. In section 2 we focus on the motion of electrons only. In many experimental situations, however, the nuclear motion and its coupling to the electronic motion is important as well. If, for example, a molecule is placed in the focus of a strong laser, the electric field of the laser can either couple directly to the nuclei (in the infrared frequency regime) or the coupling to the electrons can lead to photoionization with subsequent Coulomb explosion (dissociation) of the molecule. To deal with situations of this type a DF formalism for the coupled system of electrons and nuclei is developed in section 3. The central result is a set of coupled TDKS equations for the electrons and for

each nuclear species. While sections 2 and 3 exclusively deal with time-dependent electric fields, magnetic effects will be considered in section 4. Both the ordinary Zeeman coupling and the coupling of magnetic fields to the orbital currents will be included.

To date, most applications of TDDFT fall in the regime of linear response. The linear response limit of time-dependent density functional theory will be discussed in section 5.1. After that, in section 5.2, we shall describe the density-functional calculation of higher orders of the density response. For practical applications, approximations of the time-dependent xc potential are needed. In section 6 we shall describe in detail the construction of such approximate functionals. Some exact constraints, which serve as guidelines in the construction, will also be derived in this section. Finally, in sections 7 and 8, we shall discuss applications of TDDFT within and beyond the perturbative regime. Apart from linear response calculations of the photoabsorption spectrum (section 7.1) which, by now, is a mature and widely applied subject, we also describe some very recent developments such as the density functional calculation of excitation energies (section 7.2), van der Waals forces (section 7.3) and atoms in superintense laser pulses (section 8).

## 2 Basic formalism for electrons in time-dependent electric fields

### 2.1 One-to-one mapping between time-dependent potentials and time-dependent densities

Density functional theory is based on the existence of an exact mapping between densities and external potentials. In the ground-state formalism [1], the existence proof relies on the Rayleigh-Ritz minimum principle for the energy. Straightforward extension to the time-dependent domain is not possible since a minimum principle is not available in this case. The proof given by Runge and Gross [7] for time-dependent systems is based directly on the Schrödinger equation (atomic units are used throughout):

$$i\frac{\partial}{\partial t}\Psi(t) = \hat{H}(t)\Psi(t). \quad (2)$$

We shall investigate the densities  $n(\mathbf{r}, t)$  of electronic systems evolving from a *fixed* initial (many-particle) state

$$\Psi(t_0) = \Psi_0 \quad (3)$$

under the influence of different external potentials of the form

$$\hat{V}(t) = \sum_{i=1}^N v(\mathbf{r}_i, t). \quad (4)$$

In the following discussion, the initial time  $t_0$  is assumed to be finite and the potentials are required to be expandable in a Taylor series about  $t_0$ . No further assumptions concerning the size of the radius of convergence are made. It is sufficient that the radius of convergence is greater than zero. The initial state  $\Psi_0$  is not required to be the ground state or some other eigenstate of the initial potential  $v(\mathbf{r}, t_0) = v_0(\mathbf{r})$ . This means that the case of sudden switching is included in the formalism. On the other hand, potentials that are switched-on adiabatically from  $t_0 = -\infty$  are excluded by the Taylor-expandability condition because adiabatic switching involves an *essential* singularity at  $t_0 = -\infty$ .

Besides an external potential of the form (4), the Hamiltonian in Eq. (2) contains the kinetic energy of the electrons and their mutual Coulomb repulsion:

$$\hat{H}(t) = \hat{T} + \hat{U} + \hat{V}(t) \quad (5)$$

with

$$\hat{T} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 \quad (6)$$

and

$$\hat{U} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (7)$$

With these preliminaries, we can formulate the following Hohenberg-Kohn-type theorem: The densities  $n(\mathbf{r}, t)$  and  $n'(\mathbf{r}, t)$  evolving from a common initial state  $\Psi_0 = \Psi(t_0)$  under the influence of two potentials  $v(\mathbf{r}, t)$  and  $v'(\mathbf{r}, t)$  (both Taylor expandable about the initial time  $t_0$ ) are always different provided that the potentials differ by more than a purely time-dependent ( $\mathbf{r}$ -independent) function:<sup>1</sup>

$$v(\mathbf{r}, t) \neq v'(\mathbf{r}, t) + c(t). \quad (8)$$

To prove this theorem, we use the condition that the potentials  $v$  and  $v'$  can be expanded in Taylor series:

$$v(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(\mathbf{r})(t - t_0)^k, \quad (9)$$

$$v'(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v'_k(\mathbf{r})(t - t_0)^k. \quad (10)$$

Equation (8) is equivalent to the statement that for the expansion coefficients  $v_k(\mathbf{r})$  and  $v'_k(\mathbf{r})$  there exists a smallest integer  $k \geq 0$  such that

$$v_k(\mathbf{r}) - v'_k(\mathbf{r}) = \left. \frac{\partial^k}{\partial t^k} (v(\mathbf{r}, t) - v'(\mathbf{r}, t)) \right|_{t=t_0} \neq \text{const.} \quad (11)$$

From this inequality we prove in a first step that the current densities

$$\mathbf{j}(\mathbf{r}, t) = \langle \Psi(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi(t) \rangle \quad (12)$$

and

$$\mathbf{j}'(\mathbf{r}, t) = \langle \Psi'(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi'(t) \rangle \quad (13)$$

are different for different potentials  $v$  and  $v'$ . Here,

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2i} \sum_{j=1}^N (\nabla_{\mathbf{r}_j} \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \nabla_{\mathbf{r}_j}) \quad (14)$$

is the usual paramagnetic current density operator. In a second step we shall show that the densities  $n$  and  $n'$  are different.

Using the quantum mechanical equation of motion for the expectation value of an operator  $\hat{Q}(t)$ ,

$$\frac{\partial}{\partial t} \langle \Psi(t) | \hat{Q}(t) | \Psi(t) \rangle = \langle \Psi(t) | \left( \frac{\partial \hat{Q}}{\partial t} - i[\hat{Q}(t), \hat{H}(t)] \right) | \Psi(t) \rangle, \quad (15)$$

---

<sup>1</sup>If  $v$  and  $v'$  differ by a purely time-dependent function, the resulting wave functions  $\Psi(t)$  and  $\Psi'(t)$  differ by a purely time-dependent phase factor and, consequently, the resulting densities  $\rho$  and  $\rho'$  are identical. This trivial case is excluded by the condition (8), in analogy to the ground-state formalism where the potentials are required to differ by more than a constant.

we obtain for the current densities:

$$\frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}, t) = \frac{\partial}{\partial t} \langle \Psi(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi(t) \rangle = -i \langle \Psi(t) | [\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle \quad (16)$$

$$\frac{\partial}{\partial t} \mathbf{j}'(\mathbf{r}, t) = \frac{\partial}{\partial t} \langle \Psi'(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi'(t) \rangle = -i \langle \Psi'(t) | [\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}'(t)] | \Psi'(t) \rangle \quad (17)$$

Since  $\Psi$  and  $\Psi'$  evolve from the same initial state

$$\Psi(t_0) = \Psi'(t_0) = \Psi_0 \quad (18)$$

we can write

$$\begin{aligned} \left. \frac{\partial}{\partial t} (\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t)) \right|_{t=t_0} &= -i \langle \Psi_0 | [\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Psi_0 \rangle \\ &= -n_0(\mathbf{r}) \nabla (v(\mathbf{r}, t_0) - v'(\mathbf{r}, t_0)) \end{aligned} \quad (19)$$

with the initial density

$$n_0(\mathbf{r}) = n(\mathbf{r}, t_0) \quad (20)$$

If the condition (11) is satisfied for  $k = 0$  the right-hand side of (19) cannot vanish identically and  $\mathbf{j}$  and  $\mathbf{j}'$  will become different infinitesimally later than  $t_0$ . If (11) holds for some finite  $k > 0$  we use Eq. (15) ( $k + 1$ ) times and obtain after some algebra:

$$\left( \frac{\partial}{\partial t} \right)^{k+1} (\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t)) \Big|_{t=t_0} = -n_0(\mathbf{r}) \nabla w_k(\mathbf{r}) \neq 0 \quad (21)$$

with

$$w_k(\mathbf{r}) = \left( \frac{\partial}{\partial t} \right)^k (v(\mathbf{r}, t) - v'(\mathbf{r}, t)) \Big|_{t=t_0} \quad (22)$$

Once again, we conclude that

$$\mathbf{j}(\mathbf{r}, t) \neq \mathbf{j}'(\mathbf{r}, t) \quad (23)$$

provided that (11) holds for  $v$  and  $v'$ . To prove the corresponding statement for the densities we use the continuity equation

$$\frac{\partial}{\partial t} (n(\mathbf{r}, t) - n'(\mathbf{r}, t)) = -\nabla \cdot (\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t)) \quad (24)$$

and calculate the  $(k + 1)$ th time derivative of Eq. (24) at  $t = t_0$ :

$$\left( \frac{\partial}{\partial t} \right)^{k+2} (n(\mathbf{r}, t) - n'(\mathbf{r}, t)) \Big|_{t=t_0} = \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) \quad (25)$$

In order to prove that the densities  $n(\mathbf{r}, t)$  and  $n'(\mathbf{r}, t)$  will become different infinitesimally later than  $t_0$ , we have to demonstrate that the right-hand side of Eq. (25) cannot vanish identically. This is done by reductio ad absurdum: Assume

$$\nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) \equiv 0 \quad (26)$$

and evaluate the integral

$$\begin{aligned} &\int d^3r n_0(\mathbf{r}) [\nabla w_k(\mathbf{r})]^2 \\ &= - \int d^3r w_k(\mathbf{r}) \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) + \oint d\mathbf{S} \cdot (n_0(\mathbf{r}) w_k(\mathbf{r}) \nabla w_k(\mathbf{r})) \quad , \end{aligned} \quad (27)$$

where we have used Green's theorem. The first integral on the right-hand side of (27) vanishes by assumption. For physically realistic potentials (i. e. potentials arising from normalizable external charge densities), the surface integral vanishes as well, because for such potentials the quantities  $w_k(\mathbf{r})$  fall off at least as  $1/r$ . Since the integrand on the left-hand side is non-negative one concludes that

$$n_0(\mathbf{r})[\nabla w_k(\mathbf{r})]^2 \equiv 0 \quad (28)$$

in contradiction to  $w_k(\mathbf{r}) \neq \text{const.}$  This completes the proof of the theorem. We mention that more general potentials may also be considered. The precise conditions have been formulated in [19].

We note in passing that the right-hand side of Eq. (25) is linear in  $w_k$ . Consequently, the difference between  $n(\mathbf{r}, t)$  and  $n'(\mathbf{r}, t)$  is non-vanishing already in first order of  $v(\mathbf{r}, t) - v'(\mathbf{r}, t)$ . This result will be of importance in section 5 because it ensures the invertibility of linear response operators.

By virtue of the 1-1 correspondence established above (for a given  $\Psi_0$ ), the time-dependent density determines the external potential uniquely up to within an additive purely time-dependent function. The potential, on the other hand, determines the time-dependent wave function, which can therefore be considered as a functional of the time-dependent density, unique up to within a purely time-dependent phase  $\alpha(t)$ :

$$\Psi(t) = e^{-i\alpha(t)} \tilde{\Psi}[n](t) \quad . \quad (29)$$

As a consequence, the expectation value of any quantum mechanical operator  $\hat{Q}(t)$  is a *unique* functional of the density:

$$Q[n](t) = \langle \tilde{\Psi}[n](t) | \hat{Q}(t) | \tilde{\Psi}[n](t) \rangle \quad . \quad (30)$$

The ambiguity in the phase cancels out. As a particular example, the right-hand side of Eq. (16) can be considered as a density functional which depends parametrically on  $\mathbf{r}$  and  $t$ :

$$\mathbf{P}[n](\mathbf{r}, t) \equiv -i \langle \Psi[n](t) | [\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}(t)] | \Psi[n](t) \rangle \quad . \quad (31)$$

This implies that the time-dependent particle and current densities can always be calculated (in principle exactly) from the following set of ‘‘hydrodynamical’’ equations:

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad (32)$$

$$\frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}, t) = \mathbf{P}[n](\mathbf{r}, t) \quad . \quad (33)$$

In practice, of course, the functional  $\mathbf{P}[n]$  is only known approximately.

## 2.2 Stationary-action principle

The solution of the time-dependent Schrödinger equation (2) with initial condition (3) corresponds to a stationary point of the quantum mechanical action integral

$$\mathcal{A} = \int_{t_0}^{t_1} dt \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle \quad (34)$$

Since there is a 1-1 mapping between time-dependent wave functions,  $\Psi(t)$ , and time-dependent densities,  $n(\mathbf{r}, t)$ , the corresponding density functional

$$\mathcal{A} = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi[n](t) \rangle \quad (35)$$

must have a stationary point at the correct time-dependent density (corresponding to the Hamiltonian  $\hat{H}(t)$  and the initial state  $\Psi_0$ ). Thus the correct density can be obtained by solving the Euler equation

$$\frac{\delta \mathcal{A}[n]}{\delta n(\mathbf{r}, t)} = 0 \quad (36)$$

with appropriate boundary conditions. The functional  $\mathcal{A}[n]$  can be written as

$$\mathcal{A}[n] = \mathcal{B}[n] - \int_{t_0}^{t_1} dt \int d^3r n(\mathbf{r}, t) v(\mathbf{r}, t) \quad (37)$$

with a *universal* ( $\Psi_0$ -dependent) functional  $\mathcal{B}[n]$ , formally defined as

$$\mathcal{B}[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | i \frac{\partial}{\partial t} - \hat{T} - \hat{U} | \Psi[n](t) \rangle. \quad (38)$$

On the exact level, the hydrodynamical equations (32, 33) and the variational equation (36) are of course equivalent. The functionals  $\mathbf{P}[n]$ ,  $\mathcal{A}[n]$ ,  $\mathcal{B}[n]$  are well-defined only for  $v$ -representable densities, i. e. for densities that come from some time-dependent potential satisfying Eq. (9). In view of this, a Levy-Lieb-type [20, 21, 22] extension of the respective functionals to arbitrary (non-negative, normalizable) functions  $n(\mathbf{r}, t)$  appears desirable. Two different proposals of this type have been put forward so far [23, 24].

### 2.3 Time-dependent Kohn-Sham scheme

The 1–1 correspondence between time-dependent densities and time-dependent potentials can be established for any *given* interaction  $\hat{U}$ , in particular also for  $\hat{U} \equiv 0$ , i. e. for non-interacting particles. Therefore the external potential  $v_s[n](\mathbf{r}, t)$  of a non-interacting system reproducing a given density  $n(\mathbf{r}, t)$  is uniquely determined. However, the 1–1 correspondence only ensures the uniqueness of  $v_s[n]$  for all  $v$ -representable densities but not its existence for an *arbitrary*  $n(\mathbf{r}, t)$ . In order to derive a time-dependent KS scheme we have to assume, similar to the static case, non-interacting  $v$ -representability, i.e., we have to assume that a potential  $v_s$  exists that reproduces the time-dependent density of the *interacting* system of interest. Under this assumption, the density of the interacting system can be obtained from

$$n(\mathbf{r}, t) = \sum_{j=1}^N |\varphi_j(\mathbf{r}, t)|^2 \quad (39)$$

with orbitals  $\varphi_j(\mathbf{r}, t)$  satisfying the time-dependent KS equation

$$i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = \left( -\frac{\nabla^2}{2} + v_s[n](\mathbf{r}, t) \right) \varphi_j(\mathbf{r}, t) \quad (40)$$

Usually, the single-particle potential  $v_s$  is written as

$$v_s[n](\mathbf{r}, t) = v(\mathbf{r}, t) + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}, t) \quad , \quad (41)$$

where  $v(\mathbf{r}, t)$  is the external time-dependent field. Equation (41) *defines* the time-dependent xc potential. In practice, this quantity has to be approximated. As in the static case, the great advantage of the time-dependent KS scheme lies in its computational simplicity compared to other methods such as time-dependent Hartree-Fock or time-dependent configuration interaction [25]– [32]. One has to emphasize that, in contrast to time-dependent Hartree-Fock, the effective single-particle potential  $v_s$  is a *local* potential, i.e., a multiplicative operator in configuration space.

A few remarks are in order at this point:

- (i) An important difference between the ordinary ground state density functional theory and the time-dependent formalism developed above is that in the time-dependent case the 1–1 correspondence between potentials and densities can be established only for a *fixed* initial many-body state  $\Psi_0$ . Consequently, the functionals  $\mathbf{P}[n]$ ,  $\mathcal{A}[n]$  and  $\mathcal{B}[n]$  implicitly depend on  $\Psi_0$ . In the same way,  $v_s[n]$  and  $v_{xc}[n]$  implicitly depend on the initial KS Slater determinant. The formalism provides no guideline of how to choose the initial KS orbitals  $\varphi_j(\mathbf{r}, t_0)$  as long as they reproduce the initial interacting density  $n_0$  corresponding to  $\Psi_0$ . In general, there exist infinitely many Slater determinants reproducing a given density [33, 34]. From a formal point of view there is no problem with that; any choice of initial orbitals  $\varphi_j(\mathbf{r}, t_0)$  reproducing the initial interacting density  $n_0$  will do the job because the dependence of  $v_s[n]$  on the initial state is such that the interacting density will be reproduced in each case. In practice, however, the dependence on the initial state is a nuisance. Of course one would prefer to have functionals of the density alone rather than functionals of  $n(\mathbf{r}, t)$  and  $\Psi_0$ . One has to emphasize, however, that for a large class of systems, namely those where both  $\Psi_0$  and the initial KS Slater determinant are non-degenerate ground states,  $\mathbf{P}[n]$  and  $v_s[n]$  are indeed functionals of the density *alone*. This is because any non-degenerate ground state  $\Psi_0$  is a unique functional of its density  $n_0(\mathbf{r})$  by virtue of the traditional HK theorem. In particular, the initial KS orbitals are *uniquely* determined as well in this case.
- (ii) We emphasize that the KS scheme does *not* follow from the variational principle. Incidentally, the same statement holds true in the static case as well. The KS scheme follows from the basic 1-1 mapping (applied to non-interacting particles) and the assumption of non-interacting  $v$ -representability. The variational principle yields an additional piece of information, namely the equation

$$v_{xc}[n](\mathbf{r}, t) = \frac{\delta \mathcal{A}_{xc}[n]}{\delta n(\mathbf{r}, t)}, \quad (42)$$

where  $\mathcal{A}_{xc}$  is the xc part of the action functional, formally defined by

$$\mathcal{A}_{xc}[n] = \mathcal{B}_s[n] - \mathcal{B}[n] - \frac{1}{2} \int_{t_0}^{t_1} dt \int d^3 r \int d^3 r' \frac{n(\mathbf{r}, t) n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (43)$$

Here  $\mathcal{B}_s[n]$  is the non-interacting analogue of the functional  $\mathcal{B}[n]$ , i. e. ,

$$\mathcal{B}_s[n] = \int_{t_0}^{t_1} dt \langle \Phi[n](t) | i \frac{\partial}{\partial t} - \hat{T} | \Phi[n](t) \rangle \quad (44)$$

where  $\Phi[n](t)$  is the unique time-dependent Slater determinant corresponding to the density  $n$ .

- (iii) The current density

$$\mathbf{j}(\mathbf{r}, t) = \frac{1}{2i} \sum_{k=1}^N (\varphi_k^*(\mathbf{r}, t) \nabla \varphi_k(\mathbf{r}, t) - \varphi_k(\mathbf{r}, t) \nabla \varphi_k^*(\mathbf{r}, t)) \quad (45)$$

following from the TDKS orbitals is identical with the true current density of the interacting system at hand. In order to prove this statement we recall that the first part of the Runge-Gross proof described above establishes a 1-1 mapping,  $v(\mathbf{r}, t) \leftrightarrow \mathbf{j}(\mathbf{r}, t)$ , between external potentials and current densities of interacting particles and likewise, for  $\hat{U} \equiv 0$ , a 1-1 mapping,  $v_s(\mathbf{r}, t) \leftrightarrow \mathbf{j}_s(\mathbf{r}, t)$ , between external potentials and current densities of noninteracting particles.



Making once again the assumption of non-interacting  $v$ -representability of the interacting current density  $\mathbf{j}(\mathbf{r}, t)$ , one can establish an alternative “current-density version” of the KS scheme,

$$i \frac{\partial}{\partial t} \tilde{\varphi}_j(\mathbf{r}, t) = \left( -\frac{1}{2} \nabla^2 + \tilde{v}_s[\mathbf{j}](\mathbf{r}, t) \right) \tilde{\varphi}_j(\mathbf{r}, t) \quad (46)$$

$$\mathbf{j}(\mathbf{r}, t) = \frac{1}{2i} \sum_{k=1}^N (\tilde{\varphi}_k^*(\mathbf{r}, t) \nabla \tilde{\varphi}_k(\mathbf{r}, t) - \tilde{\varphi}_k(\mathbf{r}, t) \nabla \tilde{\varphi}_k^*(\mathbf{r}, t)) \quad (47)$$

whose solution reproduces the current density,  $\mathbf{j}$ , of the *interacting* system of interest. To prove Eq. (45), we show that the solutions  $\tilde{\varphi}_j(\mathbf{r}, t)$  of (46,47) are in fact identical with the solutions  $\varphi_j$  of the ordinary TDKS scheme (39-41). To this end we prove that the density

$$\tilde{n}(\mathbf{r}, t) = \sum_{k=1}^N |\tilde{\varphi}_k(\mathbf{r}, t)|^2 \quad (48)$$

is identical with the density resulting from (39-41):

$$\tilde{n}(\mathbf{r}, t) = n(\mathbf{r}, t). \quad (49)$$

Then the uniqueness of the potential  $v_s[n]$  reproducing  $n(\mathbf{r}, t)$  implies that  $\tilde{v}_s(\mathbf{r}, t) = v_s(\mathbf{r}, t)$  so that the solutions of (46) and (40) are identical. In order to prove Eq. (49) we observe that the full many-body Schrödinger Eq. (2) implies the continuity equation

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad (50)$$

while the Schrödinger equation (46) implies the continuity equation

$$\frac{\partial \tilde{n}(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t). \quad (51)$$

Comparing (50) and (51) we find that  $n(\mathbf{r}, t)$  and  $\tilde{n}(\mathbf{r}, t)$  can differ at most by a *time-independent* function  $\eta(\mathbf{r})$  so that, at the initial time  $t_0$ ,

$$n(\mathbf{r}, t_0) = \tilde{n}(\mathbf{r}, t_0) + \eta(\mathbf{r}). \quad (52)$$

Hence, if the initial orbitals are chosen to be identical,

$$\varphi_k(\mathbf{r}, t_0) = \tilde{\varphi}_k(\mathbf{r}, t_0) \quad k = 1, \dots, N, \quad (53)$$

it follows that  $\eta(\mathbf{r}) \equiv 0$  and Eq. (49) will be satisfied for all times. It remains to be shown that the choice (53) is always possible. This is not obvious a priori because, by construction, the orbitals  $\varphi_k(\mathbf{r}, t_0)$  must reproduce the initial density  $n(\mathbf{r}, t_0)$  while the orbitals  $\tilde{\varphi}_k(\mathbf{r}, t_0)$  must yield the initial current density  $\mathbf{j}(\mathbf{r}, t_0)$ . In order to prove that the choice (53) is possible we show that a given density  $n_0(\mathbf{r})$  and a given current density  $j_0(\mathbf{r})$  can always be simultaneously reproduced by a single Slater determinant

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \det\{\phi_j(\mathbf{r}_i)\}. \quad (54)$$

This can be shown with a current-density generalization [24] of the so-called Harriman construction [33]. Here we reproduce the construction for one spatial dimension. The three dimensional case can be treated in analogy to

Ref. [34]. Given the densities  $n_0(x)$  and  $j_0(x)$  we define the following functions

$$q(x) := \frac{2\pi}{N} \int_a^x dx' n_0(x') \quad (55)$$

$$s(x) := \int_a^x dx' \frac{j_0(x')}{n_0(x')} \quad (56)$$

so that

$$\frac{dq(x)}{dx} = \frac{2\pi}{N} n_0(x) \quad (57)$$

and

$$\frac{ds(x)}{dx} = \frac{j_0(x)}{n_0(x)}. \quad (58)$$

In terms of these quantities and the particle number  $N$  we define the single-particle orbitals

$$\phi_k(x) := \sqrt{\frac{n_0(x)}{N}} e^{i(kq(x)+s(x)-\frac{M}{N}q(x))} \quad (59)$$

where  $k$  is an arbitrary integer while  $M$  is a fixed integer to be determined below. The functions  $\{\phi_k : k \text{ integer}\}$  form a complete and orthonormal set (see e. g. [4]). Constructing the Slater determinant (54) from these orbitals it is readily verified that

$$\sum_{j=1}^N |\phi_{k_j}(x)|^2 = n_0(x) \quad (60)$$

and

$$\begin{aligned} \frac{1}{2i} \sum_{j=1}^N \left( \phi_{k_j}^*(x) \frac{d}{dx} \phi_{k_j}(x) - \phi_{k_j}(x) \frac{d}{dx} \phi_{k_j}^*(x) \right) = \\ n_0(x) \frac{ds}{dx} + \frac{n_0(x)}{N} \frac{dq}{dx} \left[ \left( \sum_{j=1}^N k_j \right) - M \right]. \end{aligned} \quad (61)$$

Hence, by virtue of Eq. (58), Eq. (61) reproduces the given current density  $j_0(x)$  if  $M$  is chosen equal to  $\left( \sum_{j=1}^N k_j \right)$ . This completes the proof.

## 3 Motion of the nuclei

### 3.1 Quantum mechanical treatment of nuclear motion

The formalism developed so far is adequate whenever the motion of the atomic nuclei can be neglected. Then the electron-nucleus interaction only enters as a *static* contribution to the potential  $v(\mathbf{r}t)$  in Eq. (41). This is a good approximation for atoms in strong laser fields above the infrared frequency regime. When the nuclei are allowed to move, the nuclear motion couples dynamically to the electronic motion and the situation becomes more complicated.

In this section we shall describe a TDDFT for systems consisting of  $N$  electrons and  $N_A$  nuclei of charge  $Z_A$  and mass  $M_A$  (in a.u.),  $A = 1, \dots, K$ .  $K$  is the number of different nuclear species. Let  $\mathbf{R}_{A\alpha}$  be the configuration space vector of the  $\alpha$ th

nucleus of species  $A$ . Then the complete system of electrons and nuclei is described by the Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r}_1 \dots \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}, t) = \left[ \hat{H}_e(\mathbf{r}_1 \dots \mathbf{r}_N, t) + \hat{H}_n(\{\mathbf{R}_{A\alpha}\}, t) + \hat{H}_{en}(\mathbf{r}_1 \dots \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}) \right] \Psi(\mathbf{r}_1 \dots \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}, t) \quad (62)$$

with the electronic Hamiltonian,

$$\hat{H}_e = \sum_{j=1}^N \left( -\frac{1}{2} \nabla_{\mathbf{r}_j}^2 + v_{\text{ext}}(\mathbf{r}_j, t) \right) + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}, \quad (63)$$

the nuclear Hamiltonian

$$\hat{H}_n = \sum_{A=1}^K \sum_{\alpha=1}^{N_A} \left( -\frac{1}{2M_A} \nabla_{\mathbf{R}_{A\alpha}}^2 + V_{\text{ext}}^A(\mathbf{R}_{A\alpha}, t) \right) + \frac{1}{2} \underbrace{\sum_{A=1}^K \sum_{\alpha=1}^{N_A} \sum_{B=1}^K \sum_{\beta=1}^{N_B}}_{(A\alpha) \neq (B\beta)} \frac{Z_A Z_B}{|\mathbf{R}_{A\alpha} - \mathbf{R}_{B\beta}|} \quad (64)$$

and the electron-nucleus interaction

$$\hat{H}_{en} = - \sum_{j=1}^N \sum_{A=1}^K \sum_{\alpha=1}^{N_A} \frac{Z_A}{|\mathbf{r}_j - \mathbf{R}_{A\alpha}|}. \quad (65)$$

Based on an extension [35] of the Runge-Gross theorems described in sect. 2 to arbitrary multicomponent systems one can develop [36] a TDDFT for the coupled system of electrons and nuclei described above. In analogy to sections 2.1 – 2.3, one can establish three basic statements: First of all, there exists a rigorous 1-1 mapping between the vector of external potentials and the vector of electronic and nuclear densities,

$$(v_{\text{ext}}(\mathbf{r}, t); V_{\text{ext}}^1(\mathbf{R}, t), \dots, V_{\text{ext}}^K(\mathbf{R}, t)) \xleftrightarrow{1-1} (n(\mathbf{r}, t); n_1(\mathbf{R}, t), \dots, n_K(\mathbf{R}, t)). \quad (66)$$

Once again, this 1-1 correspondence is valid for a fixed initial many-body state  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}; t_0)$ . Besides this HK-type statement, one can derive a stationary-action principle and a set of coupled TDKS equations for electrons and nuclei. The latter read as follows:

$$i\frac{\partial}{\partial t}\varphi_j(\mathbf{r}, t) = \left( -\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_s[n, \{n_B\}](\mathbf{r}, t) \right) \varphi_j(\mathbf{r}, t), \quad (67)$$

$j = 1, \dots, N$

$$i\frac{\partial}{\partial t}\psi_{A\alpha}(\mathbf{R}, t) = \left( -\frac{1}{2M_A} \nabla_{\mathbf{R}}^2 + V_s^A[n, \{n_B\}](\mathbf{R}, t) \right) \psi_{A\alpha}(\mathbf{R}, t), \quad (68)$$

$A = 1, \dots, K; \quad \alpha = 1, \dots, N_A$

with the nuclear densities

$$n_A(\mathbf{R}, t) = \sum_{\alpha=1}^{N_A} n_{A\alpha}(\mathbf{R}, t), \quad n_{A\alpha}(\mathbf{R}, t) = |\psi_{A\alpha}(\mathbf{R}, t)|^2, \quad (69)$$

the electronic density

$$n(\mathbf{r}, t) = \sum_{j=1}^N |\varphi_j(\mathbf{r}, t)|^2, \quad (70)$$

and the KS potentials

$$v_s[n, \{n_B\}](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} - \sum_{B=1}^K \int d^3 R \frac{Z_B n_B(\mathbf{R}, t)}{|\mathbf{r} - \mathbf{R}|} + v_{\text{xc}}[n, \{n_B\}](\mathbf{r}, t), \quad (71)$$

$$V_s^A[n, \{n_B\}](\mathbf{R}, t) = V_{\text{ext}}^A(\mathbf{R}, t) - Z_A \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{R} - \mathbf{r}'|} + Z_A \sum_{B=1}^K \int d^3 R' \frac{Z_B n_B(\mathbf{R}', t)}{|\mathbf{R} - \mathbf{R}'|} + V_{\text{xc}}^A[n, \{n_B\}](\mathbf{R}, t). \quad (72)$$

The xc potentials in (71) and (72) are formally given by functional derivatives of the xc part of the quantum mechanical action functionals:

$$v_{\text{xc}}(\mathbf{r}, t) = \frac{\delta \mathcal{A}_{\text{xc}}[n, \{n_B\}]}{\delta n(\mathbf{r}, t)} \quad (73)$$

$$V_{\text{xc}}^A(\mathbf{R}, t) = \frac{\delta \mathcal{A}_{\text{xc}}[n, \{n_B\}]}{\delta n_A(\mathbf{R}, t)}. \quad (74)$$

In molecules and clusters, *genuine* exchange (as well as correlation) among identical nuclei is very small because, at typical internuclear separations, the overlap of nuclear wave functions is rather small.<sup>2</sup> However, the exact xc functional also contains self-exchange contributions which are not small and which cancel the self-interaction terms contained in the Hartree potentials in Eqs. (71) and (72). Hence it will be a very good approximation to represent  $V_{\text{xc}}^A$  by the self-exchange terms alone. This leads to

$$V_s^{A\alpha}[n, \{n_B\}](\mathbf{R}, t) = V_{\text{ext}}^A(\mathbf{R}, t) - Z_A \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{R} - \mathbf{r}'|} + Z_A \sum_{\substack{B=1 \\ B \neq A}}^K \int d^3 R' \frac{Z_B n_B(\mathbf{R}', t)}{|\mathbf{R} - \mathbf{R}'|} + Z_A \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^{N_A} \int d^3 R' \frac{Z_A n_{A\beta}(\mathbf{R}', t)}{|\mathbf{R} - \mathbf{R}'|}. \quad (75)$$

Note that, within this approximation, the nuclear KS potential depends on the state  $\psi_{A\alpha}$  it acts on. This is analogous to the SIC scheme of Perdew and Zunger [37].

Clearly, a complete numerical solution of the coupled KS equations (67, 68) for electrons and nuclei will be rather involved. Usually only the valence electrons need to be treated dynamically. The core electrons can be taken into account approximately by replacing the electron-nucleus interaction (65) by suitable pseudopotentials and by replacing the nuclear Coulomb potential in Eq. (64) by the appropriate *ionic* Coulomb potential [38]. This procedure reduces the number of electronic KS equations and hence the numerical effort considerably.

### 3.2 Classical treatment of nuclear motion

Further simplification is achieved by treating the nuclear motion classically. Numerical schemes of this type have been derived in various ways [38, 39, 40, 41, 42, 43]. In this section we shall use the multicomponent formalism developed in section 3.1 as a starting point to derive classical equations of motion for the nuclei.

Applying Ehrenfest's theorem to the nuclear KS equation (68), the classical trajectory

$$\mathbf{R}_{A\alpha}^{\text{class}}(t) = \langle \psi_{A\alpha}(t) | \hat{\mathbf{R}} | \psi_{A\alpha}(t) \rangle = \int d^3 R \mathbf{R} n_{A\alpha}(\mathbf{R}, t) \quad (76)$$

<sup>2</sup>In atomic scattering processes this is not necessarily the case.

of the  $\alpha$ th nucleus of species  $A$  satisfies the equation of motion

$$M_A \frac{d^2}{dt^2} \mathbf{R}_{A\alpha}^{\text{class}}(t) = \mathbf{F}_{A\alpha}(t) \quad (77)$$

where the force is given by

$$\mathbf{F}_{A\alpha}(t) = -\langle \psi_{A\alpha}(t) | \nabla_{\mathbf{R}} V_s^A | \psi_{A\alpha}(t) \rangle. \quad (78)$$

Since the TDKS equations (67) – (72) reproduce the exact nuclear densities, Eq. (76) yields the *exact* classical trajectory whenever species  $A$  contains only one nucleus. When species  $A$  contains more than one nucleus we have a system of *indistinguishable* particles and then, strictly speaking, the trajectories of *single* nuclei cannot be told apart: Only the total density  $n_A(\mathbf{R}, t)$  and hence the center-of-mass trajectory of species  $A$  can be measured. In this case, trajectories of single nuclei can be *defined* by Eq. (76) within some effective single-particle theory. TDKS theory is particularly suitable for this purpose since the TDKS partial densities  $n_{A\alpha}$  lead to the *exact* total density  $n_A$ .

Employing the approximation (75) for the nuclear KS potential the force (78) on the nucleus ( $A\alpha$ ) simplifies to

$$\begin{aligned} \mathbf{F}_{A\alpha}(t) = & - \int d^3 R n_{A\alpha}(\mathbf{R}, t) \left[ \nabla_{\mathbf{R}} V_{\text{ext}}^A(\mathbf{R}, t) - Z_A \int d^3 r \nabla_{\mathbf{R}} \frac{n(\mathbf{r}, t)}{|\mathbf{R} - \mathbf{r}|} \right. \\ & \left. + Z_A \sum_{\substack{B=1 \\ B \neq A}}^K \int d^3 R' \nabla_{\mathbf{R}} \frac{Z_B n_B(\mathbf{R}', t)}{|\mathbf{R} - \mathbf{R}'|} + Z_A \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^{N_A} \int d^3 R' \nabla_{\mathbf{R}} \frac{Z_A n_{A\beta}(\mathbf{R}', t)}{|\mathbf{R} - \mathbf{R}'|} \right]. \quad (79) \end{aligned}$$

In many cases, the nuclear densities  $n_{A\alpha}(\mathbf{R}, t)$  will be rather narrow functions, with a strong peak at the classical trajectory  $\mathbf{R}_{A\alpha}^{\text{class}}(t)$ . In such a situation, integrals of the form  $\int d^3 R n_{A\alpha}(\mathbf{R}, t) G(\mathbf{R})$  are well represented by Taylor-expanding  $G(\mathbf{R})$  around the classical trajectory. This leads to

$$\int d^3 R n_{A\alpha}(\mathbf{R}, t) G(\mathbf{R}) = G(\mathbf{R}_{A\alpha}^{\text{class}}(t)) + O(\mathbf{R} - \mathbf{R}_{A\alpha}^{\text{class}})^2. \quad (80)$$

The first-order term vanishes due to the definition (76) of the classical trajectory. Neglecting terms of second and higher order is equivalent to replacing the nuclear densities by  $\delta$ -functions:

$$n_{A\alpha}(\mathbf{R}, t) = \delta(\mathbf{R} - \mathbf{R}_{A\alpha}^{\text{class}}(t)). \quad (81)$$

In this way the Newton equations (77,79) reduce to

$$\begin{aligned} M_A \frac{d^2}{dt^2} \mathbf{R}_{A\alpha}^{\text{class}}(t) = & - \nabla_{\mathbf{R}_{A\alpha}^{\text{class}}} \left[ V_{\text{ext}}^A(\mathbf{R}_{A\alpha}^{\text{class}}, t) \right. \\ & \left. - \int d^3 r \frac{Z_A n(\mathbf{r}, t)}{|\mathbf{R}_{A\alpha}^{\text{class}} - \mathbf{r}|} + \underbrace{\sum_{B=1}^K \sum_{\beta=1}^{N_B}}_{(B\beta) \neq (A\alpha)} \frac{Z_A Z_B}{|\mathbf{R}_{A\alpha}^{\text{class}} - \mathbf{R}_{B\beta}^{\text{class}}|} \right] \quad (82) \end{aligned}$$

and the electronic KS equations simplify to

$$\begin{aligned} i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = & \left( -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}, t) + \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \right. \\ & \left. - \sum_{B=1}^K \sum_{\beta=1}^{N_B} \frac{Z_B}{|\mathbf{r} - \mathbf{R}_{B\beta}^{\text{class}}(t)|} + v_{\text{xc}}[n, \{\mathbf{R}_{B\beta}^{\text{class}}(t)\}](\mathbf{r}, t) \right) \varphi_j(\mathbf{r}, t). \quad (83) \end{aligned}$$

Equations (82) and (83) are coupled and have to be solved simultaneously. This scheme has been applied rather successfully to describe the melting of bulk sodium [38]. Compared to the Car-Parrinello method [44, 45, 46] the scheme has the advantage of not requiring the imposition of orthonormality constraints in the electronic equations of motion.

One has to emphasize that Eqs. (82) and (83) do not involve the Born-Oppenheimer approximation although the nuclear motion is treated classically. This is an important advantage over the quantum molecular dynamics approach [47, 48, 49, 50, 51, 52, 53, 54] where the nuclear Newton equations (82) are solved simultaneously with a set of *ground-state* KS equations at the instantaneous nuclear positions. In spite of the obvious numerical advantages one has to keep in mind that the classical treatment of nuclear motion is justified only if the probability densities  $n_{A\alpha}(\mathbf{R}, t)$  remain narrow distributions during the whole process considered. The splitting of the nuclear wave packet found, e. g., in pump-probe experiments [55, 56, 57, 58] cannot be properly accounted for by treating the nuclear motion classically. In this case, one has to face the complete system (67 - 72) of coupled TDKS equations for electrons and nuclei.

## 4 Electrons in time-dependent electromagnetic fields

Up to this point we have exclusively dealt with time-dependent electric fields. The objective of the present chapter is to incorporate magnetic effects. For simplicity, only the electronic degrees of freedom are being discussed, i.e., the nuclear motion is not considered. Magnetic fields couple both to the spin and to the electronic orbital currents. Hence, the most general TDDFT should encompass both of these couplings at the same time. However, to keep matters as simple as possible, we shall treat the two couplings separately in the following sections.

### 4.1 Coupling to spin

In order to account for the coupling of a magnetic field  $\mathbf{B}(\mathbf{r}, t)$  to the electronic spin, the external potential

$$\hat{V}(t) = \sum_{j=1}^N v(\mathbf{r}_j, t) = \int d^3r \hat{n}(\mathbf{r}) v(\mathbf{r}, t) \quad (84)$$

represented in terms of the density operator

$$\hat{n}(\mathbf{r}) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) \quad (85)$$

has to be complemented by a Zeeman term, i.e.,  $\hat{V}(t)$  has to be replaced by

$$\hat{V}_B(t) = \int d^3r \hat{n}(\mathbf{r}) v(\mathbf{r}, t) - \int d^3r \hat{\mathbf{m}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}, t) \quad (86)$$

where  $\hat{\mathbf{m}}(\mathbf{r})$  represents the operator of the spin magnetization. For simplicity we assume that the vector  $\mathbf{B}$  has only one non-vanishing component, the  $z$ -component, so that

$$\hat{V}_B(t) = \int d^3r \hat{n}(\mathbf{r}) v(\mathbf{r}, t) - \int d^3r \hat{m}_z(\mathbf{r}) B_z(\mathbf{r}, t). \quad (87)$$

If the system contains  $N_\uparrow$  spin-up electrons and  $N_\downarrow = N - N_\uparrow$  spin-down electrons we can define spin-up and spin-down density operators by

$$\hat{n}_\uparrow(\mathbf{r}) := \sum_{j=1}^{N_\uparrow} \delta(\mathbf{r} - \mathbf{r}_j) \quad (88)$$

$$\hat{n}_\downarrow(\mathbf{r}) := \sum_{j=N_\uparrow+1}^N \delta(\mathbf{r} - \mathbf{r}_j). \quad (89)$$

In terms of these operators the total density  $\hat{n}(\mathbf{r})$  and the magnetization  $\hat{m}_z(\mathbf{r})$  can be expressed as

$$\hat{n}(\mathbf{r}) = \hat{n}_\uparrow(\mathbf{r}) + \hat{n}_\downarrow(\mathbf{r}) \quad (90)$$

$$\hat{m}_z(\mathbf{r}) = -\mu_0 [\hat{n}_\uparrow(\mathbf{r}) - \hat{n}_\downarrow(\mathbf{r})] \quad (91)$$

where  $\mu_0$  is the Bohr magneton.

Defining furthermore the spin-up and spin-down potentials

$$v_\uparrow(\mathbf{r}, t) = v(\mathbf{r}, t) + \mu_0 B_z(\mathbf{r}, t) \quad (92)$$

and

$$v_\downarrow(\mathbf{r}, t) = v(\mathbf{r}, t) - \mu_0 B_z(\mathbf{r}, t), \quad (93)$$

Eq. (87) simplifies to

$$\hat{V}_B(t) = \int d^3r \hat{n}_\uparrow(\mathbf{r}) v_\uparrow(\mathbf{r}, t) + \int d^3r \hat{n}_\downarrow(\mathbf{r}) v_\downarrow(\mathbf{r}, t). \quad (94)$$

Starting from the time-dependent many-body Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi(t) = \left( \hat{T} + \hat{U} + \hat{V}_B(t) \right) \Psi(t), \quad (95)$$

a time-dependent HKS formalism can be established [59] in analogy to section 2: The time-dependent spin densities

$$n_\uparrow(\mathbf{r}, t) = \langle \Psi(t) | \hat{n}_\uparrow(\mathbf{r}) | \Psi(t) \rangle \quad (96)$$

$$n_\downarrow(\mathbf{r}, t) = \langle \Psi(t) | \hat{n}_\downarrow(\mathbf{r}) | \Psi(t) \rangle \quad (97)$$

evolving from a fixed initial many-body state  $\Psi(t_0)$  are in 1-1 correspondence with the potentials  $(v_\uparrow(\mathbf{r}, t), v_\downarrow(\mathbf{r}, t))$  provided that the latter can be expanded in Taylor series around the initial time  $t_0$ . The spin densities thus determine the potentials  $v_\uparrow = v_\uparrow[n_\uparrow, n_\downarrow]$ ,  $v_\downarrow = v_\downarrow[n_\uparrow, n_\downarrow]$  uniquely up to within purely time-dependent ( $\mathbf{r}$ -independent) additive functions. Consequently the many-body wave function can be considered as a functional  $\Psi(t) = \Psi[n_\uparrow, n_\downarrow](t)$  of the spin densities which is unique up to within a purely time-dependent phase factor. Furthermore, following the arguments in section 2.2, the spin densities of a given interacting system can be determined variationally by solving the Euler-Lagrange equations

$$\frac{\delta \mathcal{A}_B[n_\uparrow, n_\downarrow]}{\delta n_\uparrow(\mathbf{r}, t)} = 0 \quad (98)$$

$$\frac{\delta \mathcal{A}_B[n_\uparrow, n_\downarrow]}{\delta n_\downarrow(\mathbf{r}, t)} = 0, \quad (99)$$

where the action functional is formally defined as

$$\mathcal{A}_B[n_\uparrow, n_\downarrow] := \int_{t_0}^{t_1} dt \langle \Psi[n_\uparrow, n_\downarrow](t) | i \frac{\partial}{\partial t} - \hat{T} - \hat{U} - \hat{V}_B | \Psi[n_\uparrow, n_\downarrow](t) \rangle. \quad (100)$$

Finally, assuming non-interacting  $v$ -representability, the spin densities of the interacting system of interest can be obtained from time-dependent spin orbitals

$$n_\sigma(\mathbf{r}, t) = \sum_{j=1}^{N_\sigma} |\varphi_{j\sigma}(\mathbf{r}, t)|^2 \quad (101)$$

coming from the time-dependent KS equations

$$i \frac{\partial}{\partial t} \varphi_{j\sigma}(\mathbf{r}, t) = \left( -\frac{1}{2} \nabla^2 + v_{s\sigma}[n_\uparrow, n_\downarrow](\mathbf{r}, t) \right) \varphi_{j\sigma}(\mathbf{r}, t) \quad (102)$$

$$j = 1 \dots N_\sigma, \quad \sigma = \uparrow \downarrow$$

where the spin-dependent effective single-particle potential for electrons with spin  $\sigma = \uparrow, \downarrow$  is given by

$$v_{s\sigma}[n_\uparrow, n_\downarrow](\mathbf{r}, t) = v_\sigma(\mathbf{r}, t) + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc\sigma}[n_\uparrow, n_\downarrow](\mathbf{r}, t). \quad (103)$$

Eqs. (101) – (103) constitute the KS scheme of time-dependent spin-density functional theory. With the xc action functional  $\mathcal{A}_{xc}[n_\uparrow, n_\downarrow]$  defined in analogy to Eq. (43), the spin-dependent xc potentials can be represented as functional derivatives:

$$v_{xc\sigma}[n_\uparrow, n_\downarrow](\mathbf{r}, t) = \frac{\delta \mathcal{A}_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r}, t)}. \quad (104)$$

In the limit of vanishing magnetic field the *external* potentials in Eq. (103) become identical

$$v_\uparrow(\mathbf{r}, t) = v_\downarrow(\mathbf{r}, t) = v(\mathbf{r}, t) \quad \text{for} \quad \mathbf{B}(\mathbf{r}, t) \equiv 0. \quad (105)$$

Nevertheless, Eqs. (102) and (103) do not necessarily reduce to the ordinary TDKS equations (40) and (41) in this limit. This is because the spin-dependent xc potentials  $v_{xc\uparrow}$  and  $v_{xc\downarrow}$  are not identical except for the case of spin-saturated systems ( $n_\uparrow \equiv n_\downarrow$ ).

## 4.2 Coupling to orbital currents

In order to describe the coupling of time-dependent magnetic fields to the electronic orbital currents, the kinetic energy  $\hat{T}$  has to be replaced by

$$\hat{T}_{\mathbf{A}}(t) = \sum_{j=1}^N \frac{1}{2} \left( -i \nabla_{\mathbf{r}_j} + \frac{1}{c} \mathbf{A}(\mathbf{r}_j, t) \right)^2 \quad (106)$$

where  $\mathbf{A}(\mathbf{r}, t)$  is the time-dependent vector potential related to the magnetic field by

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t). \quad (107)$$

Since the vector potential is not a gauge-invariant quantity, particular attention has to be paid to gauge transformations: If  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)$  is a solution of the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi(t) = \left( \hat{T}_{\mathbf{A}}(t) + \hat{U} + \hat{V}(t) \right) \Psi(t), \quad (108)$$

then the transformed wave function

$$\tilde{\Psi}(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \exp \left\{ -\frac{i}{c} \sum_{j=1}^N \Lambda(\mathbf{r}_j, t) \right\} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) \quad (109)$$



is a solution of (108) with the gauge-transformed potentials <sup>3</sup>

$$\tilde{v}(\mathbf{r}, t) = v(\mathbf{r}, t) + \frac{1}{c} \frac{\partial}{\partial t} \Lambda(\mathbf{r}, t) \quad (110)$$

$$\tilde{\mathbf{A}}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}, t) + \nabla \Lambda(\mathbf{r}, t). \quad (111)$$

The physical (i.e. gauge-invariant) current density is given by

$$\mathbf{j}(\mathbf{r}, t) = \langle \Psi(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi(t) \rangle + \frac{1}{c} n(\mathbf{r}, t) \mathbf{A}(\mathbf{r}, t) \quad (112)$$

where  $\hat{\mathbf{j}}_p(\mathbf{r})$  is the paramagnetic current density operator defined in Eq. (14). With these preliminaries, the central Hohenberg-Kohn-like theorem [24, 60] to be proven subsequently can be formulated as follows:

The current densities  $\mathbf{j}(\mathbf{r}, t)$  and  $\mathbf{j}'(\mathbf{r}, t)$  evolving from a common initial state  $\Psi_0 = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t_0)$  under the influence of two four-potentials  $(v(\mathbf{r}, t), \mathbf{A}(\mathbf{r}, t))$  and  $(v'(\mathbf{r}, t), \mathbf{A}'(\mathbf{r}, t))$  which differ by more than a gauge transformation with  $\Lambda(\mathbf{r}, t_0) = 0$  are always different provided that the potentials can be expanded in Taylor series around the initial time  $t_0$ .

Since the current density is gauge invariant the proof of the theorem can be carried out with an arbitrary representative of the gauge class of  $(v, \mathbf{A})$  and an arbitrary representative of the gauge class of  $(v', \mathbf{A}')$ . As representatives we choose those four-potentials having a vanishing electric potential, i.e., for  $v(\mathbf{r}, t)$  we make a gauge transformation (110) satisfying

$$\frac{\partial}{\partial t} \Lambda(\mathbf{r}, t) = -c v(\mathbf{r}, t), \quad \Lambda(\mathbf{r}, t_0) = 0 \quad (113)$$

and for  $v'(\mathbf{r}, t)$  we make a gauge transformation satisfying

$$\frac{\partial}{\partial t} \Lambda'(\mathbf{r}, t) = -c v'(\mathbf{r}, t), \quad \Lambda'(\mathbf{r}, t_0) = 0. \quad (114)$$

The corresponding gauge-transformed vector potentials are denoted by  $\tilde{\mathbf{A}}(\mathbf{r}, t)$  and  $\tilde{\mathbf{A}}'(\mathbf{r}, t)$ . Thus we have to show that

$$\left(0, \tilde{\mathbf{A}}(\mathbf{r}, t)\right) \neq \left(0, \tilde{\mathbf{A}}'(\mathbf{r}, t)\right) \quad (115)$$

implies

$$\mathbf{j}(\mathbf{r}, t) \neq \mathbf{j}'(\mathbf{r}, t). \quad (116)$$

If  $\tilde{\mathbf{A}}(\mathbf{r}, t_0) \neq \tilde{\mathbf{A}}'(\mathbf{r}, t_0)$ , then the statement of the theorem is trivially true because the initial paramagnetic currents and the initial densities are identical so that

$$\mathbf{j}(\mathbf{r}, t_0) - \mathbf{j}'(\mathbf{r}, t_0) = \frac{1}{c} n(\mathbf{r}, t_0) \left( \tilde{\mathbf{A}}(\mathbf{r}, t_0) - \tilde{\mathbf{A}}'(\mathbf{r}, t_0) \right) \neq 0. \quad (117)$$

If  $\tilde{\mathbf{A}}(\mathbf{r}, t_0) = \tilde{\mathbf{A}}'(\mathbf{r}, t_0)$  the potentials must differ in some higher Taylor coefficient, i.e.,

$$\left. \frac{\partial^k}{\partial t^k} \left( \tilde{\mathbf{A}}(\mathbf{r}, t) - \tilde{\mathbf{A}}'(\mathbf{r}, t) \right) \right|_{t=t_0} \begin{cases} = 0 & ; \quad k < l \\ \neq 0 & ; \quad k = l \end{cases} \quad (118)$$

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<sup>3</sup>In the context of electrodynamics, the gauge transformation (111) is usually complemented by the transformation  $\tilde{\varphi}(\mathbf{r}, t) = \varphi(\mathbf{r}, t) - 1/c \partial \Lambda(\mathbf{r}, t) / \partial t$  where  $\varphi(\mathbf{r}, t)$  is the electric *potential*. In quantum mechanics, on the other hand, one works with the *potential energy*  $v(\mathbf{r}, t) = q\varphi(\mathbf{r}, t)$ . For electrons ( $q = -e$ ) the gauge transformation of  $\phi$  then leads to (110) in atomic units.

must be satisfied with an integer  $l > 0$ . Calculating the  $l$ -th time derivative of the densities  $\mathbf{j}(\mathbf{r}, t)$  and  $\mathbf{j}'(\mathbf{r}, t)$  by applying the Heisenberg equation of motion  $l$  times and taking the difference at the initial time  $t_0$  we obtain

$$\left(i\frac{\partial}{\partial t}\right)^l (\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t))\Big|_{t=t_0} = \frac{1}{c}n(\mathbf{r}, t_0) \left(i\frac{\partial}{\partial t}\right)^l (\tilde{\mathbf{A}}(\mathbf{r}, t) - \tilde{\mathbf{A}}'(\mathbf{r}, t))\Big|_{t=t_0} \neq 0, \quad (119)$$

where  $n(\mathbf{r}, t_0)$  is the particle density at  $t_0$ . By virtue of (119) the current densities  $\mathbf{j}(\mathbf{r}, t)$  and  $\mathbf{j}'(\mathbf{r}, t)$  will become different at times infinitesimally later than  $t_0$ . This completes the proof. As a consequence of this theorem the physical current density  $\mathbf{j}(\mathbf{r}, t)$  determines the potentials  $v[\mathbf{j}]$ ,  $\mathbf{A}[\mathbf{j}]$  uniquely up to within a gauge transformation (110), (111). Hence, by virtue of the Schrödinger equation (108), the many-body wave function is a current-density functional  $\Psi[\mathbf{j}](\mathbf{r}_1, \dots, \mathbf{r}_N, t)$ , unique up to within a gauge transformation (109). In a *fixed* gauge, of course,  $v$ ,  $\mathbf{A}$  and  $\Psi$  are determined uniquely by the current density. Applying the theorem to noninteracting particles then, once again, the potentials  $v_s[\mathbf{j}]$ ,  $\mathbf{A}_s[\mathbf{j}]$  and the Slater determinant  $\Phi[\mathbf{j}]$  leading to the current density  $\mathbf{j}(\mathbf{r}, t)$  are uniquely determined in a fixed gauge.

In order to derive a TDKS scheme we consider a particular interacting system with current density  $\mathbf{j}_0(\mathbf{r}, t)$ , produced by the external potentials  $v_0(\mathbf{r}, t)$ ,  $\mathbf{A}_0(\mathbf{r}, t)$  (in a given gauge). Assuming noninteracting  $v$ -representability, i.e., assuming the existence of potentials  $v_{s,0}$ ,  $\mathbf{A}_{s,0}$  leading to  $\mathbf{j}_0$ , we can calculate  $\mathbf{j}_0$  from the equations

$$\begin{aligned} i\frac{\partial}{\partial t}\varphi_j(\mathbf{r}, t) &= \left(\frac{1}{2}\left(-i\nabla + \frac{1}{c}\mathbf{A}_{s,0}[\mathbf{j}_0](\mathbf{r}, t)\right)^2 + v_{s,0}[\mathbf{j}_0](\mathbf{r}, t)\right)\varphi_j(\mathbf{r}, t) \quad (120) \\ \mathbf{j}_0(\mathbf{r}, t) &= \frac{1}{2i}\sum_{k=1}^N (\varphi_k^*(\mathbf{r}, t)\nabla\varphi_k(\mathbf{r}, t) - \varphi_k(\mathbf{r}, t)\nabla\varphi_k^*(\mathbf{r}, t)) \\ &+ \frac{1}{c}\left(\sum_{k=1}^N |\varphi_k(\mathbf{r}, t)|^2\right)\mathbf{A}_{s,0}(\mathbf{r}, t). \quad (121) \end{aligned}$$

Once the existence of  $v_{s,0}$  and  $\mathbf{A}_{s,0}$  is assumed, uniqueness follows from the above theorem. Up to this point the time-dependent HKS formalism is quite similar to the case without magnetic fields developed in section 2. The variational representation of  $v_{s,0}$  and  $\mathbf{A}_{s,0}$ , however, turns out to be much more complicated. Following Wacker, Kümmel and Gross [60] the quantum mechanical action functional

$$\mathcal{A}_{v_0, \mathbf{A}_0}[\mathbf{j}] = \int_{t_0}^{t_1} dt \langle \Psi[\mathbf{j}](t) | i\frac{\partial}{\partial t} - \hat{T}_{\mathbf{A}_0}(t) - \hat{U} - \hat{V}_0(t) | \Psi[\mathbf{j}](t) \rangle \quad (122)$$

has a stationary point at the true current density  $\mathbf{j}_0$ , i.e., the latter can be determined from the variational equation

$$\left.\frac{\delta\mathcal{A}_{v_0, \mathbf{A}_0}[\mathbf{j}]}{\delta\mathbf{j}(\mathbf{r}, t)}\right|_{\mathbf{j}_0} = 0. \quad (123)$$

Correspondingly, the action functional

$$\mathcal{A}_{v_{s,0}, \mathbf{A}_{s,0}}^s[\mathbf{j}] = \int_{t_0}^{t_1} dt \langle \Phi[\mathbf{j}](t) | i\frac{\partial}{\partial t} - \hat{T}_{\mathbf{A}_{s,0}}(t) - \hat{V}_{s,0}(t) | \Phi[\mathbf{j}](t) \rangle \quad (124)$$

of noninteracting particles moving in the external potentials  $v_{s,0}$ ,  $\mathbf{A}_{s,0}$  has a stationary point at  $\mathbf{j}_0$  as well, i.e.,

$$\left.\frac{\delta\mathcal{A}_{v_{s,0}, \mathbf{A}_{s,0}}^s[\mathbf{j}]}{\delta\mathbf{j}(\mathbf{r}, t)}\right|_{\mathbf{j}_0} = 0. \quad (125)$$

In order to deduce an integral equation determining the potentials  $v_{s0}$ ,  $\mathbf{A}_{s0}$ , we decompose  $\mathcal{A}_{v_0, \mathbf{A}_0}[\mathbf{j}]$  into a universal part,  $\mathcal{B}[\mathbf{j}]$ , and a functional  $\mathcal{Q}_{v_0, \mathbf{A}_0}[\mathbf{j}]$  that depends on the external potentials  $v_0(\mathbf{r}, t)$ ,  $\mathbf{A}_0(\mathbf{r}, t)$ :

$$\mathcal{A}_{v_0, \mathbf{A}_0}[\mathbf{j}] = \mathcal{B}[\mathbf{j}] - \mathcal{Q}_{v_0, \mathbf{A}_0}[\mathbf{j}]. \quad (126)$$

The universal part is given by

$$\mathcal{B}[\mathbf{j}] = \int_{t_0}^{t_1} dt \langle \Psi[\mathbf{j}](t) | i \frac{\partial}{\partial t} - \hat{T} - \hat{U} | \Psi[\mathbf{j}](t) \rangle, \quad (127)$$

where  $\hat{T}$  is the kinetic energy (6). In terms of the functionals

$$n[\mathbf{j}](\mathbf{r}, t) = - \int_{t_0}^t dt' \operatorname{div} \mathbf{j}(\mathbf{r}, t') \quad (128)$$

and

$$\mathbf{j}_p[\mathbf{j}](\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) - \frac{1}{c} n[\mathbf{j}](\mathbf{r}, t) \cdot \mathbf{A}[\mathbf{j}](\mathbf{r}, t) \quad (129)$$

the non-universal contribution to  $\mathcal{A}[\mathbf{j}]$  can be expressed as

$$\mathcal{Q}_{v_0, \mathbf{A}_0}[\mathbf{j}] = \int_{t_0}^{t_1} dt \int d^3r \left\{ \left( v_0(\mathbf{r}, t) + \frac{1}{2c^2} \mathbf{A}_0(\mathbf{r}, t)^2 \right) n[\mathbf{j}](\mathbf{r}, t) + \frac{1}{c} \mathbf{A}_0(\mathbf{r}, t) \cdot \mathbf{j}_p[\mathbf{j}](\mathbf{r}, t) \right\}. \quad (130)$$

Similarly, the action functional of noninteracting particles can be written as

$$\mathcal{A}_{v_{s0}, \mathbf{A}_{s0}}^s[\mathbf{j}] = \mathcal{B}^s[\mathbf{j}] - \mathcal{Q}_{v_{s0}, \mathbf{A}_{s0}}^s[\mathbf{j}]. \quad (131)$$

where

$$\mathcal{B}^s[\mathbf{j}] = \int_{t_0}^{t_1} dt \langle \Phi[\mathbf{j}](t) | i \frac{\partial}{\partial t} - \hat{T} | \Phi[\mathbf{j}](t) \rangle \quad (132)$$

$$\begin{aligned} \mathcal{Q}_{v_{s0}, \mathbf{A}_{s0}}^s[\mathbf{j}] &= \int_{t_0}^{t_1} dt \int d^3r \left\{ \left( v_{s0}(\mathbf{r}, t) + \frac{1}{2c^2} \mathbf{A}_{s0}(\mathbf{r}, t)^2 \right) n[\mathbf{j}](\mathbf{r}, t) \right. \\ &\quad \left. + \frac{1}{c} \mathbf{A}_{s0}(\mathbf{r}, t) \cdot \mathbf{j}_{ps}[\mathbf{j}](\mathbf{r}, t) \right\}. \end{aligned} \quad (133)$$

Note that the functional

$$\mathbf{j}_{ps}[\mathbf{j}] = \mathbf{j}(\mathbf{r}, t) - \frac{1}{c} n[\mathbf{j}](\mathbf{r}, t) \mathbf{A}_s[\mathbf{j}](\mathbf{r}, t) \quad (134)$$

is different, in general, from the functional  $\mathbf{j}_p[\mathbf{j}]$  given by Eq. (129). Defining the universal xc functional as

$$\mathcal{A}_{xc}[\mathbf{j}] = \mathcal{B}^s[\mathbf{j}] - \mathcal{B}[\mathbf{j}] \quad (135)$$

the total action functional of the interacting system can be expressed as

$$\mathcal{A}_{v_0, \mathbf{A}_0}[\mathbf{j}] = \mathcal{B}^s[\mathbf{j}] - \mathcal{Q}_{v_0, \mathbf{A}_0}[\mathbf{j}] - \mathcal{A}_{xc}[\mathbf{j}]. \quad (136)$$

Equating the functional derivatives in (123) and (125) and inserting the expressions (131) and (136) we obtain

$$\left. \frac{\delta \mathcal{Q}_{v_{s0}, \mathbf{A}_{s0}}^s[\mathbf{j}]}{\delta \mathbf{j}(\mathbf{r}, t)} \right|_{\mathbf{j}_0} = \left. \frac{\delta \mathcal{Q}_{v_0, \mathbf{A}_0}[\mathbf{j}]}{\delta \mathbf{j}(\mathbf{r}, t)} \right|_{\mathbf{j}_0} + \left. \frac{\delta \mathcal{A}_{xc}[\mathbf{j}]}{\delta \mathbf{j}(\mathbf{r}, t)} \right|_{\mathbf{j}_0}. \quad (137)$$

This equation defines the TDKS potentials  $v_{s0}$ ,  $\mathbf{A}_{s0}$  implicitly in terms of the functionals  $\mathbf{A}[\mathbf{j}]$  and  $\mathbf{A}_s[\mathbf{j}]$ . Clearly, Eq. (137) is rather complicated. The external-potential terms  $\mathcal{Q}$  and  $\mathcal{Q}^s$  are *simple* functionals of the *density* and the *paramagnetic*

*current density*. The complexity of Eq. (137) arises from the fact that the density, Eq. (128), and the paramagnetic currents, Eqs. (129), (134), are complicated functionals of  $\mathbf{j}$ . Hence a formulation directly in terms of the density and the *paramagnetic* current density would be desirable. For electrons in *static* electromagnetic fields, Vignale and Rasolt [61, 62, 63] have formulated a current-density functional theory in terms of the density and the paramagnetic current density which has been successfully applied to a variety of systems [63]. A time-dependent HKS formalism in terms of the density and the paramagnetic current density, however, has not been achieved so far.

Several extensions of the formalism presented here have been proposed to deal with more general situations. Those include superconductors in time-dependent electromagnetic fields [60, 64] and time-dependent ensembles either for the electrons alone [65, 66] or for the coupled system of electrons and ions [42, 67]. As long as the number of photons is large, i.e.,  $\gg 1$  in a volume given by the wave length cubed, the electromagnetic fields can be treated as *classical* fields. For smaller photon densities the quantum nature of electromagnetic radiation becomes important. In this case, a time-dependent functional theory can be formulated [68] on the basis of quantum electrodynamics. In this formulation the electromagnetic field is treated as a quantum field to be determined self-consistently with the four-current vector of the Dirac matter field.

## 5 Perturbative regime, basic equations

### 5.1 Time-dependent linear density response

In this section we shall derive [69] a formally exact representation of the linear density response  $n_1(\mathbf{r}\omega)$  of an interacting many-electron system in terms of the response function of the corresponding (non-interacting) Kohn-Sham system and a frequency-dependent xc kernel.

We consider electronic systems subject to external potentials of the form

$$v_{\text{ext}}(\mathbf{r}, t) = \begin{cases} v_0(\mathbf{r}) & ; t \leq t_0 \\ v_0(\mathbf{r}) + v_1(\mathbf{r}, t) & ; t > t_0 \end{cases} \quad (138)$$

where  $v_0(\mathbf{r})$  denotes the static external potential of the unperturbed system (typically the nuclear Coulomb attraction) and  $v_1(\mathbf{r}, t)$  is a time-dependent perturbation. We assume, that at times  $t \leq t_0$  the system is in the *ground state* corresponding to  $v_0(\mathbf{r})$ . In this case, the initial density  $n_0(\mathbf{r})$  can be obtained from the self-consistent solution of the ordinary ground-state Kohn-Sham equations:

$$\left( -\frac{1}{2}\nabla^2 + v_0(\mathbf{r}) + \int d^3r' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n_0](\mathbf{r}) \right) \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r}), \quad (139)$$

$$n_0(\mathbf{r}) = \sum_{j=1}^N |\phi_j(\mathbf{r})|^2. \quad (140)$$

By virtue of the static HK-theorem, the initial many-body ground state is uniquely determined by the initial ground-state density  $n_0$ . Hence, in this case, the time-dependent density  $n(\mathbf{r}, t)$  is a functional of the external potential alone,

$$n(\mathbf{r}, t) = n[v_{\text{ext}}](\mathbf{r}, t), \quad (141)$$

i.e., there is no additional dependence on the initial many-body state. By virtue of the fundamental 1-1 correspondence between time-dependent densities and time-dependent potentials, proven by Runge and Gross [7], the functional  $n[v_{\text{ext}}]$  can be

inverted, i.e.,

$$v_{\text{ext}}(\mathbf{r}, t) = v_{\text{ext}}[n](\mathbf{r}, t). \quad (142)$$

Within the realm of perturbation theory, i.e., for sufficiently small  $v_1(\mathbf{r}, t)$  the functional  $n[v_{\text{ext}}]$  can be expanded into a functional Taylor series with respect to the perturbation  $v_1(\mathbf{r}, t)$ ,

$$n(\mathbf{r}, t) - n_0(\mathbf{r}) = n_1(\mathbf{r}, t) + n_2(\mathbf{r}, t) + n_3(\mathbf{r}, t) + \dots, \quad (143)$$

where the lower indices denote the orders in  $v_1$ . The *first* order density response  $n_1$  is given by

$$n_1(\mathbf{r}, t) = \int dt' \int d^3 r' \chi(\mathbf{r}, t, \mathbf{r}', t') v_1(\mathbf{r}', t') \quad (144)$$

with the density-density response function

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta n[v_{\text{ext}}](\mathbf{r}, t)}{\delta v_{\text{ext}}(\mathbf{r}', t')} \right|_{v_0}. \quad (145)$$

Owing to the static HK theorem, the initial potential  $v_0 = v_{\text{ext}}[n_0]$  is a functional of the unperturbed ground-state density  $n_0$ , so that the response function  $\chi$ , by Eq. (145), is a functional of  $n_0$  as well.

For *non-interacting* particles moving in external potentials  $v_s(\mathbf{r}, t)$ , the Runge-Gross theorem holds as well. Therefore the functional

$$n(\mathbf{r}, t) = n[v_s](\mathbf{r}, t) \quad (146)$$

can be inverted,

$$v_s(\mathbf{r}, t) = v_s[n](\mathbf{r}, t), \quad (147)$$

and the Kohn-Sham response function, i.e., the density-density response function of non-interacting particles with unperturbed density  $n_0$  is given by

$$\chi_s(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta n[v_s](\mathbf{r}, t)}{\delta v_s(\mathbf{r}', t')} \right|_{v_s[n_0]}. \quad (148)$$

By inserting the functional (141) into the right-hand side of Eq. (147) one has formally constructed a unique functional  $v_s[v_{\text{ext}}]$  such that the time-dependent density of *noninteracting* particles moving in  $v_s(\mathbf{r}, t)$  is identical with the density of Coulomb-interacting particles moving in  $v_{\text{ext}}(\mathbf{r}, t)$ . The potential  $v_s(\mathbf{r}, t)$  corresponding to a *given*  $v_{\text{ext}}(\mathbf{r}, t)$ , is the time-dependent Kohn-Sham potential (41):

$$v_s(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r}, t). \quad (149)$$

By virtue of the functional chain rule, the functional derivative of  $v_s$  with respect to  $v_{\text{ext}}$  provides a link of the interacting response function (145) to its noninteracting counterpart:

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \int d^3 x \int d\tau \left. \frac{\delta n(\mathbf{r}, t)}{\delta v_s(\mathbf{x}, \tau)} \frac{\delta v_s(\mathbf{x}, \tau)}{\delta v_{\text{ext}}(\mathbf{r}', t')} \right|_{n_0}. \quad (150)$$

Making use of the functional chain rule once more to calculate the functional derivative of  $v_s$  with respect to  $v_{\text{ext}}$  one gets

$$\begin{aligned} \left. \frac{\delta v_s(\mathbf{r}, t)}{\delta v_{\text{ext}}(\mathbf{r}', t')} \right|_{n_0} &= \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \\ &+ \int d^3 x \int d\tau \left( \frac{\delta(t - \tau)}{|\mathbf{r} - \mathbf{x}|} + \frac{\delta v_{\text{xc}}(\mathbf{r}, t)}{\delta n(\mathbf{x}, \tau)} \right) \frac{\delta n(\mathbf{x}, t)}{\delta v_{\text{ext}}(\mathbf{r}', t')}. \end{aligned} \quad (151)$$

By inserting (151) into (150) and using the definitions (145) and (148) we end up with a Dyson-type equation relating the interacting and the noninteracting response functions to each other:

$$\begin{aligned} \chi(\mathbf{r}, t, \mathbf{r}', t') &= \chi_s(\mathbf{r}, t, \mathbf{r}', t') + \int d^3x \int d\tau \int d^3x' \int d\tau' \chi_s(\mathbf{r}, t, \mathbf{x}, \tau) \\ &\quad \times \left( \frac{\delta(\tau - \tau')}{|\mathbf{x} - \mathbf{x}'|} + f_{xc}[n_0](\mathbf{x}, \tau, \mathbf{x}', \tau') \right) \chi(\mathbf{x}', \tau', \mathbf{r}', t'), \end{aligned} \quad (152)$$

where the so-called time-dependent xc kernel

$$f_{xc}[n_0](\mathbf{r}, t, \mathbf{r}', t') := \left. \frac{\delta v_{xc}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{n_0} \quad (153)$$

is a functional of the initial ground-state density  $n_0$ . Equations (152) - (153) are the central result of our analysis. In previous work, see e.g. Ref. [70], it has been common practice to define  $f_{xc}$  by Eq. (152). The present derivation of Eq. (152) from TDDFT shows that  $f_{xc}$ , apart from its relation to the response functions  $\chi$  and  $\chi_s$ , can also be represented as the functional derivative of the TD xc potential. Multiplying Eq. (152) by the perturbing potential  $v_1(\mathbf{r}', t')$  and integrating over  $\mathbf{r}'$  and  $t'$  leads to the time-dependent Kohn-Sham equations for the linear density response:

$$n_1(\mathbf{r}, t) = \int dt' \int d^3r' \chi_s(\mathbf{r}, t, \mathbf{r}', t') v_{s,1}(\mathbf{r}', t'), \quad (154)$$

where the effective potential

$$v_{s,1}(\mathbf{r}, t) = v_1(\mathbf{r}, t) + \int d^3r' \frac{n_1(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r' \int dt' f_{xc}[n_0](\mathbf{r}, t, \mathbf{r}', t') n_1(\mathbf{r}', t') \quad (155)$$

consists of the external perturbation  $v_1$  and the Hartree- and exchange-correlation contributions to first order in the perturbing potential  $v_1$ . We emphasize that Eqs. (154) and (155), postulated in previous work [10, 71, 72], constitute an exact representation of the linear density response. In other words, the *exact* linear density response  $n_1(\mathbf{r}, t)$  of an interacting system can be written as the linear density response of a *noninteracting* system to the effective perturbation  $v_{s,1}(\mathbf{r}, t)$ . Combining Eqs. (154) and (155) and taking the Fourier transform with respect to time, the *exact* frequency-dependent linear density response is seen to be

$$\begin{aligned} n_1(\mathbf{r}, \omega) &= \int d^3y \chi_s(\mathbf{r}, \mathbf{y}; \omega) v_1(\mathbf{y}, \omega) \\ &\quad + \int d^3y \int d^3y' \chi_s(\mathbf{r}, \mathbf{y}; \omega) \left( \frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc}[n_0](\mathbf{y}, \mathbf{y}'; \omega) \right) n_1(\mathbf{y}', \omega). \end{aligned} \quad (156)$$

The Kohn-Sham response function  $\chi_s$  is readily expressed in terms of the static unperturbed Kohn-Sham orbitals  $\phi_k$ :

$$\chi_s(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{j,k} (f_k - f_j) \frac{\phi_j(\mathbf{r}) \phi_k^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}. \quad (157)$$

Here,  $(f_k, f_j)$  are the occupation numbers (0 or 1) of the KS orbitals. The summation in (157) ranges over both occupied and unoccupied orbitals, including the continuum states.

In this section we only dealt with the linear response to time-dependent electric fields of systems at zero temperature. The corresponding formalism for systems at finite temperature in thermal equilibrium was developed in [73, 74]. The

current-density-functional response theory for arbitrary time-dependent electromagnetic fields has been worked out by Ng [75]. The exchange-correlation kernel  $f_{xc}$ , given by Eq. (153), comprises all dynamic exchange and correlation effects to linear order in the perturbing potential. Depending on physical context,  $f_{xc}$  has different names: In the theory of the homogeneous electron gas [70, 76, 77, 78] the Fourier transform,  $f_{xc}(q, \omega)$ , of  $f_{xc}(\mathbf{r}, t, \mathbf{r}', t')$  with respect to  $(\mathbf{r} - \mathbf{r}')$  and  $(t - t')$  is proportional to the so-called *local field correction*

$$\mathcal{G}(q, \omega) = -\frac{q^2}{4\pi} f_{xc}(q, \omega). \quad (158)$$

In the theory of classical liquids [79],  $f_{xc}$  plus the particle-particle interaction is known as *Ornstein-Zernike function*. In practice, of course, this quantity is only approximately known. Suitable approximations of  $f_{xc}$  will be discussed in section 6. In order to construct such approximate functionals, it is useful to express  $f_{xc}$  in terms of the full response function  $\chi$ . An exact representation of  $f_{xc}$  is readily obtained by solving Eq. (144) for  $v_1$  and inserting the result in Eq. (155). Eq. (154) then yields

$$f_{xc}[n_0](\mathbf{r}, t, \mathbf{r}', t') = \chi_s^{-1}[n_0](\mathbf{r}, t, \mathbf{r}', t') - \chi^{-1}[n_0](\mathbf{r}, t, \mathbf{r}', t') - \frac{\delta(t - t')}{|\mathbf{r} - \mathbf{r}'|}, \quad (159)$$

where  $\chi_s^{-1}$  and  $\chi^{-1}$  stand for the kernels of the corresponding inverse integral operators whose existence on the set of densities specified by Eqs. (138) and (144) follows from Eq. (25), as mentioned in section 2.1. The frequency-dependent response operators  $\chi(\mathbf{r}, \mathbf{r}'; \omega)$  and  $\chi_s(\mathbf{r}, \mathbf{r}'; \omega)$ , on the other hand, can be non-invertible at isolated frequencies [80, 81]. Ng and Singwi [73, 82] have argued, however, that these examples are typical of *finite* systems while for large systems in the thermodynamic limit invertibility of the frequency-dependent response operators is guaranteed by the second law of thermodynamics.

As a consequence of causality, the response functions  $\chi(\mathbf{r}, t, \mathbf{r}', t')$  and  $\chi_s(\mathbf{r}, t, \mathbf{r}', t')$  vanish for  $t' > t$ . The same statement holds true for the kernels  $\chi^{-1}(\mathbf{r}, t, \mathbf{r}', t')$  and  $\chi_s^{-1}(\mathbf{r}, t, \mathbf{r}', t')$  of the inverse response operators and hence, by Eq. (159), the xc kernel must satisfy

$$f_{xc}(\mathbf{r}, t, \mathbf{r}', t') = 0 \quad \text{for } t' > t. \quad (160)$$

In particular,  $f_{xc}(\mathbf{r}, t, \mathbf{r}', t')$  is not symmetric under exchange of  $(\mathbf{r}, t)$  and  $(\mathbf{r}', t')$ . Hence, by virtue of Schwarz' lemma for functionals [83],  $f_{xc}(\mathbf{r}, t, \mathbf{r}', t')$  cannot be a second functional derivative  $\delta^2 \mathcal{A}_{xc} / \delta n(\mathbf{r}, t) \delta n(\mathbf{r}', t')$ . Since, on the other hand,  $f_{xc}$  is the functional derivative of  $v_{xc}$  one concludes that the exact  $v_{xc}[n](\mathbf{r}, t)$  cannot be a functional derivative. This is in contradiction to the stationary action principle described in section 2.2. which leads to the representation (42) of  $v_{xc}$  as a functional derivative. This contradiction is currently an unresolved problem. It appears that causality somehow has to be taken into account explicitly in the variational principle (36). We emphasize once more that these considerations do not affect the validity of the TDKS equations (39) – (41) nor do they affect the validity of the response equations (152) – (156). Only the variational representation (42) of  $v_{xc}$  appears doubtful.

We finally mention that the chain of arguments leading to Eq. (152) can be repeated within *static* HKS theory as well. This yields

$$\begin{aligned} & \chi^{\text{stat}}(\mathbf{r}, \mathbf{r}') = \chi_s^{\text{stat}}(\mathbf{r}, \mathbf{r}') \\ & + \int d^3x \int d^3x' \chi_s^{\text{stat}}(\mathbf{r}, \mathbf{x}) \left( \frac{1}{|\mathbf{x} - \mathbf{x}'|} + f_{xc}^{\text{stat}}[n_0](\mathbf{x}, \mathbf{x}') \right) \chi^{\text{stat}}(\mathbf{x}', \mathbf{r}'), \quad (161) \end{aligned}$$

where  $\chi^{\text{stat}}$  and  $\chi_s^{\text{stat}}$  are the full and the KS response functions to static perturbations and

$$f_{\text{xc}}[n_0](\mathbf{x}, \mathbf{x}') := \left. \frac{\delta v_{\text{xc}}[n](\mathbf{x})}{\delta n(\mathbf{x}')} \right|_{n_0} = \left. \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{x}) \delta n(\mathbf{x}')} \right|_{n_0}. \quad (162)$$

On the other hand, taking the Fourier transform of Eq. (152) with respect to  $(t-t')$  one obtains

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}'; \omega) &= \chi_s(\mathbf{r}, \mathbf{r}'; \omega) \\ + \int d^3x \int d^3x' \chi_s(\mathbf{r}, \mathbf{x}; \omega) &\left( \frac{1}{|\mathbf{x} - \mathbf{x}'|} + f_{\text{xc}}[n_0](\mathbf{x}, \mathbf{x}'; \omega) \right) \chi(\mathbf{x}', \mathbf{r}'; \omega). \end{aligned} \quad (163)$$

Subtracting the zero-frequency limit of this equation from Eq. (161) and using the fact that

$$\chi_s^{\text{stat}}(\mathbf{r}, \mathbf{r}') = \chi_s(\mathbf{r}, \mathbf{r}'; \omega = 0) \quad (164)$$

$$\chi^{\text{stat}}(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}, \mathbf{r}'; \omega = 0) \quad (165)$$

one concludes that

$$\int d^3x \int d^3x' \chi_s(\mathbf{r}, \mathbf{x}; \omega = 0) (f_{\text{xc}}[n_0](\mathbf{x}, \mathbf{x}'; \omega = 0) - f_{\text{xc}}^{\text{stat}}[n_0](\mathbf{x}, \mathbf{x}')) \chi(\mathbf{x}', \mathbf{r}'; \omega = 0) = 0. \quad (166)$$

Acting on this equation with  $\hat{\chi}_s^{-1}$  from the left and with  $\hat{\chi}^{-1}$  from the right, one obtains the rigorous identity [84]

$$\lim_{\omega \rightarrow 0} f_{\text{xc}}[n_0](\mathbf{x}, \mathbf{x}'; \omega) = \left. \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{x}) \delta n(\mathbf{x}')} \right|_{n_0}. \quad (167)$$

## 5.2 Time-dependent higher-order response

Recently there has been a great deal of interest in nonlinear phenomena, both from a fundamental point of view, and for the development of new nonlinear optical and optoelectronic devices. Even in the optical case, the nonlinearity is usually engendered by a solid or molecular medium whose properties are typically determined by nonlinear response of an interacting many-electron system. To be able to predict these response properties we need an efficient description of exchange and correlation phenomena in many-electron systems which are not necessarily near to equilibrium. The objective of this chapter is to develop the basic formalism of time-dependent nonlinear response within density functional theory, i.e., the calculation of the higher-order terms of the functional Taylor expansion Eq. (143). In the following this will be done explicitly for the second- and third-order terms

$$n_2(x) = \frac{1}{2!} \int dy \int dy' \chi^{(2)}(x, y, y') v_1(y) v_1(y') \quad (168)$$

$$n_3(x) = \frac{1}{3!} \int dy \int dy' \int dy'' \chi^{(3)}(x, y, y', y'') v_1(y) v_1(y') v_1(y''). \quad (169)$$

The extension to terms of arbitrary order is straightforward. For convenience, we use the four-vector notation

$$x \equiv (\mathbf{r}, t) \quad \text{and} \quad \int dx \equiv \int d^3r \int dt. \quad (170)$$

The second- and third-order response functions of the interacting system are formally given by the functional derivatives

$$\chi^{(2)}(x, y, y') = \left. \frac{\delta^2 n(x)}{\delta v_{\text{ext}}(y) \delta v_{\text{ext}}(y')} \right|_{n_0} \quad (171)$$

$$\chi^{(3)}(x, y, y', y'') = \left. \frac{\delta^3 n(x)}{\delta v_{\text{ext}}(y) \delta v_{\text{ext}}(y') \delta v_{\text{ext}}(y'')} \right|_{n_0} \quad (172)$$



of the time-dependent density with respect to the time-dependent external potential  $v_{\text{ext}}$  evaluated at the initial ground-state density  $n_0$ . From ordinary time-dependent perturbation theory, these quantities are given by [85]

$$\chi^{(2)}(x, y, y') = (-i)^2 \sum_{\mathcal{P}} \theta(t - \tau) \theta(t - \tau') \langle \Psi_0 | [[\hat{n}_H(x), \hat{n}_H(y)], \hat{n}_H(y')] | \Psi_0 \rangle \quad (173)$$

$$\chi^{(3)}(x, y, y', y'') = (-i)^3 \sum_{\mathcal{P}} \theta(t - \tau) \theta(t - \tau') \theta(t' - \tau'') \langle \Psi_0 | [[[ \hat{n}_H(x), \hat{n}_H(y) ], \hat{n}_H(y') ], \hat{n}_H(y'')] | \Psi_0 \rangle \quad (174)$$

where the sum has to be taken over all permutations  $\mathcal{P}$  of  $y, y', y''$  and the index H denotes the Heisenberg picture corresponding to the unperturbed Hamiltonian. From the time-translational invariance of the unperturbed system it follows that the response functions (145), (171) and (172) only depend on the differences of the time-arguments. Obviously, the full response functions (171) and (172) are very hard to calculate.

The response functions of systems of noninteracting particles, on the other hand, are functional derivatives of the density with respect to the time-dependent single-particle potential  $v_s$ :

$$\chi_s^{(2)}(x, y, y') = \left. \frac{\delta^2 n(x)}{\delta v_s(y) \delta v_s(y')} \right|_{n_0} \quad (175)$$

$$\chi_s^{(3)}(x, y, y', y'') = \left. \frac{\delta^3 n(x)}{\delta v_s(y) \delta v_s(y') \delta v_s(y'')} \right|_{n_0}. \quad (176)$$

These functions can be expressed in terms of single-particle orbitals, similar to the linear response function (157).

To obtain the higher-order expressions of the density response, we use the functional chain rule in Eq. (171):

$$\begin{aligned} \frac{\delta^2 n(x)}{\delta v_{\text{ext}}(y) \delta v_{\text{ext}}(y')} &= \frac{\delta}{\delta v_{\text{ext}}(y)} \int dz \frac{\delta n(x)}{\delta v_s(z)} \frac{\delta v_s(z)}{\delta v_{\text{ext}}(y')} \\ &= \int dz \int dz' \frac{\delta^2 n(x)}{\delta v_s(z') \delta v_s(z)} \frac{\delta v_s(z')}{\delta v_{\text{ext}}(y)} \frac{\delta v_s(z)}{\delta v_{\text{ext}}(y')} \\ &\quad + \int dz \frac{\delta n(x)}{\delta v_s(z)} \frac{\delta^2 v_s(z)}{\delta v_{\text{ext}}(y) v_{\text{ext}}(y')}. \end{aligned} \quad (177)$$

As has been outlined in Section 2, the full time-dependent Kohn-Sham potential

$$v_s(x) = v_{\text{ext}}(x) + v_H(x) + v_{\text{xc}}(x) \quad (178)$$

is a unique functional of the external potential  $v_{\text{ext}}$ . Hence, we get

$$\begin{aligned} \frac{\delta^2 v_s(z)}{\delta v_{\text{ext}}(y) \delta v_{\text{ext}}(y')} &= \frac{\delta}{\delta v_{\text{ext}}(y)} \int dz' \frac{\delta (v_H(z) + v_{\text{xc}}(z))}{\delta n(z')} \frac{\delta n(z')}{\delta v_{\text{ext}}(y')} \\ &= \int dz' \int dz'' \frac{\delta^2 (v_H(z) + v_{\text{xc}}(z))}{\delta n(z'') \delta n(z')} \frac{\delta n(z'')}{\delta v_{\text{ext}}(y)} \frac{\delta n(z')}{\delta v_{\text{ext}}(y')} \\ &\quad + \int dz' \frac{\delta (v_H(z) + v_{\text{xc}}(z))}{\delta n(z')} \frac{\delta^2 n(z')}{\delta v_{\text{ext}}(y) \delta v_{\text{ext}}(y')}. \end{aligned} \quad (179)$$

Combining Eqs. (177) and (179) and evaluating all functionals at the ground-state density  $n_0$ , we obtain a Dyson-type relation for the second-order response function

(171):

$$\begin{aligned}
\chi^{(2)}(x, y, y') &= \int dz \int dz' \chi_s^{(2)}(x, z, z') \left. \frac{\delta v_s(z)}{\delta v_{\text{ext}}(y)} \right|_{n_0} \left. \frac{\delta v_s(z')}{\delta v_{\text{ext}}(y')} \right|_{n_0} \\
&+ \int dz \chi_s(x, z) \int dz' \int dz'' g_{\text{xc}}(z, z', z'') \chi(z', y) \chi(z'', y') \\
&+ \int dz \chi_s(x, z) \int dz' (w(z, z') + f_{\text{xc}}(z, z')) \chi^{(2)}(z', y, y'), \quad (180)
\end{aligned}$$

where the time-dependent second-order xc kernel  $g_{\text{xc}}$  is defined as:

$$g_{\text{xc}}(z, z', z'') \equiv \left. \frac{\delta^2 v_{\text{xc}}(z)}{\delta n(z') \delta n(z'')} \right|_{n_0}. \quad (181)$$

To arrive at Eq. (180) we have used the definitions (145), (148), (171) and (175) of the density response functions. Furthermore, we have abbreviated the kernel of the (instantaneous) Coulomb interaction by  $w(x, x') \equiv \delta(t - t')/|\mathbf{r} - \mathbf{r}'|$ . Finally, by inserting Eq. (180) into (168) one arrives at the time-dependent Kohn-Sham equations for the second-order density response:

$$\begin{aligned}
n_2(x) &= \frac{1}{2} \int dz \int dz' \chi_s^{(2)}(x, z, z') v_{s,1}(z) v_{s,1}(z') \\
&+ \frac{1}{2} \int dz \int dz' \int dz'' \chi_s(x, z) g_{\text{xc}}(z, z', z'') n_1(z') n_1(z'') \\
&+ \int dz \int dz' \chi_s(x, z) (w(z, z') + f_{\text{xc}}(z, z')) n_2(z'). \quad (182)
\end{aligned}$$

Solving Eqs. (154) and (155) first, allows for the subsequent solution of the selfconsistent Eq. (182) which is quadratic in the (effective) perturbing potential (155).

In similar fashion, one can set up the equation for the third-order density response (169):

$$\begin{aligned}
n_3(x) &= \frac{1}{6} \int dy \int dy' \int dy'' \chi_s^{(3)}(x, y, y', y'') v_{s,1}(y) v_{s,1}(y') v_{s,1}(y'') \\
&+ \frac{1}{2} \int dy \int dy' \int dz \int dz' \chi_s^{(2)}(x, y, y') v_{s,1}(y) g_{\text{xc}}(y', z, z') n_1(z) n_1(z') \\
&+ \int dy \int dy' \int dy'' \chi_s^{(2)}(x, y, y') v_{s,1}(y) (w(y', y'') + f_{\text{xc}}(y', y'')) n_2(y'') \\
&+ \frac{1}{6} \int dy \int dz \int dz' \int dz'' \chi_s(x, y) h_{\text{xc}}(y, z, z', z'') n_1(z) n_1(z') n_1(z'') \\
&+ \int dy \int dy' \int dy'' \chi_s(x, y) g_{\text{xc}}(y, y', y'') n_1(y') n_2(y'') \\
&+ \int dy \int dy' \chi_s(x, y) (w(y, y') + f_{\text{xc}}(y, y')) n_3(y'). \quad (183)
\end{aligned}$$

The quantity  $h_{\text{xc}}$  occurring in this equation is the third-order functional derivative of the time-dependent xc potential with respect to the time-dependent densities:

$$h_{\text{xc}}(y, z, z', z'') \equiv \left. \frac{\delta^3 v_{\text{xc}}(y)}{\delta n(z) \delta n(z') \delta n(z'')} \right|_{n_0}. \quad (184)$$

Interestingly, the equations (154), (155), (182) and (183) for the  $i$ -th order density responses all exhibit the same structure:

$$n_i(x) = \mathcal{M}_i(x) + \int dy \int dy' \chi_s(x, y) (w(y, y') + f_{\text{xc}}(y, y')) n_i(y') \quad i = 1, 2, 3, \quad (185)$$

where the functionals  $\mathcal{M}_i(x)$  are known after the solution of the  $(i - 1)$ th order. This establishes a hierarchy of Kohn-Sham equations for the time-dependent density response.

The frequency-dependent nonlinear density responses are given by the Fourier transforms of Eqs.(185). For monochromatic perturbations, the expressions for the higher-order frequency dependent density shifts decouple in the frequency variable. The corresponding formulae and explicit expressions for the Kohn-Sham response functions up to third order are given in work of Senatore and Subbaswamy [86]. The corresponding *static* higher-order response has been worked out and applied to solids by Gonze and Vigneron [87].

## 6 The time-dependent exchange-correlation potential: Rigorous properties and approximate functionals

### 6.1 Approximations based on the homogeneous electron gas

The simplest possible approximation of the time-dependent xc potential is the so-called *time-dependent* or *“adiabatic” local density approximation* (ALDA). It employs the functional form of the static LDA with a time-dependent density:

$$v_{xc}^{\text{ALDA}}[n](\mathbf{r}, t) = v_{xc}^{\text{hom}}(n(\mathbf{r}, t)) = \frac{d}{d\rho} (\rho \epsilon_{xc}^{\text{hom}}(\rho)) \Big|_{\rho=n(\mathbf{r}, t)} . \quad (186)$$

Here  $\epsilon_{xc}^{\text{hom}}$  is the xc energy per particle of the homogeneous electron gas. By its very definition, the ALDA can be expected to be a good approximation only for nearly homogeneous densities, i.e., for functions  $n(\mathbf{r}, t)$  that are slowly varying both spatially and temporally. It will turn out, however, that the ALDA gives rather accurate results even for rapidly varying densities (see sections 7 and 8). For the time-dependent xc kernel (153), Eq. (186) leads to

$$f_{xc}^{\text{ALDA}}[n_0](\mathbf{r}, t, \mathbf{r}', t') = \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') \frac{d^2}{d\rho^2} (\rho \epsilon_{xc}^{\text{hom}}(\rho)) \Big|_{\rho=n_0(\mathbf{r})} . \quad (187)$$

The Fourier-transformed quantity

$$f_{xc}^{\text{ALDA}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{d^2}{d\rho^2} (\rho \epsilon_{xc}^{\text{hom}}(\rho)) \Big|_{\rho=n_0(\mathbf{r})} . \quad (188)$$

has no frequency-dependence at all.

In order to incorporate the frequency-dependence of  $f_{xc}$  in some approximate fashion, Gross and Kohn [71] suggested to use the frequency-dependent xc kernel  $f_{xc}^{\text{hom}}$  of the homogeneous electron gas in the sense of an LDA:

$$f_{xc}^{\text{LDA}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) := f_{xc}^{\text{hom}}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega) . \quad (189)$$

The LDA of non-local quantities, such as response functions, always involves some ambiguity [1, 2] as to whether the inhomogeneous  $n_0$  is to be evaluated at  $\mathbf{r}$ , at  $\mathbf{r}'$ , or at some suitably chosen mean value of  $\mathbf{r}$  and  $\mathbf{r}'$ . Of course, in the limit of slowly varying  $n_0(\mathbf{r})$  (i. e. in the limit where the LDA should be a good approximation) the choice does not matter. In addition to the LDA replacement  $f_{xc} \rightarrow f_{xc}^{\text{hom}}$ , Gross and Kohn [71] made the assumption that  $n_1(\mathbf{r}, \omega)$  is slowly varying on the length scale given by the range of  $f_{xc}^{\text{hom}}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega)$ . Under this assumption, the change in the xc potential can be calculated as

$$v_{xc}^{(1)}(\mathbf{r}, \omega) = n_1(\mathbf{r}, \omega) \int d^3r' f_{xc}^{\text{hom}}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega) . \quad (190)$$

In terms of the Fourier transform of  $f_{xc}^{hom}$  with respect to  $(\mathbf{r}-\mathbf{r}')$ , Eq. (190) amounts to the approximation

$$f_{xc}^{GK}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') f_{xc}^{hom}(n_0(\mathbf{r}), q = 0; \omega) \quad . \quad (191)$$

This approximation requires the xc kernel of the homogeneous electron gas as input. In order to investigate this quantity we consider Eq. (159) in the homogeneous case. Fourier transformation with respect to  $(\mathbf{r} - \mathbf{r}')$  and  $(t - t')$  leads to

$$f_{xc}^{hom}(n_0, q; \omega) = \frac{1}{\chi_s^{hom}(n_0, q; \omega)} - \frac{1}{\chi^{hom}(n_0, q; \omega)} - \frac{4\pi}{q^2} \quad . \quad (192)$$

The response function  $\chi_s^{hom}$  of a non-interacting homogeneous system is the well-known Lindhard function. The full response function  $\chi^{hom}$ , on the other hand, is not known analytically. However, some exact features of  $\chi^{hom}$  are known. From these, the following exact properties of  $f_{xc}^{hom}$  can be deduced:

1. As a consequence of the compressibility sum rule one finds [76]

$$\lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = 0) = \frac{d^2}{dn^2}(n\epsilon_{xc}^{hom}(n)) \equiv f_0(n) \quad . \quad (193)$$

This shows that  $f_{xc}^{ALDA}$ , as given by Eq. (188), is identical with the zero-frequency limit of  $f_{xc}^{GK}$ .

2. The third-frequency-moment sum rule leads to [88]

$$\begin{aligned} & \lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = \infty) \\ &= -\frac{4}{5}n^{2/3} \frac{d}{dn} \left( \frac{\epsilon_{xc}^{hom}(n)}{n^{2/3}} \right) + 6n^{1/3} \frac{d}{dn} \left( \frac{\epsilon_{xc}^{hom}(n)}{n^{1/3}} \right) \equiv f_\infty(n) \quad . \quad (194) \end{aligned}$$

3. According to the best estimates [89, 90] of  $\epsilon_{xc}^{hom}$ , the following relation holds for all densities:

$$f_0(n) < f_\infty(n) < 0 \quad . \quad (195)$$

4. The large- $q$  behavior at zero frequency is given by [91]

$$\lim_{q \rightarrow \infty} f_{xc}^{hom}(q, \omega = 0) = -2n^{1/3} \frac{d}{dn} \left( n^{-1/3} \epsilon_{xc}^{hom}(n) \right) - \frac{4\pi}{q^2} B(n) \quad . \quad (196)$$

The function  $B(n)$  has been fitted [92] to Monte-Carlo results. The resulting parametrization

$$B(n) = \frac{1 + 2.15x + 0.435x^3}{3 + 1.57x + 0.409x^3}, \quad x = \sqrt{r_s} = \left( \frac{3}{4\pi n} \right)^{1/6} \quad (197)$$

reproduces the Monte-Carlo results with a precision of about 1% in the density range  $0 \leq r_s \leq 10$ .

5. The short-wavelength behavior in the high-frequency limit is given by [93, 94]

$$\lim_{q \rightarrow \infty} f_{xc}^{hom}(q, \omega = \infty) = -\frac{2}{3} \cdot \frac{4\pi}{q^2} (1 - g(0)) + 6n^{1/3} \frac{d}{dn} \left( n^{-1/3} \epsilon_{xc}^{hom}(n) \right) \quad (198)$$

where  $g(r)$  denotes the pair correlation function.

6.  $f_{xc}^{hom}(q, \omega)$  is a complex-valued function satisfying the symmetry relations

$$\Re f_{xc}^{hom}(q, \omega) = \Re f_{xc}^{hom}(q, -\omega) \quad (199)$$

$$\Im f_{xc}^{hom}(q, \omega) = -\Im f_{xc}^{hom}(q, -\omega) \quad . \quad (200)$$

7.  $f_{xc}^{hom}(q, \omega)$  is an analytic function of  $\omega$  in the upper half of the complex  $\omega$ -plane and approaches a real function  $f_\infty(q)$  for  $\omega \rightarrow \infty$  [70]. Therefore, the function  $(f_{xc}^{hom}(q, \omega) - f_\infty(q))$  satisfies standard Kramers-Kronig relations:

$$\Re f_{xc}^{hom}(q, \omega) - f_\infty(q) = \mathbf{P} \int \frac{d\omega'}{\pi} \frac{\Im f_{xc}^{hom}(q, \omega')}{\omega' - \omega} \quad (201)$$

$$\Im f_{xc}^{hom}(q, \omega) = -\mathbf{P} \int \frac{d\omega'}{\pi} \frac{\Re f_{xc}^{hom}(q, \omega') - f_\infty(q)}{\omega' - \omega} \quad . \quad (202)$$

8. The imaginary part of  $f_{xc}^{hom}$  exhibits the high-frequency behavior

$$\lim_{\omega \rightarrow \infty} \Im f_{xc}^{hom}(q, \omega) = -\frac{c}{\omega^{3/2}} \quad (203)$$

for any  $q < \infty$  [95]. A second-order perturbation expansion [95, 96] of the irreducible polarization propagator leads to the high-density limit

$$c = \frac{23\pi}{15} \quad . \quad (204)$$

Other authors [97, 98] find  $c = 46\pi/15$ ; see also Ref. [94].

9. In the same limit, the real part of  $f_{xc}^{hom}$  behaves like [71]

$$\lim_{\omega \rightarrow \infty} \Re f_{xc}^{hom}(q, \omega) = f_\infty(q) + \frac{c}{\omega^{3/2}} \quad . \quad (205)$$

Since  $c > 0$ , the infinite-frequency value  $f_\infty$  is approached from above. This implies, in view of the relation (195), that  $\Re f_{xc}^{hom}(q = 0, \omega)$  cannot grow monotonically from  $f_0$  to  $f_\infty$ .

The above features of  $f_{xc}^{hom}$  are valid for a three-dimensional electron gas. Analogous results have been obtained for the two-dimensional case [95, 99, 100].

Taking into account the exact high- and low-frequency limits, Gross and Kohn [71] proposed the following parametrization for the imaginary part of  $f_{xc}^{hom}$ :

$$\Im f_{xc}^{hom}(q = 0, \omega) = \frac{a(n)\omega}{(1 + b(n)\omega^2)^{5/4}} \quad , \quad (206)$$

where

$$a(n) = -c(\gamma/c)^{5/3}(f_\infty(n) - f_0(n))^{5/3} \quad (207)$$

$$b(n) = (\gamma/c)^{4/3}(f_\infty(n) - f_0(n))^{4/3} \quad (208)$$

$$\gamma = \frac{(\Gamma(1/4))^2}{4\sqrt{2\pi}} \quad . \quad (209)$$

$f_0$ ,  $f_\infty$ , and  $c$  are given by Eqs. (193), (194), and (204), respectively. Using the Kramers-Kronig relation (201), the real part can be expressed as

$$\begin{aligned} & \Re f_{xc}^{hom}(q = 0, \omega) \\ &= f_\infty + \frac{a}{\pi s^2} \sqrt{\frac{8}{b}} \left[ 2E\left(\frac{1}{\sqrt{2}}\right) - \frac{1+s}{2} \Pi\left(\frac{1-s}{2}, \frac{1}{\sqrt{2}}\right) \right. \\ & \quad \left. - \frac{1-s}{2} \Pi\left(\frac{1+s}{2}, \frac{1}{\sqrt{2}}\right) \right] \quad , \quad s^2 = 1 + b\omega^2 \quad . \quad (210) \end{aligned}$$

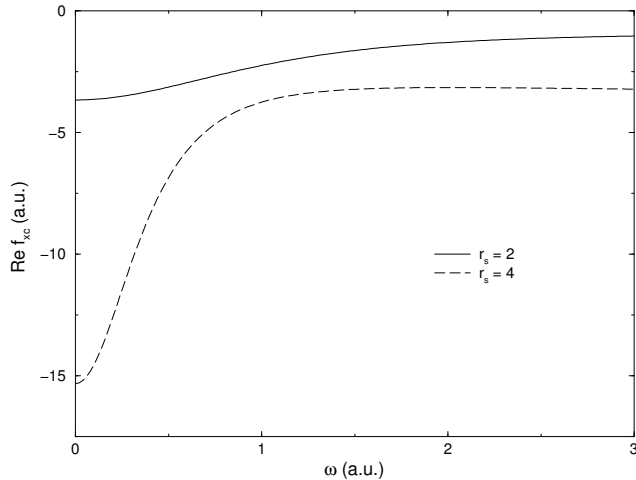


Figure 1: *Real part of the parametrization for  $f_{xc}^{hom}(q = 0, \omega)$ , from Ref. [88].*

$E$  and  $\Pi$  are complete elliptic integrals of the second and third kind in the standard notation of Byrd and Friedman [101]. This completes the explicit form of the Gross-Kohn approximation (191).

Figs. 1 and 2 show the real and imaginary part of  $f_{xc}^{hom}$  as calculated from (206) and (210). The functions are plotted for the two density values corresponding to  $r_s = 2$  and  $r_s = 4$ . For the lower density value ( $r_s = 4$ ), a considerable frequency dependence is found. The dependence on  $\omega$  becomes less pronounced for higher densities. In the extreme high-density limit, the difference between  $f_0$  and  $f_\infty$  tends to zero. One finds the exact result

$$f_\infty - f_0 \sim r_s^2 \quad \text{for } r_s \rightarrow 0 \quad . \quad (211)$$

At the same time, the depth of the minimum of  $\Im f_{xc}^{hom}$  decreases, within the parametrization (206) proportional to  $r_s^2$ .

We finally mention that an extension of the parametrization (206) to non-vanishing  $q$  was given by Dabrowski [102]. The spin-dependent case was treated by Liu [103]. A similar interpolation for the exchange-correlation kernel of the 2-dimensional electron gas has been derived by Holas and Singwi [95].

In the construction and improvement of static ground-state density functionals, various exact constraints such as xc hole normalization [104] and scaling relations [105] have been extremely useful. While the development of explicit time-dependent functionals is at a comparatively early stage, there are some constraint conditions which can be useful in the time-dependent context. First of all, some of the exact properties of the homogeneous-electron-gas kernel  $f_{xc}^{hom}$  are readily generalized to the inhomogeneous case: Causality leads to Kramers-Kronig relations for  $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$  analogous to Eqs. (201) and (202), and the fact that  $f_{xc}(\mathbf{r}, t, \mathbf{r}', t')$  is a real-valued quantity implies that

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = f_{xc}(\mathbf{r}, \mathbf{r}'; -\omega)^* . \quad (212)$$

Besides that, the response functions  $\chi_s$  and  $\chi$  satisfy the symmetry relations [106]

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \chi(\mathbf{r}', \mathbf{r}; \omega) \quad (213)$$

$$\chi_s(\mathbf{r}, \mathbf{r}'; \omega) = \chi_s(\mathbf{r}', \mathbf{r}; \omega) \quad (214)$$

provided that the unperturbed system has time-reversal symmetry. Equation (163) then implies that

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = f_{xc}(\mathbf{r}', \mathbf{r}; \omega) . \quad (215)$$

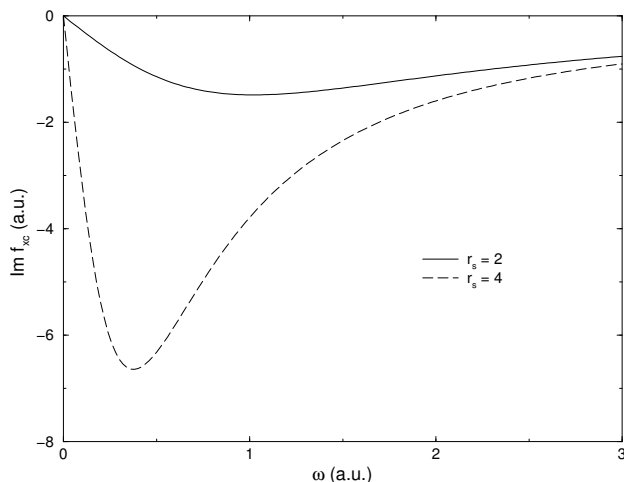


Figure 2: *Imaginary part of the parametrization for  $f_{xc}^{hom}(q=0, \omega)$ , from Ref. [88].*

Further exact constraints can be deduced from the quantum mechanical equation of motion (15). For the operator

$$\hat{\mathbf{r}} = \int d^3r \mathbf{r} \hat{n}(\mathbf{r}) \quad (216)$$

Eq. (15) leads to

$$\frac{d}{dt} \langle \Psi(t) | \mathbf{r} | \Psi(t) \rangle = \frac{d}{dt} \int d^3r \mathbf{r} n(\mathbf{r}, t) = i \langle \Psi(t) | [\hat{H}(t), \hat{\mathbf{r}}] | \Psi(t) \rangle \quad (217)$$

where

$$\hat{H}(t) = \hat{T} + \hat{U} + \hat{V}_{\text{ext}}(t). \quad (218)$$

Taking the time derivative of Eq. (217) and employing the equation of motion (15) once more one obtains

$$\frac{d^2}{dt^2} \int d^3r \mathbf{r} n(\mathbf{r}, t) = - \langle \Psi(t) | [\hat{H}(t), [\hat{H}(t), \hat{\mathbf{r}}]] | \Psi(t) \rangle \quad (219)$$

because  $\frac{\partial}{\partial t} [\hat{H}(t), \hat{\mathbf{r}}] \equiv 0$ . Using the translational invariance of the Coulomb interaction  $\hat{U}$  the double commutator in (219) is readily calculated, leading to the traditional Ehrenfest theorem:

$$\frac{d^2}{dt^2} \int d^3r \mathbf{r} n(\mathbf{r}, t) = - \int d^3r n(\mathbf{r}, t) \nabla v_{\text{ext}}(\mathbf{r}, t). \quad (220)$$

Likewise, for noninteracting systems described by Hamiltonians of the form

$$\hat{H}_s(t) = \hat{T} + \hat{V}_s(t) \quad (221)$$

one obtains

$$\frac{d^2}{dt^2} \int d^3r \mathbf{r} n_s(\mathbf{r}, t) = - \int d^3r n_s(\mathbf{r}, t) \nabla v_s(\mathbf{r}, t). \quad (222)$$

For the unique KS potential

$$v_s[n](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_H[n](\mathbf{r}, t) + v_{xc}[n](\mathbf{r}, t) \quad (223)$$

which reproduces the density  $n(\mathbf{r}, t)$  of the interacting system, Eq. (222) leads to

$$\frac{d^2}{dt^2} \int d^3r \mathbf{r} n(\mathbf{r}, t) = - \int d^3r n(\mathbf{r}, t) \nabla (v_{\text{ext}}(\mathbf{r}, t) + v_H[n](\mathbf{r}, t) + v_{\text{xc}}[n](\mathbf{r}, t)) . \quad (224)$$

Subtracting Eq. (220) from Eq. (224) one obtains the rigorous result

$$\int d^3r n(\mathbf{r}, t) \nabla v_{\text{xc}}[n](\mathbf{r}, t) = 0 . \quad (225)$$

To arrive at Eq. (225) we have used the fact that the Hartree potential

$$v_H[n](\mathbf{r}, t) = \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \quad (226)$$

satisfies the equation

$$\int d^3r n(\mathbf{r}, t) \nabla v_H[n](\mathbf{r}, t) = 0 . \quad (227)$$

Equation (225) was first obtained by Vignale [107] from invariance properties of the xc action functional  $\mathcal{A}_{\text{xc}}$  defined in Eq. (43). The derivation given here [108, 109] has the advantage of being independent of the stationary action principle.

Applying the equation of motion (15) to the angle operator  $\hat{\varphi}$  and using the rotational invariance of the Coulomb interaction  $\hat{U}$ , one obtains

$$\frac{d^2}{dt^2} \langle \Psi(t) | \hat{\varphi} | \Psi(t) \rangle = - \int d^3r n(\mathbf{r}, t) \mathbf{r} \times \nabla v_{\text{ext}}(\mathbf{r}, t) . \quad (228)$$

Subtraction of the corresponding equation for the KS potential (223) then leads to the exact constraint

$$\int d^3r n(\mathbf{r}, t) \mathbf{r} \times \nabla v_{\text{xc}}[n](\mathbf{r}, t) = 0 . \quad (229)$$

Corresponding properties of the exact xc kernel are obtained by evaluating the left-hand sides of Eqs. (225) and (229) at the density

$$n(\mathbf{r}, t) = n_0(\mathbf{r}) + \delta n(\mathbf{r}, t) , \quad (230)$$

where  $\delta n(\mathbf{r}, t)$  is an arbitrary deviation from the ground-state density  $n_0(\mathbf{r})$ . To first order in  $\delta n$  one obtains from Eq. (225)

$$\begin{aligned} 0 &= \int d^3r n_0(\mathbf{r}) \nabla v_{\text{xc}}[n_0](\mathbf{r}) \\ &+ \int d^3r' \int dt' \delta n(\mathbf{r}', t') \left[ \delta(t - t') \nabla_{\mathbf{r}'} v_{\text{xc}}[n_0](\mathbf{r}') \right. \\ &\left. + \int d^3r n_0(\mathbf{r}) \nabla_{\mathbf{r}} f_{\text{xc}}[n_0](\mathbf{r}, t, \mathbf{r}', t') \right] . \end{aligned} \quad (231)$$

The first integral on the right-hand side of this equation must vanish. (This is the static limit [110] of Eq. (225).) Since  $\delta n$  is arbitrary, the second integral leads to the identity

$$\int d^3r n_0(\mathbf{r}) \nabla_{\mathbf{r}} f_{\text{xc}}[n_0](\mathbf{r}, t, \mathbf{r}', t') = -\delta(t - t') \nabla_{\mathbf{r}'} v_{\text{xc}}[n_0](\mathbf{r}') . \quad (232)$$

Taking the Fourier-Transform of this equation with respect to  $(t - t')$  one obtains the constraint

$$\int d^3r n_0(\mathbf{r}) \nabla_{\mathbf{r}} f_{\text{xc}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = -\nabla_{\mathbf{r}'} v_{\text{xc}}[n_0](\mathbf{r}') . \quad (233)$$



Applying the same procedure to Eq. (229) one arrives at [108, 109]

$$\int d^3r n_0(\mathbf{r}) \mathbf{r} \times \nabla_{\mathbf{r}} f_{xc}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = -\mathbf{r}' \times \nabla_{\mathbf{r}'} v_{xc}[n_0](\mathbf{r}'). \quad (234)$$

Finally, multiplying Eqs. (233) and (234) by  $n_0(\mathbf{r}')$  and integrating over  $\mathbf{r}'$  leads to

$$\int d^3r \int d^3r' n_0(\mathbf{r}) n_0(\mathbf{r}') \nabla_{\mathbf{r}} f_{xc}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = 0 \quad (235)$$

and

$$\int d^3r \int d^3r' n_0(\mathbf{r}) n_0(\mathbf{r}') \mathbf{r} \times \nabla_{\mathbf{r}} f_{xc}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = 0. \quad (236)$$

Equation (233) was first obtained by Vignale [111] from a new sum rule for the response function. The ALDA satisfies the constraints (233) and (234) while the Gross-Kohn approximation (191) is easily seen to violate them. This fact is closely related to the violation of the Harmonic Potential Theorem which will be discussed in detail below.

Another type of constraint on theories of time-dependent phenomena in interacting inhomogeneous systems is obtained by taking expectation values of repeated commutators of current operators with the Hamiltonian. In this way one obtains exact relations for frequency moments of response functions. Very recently Sturm [94] has given a detailed study of the odd frequency moments of the dielectric function in *inhomogeneous* systems, and has explored odd moments up to the seventh. The ALDA satisfies the first, third and fifth frequency moment sum rules but violates the seventh as was demonstrated by Sturm for metals in the nearly free electron approximation.

Finally, another rigorous constraint [112] is known as the Harmonic Potential Theorem (HPT), as it relates to the motion of interacting many-electron systems in an externally-imposed harmonic oscillator potential  $v(\mathbf{r}) = \frac{1}{2} \mathbf{r} \cdot \mathbf{K} \cdot \mathbf{r}$  plus the potential  $-\mathbf{F}(t) \cdot \mathbf{r}$  describing a spatially uniform, time-dependent external force  $\mathbf{F}(t)$ . Here  $\mathbf{K}$  is a spring-constant matrix which can be assumed symmetric without loss of generality. (Suitable choices of  $\mathbf{K}$  yield various physical situations: for example, the choice  $\mathbf{K} = \mathbf{diag}(k, k, k)$  corresponds to a spherical quantum dot or ‘‘Hooke’s atom’’, while the choice  $\mathbf{K} = \mathbf{diag}(0, 0, k)$  yields a parabolic quantum well such as may be grown in the  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  system by molecular beam epitaxy.) The harmonic external potential is special, being the only confining potential which retains its form when one transforms to a homogeneously accelerated reference frame. To see that it does so, consider [113] a moving frame whose origin has the space coordinate  $\mathbf{X}(t)$  relative to the rest frame. The observer in this frame sees a total external potential

$$\bar{v}(\bar{\mathbf{r}}, t) = \frac{1}{2} \mathbf{r} \cdot \mathbf{K} \cdot \mathbf{r} + m \ddot{\mathbf{X}} \cdot \bar{\mathbf{r}} - \mathbf{F}(t) \cdot \mathbf{r} \quad (237)$$

where  $\bar{\mathbf{r}} = \mathbf{r} - \mathbf{X}(t)$  is the position coordinate in the new frame, and the second term in (237) is the centrifugal or fictitious potential due to motion of the frame. If  $\mathbf{X}(t)$  satisfies the classical equation of motion

$$m \ddot{\mathbf{X}}(t) = -\mathbf{K} \cdot \mathbf{X}(t) + \mathbf{F}(t) \quad (238)$$

then one obtains the potential in the moving frame as

$$\bar{v}(\bar{\mathbf{r}}, t) = \frac{1}{2} \bar{\mathbf{r}} \cdot \mathbf{K} \cdot \bar{\mathbf{r}} + c(t). \quad (239)$$

This transformed external potential (239) has the same form as the potential for the *undriven* ( $\mathbf{F} = \mathbf{0}$ ) harmonic well problem in the rest frame, except for the term  $c$

which depends on time but not on  $\bar{\mathbf{r}}$ . Furthermore, because the (Coulomb or other) particle-particle interaction is a function only of differences  $\mathbf{r}_i - \mathbf{r}_j = \bar{\mathbf{r}}_i - \bar{\mathbf{r}}_j$ , the interaction potential is also invariant under the transformation to the accelerated frame. Thus, both classically and quantum mechanically, any state or motion in the rest frame has a counterpart motion with superimposed translation  $\mathbf{X}(t)$ , provided that (238) is satisfied. In particular

*for harmonically-confined interacting systems there exist quantum states in which the ground-state many-body wavefunction is translated rigidly (up to a phase factor) as in classical motion, and hence the ground-state number density  $n_0(\mathbf{r})$  is replaced by the rigidly moving density  $n(\mathbf{r}, t) = n_0(\mathbf{r} - \mathbf{X}(t))$ .*

(240)

This conclusion is the Harmonic Potential Theorem (HPT). It is an extension of the generalized Kohn Theorem [114]: the latter only refers to the frequency dependence of linear response and does not address the spatial profile of the moving density. The HPT can be also proved more formally [112] by explicit construction of the moving many-body wavefunction as seen in the rest frame. It is important to note that systems confined by a scalar harmonic potential (e.g. quantum dots) are spatially finite in at least one dimension, and have strong spatial inhomogeneity at their edges. Thus the HPT constitutes an *exact* result *beyond the level of linear response* for the *time-dependent* behavior of an *inhomogeneous, interacting many-body system*. As such, it poses an interesting constraint on approximate general theories of time-dependent many-body physics, such as local-density versions of TDDFT. Of course, since the HPT is valid generally it is also valid for linear response. Vignale [107] has shown that the HPT result holds even with the inclusion of a homogeneous magnetic field.

Another closely related constraint is that of Galileian invariance. Suppose that a many-body wavefunction  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  satisfies the time-independent interacting N-particle Schrödinger equation with an external one-particle potential  $v(\mathbf{r})$ . Then, provided that the inter-particle interaction depends on coordinate differences only, it is readily verified that a boosted wavefunction of the form

$$\exp(-iS(t) + i\mathbf{U} \cdot \sum_{j=1}^N \mathbf{r}_j) \Psi(\mathbf{r}_1 - \mathbf{U}t, \mathbf{r}_2 - \mathbf{U}t, \dots, \mathbf{r}_N - \mathbf{U}t), \quad (241)$$

where  $S(t)$  is the corresponding *classical* action [112], satisfies the time-dependent interacting N-body Schrödinger equation with boosted external potential  $v(\mathbf{r} - \mathbf{U}t)$ . Because the phase factor disappears in forming  $|\Psi|^2$ , this result implies that all many-body probability densities are rigidly boosted when the external one-body potential is boosted. In particular, the one-particle density is rigidly boosted, and this particular aspect of Galileian invariance should apply to TDDFT which deals directly with densities. In applying this criterion, it will clearly be necessary to relax the condition used in section 5 that the initial many-body wavefunction be the ground-state wavefunction. In fact, to represent a system boosted to constant velocity  $\mathbf{U}$ , the initial wavefunction must contain the additional phase factor shown in Eq. (241)

The following question now arises: which approximations in TDDFT satisfy the HPT and Galileian invariance? By noting that the ALDA xc potential rigidly follows the density when the latter is rigidly moved, and by examining the TDKS equations for harmonic confinement with and without a driving field Dobson [112] showed that the ALDA satisfies the HPT for motion of arbitrary amplitude. The same proof in fact shows that any approximation to TDDFT satisfies the HPT provided that the xc potential rigidly follows a rigidly translated density. This

rigid-following condition will be termed *Generalized Translational Invariance* and can be expressed as:

$$v_{xc}[n'](\mathbf{r}, t) = v_{xc}[n](\mathbf{r} - \mathbf{X}(t)) \quad (242)$$

Here  $n(\mathbf{r})$  is an arbitrary time-independent density and  $n'(\mathbf{r}, t) = n(\mathbf{r} - \mathbf{X}(t))$  is the same density rigidly boosted. (The otherwise-arbitrary displacement function  $\mathbf{X}(t)$  will need to be zero at the initial time  $t_0$ , and the initial many body state will need to be the ground-state, in order for  $v_{xc}$  in (242) to be defined in the same manner used earlier in this chapter.) Eq. (242) simply says that a rigid (possibly accelerated) motion of the density implies a similar rigid motion of the xc potential. Equation (242) was first demonstrated by Vignale [107] from the covariance of the time-dependent Schrödinger equation under transformation to an accelerated rest frame. Vignale also generalized the treatment to include a magnetic field. The same condition (242) with  $\mathbf{X}(t) = \mathbf{U}t$  will also ensure that an approximation to  $v_{xc}$  satisfies Galileian invariance.

Perhaps surprisingly, the Gross-Kohn approximation (191) unlike the ALDA, does *not* satisfy the HPT constraint. This was proved in Ref. [112] by exhibiting a specific counterexample.

The question now arises how one might correct this situation. One attempt [112] is based on the heuristic picture that, in the rigid HPT motion, all the *relative* particle motions [115], and therefore the exchange and correlation phenomena, are exactly as in the ground-state. In particular, the *static* exchange-correlation kernel  $f_{xc}(n, \omega = 0)$  is appropriate for this very special motion, even though the frequency of the HPT motion has the high value  $\omega = \omega_P$ . This is why the ALDA succeeds with the HPT motion: it uses  $f_{xc}(n, \omega = 0)$  in all circumstances and therefore is fortuitously exact for HPT motion. The original GK formalism requires the use of  $f_{xc}(n, \omega = \omega_P)$ , and this is the core of the difficulty. (A similar difficulty was also demonstrated [112] for hydrodynamic theory of plasmons where, once again, the frequency dependence of a coefficient,  $\beta^2(\omega \rightarrow \infty) \neq \beta^2(\omega \rightarrow 0)$ , is to blame,  $\beta$  being the pressure or diffusion coefficient.)

While most motions are not simple rigid displacements, there will be an element of this type of motion, as well as an element of compression, in more general motions provided that the original density is spatially inhomogeneous. In the linear response regime, a well-defined separation between these two components of the motion can be made [112] by first introducing the fluid velocity  $\mathbf{u}(\mathbf{r}, t) = \mathbf{J}(\mathbf{r}, t)/n(\mathbf{r}, t)$  where the *exact* current density  $\mathbf{J}$  can be obtained from the TDKS orbitals as demonstrated in section 2.3. A fluid element displacement  $\mathbf{X}(\mathbf{r}, t)$  is then defined for a general motion by

$$\mathbf{X}(\mathbf{r}, t) = \mathbf{r} + \int_{t_0}^t \mathbf{u}(\mathbf{r}, t') dt', \quad \mathbf{u} = \frac{\partial \mathbf{X}}{\partial t} \quad (243)$$

and by integrating the linearized continuity equation with respect to  $t$  at fixed  $\mathbf{r}$  we obtain an expression for the perturbation to the equilibrium density  $n_0(\mathbf{r})$  in a small motion:

$$n_1(\mathbf{r}, t) = -\nabla \cdot [n_0(\mathbf{r})\mathbf{X}(\mathbf{r}, t)] = -n_0(\mathbf{r})\nabla \cdot \mathbf{X}(\mathbf{r}, t) - \mathbf{X}(\mathbf{r}, t) \cdot \nabla n_0(\mathbf{r}). \quad (244)$$

For an arbitrary motion, we denote the first term in (244) as

$$n_{1a}(\mathbf{r}, t) = -n_0(\mathbf{r})\nabla \cdot \mathbf{X}(\mathbf{r}, t) \quad (245)$$

and interpret  $n_{1a}$  as the compressive part of the density perturbation, to be associated with  $f_{xc}(\omega)$  where  $\omega$  is the actual frequency of the linear motion. The other density component from (244) is

$$n_{1b}(\mathbf{r}, t) = -\mathbf{X}(\mathbf{r}, t) \cdot \nabla n_0(\mathbf{r}) \quad (246)$$

and this is the part one would have obtained if the equilibrium density had been rigidly translated, suggesting that it should be associated with a zero-frequency kernel  $f_{xc}(\omega = 0)$ . These two components make up the total density perturbation,

$$n_1 = n_{1a} + n_{1b}, \quad (247)$$

and the above arguments suggest that the xc potential for small-amplitude motion at frequency  $\omega$  should be

$$v_{1xc}(\mathbf{r}, \omega) = f_{xc}(n_0(\mathbf{r}), \omega)n_{1a}(\mathbf{r}, \omega) + f_{xc}(n_0(\mathbf{r}), \omega = 0)n_{1b}(\mathbf{r}, \omega). \quad (248)$$

It is immediately apparent that (248) will give the correct zero-frequency xc potential value for Harmonic Potential Theorem motion. For this motion, the gas moves rigidly implying  $\mathbf{X}$  is independent of  $\mathbf{r}$  so that the compressive part,  $n_{1a}$ , of the density perturbation from (245) is zero. Equally, for perturbations to a uniform electron gas,  $\nabla n_0$  and hence  $n_{1b}$  is zero, so that (248) gives the uniform-gas xc kernel  $f_{xc}(\omega)$  at the actual frequency  $\omega$ , as required.

A modification similar to (248) was also proposed in [112] for the pressure or diffusion term in hydrodynamics, and the resulting formalism has had some success with a unified description of boundary conditions and plasmon modes on parabolic wells [116].

Since the fluid displacement during linear response at a definite frequency  $\omega$  is given by  $\mathbf{X} = \mathbf{J}/(i\omega n)$ , the postulated Eq. (248) suggests that  $v_{xc}$  is not a local function of the density but rather of the *current* density  $\mathbf{J}$ . There are, however, preliminary indications that, for nonlinear phenomena such that a definite frequency cannot be assigned to the motion the fluid displacement  $\mathbf{X}$  may yield a more direct formulation of xc phenomena than does the current density (see later in this chapter).

Numerical applications of the new formalism implied by (248) are under development [117]. Preliminary indications are that the ALDA, the Gross-Kohn approximation (191) and (248) will all give substantially different results for at least one of the plasmon modes of a low-density parabolic quantum well, say for  $r_s = 6$ . (The modes in question are the HPT (“Kohn” or “sloshing”) mode, the standing plasmon modes [118], and also the 2D plasmon mode at substantial surface-directed wavenumber  $q_{\parallel}$  for which case the frequency is not constrained by model-independent theorems [119].)

Vignale [107] has given an alternative method to ensure that any xc formalism with finite memory (i.e. with frequency-dependent xc kernel) will satisfy the HPT. Starting from a simple *Ansatz* for the action integral, he derived an xc potential

$$v_{1xc}(\mathbf{r}, t) = \int_{t_0}^t f_{xc}(n_0(\mathbf{r}), t - t') \delta n_{rel}(\mathbf{r}, t') dt' \quad (249)$$

where

$$\delta n_{rel}(\mathbf{r}, t) = n(\mathbf{r} + \mathbf{R}_{cm}(t)) - n_0(\mathbf{r}) \quad (250)$$

is the density perturbation seen by an observer moving with the global center of mass

$$\mathbf{R}_{cm}(t) = \frac{1}{N} \int \mathbf{r} n(\mathbf{r}, t) d^3 r. \quad (251)$$

This approach does ensure satisfaction of the HPT. It differs from the method described above in that it is very much less local, requiring a determination of the global center of mass from (251) at each instant  $t$ . One can imagine situations where the two formalisms will give very different results. For example, consider two well-separated layers of electron gas confined in parallel parabolic wells. At the Hartree

and Hartree-Fock levels there is no interaction between these wells in the absence of significant wavefunction overlap (and in the absence of any perturbation which might break the symmetry in the plane of the electron gas layers). For sufficient separations any residual van der Waals interaction can be made as small as desired, so the  $q_{\parallel} = 0$  modes of oscillation of the two wells will be uncoupled. First consider a motion in which the two electron gases execute HPT motion (sloshing sideways) *in phase*. Then the global electronic center of mass also executes HPT motion and the Vignale method will give the correct HPT motion of the combined system. Secondly, however, consider the mode in which the two sloshing motions are 180 degrees out of phase. Then the global center of mass is stationary and the Vignale correction makes no difference, leaving the GK formalism unmodified. But this method is known not give the HPT motion correctly, as discussed above. The method described by Eq. (248), on the other hand, is more local in its effect and it corrects the motion of each well separately, giving the correct HPT motion of each gas even for the 180 degrees phase mode.

In general, for systems far from equilibrium it is not at all clear how one should approximate the full xc potential  $v_{xc}[n](\mathbf{r}, t)$ . The most general possible nonlinear dependence of  $v_{xc}[n](\mathbf{r}, t)$  on  $n$  must involve at least terms with  $n$  evaluated at one space-time point  $\xi' \equiv (\mathbf{r}', t')$ , terms with  $n$  evaluated at two spacetime points  $\xi'$  and  $\xi''$ , terms with  $n$  evaluated at three points  $\xi', \xi'', \xi'''$ , and so on. (Even this might not cover all possibilities, but the only counterexamples so far noted have involved essentially singular functions [120].) Thus in general we expect to require nonlinear functions  $W^{(i)}$  such that

$$v_{xc}[n](\xi) = \int d\xi' W^{(1)}(n(\xi'), \xi, \xi') + \int d\xi' d\xi'' W^{(2)}(n(\xi'), n(\xi''), \xi, \xi', \xi'') + \dots \quad (252)$$

The functional derivative of (252) is

$$\frac{\delta v_{xc}(\xi)}{\delta n(\xi')} = \frac{\partial W^{(1)}}{\partial n}(n(\xi'), \xi, \xi') + \int d\xi'' [W_1^{(2)}(n(\xi'), n(\xi''), \xi, \xi', \xi'') + W_2^{(2)}(n(\xi''), n(\xi'), \xi, \xi'', \xi')] + \dots \quad (253)$$

where  $W_1^{(2)} \equiv \partial W^{(2)}(n', n'', \xi, \xi', \xi'') / \partial n'$  and  $W_2^{(2)} \equiv \partial W^{(2)}(n', n'', \xi, \xi', \xi'') / \partial n''$ . Considerable simplification is achieved by postulating the following local-density *Ansatz* (254) [121] for the functional derivative

$$\frac{\delta v_{xc}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \approx f_{xc}^{\text{hom}}(n(\mathbf{r}', t'), |\mathbf{r} - \mathbf{r}'|, t - t') \quad (254)$$

where  $f_{xc}^{\text{hom}}(n, |\mathbf{r} - \mathbf{r}'|, t - t')$  is the nonlocal, delayed xc kernel of the uniform electron gas of density  $n$ . Clearly, in the limit of weakly inhomogeneous systems, i.e., for systems with densities  $n(\mathbf{r}', t') \rightarrow \text{const}$  this *Ansatz* becomes exact. We now seek a functional  $v_{xc}[n](\mathbf{r}, t)$  whose functional derivative  $\delta v_{xc}(\mathbf{r}, t) / \delta n(\mathbf{r}', t')$  is given by (254). The task of finding such a  $v_{xc}$  is possible because (254) is a function of density at one point only. Hence the integral terms in (252) and (253) involving  $W^{(2)}$  and higher must be discarded and it follows that

$$\frac{\partial W^{(1)}}{\partial n}(n(\mathbf{r}', t'), \mathbf{r}, \mathbf{r}') = f_{xc}^{\text{hom}}(n(\mathbf{r}', t'), |\mathbf{r} - \mathbf{r}'|, t - t'). \quad (255)$$

Thus  $W^{(1)}$  is a density integral of  $f_{xc}^{\text{hom}}(n, r, \tau)$ . Assuming that  $v_{xc}$  is zero in a zero-density system, and defining

$$W_{xc}(n, r, \tau) = \int_0^n f_{xc}^{\text{hom}}(\rho, r, \tau) d\rho \quad (256)$$

we then obtain

$$v_{\text{xc}}[n](\mathbf{r}, t) = \int dt' d^3r' W_{\text{xc}}(n(\mathbf{r}', t'), |\mathbf{r} - \mathbf{r}'|, t - t'). \quad (257)$$

The *Ansatz* (257) makes  $v_{\text{xc}}(\mathbf{r}, t)$  depend principally on the density near the point  $\mathbf{r}$ , at a range of times  $t'$  which are near to, but earlier than,  $t$ . In the following we propose to improve this by noting that, if there is streaming in the many-body fluid, the memory of past densities is likely to be greatest when one remains with the same fluid element rather than remaining with the same spatial point  $\mathbf{r}$ . Thus we propose [122] instead of (257)

$$v_{\text{xc}}[n](\mathbf{r}, t) = \int dt' d^3r' W_{\text{xc}}(n(\mathbf{r}', t'), |\mathbf{R}(t' | \mathbf{r}, t) - \mathbf{r}'|, t - t'). \quad (258)$$

where  $W_{\text{xc}}$  is still given by (256).

In (258) the density from a past time  $t'$  which most strongly influences  $v_{\text{xc}}(\mathbf{r}, t)$  is the density at position  $\mathbf{r}' = \mathbf{R}(t' | \mathbf{r}, t)$ , where the trajectory function  $\mathbf{R}(t' | \mathbf{r}, t)$  of a fluid element is its position at time  $t'$ , given that its position at time  $t$  is  $\mathbf{r}$ .  $\mathbf{R}$  can be defined unambiguously by demanding that its time derivative is the fluid velocity  $\mathbf{u} = \mathbf{J}/n$  formed from the current density  $\mathbf{J}(\mathbf{r}, t)$ :

$$\frac{\partial}{\partial t'} \mathbf{R}(t' | \mathbf{r}, t) = \mathbf{u}(\mathbf{R}, t') \equiv \mathbf{J}(\mathbf{R}, t')/n(\mathbf{R}, t') \quad (259)$$

where all occurrences of  $\mathbf{R}$  have the same arguments as on the left-hand side of Eq. (259). The boundary condition on (259) is

$$\mathbf{R}(t | \mathbf{r}, t) = \mathbf{r}. \quad (260)$$

In (258) one acknowledges that the physics of delayed correlation will have its maximum degree of spatial locality if the observer is riding on a fluid element rather than observing from a fixed location  $\mathbf{r}$ . Eqs. (258) – (260) represent our general expression for the dynamic xc potential. The use of (258) in place of (257) will turn out to provide a nonlinear theory which, regardless of its validity in other respects, at least satisfies both the nonlinear Harmonic Potential Theorem [112] and the requirements of Galileian invariance [107]. To demonstrate that (258) satisfies the HPT, we show that it satisfies the generalized Galileian invariance condition (242). The only difficulty is that (258) has an implicit and highly nonlocal dependence on  $n(\mathbf{r}', t)$  via the current density dependence of  $\mathbf{R}$ . From [112], however, it follows that for HPT motion the TDKS equations involve not only a rigidly boosted density  $n'(\mathbf{r}, t) = n_0(\mathbf{r} - \mathbf{X}(t))$ , but also a boosted current  $\mathbf{J}'(\mathbf{r}, t) = n'(\mathbf{r}, t)\dot{\mathbf{X}}(t)$  because of the phase factor introduced by the motion into the KS wavefunctions. Thus the fluid velocity is just  $\mathbf{u}(\mathbf{r}, t) = \dot{\mathbf{X}}(t)$ . From (259) and (260) it then follows that

$$\mathbf{R}[n'](t' | \mathbf{r}, t) = \mathbf{r} + \mathbf{X}(t') - \mathbf{X}(t) \quad (261)$$

Putting this into (258) we find

$$\begin{aligned} v_{\text{xc}}[n'](\mathbf{r}, t) &= \int dt' d^3r' W_{\text{xc}}(n(\mathbf{r}' - \mathbf{X}(t'), t'), |\mathbf{r} + \mathbf{X}(t') - \mathbf{X}(t) - \mathbf{r}'|, t - t') \\ &= \int dt' d^3r' W_{\text{xc}}(n(\mathbf{r}' - \mathbf{X}(t'), t'), |(\mathbf{r} - \mathbf{X}(t)) - (\mathbf{r}' - \mathbf{X}(t'))|, t - t') \\ &= v_{\text{xc}}[n](\mathbf{r} - \mathbf{X}(t), t). \end{aligned} \quad (262)$$

Thus (258) satisfies (242). Hence the HPT and Galileian invariance requirements are satisfied.

Apart from its presumed nonlinear capabilities, (258), is also more general than the linear response work in preceding sections because it invokes the *spatial* nonlocality of the uniform gas xc kernel  $f_{xc}$ , making it more comparable to the work of Dabrowski [102]. To compare it with the discussions above, we now make the local approximation

$$f_{xc}^{hom}(\mathbf{r}, t; \mathbf{r}'t') \approx \delta(\mathbf{r} - \mathbf{r}')f_{xc}^{hom}(n, q = 0, t - t') \quad (263)$$

If this local approximation is employed in Eqs. (256) and (257), the resulting  $v_{xc}[n](\mathbf{r}, t)$  does not satisfy the HPT and the requirements of Galileian invariance because, when linearized, it reduces to the Gross-Kohn form (191) and this is known [112] not to satisfy the HPT. However, combined with Eq. (258), the local approximation (263) leads to

$$v_{xc}[n](\mathbf{r}, t) = \int dt' w_{xc}(n(\mathbf{R}(t' | \mathbf{r}, \mathbf{t}), t'), t - t') \quad (264)$$

where

$$w_{xc}(n, \tau) = \int_0^n f_{xc}^{hom}(\rho, q = 0, \tau) d\rho. \quad (265)$$

We now show that the functional (264), when linearized, gives precisely the modified linear-response xc kernel  $f_{xc}$  of Eq. (248). To this end we consider small motions around a static equilibrium, in the sense that the displacement

$$\mathbf{x}(\mathbf{r}, t) \equiv \mathbf{R}(t | \mathbf{r}, t_0) - \mathbf{r} \quad (266)$$

of each fluid element from its initial ( $t = t_0$ ) position  $\mathbf{r}$  is small. Under these circumstances both the fluid displacement  $\mathbf{X}$  and the current  $\mathbf{J}$  in (259) are small (first-order) quantities. Thus we may write

$$\mathbf{R}(t' | \mathbf{r}, t) = \mathbf{r} + O(\mathbf{x}) = \mathbf{R}(t' | \mathbf{r}, t_0) + O(\mathbf{x}) \quad (267)$$

and using this in (259) we find

$$\frac{\partial}{\partial t'} \mathbf{R}(t' | \mathbf{r}, t) = \mathbf{J}(\mathbf{R}(t' | \mathbf{r}, t_0)) / n_0(\mathbf{r}) + O(\mathbf{x}^2) = \frac{\partial}{\partial t'} \mathbf{R}(t' | \mathbf{r}, t_0) + O(\mathbf{x}^2). \quad (268)$$

Integrating both sides of (268) with respect to  $t'$ , starting from  $t' = t$ , we find

$$\mathbf{R}(t' | \mathbf{r}, t) - \mathbf{R}(t | \mathbf{r}, t) = \mathbf{R}(t' | \mathbf{r}, t_0) - \mathbf{R}(t | \mathbf{r}, t_0) + O(\mathbf{x}^2), \quad (269)$$

so that, by (269) and (266)

$$\mathbf{R}(t' | \mathbf{r}, t) = \mathbf{r} + \mathbf{x}(t') - \mathbf{x}(t) + O(\mathbf{x}^2). \quad (270)$$

In the linear limit we can also integrate the linearized continuity equation

$$\frac{\partial n_1}{\partial t} + \nabla \cdot [n_0(\mathbf{r})\mathbf{u}(\mathbf{r}, t)] = 0 \quad (271)$$

to give the density perturbation  $n_1$  in terms of the fluid displacement  $\mathbf{x}$ :

$$n_1(\mathbf{r}, t) = -\nabla \cdot [n_0(\mathbf{r})\mathbf{x}(\mathbf{r}, t)] + O(\mathbf{x}^2). \quad (272)$$

We can now use (270) and (272) to expand the density argument of  $w_{xc}$  in the nonlinear functional (264):

$$n(\mathbf{R}(t' | \mathbf{r}, t), t') = n(\mathbf{r} + \mathbf{x}(\mathbf{r}, t') - \mathbf{x}(\mathbf{r}, t), t') + O(\mathbf{x}^2)$$

$$\begin{aligned}
&= n_0(\mathbf{r}) + \nabla n_0(\mathbf{r}) \cdot (\mathbf{x}(\mathbf{r}, t') - \mathbf{x}(\mathbf{r}, t)) + n_1(\mathbf{r}, t') + O(\mathbf{x}^2) \\
&= n_0(\mathbf{r}) - \nabla n_0(\mathbf{r}) \cdot \mathbf{x}(\mathbf{r}, t) - n_0(\mathbf{r}) \nabla \cdot \mathbf{x}(\mathbf{r}, t') + O(\mathbf{x}^2).
\end{aligned} \tag{273}$$

In deriving (273), we used (270) in the first step, standard linearization in the second step and (272) in the third step. Putting (273) into the proposed nonlinear xc potential (264) we find

$$\begin{aligned}
v_{xc}(\mathbf{r}, t) &= \int_{-\infty}^{\infty} w_{xc}(n_0(\mathbf{r}), t - t') dt' - \nabla n_0(\mathbf{r}) \cdot \mathbf{x}(\mathbf{r}, t) \int_{-\infty}^{\infty} \frac{\partial w_{xc}}{\partial n}(n_0(\mathbf{r}), t - t') dt' \\
&\quad - n_0(\mathbf{r}) \int_{-\infty}^{\infty} \frac{\partial w_{xc}}{\partial n}(n_0(\mathbf{r}), t - t') \nabla \cdot \mathbf{x}(\mathbf{r}, t') dt' + O(\mathbf{x}^2)
\end{aligned} \tag{274}$$

Integrating (256) with respect to time and using  $f_{xc}^{\text{hom}}(n) = dv_{xc}^{\text{hom}}(n)/dn$ , we find that the first term in (274) is just the xc potential  $v_{xc}^{\text{hom}}(n_0(\mathbf{r}))$  of the static, unperturbed problem. The linear correction to this equilibrium value of the xc potential is then, by (274) and (256),

$$v_{1xc}(\mathbf{r}, t) = \left( \int_{-\infty}^{\infty} f_{xc}(n_0(\mathbf{r}), t - t') dt' \right) n_{1B}(\mathbf{r}, t) + \int_{-\infty}^{\infty} f_{xc}(n_0(\mathbf{r}), t - t') n_{1A}(\mathbf{r}, t') dt'. \tag{275}$$

where

$$n_{1A}(\mathbf{r}, t) = -n_0(\mathbf{r}) \nabla \cdot \mathbf{x}(\mathbf{r}, t), \quad n_{1B}(\mathbf{r}, t) = -\mathbf{x}(\mathbf{r}, t) \cdot \nabla n_0(\mathbf{r}) \tag{276}$$

Fourier-transforming (275) and writing the terms in reverse order we find

$$v_{1xc}(\mathbf{r}, \omega) = f_{xc}(n_0(\mathbf{r}), \omega) n_{1A}(\mathbf{r}, \omega) + f_{xc}(n_0(\mathbf{r}), \omega = 0) n_{1B}(\mathbf{r}, \omega). \tag{277}$$

This is identical to the form (248). To summarize, we have proposed a rather bold *Ansatz*, Eq. (258), for the time-dependent xc potential  $v_{xc}(\mathbf{r}, t)$  of an arbitrary system which could be far from equilibrium. This *Ansatz* carries a nonlocal space and time dependence based on uniform-gas data, but accesses the actual system density  $n(\mathbf{r}, t)$  in a simple local fashion. The assumption of local space dependence in the uniform gas yields a simpler form again, Eq. (264). It remains to be seen whether our relatively simple forms can cope with the gamut of nonlinear phenomena in systems far from equilibrium. As a first step it would be interesting to investigate second- and higher-order nonlinear susceptibilities described in section 5.2. Computer codes for investigating the fully nonlinear case may be adaptable from the work of Galdrikian *et al.* [123], who have investigated strongly driven quantum wells. Regardless of the applicability of our method to general nonlinear phenomena, the use of the trajectory function  $\mathbf{R}(t' | \mathbf{r}, t)$  in (258) and (264) guarantees two things: firstly, satisfaction of the generalized Galileian invariance condition (242) and hence of the Harmonic Potential Theorem (240), for motion of arbitrarily large amplitude; and secondly, for systems close to equilibrium the more local version (264) reduces to the linear time-delayed or frequency-dependent formalism previously proposed by Dobson [112].

## 6.2 Time-dependent optimized effective potential

The approximate xc potentials described so far were derived from the homogeneous electron gas in one or another way. All of them have one deficiency in common: They contain spurious self-interaction contributions. It is known from static DFT that the removal of self-interaction is an important ingredient in the construction of good xc potentials. Various approaches to the construction of self-interaction-free functionals are known in the static case [37, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135]. One of these is the so-called optimized potential method (OPM) [133, 134, 135]. This method takes as starting point a given expression for the total



energy  $E[\phi_1 \dots \phi_N]$  of an  $N$ -electron system as a functional of a set of single-particle orbitals  $\{\phi_j(\mathbf{r})\}$  (e. g. the Hartree-Fock total energy functional in the exchange-only case). Then, the variationally best *local* effective potential is determined such that, when inserted in a stationary single-particle Schrödinger equation, it yields the set of  $N$  eigenfunctions (corresponding to the  $N$  lowest eigenvalues) that minimize  $E[\phi_1 \dots \phi_N]$ . In practice, the full OPM scheme is computationally quite involved since it requires the numerical solution of an integral equation for  $v_{\text{xc}}(\mathbf{r})$ . As a consequence, complete OPM calculations have been performed mainly for problems where the potential is a function of a single variable, e. g. for spherically symmetric atoms [134]–[140]. There exists, however, an approximate OPM scheme, recently proposed by Krieger, Li, and Iafrate (KLI) [141]–[149], which is numerically as easy to handle as the ordinary KS scheme. This simplified OPM has been applied very successfully to the calculation of atomic properties [6]. In many respects this method is currently the most accurate density-functional scheme.

In the present section we shall describe the construction of a self-interaction-free xc potential which can be viewed as a time-dependent version of the optimized potential method (TDOPM). The approach leads to  $v_{\text{xc}}$  as a function of  $(\mathbf{r}, t)$  rather than to  $v_{\text{xc}}$  as an explicit functional of the density. In order to derive such a time-dependent generalization of the OPM we consider an  $N$ -electron system at some finite time  $t_0$  which, for all times up until  $t_0$ , has been in the ground state associated with an external potential  $v_0(\mathbf{r})$  (e.g., a nuclear Coulomb potential). We assume that the corresponding stationary OPM problem has been solved for that system, i. e. a local effective potential and a set of  $N$  single-particle orbitals  $\{\phi_j\}$  (with energy eigenvalues  $\varepsilon_j$ ) minimizing a given energy functional  $E[\phi_1 \dots \phi_N]$  are assumed to be known. Again, at  $t = t_0$  an additional time-dependent potential  $v_1(\mathbf{r}, t)$  is switched on. Our goal is to determine the time evolution of the system under the influence of the total external potential  $v(\mathbf{r}, t) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t)$  from  $t_0$  up until an arbitrary later time  $t_1$ . To construct an optimized local effective potential we start with the quantum mechanical action [150]

$$\begin{aligned} \mathcal{A}[\varphi_1 \dots \varphi_N] &= \sum_j^N \int_{-\infty}^{t_1} dt \int d^3r \varphi_j^*(\mathbf{r}, t) \left( i \frac{\partial}{\partial t} + \frac{\nabla^2}{2} \right) \varphi_j(\mathbf{r}, t) \\ &- \int_{-\infty}^{t_1} dt \int d^3r n(\mathbf{r}, t) v(\mathbf{r}, t) - \frac{1}{2} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{n(\mathbf{r}, t) n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} - \mathcal{A}_{\text{xc}}[\varphi_1 \dots \varphi_N] \end{aligned} \quad (278)$$

written as a functional of  $N$  time-dependent single-particle orbitals  $\{\varphi_j(\mathbf{r}, t)\}$  where  $n(\mathbf{r}, t) = \sum_j^N |\varphi_j(\mathbf{r}, t)|^2$ . In a time-dependent exchange-only theory  $\mathcal{A}_{\text{xc}}[\varphi_1 \dots \varphi_N]$ —the xc part of the quantum mechanical action—would be replaced by the time-dependent Fock expression

$$\mathcal{A}_{\text{xc}} \approx \mathcal{A}_{\text{x}} = -\frac{1}{2} \sum_{i,j}^N \delta_{\sigma_i \sigma_j} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{\varphi_i^*(\mathbf{r}', t) \varphi_j(\mathbf{r}', t) \varphi_i(\mathbf{r}, t) \varphi_j^*(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} \quad (279)$$

( $\sigma_j$  denotes the spin orientation of the  $j$ th orbital). We note that the integrand of (279) is a *local* expression with respect to the time-coordinate, i.e., all orbitals depend on the same time argument  $t$ . With approximate functionals of this type, the causality problem described in section 5.2 does not occur. The orbitals are solutions of the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = \left( -\frac{\nabla^2}{2} + v_s(\mathbf{r}, t) \right) \varphi_j(\mathbf{r}, t) \quad , \quad j = 1, \dots, N \quad , \quad (280)$$

with  $\varphi_j(\mathbf{r}, t) = \phi_j(\mathbf{r}) \exp[-i\varepsilon_j(t - t_0)]$  for  $-\infty < t \leq t_0$ . The local effective potential is given by

$$v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + v_{\text{H}}(\mathbf{r}, t) + v_{\text{xc}}^{\text{TDOPM}}(\mathbf{r}, t) \quad , \quad (281)$$

where  $v_H(\mathbf{r}, t) = \int d^3r' n(\mathbf{r}', t)/|\mathbf{r}-\mathbf{r}'|$  denotes the time-dependent Hartree potential. The total potential  $v_s(\mathbf{r}, t)$  has to be determined in such a way that the  $\{\varphi_j(\mathbf{r}, t)\}$ , resulting from Eq. (280), render the total action functional  $\mathcal{A}[\varphi_1 \dots \varphi_N]$  stationary. Therefore, we have to solve the following variational problem:

$$\begin{aligned} \frac{\delta \mathcal{A}[\varphi_1 \dots \varphi_N]}{\delta v_s(\mathbf{r}, t)} &= \sum_j^N \int_{-\infty}^{+\infty} dt' \int d^3r' \left( \frac{\delta \mathcal{A}[\varphi_1 \dots \varphi_N]}{\delta \varphi_j(\mathbf{r}', t')} \frac{\delta \varphi_j(\mathbf{r}', t')}{\delta v_s(\mathbf{r}, t)} + \frac{\delta \mathcal{A}[\varphi_1 \dots \varphi_N]}{\delta \varphi_j^*(\mathbf{r}', t')} \frac{\delta \varphi_j^*(\mathbf{r}', t')}{\delta v_s(\mathbf{r}, t)} \right) \\ &= 0 \quad . \end{aligned} \quad (282)$$

We first compute the functional derivatives  $\delta \mathcal{A}/\delta \varphi_j$  and  $\delta \mathcal{A}/\delta \varphi_j^*$ : defining

$$u_{xcj}(\mathbf{r}, t) = \frac{1}{\varphi_j^*(\mathbf{r}, t)} \frac{\delta \mathcal{A}_{xc}[\varphi_1 \dots \varphi_N]}{\delta \varphi_j(\mathbf{r}, t)} \quad , \quad (283)$$

we obtain

$$\frac{\delta \mathcal{A}[\varphi_1 \dots \varphi_N]}{\delta \varphi_j(\mathbf{r}', t')} = \left[ -i \frac{\partial}{\partial t'} - \left( -\frac{\nabla'^2}{2} + v(\mathbf{r}', t') + v_H(\mathbf{r}', t') + u_{xcj}(\mathbf{r}', t') \right) \right] \varphi_j^*(\mathbf{r}', t') \theta(t_1 - t') \quad (284)$$

and an analogous expression for  $\delta \mathcal{A}/\delta \varphi_j^*$  which, for all reasonable (i. e. real) functionals  $\mathcal{A}[\varphi_1 \dots \varphi_N]$ , is the complex conjugate of (284).  $\theta(x)$  denotes the usual step function (1 for  $x > 0$ , 0 for  $x < 0$ ). To arrive at Eq. (284) the first term of Eq. (278) has to be integrated by parts with respect to the time coordinate. We impose the usual boundary condition on  $\varphi_j(\mathbf{r}, t)$  at  $t = t_1$ , i. e.  $\delta \varphi_j(\mathbf{r}, t_1) = 0$ , thus obtaining a zero boundary contribution. The other boundary contribution at  $t = -\infty$  vanishes, too, because the action functional (278), in order to be well-defined, is to be calculated by introducing the usual factor  $e^{\eta t}$  in the integrand and taking  $\lim_{\eta \rightarrow 0^+}$  after the integration. Substituting Eq. (281) into (284) and making use of the fact that  $\varphi_j^*$  solves the complex conjugate of the Schrödinger equation (280), we find

$$\frac{\mathcal{A}[\varphi_1 \dots \varphi_N]}{\delta \varphi_j(\mathbf{r}', t')} = [v_{xc}^{\text{TDOPM}}(\mathbf{r}', t') - u_{xcj}(\mathbf{r}', t')] \varphi_j^*(\mathbf{r}', t') \theta(t_1 - t') \quad . \quad (285)$$

In order to evaluate  $\delta \mathcal{A}/\delta v_s$  from Eq. (282), we further need the functional derivatives  $\delta \varphi_j/\delta v_s$  and  $\delta \varphi_j^*/\delta v_s$ . The stationary OPM eigenfunctions  $\{\phi_j(\mathbf{r}), j = 1, \dots, \infty\}$  form a complete orthonormal set, and so do the time-evolved states  $\{\varphi_j(\mathbf{r}, t), j = 1, \dots, \infty\}$  for any time  $t \in [-\infty, t_1]$ , and we denote this set by  $\Phi_t$ . Now consider  $\Phi_t$  as unperturbed states, remembering that at  $t = t_1$  the orbitals are held *fixed* with respect to variations in the total potential. We therefore start from  $t = t_1$ , subject the system to an *additional* small perturbation  $\delta v_s(\mathbf{r}, t)$  and let it evolve *backward* in time. The corresponding perturbed wave functions  $\varphi'_j(\mathbf{r}, t)$  are determined by the backward Schrödinger equation

$$i \frac{\partial}{\partial t} \varphi'_j(\mathbf{r}, t) = \left( -\frac{\nabla^2}{2} + v_s(\mathbf{r}, t) + \delta v_s(\mathbf{r}, t) \right) \varphi'_j(\mathbf{r}, t) \quad , \quad j = 1, \dots, N \quad (286)$$

with the initial condition  $\varphi'_j(\mathbf{r}, t_1) = \varphi_j(\mathbf{r}, t_1)$ . This problem cannot be treated directly with time-dependent perturbation theory as described in standard text books because the unperturbed Hamiltonian is already time-dependent. Nevertheless, Dirac's method of variation of constants can be applied in a straightforward manner. We expand, at each given  $t$ , the perturbed wave function  $\varphi'_j(\mathbf{r}, t)$  in terms of the set  $\Phi_t$ ,

$$\varphi'_j(\mathbf{r}, t) = \sum_{k=1}^{\infty} c_{jk}(t) \varphi_k(\mathbf{r}, t) \quad , \quad (287)$$

and insert this expansion in (286), utilizing Eq. (280). The resulting equation

$$i \sum_{k=1}^{\infty} \dot{c}_{jk}(t) \varphi_k(\mathbf{r}, t) = \sum_{k=1}^{\infty} c_{jk}(t) \delta v_s(\mathbf{r}, t) \varphi_k(\mathbf{r}, t) \quad (288)$$

is then multiplied by  $\varphi_l^*(\mathbf{r}, t)$  and integrated over all space; the orthonormality of  $\Phi_t$  yields

$$\dot{c}_{jl}(t) = \frac{1}{i} \sum_{k=1}^{\infty} c_{jk}(t) \int d^3r \varphi_l^*(\mathbf{r}, t) \delta v_s(\mathbf{r}, t) \varphi_k(\mathbf{r}, t) \quad (289)$$

We now make the usual ansatz for a perturbation expansion,

$$c_{jk}(t) = c_{jk}^{(0)}(t) + c_{jk}^{(1)}(t) + \dots \quad (290)$$

and collect corresponding orders on each side of Eq. (289). This yields

$$\begin{aligned} \dot{c}_{jl}^{(0)}(t) &= 0 \\ \dot{c}_{jl}^{(1)}(t) &= \frac{1}{i} \sum_{k=1}^{\infty} c_{jk}^{(0)}(t) \int d^3r \varphi_l^*(\mathbf{r}, t) \delta v_s(\mathbf{r}, t) \varphi_k(\mathbf{r}, t) \\ &\vdots \end{aligned} \quad (291)$$

Since, in our case, the wave function evolves backward from the fixed state  $\varphi_j(\mathbf{r}, t_1)$  we find  $c_{jk}^{(0)}(t) = \delta_{jk}$  and  $c_{jk}^{(1)}(t_1) = 0$ , leading to

$$c_{jl}^{(1)}(t) = \frac{1}{i} \int_{t_1}^t dt' \int d^3r \varphi_l^*(\mathbf{r}, t') \delta v_s(\mathbf{r}, t') \varphi_j(\mathbf{r}, t') \quad (292)$$

It follows that the first-order correction to the wave function  $\varphi_j(\mathbf{r}, t)$  under the influence of  $\delta v_s(\mathbf{r}, t)$  is given by

$$\delta \varphi_j(\mathbf{r}, t) = \sum_{k=1}^{\infty} c_{jk}^{(1)}(t) \varphi_k(\mathbf{r}, t) = i \sum_{k=1}^{\infty} \int_t^{t_1} dt' \int d^3r' \varphi_k^*(\mathbf{r}', t') \delta v_s(\mathbf{r}', t') \varphi_j(\mathbf{r}', t') \varphi_k(\mathbf{r}, t) \quad (293)$$

Therefore, the desired functional derivative is

$$\frac{\delta \varphi_j(\mathbf{r}', t')}{\delta v_s(\mathbf{r}, t)} = i \sum_{k=1}^{\infty} \varphi_k^*(\mathbf{r}, t) \varphi_j(\mathbf{r}, t) \varphi_k(\mathbf{r}', t') \theta(t_1 - t) \theta(t - t') \quad (294)$$

Once again,  $\delta \varphi_j^* / \delta v_s$  leads to the complex conjugate expression. We can now insert (285) and (294) in the variational equation (282), and the result is the TDOPM integral equation for the local exchange-correlation potential  $v_{xc}(\mathbf{r}, t)$ :

$$i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3r' [v_{xc}^{\text{TDOPM}}(\mathbf{r}', t') - u_{xcj}(\mathbf{r}', t')] \varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}', t') K(\mathbf{r}, t, \mathbf{r}', t') + c.c. = 0 \quad (295)$$

The kernel

$$K(\mathbf{r}, t, \mathbf{r}', t') = \sum_{k=1}^{\infty} \varphi_k^*(\mathbf{r}, t) \varphi_k(\mathbf{r}', t') \theta(t - t') \quad (296)$$

can be identified with the Green's function of the system, which satisfies the differential equation

$$\left[ i \frac{\partial}{\partial t'} - \left( -\frac{\nabla'^2}{2} + v_s(\mathbf{r}', t') \right) \right] K(\mathbf{r}, t, \mathbf{r}', t') = -i \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (297)$$

with the initial condition  $K(\mathbf{r}, t, \mathbf{r}', t') = 0$  for  $t' > t$ . The TDOPM scheme is now complete: the integral equation (295) has to be solved for  $v_{xc}(\mathbf{r}, t)$  in combination with the Schrödinger equation (280) and the differential equation (297) for  $K(\mathbf{r}, t, \mathbf{r}', t')$ , both with the appropriate initial conditions. It is easy to show that in the time interval  $[-\infty, t_1]$  the exchange-correlation potential  $v_{xc}(\mathbf{r}, t)$  is only determined up to within a purely time-dependent function  $c(t)$  (as expected in view of the time-dependent HK theorem discussed in section 2).

We now demonstrate that for  $t < t_0$  or for a time-independent external potential ( $v_1(\mathbf{r}, t) \equiv 0$ ) the TDOPM reduces to the stationary OPM. For this purpose we rewrite Eq. (295) in the following way (using the fact that  $v_{xc}$  is real):

$$\begin{aligned} i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3 r' [v_{xc}^{\text{TDOPM}}(\mathbf{r}', t') - u_{xcj}(\mathbf{r}', t')] \varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}', t') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \varphi_k^*(\mathbf{r}, t) \varphi_k(\mathbf{r}', t') \theta(t - t') + c.c. \\ = i \sum_j^N \varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}, t) \int_{-\infty}^t dt' \int d^3 r' (u_{xcj}(\mathbf{r}', t') - u_{xcj}^*(\mathbf{r}', t')) \varphi_j(\mathbf{r}', t') \varphi_j^*(\mathbf{r}', t') \quad . \end{aligned} \quad (298)$$

In the static case, the orbitals  $\{\varphi_j(\mathbf{r}, t)\}$  are replaced by  $\{\phi_j(\mathbf{r}) \exp[-i\varepsilon_j(t-t_0)]\}$ . It is reasonable to assume that the exchange-correlation functional  $\mathcal{A}_{xc}$  then becomes

$$\mathcal{A}_{xc}[\varphi_1 \dots \varphi_N] \longrightarrow \int_{-\infty}^{t_1} dt' E_{xc}[\varphi_1(t') \dots \varphi_N(t')] \quad , \quad (299)$$

where  $E_{xc}[\phi_1 \dots \phi_N]$  is the corresponding ground state exchange-correlation energy functional. Definition (283) then yields

$$u_{xcj}^{\text{static}}(\mathbf{r}, t) = \left[ \frac{1}{\tilde{\phi}_j^*(\mathbf{r})} \frac{\delta E_{xc}[\tilde{\phi}_1 \dots \tilde{\phi}_N]}{\delta \tilde{\phi}_j(\mathbf{r})} \right]_{\tilde{\phi}_j(\mathbf{r}) = \phi_j(\mathbf{r}) e^{-i\varepsilon_j(t-t_0)}} \quad . \quad (300)$$

We assume that the value of  $E_{xc}[\phi_1 \dots \phi_N]$  remains unchanged if the arguments  $\{\phi_j(\mathbf{r})\}$  are multiplied by phase factors  $e^{i\alpha_j}$ . If this is the case, we can use the identity

$$\varphi_j(\mathbf{r}, t) = \sqrt{\frac{\varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}_0, t)}{|\varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}_0, t)|}} \varphi_j(\mathbf{r}_0, t) e^{i \arg(\varphi_j(\mathbf{r}_0, t))} \quad (301)$$

(where  $\mathbf{r}_0$  is an arbitrary reference point) and write  $E_{xc}$  in Eq. (299) as a functional of the combinations  $\varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}', t)$ . Then it is not difficult to show that  $u_{xcj}^{\text{static}}$  is independent of time and that the right-hand side of (298) is zero. We therefore obtain

$$\begin{aligned} i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3 r' [v_{xc}^{\text{OPM}}(\mathbf{r}') - u_{xcj}^{\text{static}}(\mathbf{r}')] \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \phi_k^*(\mathbf{r}) \phi_k(\mathbf{r}') e^{-i(\varepsilon_j - \varepsilon_k)(t-t')} \theta(t - t') \\ + c.c. = 0 \quad . \end{aligned} \quad (302)$$

Performing the integration over  $t'$  we find the stationary OPM integral equation [134]

$$\lim_{\eta \rightarrow 0^+} \sum_j^N \int d^3 r' [v_{xc}^{\text{OPM}}(\mathbf{r}') - u_{xcj}^{\text{static}}(\mathbf{r}')] \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\phi_k^*(\mathbf{r}) \phi_k(\mathbf{r}')}{\varepsilon_j - \varepsilon_k - i\eta} + c.c. = 0 \quad . \quad (303)$$

The derivation of Eq. (303) shows that in order to recover the static limit from the time-dependent formalism one had to extend the time integral in Eq. (278) to  $-\infty$ ;

a *finite* lower time boundary does not correctly account for memory effects in  $v_{xc}$  and therefore results in an unphysical time dependence even in the static case.

The numerical implementation of the full TDOPM is an extremely demanding task. It is therefore most desirable to obtain a simplified scheme. To this end we shall perform a transformation of Eq. (295) similar to the one proposed by KLI in the stationary case [146, 149]. This will lead to an alternative but still exact form of the TDOPM scheme which allows one to construct approximations of  $v_{xc}(\mathbf{r}, t)$  which are *explicit* functionals of the orbitals  $\{\varphi_j\}$ , thereby avoiding the need to solve the integral equation. Following Refs. [146, 149], we define

$$p_j(\mathbf{r}, t) = \frac{-i}{\varphi_j^*(\mathbf{r}, t)} \int_{-\infty}^{t_1} dt' \int d^3 r' [v_{xc}^{\text{TDOPM}}(\mathbf{r}', t') - u_{xcj}(\mathbf{r}', t')] \varphi_j^*(\mathbf{r}', t') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \varphi_k^*(\mathbf{r}, t) \varphi_k(\mathbf{r}', t') \theta(t-t') \quad (304)$$

and

$$\bar{u}_{xcj}(t) = \int d^3 r n_j(\mathbf{r}, t) u_{xcj}(\mathbf{r}, t) \quad (305)$$

where  $n_j(\mathbf{r}, t) = |\varphi_j(\mathbf{r}, t)|^2$ . Eq. (298) can then be written as

$$\sum_j^N n_j(\mathbf{r}, t) p_j(\mathbf{r}, t) + c.c. = -i \sum_j^N n_j(\mathbf{r}, t) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \quad , \quad (306)$$

and it is easy to show that

$$\int d^3 r n_j(\mathbf{r}, t) p_j(\mathbf{r}, t) = 0 \quad . \quad (307)$$

Evaluating  $\varphi_j(\mathbf{r}, t)[-i \partial/\partial t + \nabla^2/2 - v_s(\mathbf{r}, t)]\varphi_j^*(\mathbf{r}, t)p_j(\mathbf{r}, t)$  one finds that  $p_j(\mathbf{r}, t)$  satisfies the following differential equation:

$$\begin{aligned} \frac{1}{2} \nabla \cdot (n_j(\mathbf{r}, t) \nabla p_j(\mathbf{r}, t)) - i n_j(\mathbf{r}, t) \frac{\partial}{\partial t} p_j(\mathbf{r}, t) - i \mathbf{J}_j(\mathbf{r}, t) \cdot \nabla p_j(\mathbf{r}, t) \\ = -n_j(\mathbf{r}, t) \left[ v_{xc}^{\text{TDOPM}}(\mathbf{r}, t) - u_{xcj}(\mathbf{r}, t) - (\bar{v}_{xcj}(t) - \bar{u}_{xcj}(t)) \right] \end{aligned} \quad (308)$$

with the current density  $\mathbf{J}_j(\mathbf{r}, t) = (2i)^{-1} (\varphi_j^*(\mathbf{r}, t) \nabla \varphi_j(\mathbf{r}, t) - \varphi_j(\mathbf{r}, t) \nabla \varphi_j^*(\mathbf{r}, t))$  and  $\bar{v}_{xcj}(t) = \int d^3 r n_j(\mathbf{r}, t) v_{xc}^{\text{TDOPM}}(\mathbf{r}, t)$ . Finally, operating with  $\nabla^2$  on Eq. (306) and using Eq. (308) we find

$$\begin{aligned} v_{xc}^{\text{TDOPM}}(\mathbf{r}, t) &= \frac{1}{n(\mathbf{r}, t)} \sum_j^N n_j(\mathbf{r}, t) \frac{1}{2} (u'_{xcj}(\mathbf{r}, t) + u'^*_{xcj}(\mathbf{r}, t)) \\ &+ \frac{1}{n(\mathbf{r}, t)} \sum_j^N n_j(\mathbf{r}, t) \left[ \bar{v}_{xcj}(t) - \frac{1}{2} (\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t)) \right] \\ &+ \frac{i}{4n(\mathbf{r}, t)} \sum_j^N \nabla^2 n_j(\mathbf{r}, t) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \end{aligned} \quad (309)$$

where

$$u'_{xcj}(\mathbf{r}, t) = u_{xcj}(\mathbf{r}, t) + \frac{1}{n_j(\mathbf{r}, t)} \left[ \frac{1}{2} \nabla \cdot (p_j(\mathbf{r}, t) \nabla n_j(\mathbf{r}, t)) + i n_j(\mathbf{r}, t) \frac{\partial}{\partial t} p_j(\mathbf{r}, t) + i \mathbf{J}_j(\mathbf{r}, t) \cdot \nabla p_j(\mathbf{r}, t) \right]. \quad (310)$$

Eqs. (309) and (310) together with the differential equation (308) for  $p_j(\mathbf{r}, t)$  and the condition (307) (which can be used to fix the constant left undetermined by

Eq. (308)) represent an exact alternative formulation of the TDOPM scheme. The advantage of Eq. (309) lies in the fact that it is a very convenient starting point for constructing approximations of  $v_{xc}(\mathbf{r}, t)$  as explicit functionals of the  $\{\varphi_j(\mathbf{r}, t)\}$ : it is only necessary to approximate  $p_j(\mathbf{r}, t)$  in Eq. (310) by a suitably chosen functional of the orbitals. We can then readily solve Eq. (309) *analytically* for  $v_{xc}^{\text{TDOPM}}(\mathbf{r}, t)$ , as we shall show below.

We expect an *approximate* potential  $\tilde{v}_{xc}(\mathbf{r}, t)$  defined in this way to be close to the exact  $v_{xc}(\mathbf{r}, t)$ . This conjecture is based on the observation that the difference between  $\tilde{v}_{xc}$  and  $v_{xc}$  is entirely accounted for by the differences  $u'_{xcj} - u_{xcj}$  which are zero if averaged over the  $j$ th orbital, as will be demonstrated in the following. From Eq. (310) we obtain

$$\begin{aligned} \bar{u}'_{xcj}(t) - \bar{u}_{xcj}(t) = \\ \frac{1}{2} \int d^3r \nabla \cdot (p_j(\mathbf{r}, t) \nabla n_j(\mathbf{r}, t)) + i \int d^3r \left[ n_j(\mathbf{r}, t) \frac{\partial}{\partial t} p_j(\mathbf{r}, t) + \mathbf{J}_j(\mathbf{r}, t) \cdot \nabla p_j(\mathbf{r}, t) \right] \end{aligned} \quad (311)$$

Using the divergence theorem, the first term on the right-hand side can be transformed into a surface integral which vanishes if the time-dependent orbitals decrease exponentially for  $r \rightarrow \infty$ . The contribution to the second integral containing  $\mathbf{J}_j \cdot \nabla p_j$  is then integrated by parts. The surface term vanishes due to the same argument as before, and the remaining term is transformed using the continuity equation for the  $j$ th orbital to replace  $-\nabla \cdot \mathbf{J}_j(\mathbf{r}, t)$  by  $\partial n_j(\mathbf{r}, t) / \partial t$ . Hence we find

$$\bar{u}'_{xcj}(t) - \bar{u}_{xcj}(t) = i \frac{\partial}{\partial t} \int d^3r n_j(\mathbf{r}, t) p_j(\mathbf{r}, t) = 0 \quad , \quad (312)$$

where the last equality follows from Eq. (307).

The simplest approximation is obtained by replacing  $p_j$  by its average value, i. e. by setting  $p_j(\mathbf{r}, t) \equiv 0$ . The resulting approximate potential will be termed the time-dependent KLI (TDKLI) potential. It is given by the equation

$$\begin{aligned} v_{xc}^{\text{TDKLI}}(\mathbf{r}, t) &= \frac{1}{n(\mathbf{r}, t)} \sum_j^N n_j(\mathbf{r}, t) \frac{1}{2} (u_{xcj}(\mathbf{r}, t) + u_{xcj}^*(\mathbf{r}, t)) \\ &+ \frac{1}{n(\mathbf{r}, t)} \sum_j^N n_j(\mathbf{r}, t) \left[ \bar{v}_{xcj}^{\text{TDKLI}}(t) - \frac{1}{2} (\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t)) \right] \\ &+ \frac{i}{4n(\mathbf{r}, t)} \sum_j^N \nabla^2 n_j(\mathbf{r}, t) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \quad . \end{aligned} \quad (313)$$

This equation is still an integral equation for  $v_{xc}^{\text{TDKLI}}$ . It can, however, be solved semi-analytically [145]: Multiplying Eq. (313) by  $n_k(\mathbf{r}, t)$  and integrating over all space yields

$$\bar{v}_{xc}^{\text{TDKLI}}(t) = \bar{w}_{xc}(t) + \sum_j^N M_{kj}(t) \bar{v}_{xcj}^{\text{TDKLI}}(t) \quad , \quad (314)$$

where we have defined

$$\begin{aligned} w_{xc}(\mathbf{r}, t) &= \frac{1}{n(\mathbf{r}, t)} \sum_j^N n_j(\mathbf{r}, t) \frac{1}{2} (u_{xcj}(\mathbf{r}, t) + u_{xcj}^*(\mathbf{r}, t)) \\ &- \frac{1}{n(\mathbf{r}, t)} \sum_j^N n_j(\mathbf{r}, t) \frac{1}{2} (\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t)) \\ &+ \frac{i}{4n(\mathbf{r}, t)} \sum_j^N \nabla^2 n_j(\mathbf{r}, t) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \end{aligned} \quad (315)$$

and

$$M_{kj}(t) = \int d^3r \frac{n_k(\mathbf{r}, t)n_j(\mathbf{r}, t)}{n(\mathbf{r}, t)} . \quad (316)$$

Solving Eq. (314) for  $\bar{v}_{xcj}^{\text{TDKLI}}(t)$  requires inversion of the  $N \times N$  matrix

$$A_{kj}(t) = \delta_{kj} - M_{kj}(t) \quad (317)$$

and leads to

$$\bar{v}_{xcj}^{\text{TDKLI}}(t) = \sum_k^N (A^{-1}(t))_{jk} \bar{w}_{xck}(t) . \quad (318)$$

When Eq. (318) is substituted into Eq. (313), one obtains  $v_{xc}^{\text{TDKLI}}(\mathbf{r}, t)$  as an explicit functional of the orbitals  $\{\varphi_j(\mathbf{r}, t)\}$ . As the exact  $v_{xc}(\mathbf{r}, t)$  which follows from Eq. (295),  $v_{xc}^{\text{TDKLI}}(\mathbf{r}, t)$  is determined by Eq. (313) only up to within a purely time-dependent function  $c(t)$ .

The last term of Eqs. (313) and (315) vanishes identically for a large class of exchange-correlation functionals  $\mathcal{A}_{xc}$ . This class includes all functionals depending on  $\{\varphi_j\}$  only through the combinations  $\varphi_j(\mathbf{r}, t)\varphi_j^*(\mathbf{r}', t)$  (such as the time-dependent Fock functional, Eq. (279)).

One readily verifies that both the full TDOPM potential and the TDKLI approximation of it satisfy the generalized translational invariance condition (242) (and hence the harmonic potential theorem) provided that

$$\mathcal{A}_{xc}[\varphi'_1 \dots \varphi'_N] = \mathcal{A}_{xc}[\varphi_1 \dots \varphi_N] \quad (319)$$

is satisfied with  $\varphi'_j$  being the orbitals in the accelerated frame:

$$\varphi'_j(\mathbf{r}, t) = \exp(-iS(t) + i\dot{\mathbf{X}} \cdot \mathbf{r}) \phi_j(\mathbf{r} - \mathbf{X}(t)) . \quad (320)$$

The TDHF functional (279) is easily seen to satisfy the constraint (319). Equation (319) will be a strong guideline in the proper construction of approximate correlation functionals  $\mathcal{A}_c[\varphi_1 \dots \varphi_N]$ . Equation (313) combined with the Schrödinger equation (280) represents a time-dependent scheme which is numerically much less involved than, e.g., the time-dependent Hartree-Fock method. Numerical results obtained with this scheme for atoms in strong laser pulses will be described in section 8.

To conclude this section we construct in the following an approximation of the xc kernel  $f_{xc}$  on the basis of the TDOPM. A calculation analogous to Eqs. (138) - (152) shows [151, 152] that within TDOPM the central equation (152) holds for the quantity  $f_{xc}^{\text{TDOPM}}$  defined by the integral equation

$$\int_t^\infty dt' \int d^3r' \sum_{jk} \left[ \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}') \phi_k^*(\mathbf{r}) e^{-i(\epsilon_j - \epsilon_k)(t-t')} \right. \\ \left. \times \left( f_j f_{xc}^{\text{TDOPM}}(\mathbf{y}, \tau, \mathbf{r}', t') - g_{xc}^{(j)}(\mathbf{y}, \tau, \mathbf{r}', t') \right) - c.c. \right] = 0 \quad (321)$$

where

$$g_{xc}^{(j)}(\mathbf{y}, \tau, \mathbf{r}', t') = \left[ \frac{1}{2\varphi_j^*(\mathbf{r}', t')} \frac{\delta v_{xc}^{\text{TDOPM}}(\mathbf{y}, \tau)}{\delta \varphi_j(\mathbf{r}', t')} \right]_{\varphi_j(t)=\phi_j e^{-i\epsilon_j t}} . \quad (322)$$

Equation (321) has the same algebraic structure as the TDOPM integral equation (295) with the time-dependent orbitals  $\varphi_j(\mathbf{r}, t)$  replaced by  $e^{-i\epsilon_j t} \phi_j$  and with  $v_{xc}^{\text{TDOPM}}(\mathbf{r}', t')$  and  $u_{xcj}(\mathbf{r}', t')$  replaced by  $f_{xc}^{\text{TDOPM}}(\mathbf{y}, \tau, \mathbf{r}', t')$  and  $g_{xc}^{(j)}(\mathbf{y}, \tau, \mathbf{r}', t')$ , respectively. A simple analytical approximation to  $v_{xc}^{\text{TDOPM}}(\mathbf{r}, t)$  is given by

$$v_{xc}^{\text{approx}}(\mathbf{r}, t) = \sum_j \frac{|\varphi_j(\mathbf{r}, t)|^2}{2n(\mathbf{r}, t)} (u_{xcj}(\mathbf{r}, t) + u_{xcj}^*(\mathbf{r}, t)) . \quad (323)$$

Applying this approximation to (321), i.e., setting

$$f_{\text{xc}}^{\text{approx}}(\mathbf{y}, \tau, \mathbf{r}', t') = \sum_j \frac{|\phi_j(\mathbf{r})|^2}{2n(\mathbf{r})} \left( g_{\text{xc}}^{(j)}(\mathbf{y}, \tau, \mathbf{r}', t') + c.c. \right) \quad (324)$$

and using the explicit analytical form (323) to evaluate (322) one arrives in the time-dependent x-only limit (279) at the compact expression

$$f_{\text{xc}}^{\text{approx}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = - \frac{2 |\sum_k f_k \phi_k(\mathbf{r}) \phi_k^*(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'| n_0(\mathbf{r}) n_0(\mathbf{r}')}. \quad (325)$$

In general, the Fourier transform of the xc kernel defined by Eq. (321) is frequency dependent (even in the TD x-only case), a feature which is not accounted for by the present approximation (325). However, for the special case of a two-electron system treated within TD x-only theory, Eqs. (323) and (325) are the *exact* solutions of the respective integral equations.

## 7 Applications within the perturbative regime

### 7.1 Photoresponse of finite and infinite Systems

To date, most applications of TDDFT have been in the linear response regime. Calculations of the photoresponse from Eqs. (154) and (155) are, by now, a mature subject. The literature on such calculations is enormous and a whole volume [153] has been devoted to the subject. In this section we shall restrict ourselves to the basic ideas rather than describing the applicational details.

The TDKS formalism has been employed to calculate the photoresponse of atoms [10, 12, 13, 14, 154, 155], molecules [156, 157] and clusters [158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168] metallic surfaces [169, 170, 171, 172, 173, 173, 174, 175] and semiconductor heterostructures [72, 176, 177, 178, 179] bulk semiconductors [180] and bulk metals [181, 182, 183, 184]

For simplicity, we consider sufficiently low radiation frequencies, such that the electric field can be assumed to be constant across the atom or molecule. For atoms this is the case for photon energies below 3 keV. The external potential associated with a monochromatic electric field is then given by

$$v_1(\mathbf{r}, t) = E z \cos \omega t. \quad (326)$$

The induced density change  $n(\mathbf{r}, t) - n_0(\mathbf{r})$  (143) can be characterized by a series of multipole moments. The induced *dipole* moment

$$p(t) = - \int d^3 r z (n(\mathbf{r}, t) - n_0(\mathbf{r})), \quad (327)$$

can be expanded as [185]

$$p(t) = \alpha(\omega) \cdot \mathbf{E} \cos \omega t + \frac{1}{2} \beta(0) : \mathbf{E} \mathbf{E} + \frac{1}{2} \beta(2\omega) : \mathbf{E} \mathbf{E} \cos 2\omega t \quad (328)$$

$$+ \frac{1}{4} \gamma(\omega) : \mathbf{E} \mathbf{E} \mathbf{E} \cos \omega t + \frac{1}{4} \gamma(3\omega) : \mathbf{E} \mathbf{E} \mathbf{E} \cos 3\omega t, \quad (329)$$

where the notation is meant to indicate the tensorial character of the quantities  $\alpha$ ,  $\beta$  and  $\gamma$ . The first coefficient,  $\alpha$ , is termed the *dipole polarizability*;  $\beta$  and  $\gamma$  denote the second- and third-order *dipole hyperpolarizabilities*. For spherically symmetric ground states  $\beta$  is zero.



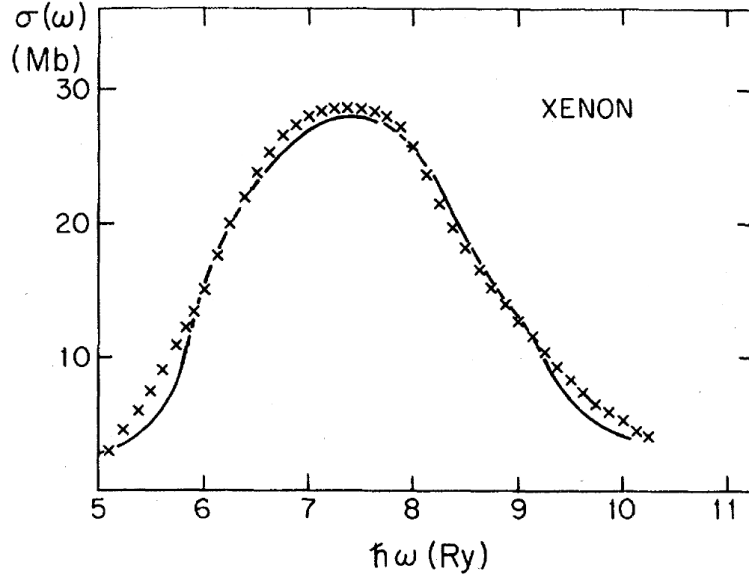


Figure 3: Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold. Solid line: self-consistent time-dependent KS calculation from [10]; crosses: experimental data from [186].

The dipole polarizability is related to the frequency-dependent linear density response  $n_1(\mathbf{r}, \omega)$  via

$$\alpha(\omega) = -\frac{2}{E} \int d^3r z n_1(\mathbf{r}, \omega) \quad (330)$$

and the photoabsorption cross section is given by

$$\sigma(\omega) = \frac{4\pi\omega}{c} \Im\alpha(\omega). \quad (331)$$

Zangwill and Soven [10] have calculated the photoabsorption spectrum of rare-gas atoms from the frequency-dependent KS equations (156) – (157) within the ALDA. As an example for the quality of the results we show, in Fig. 3, the photoabsorption cross section of Xenon just above the 4d threshold. The agreement with experiment is remarkably good. Results of similar quality have been achieved for the photoresponse of small molecules [156, 157].

It should be mentioned that the thresholds characterizing the onset of continuous absorption from the various occupied atomic shells are not well reproduced in the calculations of Zangwill and Soven. The calculated absorption edges are typically several eV below the observed thresholds. While, in principle, TDDFT should yield the correct thresholds, it appears that simple approximations such as the ALDA are not sufficient in this respect.

As a point of practical interest we mention that the KS response function is usually not calculated directly from the KS orbitals as in Eq. (157). Instead, one rewrites the response function in terms of the KS Green's function. The latter is then calculated numerically from the corresponding equation of motion, usually by multipole expansion [10, 187].

The linear photoresponse of metal clusters was successfully calculated for spherical [158, 160, 159, 163] as well as for spheroidal clusters [164] within the jellium model [188] using the LDA. The results are improved considerably by the use of self-interaction corrected functionals. In the context of response calculations, self-interaction effects occur at three different levels: First of all, the static KS orbitals, which enter the response function, have a self-interaction error if calculated within LDA. This is because the LDA xc potential of finite systems shows an exponential rather than the correct  $-1/r$  behaviour in the asymptotic region. As a

consequence, the valence electrons of finite systems are too weakly bound and the effective (ground-state) potential does not support high-lying unoccupied states. Apart from the response function  $\chi_s$ , the xc kernel  $f_{xc}[n_0]$  no matter which approximation is used for it, also has a self-interaction error. This is because  $f_{xc}[n_0]$  is evaluated at the unperturbed ground-state density  $n_0(\mathbf{r})$ , and this density exhibits self-interaction errors if the KS orbitals were calculated in LDA. Finally the ALDA form of  $f_{xc}$  itself carries another self-interaction error.

To improve upon these defects, one has to go beyond the LDA: The (*modified weighted density approximation*) [189] retains the correct asymptotic behaviour of  $v_{xc}$  and improves the response properties of metal clusters [162, 165]. A different route to improvement provides the *self-interaction correction* (SIC) of Perdew Zunger [37], where the spurious self-interaction of the LDA is compensated by additional terms in the ground-state potential [166] and in the effective perturbing potential as well [167] (Full-SIC).

In most theoretical work on the response of metallic surfaces the ionic potential is replaced by the potential due to a uniform positive charge background in a half space, say  $z > 0$ . This is the so-called jellium model for metallic surfaces. In this model are two intrinsic microscopic length scales, the inverse Fermi wave-number,  $k_F^{-1}$ , and the Thomas-Fermi screening length ( $\approx$  surface thickness),  $k_{TF}^{-1}$ . Both lengths are typically of the order  $a \approx 10^{-8}$  cm. In most applications the perturbing electric potential  $v_1$  and the perturbing vector potential  $\mathbf{A}_1$  vary on a length scale  $\ell$  which satisfies  $\ell \gg a$ . Examples are the scalar potential  $v_1(\mathbf{r})$  due to an external charge at a distance  $z \gg a$ , or the vector potential  $\mathbf{A}_1(\mathbf{r}, t)$ , associated with a light wave of wavelength  $\lambda \gg a$ . The corresponding linear responses  $n_1$  and  $\mathbf{j}_1$  vary on the scale of  $\ell$  in the  $x - y$  plane but, because of the abrupt drop of the unperturbed density at the surface (on the scale of  $a$ ), they vary on the short scale  $a$  in the  $z$ -direction. Formal arguments due to Feibelman [190] have shown that, to leading order in  $a/\ell$ , the effect of the surface on the electromagnetic fields far from the surface ( $|z| \gg a$ ) is entirely characterized by two complex frequency-dependent lengths,  $d_{\parallel}(\omega)$  and  $d_{\perp}(\omega)$ .

Actually, for the jellium model  $d_{\parallel}(\omega) \equiv 0$ . This result has been obtained in the random phase approximation (RPA) in Ref. [190]. It is easily established as a rigorous many-body result for the jellium model [191]. To define  $d_{\perp}(\omega)$  we Fourier analyze all physical quantities parallel to the surface, in the  $x - y$  plane. For example, a Fourier component of the induced charge density becomes

$$n_1(\mathbf{r}, \omega) \equiv n_1(z, \omega) e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r}}, \quad (332)$$

where  $\mathbf{q}_{\parallel} = (q_x, q_y, 0)$  (and  $|\mathbf{q}_{\parallel}| a \ll 1$ ). Then  $d_{\perp}(\omega)$  is given by

$$d_{\perp}(\omega) \equiv \frac{\int dz z n_1(z, \omega)}{\int dz n_1(z, \omega)}, \quad (333)$$

i.e., it is the (complex) center of mass of the induced surface charge.  $d_{\perp}(\omega)$  is the generalization of the static image plane introduced by Lang and Kohn [192].

This  $d_{\perp}(\omega)$  is then the subject of quantitative calculations. They require the density response  $n_1(z, \omega)$ , to a uniform external electric field perpendicular to the surface. The calculation was first carried out in the RPA equivalent to time-dependent Hartree theory, in which the xc kernel  $f_{xc}$  is neglected. These calculations led to very interesting results not present in classical Maxwell theory, such as the surface photo effect and surface plasmons. Plasmons are high-frequency charge-density oscillations of the electron gas. In a bulk material the long-wavelength plasma frequency is  $\omega_P = (4\pi n e^2 / m)^{1/2}$  in gaussian cgs units. Plasmons occur in the ultraviolet frequency region for metals, but the artificial electron gas in semiconductor quantum wells often has a plasma frequency in the infrared. The confinement of the

electron gas at metal edges introduces a range of new plasmon modes at frequencies other than  $\omega_P$ , and these could potentially yield information about inhomogeneous xc effects. Information about plasmons on films, surfaces and semiconductor wells is most easily available experimentally for small values of the surface-directed wavenumber  $q_{\parallel}$ , and unfortunately in this region there are theorems prescribing the plasmon frequencies, *regardless* of the effects of exchange and correlation. A summary of these "no-go" theorems is given in [113] and further review is given in [119] for the case of semiconductor quantum wells.

Early theoretical studies of plasmas used hydrodynamics [193]. These treatments were able to predict the main new feature of the plasmon spectrum at a metal surface due to the strong surface inhomogeneity of the electron gas, namely the surface plasmon. Its frequency approaches  $\omega_P/\sqrt{2}$  as the surface directed wavenumber  $q_{\parallel}$  approaches zero, and this is correctly predicted in hydrodynamic and microscopic theories. This result is independent both of the precise electron density edge profile and of the type of xc kernel used, if any [194, 195]. Thus, although the surface plasmon is often the strongest feature in electron energy loss measurements on thin metal films, [196] it is hard to obtain any information from it about dynamic exchange and correlation. To see such effects one needs to measure with great accuracy the *dispersion* of surface plasmons. Only in the last few years has it been possible even to confirm experimentally a result first predicted by Feibelman [190] on the basis of selfconsistent RPA calculations, namely that the dispersion of the surface plasmon on a charge-neutral metal surface is initially *negative*. This result follows basically from the very "soft" or weakly bound nature of the electron gas at a neutral jellium surface, allowing electrons to spill out substantially into the vacuum. For a review of some experimental and theoretical aspects see [197]. While the value of this negative dispersion coefficient does depend to a degree on the xc kernel  $f_{xc}$  introduced earlier, it remains to be seen whether experiments on metal films and surfaces can measure this quantity to a useful accuracy. On the theory side, an important observation by Liebsch [198] is that the KS orbitals used to construct the dynamic response must come from a static calculation using a model of exchange and correlation that is consistent with the dynamic xc kernel used in the plasmon calculation. For example, LDA calculation followed by RPA screening (with  $f_{xc} = 0$ ) is not consistent and causes false shifts in predicted surface plasmon frequencies.

The weak binding and wide inhomogeneous density layer at the edge of a neutral metal surface leads to a "multipole" surface plasmon mode in addition to the usual "monopole" surface plasmon [173, 172, 197]. This mode is in principle sensitive to  $f_{xc}$  even at  $q_{\parallel} = 0$ . Gies and Gerhardtts [173] and Dobson and Harris [199] investigated this mode both in the ALDA and the frequency dependent parametrization (206) – (210). It was found that, for an aluminium surface, the inclusion of the frequency dependence of  $f_{xc}$  has only a 3% effect on the multipole plasmon frequency, but a 20% effect on the damping of the mode. It seems likely that the frequency dependence of  $f_{xc}$  will have a much larger effect on this mode for a low-electron density metal such as Rb, and this may be worth pursuing.

In general, low-dimensional, low-density systems offer the best prospects for strong effects of xc phenomena on plasmon frequencies. A case in point is a pair of parallel quasi-two-dimensional electron layers in a semiconductor double-quantum well experiment. Interesting effects are predicted for this case [200].

Another way of probing dynamic xc effects experimentally is by inelastic X-ray scattering from bulk metals [201, 202, 203]. In this way, the so-called dynamical structure factor  $S(q, \omega)$  can be measured which is proportional to the imaginary part of the full response function in reciprocal space. With this information at hand and with a first-principles calculation of the non-interacting response function, the connection (159) between  $f_{xc}$  and the response functions can be used to deduce

information about  $f_{xc}$  [204].

All applications quoted so far were for the *linear* response. Very few investigations have dealt with the higher-order response described in section 5.2. The frequency-dependent third-order hyperpolarizabilities of rare-gas atoms were calculated by Senatore and Subbaswamy [86] within the ALDA; the calculated values turned out to be too large by a factor of two, further indicating the need for self-interaction corrected functionals in the calculation of response properties. The effect of adsorbates on second-harmonic generation at simple metal surfaces was investigated by Kuchler and Rebentrost [205, 206]. Most recently, the second-order harmonic generation in bulk insulators was calculated within the ALDA [207].

## 7.2 Calculation of excitation energies

The traditional density-functional formalism of Hohenberg, Kohn and Sham [1, 2] is a powerful tool in predicting ground-state properties of many-electron systems [3, 4, 5]. The description of excited-state properties within density-functional theory, however, is notoriously difficult. One might be tempted to interpret the Kohn-Sham single-particle energy differences  $\omega_{jk} := \epsilon_j - \epsilon_k$  as excitation energies. This interpretation, however, has no rigorous basis and in practice the Kohn-Sham orbital energy differences  $\omega_{jk}$  deviate by 10–50% from the true excitation energies  $\Omega_m := E_m - E_0$ . Several extensions of ground-state DFT have been devised to tackle excited states. They are based either on the Rayleigh-Ritz principle for the lowest eigenstate of each symmetry class [208, 209, 210] or on a variational principle for ensembles [211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222]. A fundamental difficulty is that the xc energy functionals appearing in these approaches depend on the symmetry labels of the state considered or on the particular ensemble, respectively. Until today very little is known on how these excited-state xc functionals differ from the ordinary ground-state xc energy.

In this section we are going to develop a different approach to the calculation of excitation energies which is based on TDDFT [69, 84, 152]. Similar ideas were recently proposed by Casida [223] on the basis of the one-particle density matrix. To extract excitation energies from TDDFT we exploit the fact that the frequency-dependent linear density response of a finite system has discrete poles at the excitation energies of the unperturbed system. The idea is to use the formally exact representation (156) of the linear density response  $n_1(\mathbf{r}, \omega)$ , to calculate the shift of the Kohn-Sham orbital energy differences  $\omega_{jk}$  (which are the poles of the Kohn-Sham response function) towards the true excitation energies  $\Omega_m$  in a systematic fashion.

The spin-dependent generalization [59] of TDDFT described in section 4.1 leads to the following analogue of Eq. (156) for the linear density response of electrons with spin  $\sigma$ :

$$\begin{aligned} n_{1\sigma}(\mathbf{r}, \omega) &= \sum_{\nu} \int d^3y \chi_{s\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) v_{1\nu}(\mathbf{y}, \omega) \\ &+ \sum_{\nu, \nu'} \int d^3y \int d^3y' \chi_{s\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) \left( \frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) n_{1\nu'}(\mathbf{y}', \omega). \end{aligned} \quad (334)$$

Here the spin-dependent exchange-correlation kernel is given by the Fourier transform of

$$f_{xc\sigma\sigma'}(\mathbf{r}, t, \mathbf{r}', t') := \left. \frac{\delta v_{xc\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}, t)}{\delta n_{\sigma'}(\mathbf{r}', t')} \right|_{n_{0\uparrow}, n_{0\downarrow}} \quad (335)$$

with respect to  $(t - t')$ . Note that the spin-dependent response-function of nonin-

interacting particles

$$\chi_{s\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) = \delta_{\sigma\sigma'} \sum_{j,k} (f_{k\sigma} - f_{j\sigma}) \frac{\phi_{j\sigma}(\mathbf{r}) \phi_{k\sigma}^*(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{k\sigma}(\mathbf{r}')}{\omega - (\epsilon_{j\sigma} - \epsilon_{k\sigma}) + i\eta} \quad (336)$$

is diagonal in the spin variable and exhibits poles at frequencies  $\omega_{jk\sigma} \equiv \epsilon_{j\sigma} - \epsilon_{k\sigma}$  corresponding to single-particle excitations within the same spin space. In order to calculate the shifts towards the true excitation energies  $\Omega$  of the interacting system, we rewrite Eq. (334) as

$$\sum_{\nu'} \int d^3y' \left( \delta_{\sigma\nu'} \delta(\mathbf{r} - \mathbf{y}') - \sum_{\nu} \int d^3y \chi_{s\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) \left( \frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) \right) n_{1\nu'}(\mathbf{y}', \omega) = \sum_{\nu} \int d^3y \chi_{s\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) v_{1\nu}(\mathbf{y}, \omega). \quad (337)$$

Since, in general, the true excitation energies  $\Omega$  are not identical with the Kohn-Sham excitation energies  $\omega_{jk\sigma}$ , the right-hand side of Eq. (337) remains finite for  $\omega \rightarrow \Omega$ . In contrast, the *exact* spin-density response  $n_{1\sigma}$ , has poles at the true excitation energies  $\omega = \Omega$ . Hence the integral operator acting on  $n_{1\sigma}$  on the left-hand side of Eq. (337) cannot be invertible for  $\omega \rightarrow \Omega$ . If it were invertible one could act with the inverse operator on both sides of Eq. (337) leading to a *finite* result for  $\omega \rightarrow \Omega$  on the right-hand side in contradiction to the fact that  $n_{1\sigma}$ , on the left-hand side, has a pole at  $\omega = \Omega$ .

The true excitation energies  $\Omega$  can therefore be characterized as those frequencies where the eigenvalues of the integral operator acting on the spin-density vector in Eq. (337) vanish or, if the integration over the delta-function is performed, where the eigenvalues  $\lambda(\omega)$  of

$$\sum_{\nu'} \int d^3y' \sum_{\nu} \int d^3y \chi_{s\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) \left( \frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) \zeta_{\nu'}(\mathbf{y}', \omega) = \lambda(\omega) \zeta_{\sigma}(\mathbf{r}, \omega) \quad (338)$$

satisfy

$$\lambda(\Omega) = 1. \quad (339)$$

This condition rigorously determines the true excitation spectrum of the interacting system considered.

To simplify the notation, we now introduce double indices  $q \equiv (j, k)$  so that  $\omega_{q\sigma} \equiv \epsilon_{j\sigma} - \epsilon_{k\sigma}$  denotes the excitation energy of the single-particle transition ( $k\sigma \rightarrow j\sigma$ ). Moreover, we define

$$\Phi_{q\sigma}(\mathbf{r}) := \phi_{k\sigma}(\mathbf{r})^* \phi_{j\sigma}(\mathbf{r}), \quad (340)$$

$$\alpha_{q\sigma} := f_{k\sigma} - f_{j\sigma} \quad (341)$$

and set

$$\xi_{q\sigma}(\omega) := \sum_{\nu'} \int d^3y' \sum_{\nu} \int d^3y \delta_{\sigma\nu} \Phi_{q\nu}(\mathbf{y})^* \left( \frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) \zeta_{\nu'}(\mathbf{y}', \omega). \quad (342)$$

With these definitions, Eq. (338) takes the form

$$\sum_q \frac{\alpha_{q\sigma} \Phi_{q\sigma}(\mathbf{r})}{\omega - \omega_{q\sigma} + i\eta} \xi_{q\sigma}(\omega) = \lambda(\omega) \zeta_{\sigma}(\mathbf{r}, \omega). \quad (343)$$

Solving this equation for  $\zeta_\sigma(\mathbf{r}, \omega)$  and reinserting the result on the right-hand side of Eq. (342) leads to

$$\sum_{\sigma'} \sum_{q'} \frac{M_{q\sigma q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} \xi_{q'\sigma'}(\omega) = \lambda(\omega) \xi_{q\sigma}(\omega) \quad (344)$$

with the matrix elements

$$M_{q\sigma q'\sigma'}(\omega) = \alpha_{q'\sigma'} \int d^3r \int d^3r' \Phi_{q\sigma}^*(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) \right) \Phi_{q'\sigma'}(\mathbf{r}'). \quad (345)$$

Note that the summation in Eq. (344) extends over all single-particle transitions  $q'\sigma'$  between occupied and unoccupied Kohn-Sham orbitals, including the continuum states. Up to this point, no approximations have been made. In order to actually calculate  $\lambda(\omega)$ , the eigenvalue problem (344) has to be truncated in one way or another. One possibility is to expand all quantities in Eq. (344) about one particular KS-orbital energy difference  $\omega_{p\tau}$ :

$$\xi_{q\sigma}(\omega) = \xi_{q\sigma}(\omega_{p\tau}) + \left. \frac{d\xi_{q\sigma}(\omega)}{d\omega} \right|_{\omega_{p\tau}} (\omega - \omega_{p\tau}) + \dots \quad (346)$$

$$\lambda(\omega) = \frac{A(\omega_{p\tau})}{\omega - \omega_{p\tau}} + B(\omega_{p\tau}) + \dots \quad (347)$$

The matrix elements with  $(\omega_{p\tau} \neq \omega_{q'\sigma'})$  can be written as

$$\frac{M_{q\sigma q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} = \frac{M_{q\sigma q'\sigma'}(\omega_{p\tau})}{\omega_{p\sigma} - \omega_{q'\sigma'} + i\eta} + \frac{d}{d\omega} \left[ \frac{M_{q\sigma q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} \right]_{\omega_{p\tau}} (\omega - \omega_{p\tau}) + \dots \quad (348)$$

whereas if  $(\omega_{p\tau} = \omega_{q'\sigma'})$ ,

$$\frac{M_{q\sigma q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} = \frac{M_{q\sigma q'\sigma'}(\omega_{p\tau})}{\omega - \omega_{p\tau} + i\eta} + \left. \frac{dM_{q\sigma q'\sigma'}(\omega)}{d\omega} \right|_{\omega_{p\tau}} + \dots \quad (349)$$

Inserting Eqs. (346) - (349) in Eq. (344) the coefficients  $A$  and  $B$  are readily identified. If the pole  $\omega_{p\tau}$  is non-degenerate, one finds:

$$A(\omega_{p\tau}) = M_{p\tau p\tau}(\omega_{p\tau}) \quad (350)$$

and

$$B(\omega_{p\tau}) = \left. \frac{dM_{p\tau p\tau}}{d\omega} \right|_{\omega_{p\tau}} + \frac{1}{M_{p\tau p\tau}(\omega_{p\tau})} \sum_{q'\sigma' \neq p\tau} \frac{M_{p\tau q'\sigma'}(\omega_{p\tau}) M_{q'\sigma' p\tau}(\omega_{p\tau})}{\omega_{p\tau} - \omega_{q'\sigma'} + i\eta}. \quad (351)$$

The corresponding eigenvector (in lowest order) is given by

$$\xi_{q\sigma} = \frac{1}{A(\omega_{p\tau})} M_{q\sigma p\tau}(\omega_{p\tau}) \xi_{p\tau} \quad (352)$$

with  $(p\tau)$  fixed. The number  $\xi_{p\tau}$  is free and can be chosen to properly normalize the vector  $\xi$ .

If the pole  $\omega_{p\tau}$  is  $\wp$ -fold degenerate,

$$\omega_{p_1\tau_1} = \omega_{p_2\tau_2} = \dots = \omega_{p_\wp\tau_\wp} \equiv \omega_0, \quad (353)$$

the lowest-order coefficient  $A$  in Eq. (347) is determined by the following matrix equation

$$\sum_{k=1}^{\wp} M_{p_i\tau_i p_k\tau_k}(\omega_0) \xi_{p_k\tau_k}^{(n)} = A_n(\omega_0) \xi_{p_i\tau_i}^{(n)}, \quad i = 1 \dots \wp. \quad (354)$$

In general, one obtains  $\wp$  different eigenvalues  $A_1 \dots A_\wp$ . Then the remaining components of the corresponding eigenvectors  $\xi^{(n)}$  can be calculated from

$$\xi_{q\sigma}^{(n)} = \frac{1}{A_n(\omega_0)} \sum_{k=1}^{\wp} M_{q\sigma p_k \tau_k}(\omega_0) \xi_{p_k \tau_k}^{(n)}, \quad (355)$$

once the eigenvalue problem (354) has been solved. Assuming that the true excitation energy  $\Omega$  is not too far away from  $\omega_0$  it will be sufficient to consider only the lowest-order terms of the above Laurent expansions. In particular, we set

$$\lambda_n(\omega) \approx \frac{A_n(\omega_0)}{\omega - \omega_0}. \quad (356)$$

The condition (339) and its complex conjugate,  $\lambda^*(\Omega) = 1$ , then lead to

$$\Omega_n = \omega_0 + \Re A_n(\omega_0) \quad (357)$$

This is the central result of our analysis. Eq. (357) shows that a single KS pole can lead to several many-body excitation energies. The corresponding oscillator strengths can be obtained [152] from the eigenvectors  $\xi^{(n)}$  and the KS oscillator strengths.

In the following, we exclusively consider closed-shell systems. For these systems, the Kohn-Sham orbital eigenvalues are degenerate with respect to the spin variable, which implies a lack of spin-multiplet structure. In what follows, we demonstrate how this is restored by the lowest-order corrections (357). Assuming that there are no further degeneracies besides the spin degeneracy, Eq. (354) reduces to the following  $(2 \times 2)$  eigenvalue problem:

$$\sum_{\sigma'=\uparrow,\downarrow} M_{p\sigma p\sigma'}(\omega_0) \xi_{p\sigma'}(\omega_0) = A \xi_{p\sigma}(\omega_0). \quad (358)$$

For spin-saturated systems,  $M_{p\uparrow p\uparrow} = M_{p\downarrow p\downarrow}$  and  $M_{p\uparrow p\downarrow} = M_{p\downarrow p\uparrow}$ , so that the eigenvalues of Eq.(358) are given by

$$A_{1,2} = M_{p\uparrow p\uparrow} \pm M_{p\uparrow p\downarrow}. \quad (359)$$

By Eq. (357), the resulting excitation energies are:

$$\Omega_1 = \omega_0 + \Re \{M_{p\uparrow p\uparrow} + M_{p\uparrow p\downarrow}\} \quad (360)$$

$$\Omega_2 = \omega_0 + \Re \{M_{p\uparrow p\uparrow} - M_{p\uparrow p\downarrow}\}. \quad (361)$$

Inserting the explicit form of the matrix elements (345) one finds

$$\Omega_1 = \omega_0 + 2\Re \int d^3r \int d^3r' \Phi_p^*(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}'; \omega_0) \right) \Phi_p(\mathbf{r}') \quad (362)$$

$$\Omega_2 = \omega_0 + 2\Re \int d^3r \int d^3r' \Phi_p^*(\mathbf{r}) \mu_0^2 G_{xc}(\mathbf{r}, \mathbf{r}'; \omega_0) \Phi_p(\mathbf{r}') \quad (363)$$

where, for simplicity, we have dropped the spin-index of  $\Phi_{p\sigma}$ .<sup>4</sup> Obviously, the xc kernel appearing in Eq. (362),

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{4} \sum_{\sigma, \sigma'=\pm 1} f_{xc\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) \quad (364)$$

<sup>4</sup>This is possible only if the unperturbed KS ground-state determinant is spin-saturated since, in this case,  $\phi_{j\uparrow}(\mathbf{r}) = \phi_{j\downarrow}(\mathbf{r})$  for all  $j$ .

is identical with the one already defined in section 5.1. On the other hand, Eq. (363) exhibits the kernel

$$G_{\text{xc}}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{4\mu_0^2} \sum_{\sigma, \sigma' = \pm 1} (\sigma \cdot \sigma') f_{\text{xc}\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega). \quad (365)$$

This quantity gives rise to exchange and correlation effects in the Kohn-Sham equation for the linear response of the frequency-dependent magnetization density  $m(\mathbf{r}, \omega)$  [59]. The fact that the magnetization density response naturally involves spin-flip processes, suggests that  $\Omega_2$  represents the spin triplet excitation energies of many-electron systems with spin-saturated ground states. The corresponding spin singlet excitation energies, on the other hand, are given by  $\Omega_1$ . This assignment will be given further evidence by the numerical results presented at the end of this section.

Apart from the truncation of the Laurent series, two further approximations are necessary:

- (i) The frequency-dependent xc kernels  $f_{\text{xc}}$  and  $G_{\text{xc}}$  have to be approximated.
- (ii) The static Kohn-Sham orbitals entering Eqs. (362) and (363) (cf. Eq. (340)) have to be calculated with an *approximate* (static) potential  $v_{\text{xc}}^{\text{stat}}$ .

As an application of the method, we consider the lowest excitation energies of the alkaline earth elements and the zinc series. Here, in addition to the degeneracy with respect to the spin index, the  $s \rightarrow p$  transitions under consideration are threefold degenerate in the magnetic quantum number  $m$  of the “final” state. Hence, we have six degenerate poles and Eq. (354) is a  $(6 \times 6)$  eigenvalue problem. In our case, however, the matrix  $M_{p_i \tau_i p_k \tau_k}$  in Eq. (354) consists of (three) identical  $(2 \times 2)$  blocks, leading only to two distinct corrections, independent of  $m$ , as it should be.

Tables 1 - 3 show the results of calculations based on Eqs. (362) and (363). The calculation of Table 1 employs the ordinary local density approximation (LDA) for  $v_{\text{xc}}^{\text{stat}}$  and the adiabatic LDA (188) for  $f_{\text{xc}}$  (both using the parametrization of Vosko, Wilk and Nusair [90]). In this limit, the kernel  $G_{\text{xc}}$  is approximated by [103]

$$G_{\text{xc}}^{\text{ALDA}}[n](\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{1}{\mu_0^2 n(\mathbf{r})} \alpha_{\text{xc}}(n(\mathbf{r})). \quad (366)$$

The exchange-correlation contribution to the so called “spin-stiffness coefficient”  $\alpha_{\text{xc}}$  is also approximated within the LDA of [90].

The calculation of Table 2 uses the x-only optimized effective potential (OPM) for  $v_{\text{xc}}^{\text{stat}}$  in the approximation of Krieger, Li and Iafrate (KLI) [224] and for  $f_{\text{xc}}$  the TDOPM kernel (325) derived in section 6.2. Concerning the singlet spectrum, the OPM values are clearly superior to the LDA results and are also better than the usual  $\Delta_{\text{SCF}}$  values. The unoccupied orbitals and their energy eigenvalues are very sensitive to the behavior of the potential far from the nucleus. Thus one major reason for the superiority of the optimized effective potential is the fact that it is self-interaction free and therefore has the correct  $-1/r$  tail (while the LDA potential falls off exponentially). An important point to note is that the optimized effective potential decreases *correctly* for *all* orbitals. For this reason, the x-only optimized effective potential is also superior to the Hartree-Fock (HF) potential which is self-interaction free only for the occupied orbitals but not for the unoccupied ones. As a consequence, HF orbital-energy differences are typically too large. However, in spite of the fact that the OPM provides self-interaction free orbitals, it reproduces the triplet spectrum less accurately. This hinges on the approximation the xc *kernel* is based on. Substituting the TD-Fock expression (279) for the xc action functional defined in (278) leads to a xc kernel *diagonal* in spin space, because the correlation



between antiparallel spins is neglected. Accordingly, from Eqs. (364) and (365) we have, within the x-only TDOPM

$$G_{xc}^{\text{TDOPM}}[n](\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{\mu_0^2} f_{xc}^{\text{TDOPM}}[n](\mathbf{r}, \mathbf{r}'; \omega). \quad (367)$$

This should be cured by adding appropriate correlation terms to the xc part of the action functional, which is further backed by the observation that when combining the advantage of approximating  $v_{xc}^{\text{stat}}$  by the optimized effective potential, together with a local density prescription of exchange *and* correlation in the xc kernels  $f_{xc}$  and  $G_{xc}$ , both singlet and the triplet spectrum are reproduced well by Eqs. (362) and (363), as can be seen from Table 3.

In spite of the fact that we focused our attention to the situation of closed shells, and spin-multiplets, the method is also capable of dealing with open-shell systems and spatial multiplets. More details can be found in [152].

We emphasize that the calculation of excitation energies from Eqs. (362) and (363) involves only *known ground-state* quantities, i.e., the ordinary static Kohn-Sham orbitals and the corresponding Kohn-Sham eigenvalues. Thus the scheme described here requires only one selfconsistent Kohn-Sham calculation, whereas the so-called  $\Delta_{\text{SCF}}$  procedure involves linear combinations of two or more selfconsistent total energies [209]. So far, the best results are obtained with the optimized effective potential for  $v_{xc}^{\text{stat}}$  in the KLI x-only approximation. Further improvement is expected from the inclusion of correlation terms [6, 225] in the OPM.

### 7.3 Van der Waals interactions

While TDDFT has its main applications in time-dependent phenomena, and in the calculation of excitation or promotion energies, certain aspects of *groundstate* energy calculations are also assisted by TDDFT. This development principally concerns the van der Waals (vdW) or dispersion-force component of the groundstate energy. The usual groundstate LDA and its various gradient extensions [227] do not give an adequate description of vdW forces [228], presumably because these forces arise (in one picture at least: see below) from the correlations between dynamic electron density fluctuations in widely separated positions. This makes the usual local or near-local approximations invalid. The approach to be introduced here facilitates the derivation of van der Waals functionals via a frequency integration over dynamic susceptibilities.

(i) *vdW interactions for widely-separated fragments*: Perhaps the most familiar example of a dispersion interaction is the attractive mutual energy of a pair of neutral spherical atoms separated by a large distance  $R$ , an interaction which forms the tail of the well-known Lennard-Jones potential. To lowest order this interaction energy falls off [229] as  $R^{-6}$ . This form of dispersion interaction is readily derived for a general pair of non-overlapping electronic systems by regarding the electrons on the first system as distinguishable from those on the second system. One then obtains the  $R^{-6}$  dispersion energy (in addition to some "polarization" terms relating to any static electric moments [230]) by performing second-order Rayleigh-Schrodinger perturbation theory, treating the Coulomb interaction between the two groups of electrons as the perturbation Hamiltonian. (For very large separations  $R$  the retardation of the electromagnetic interactions between the systems cannot be ignored. In this regime the  $R^{-6}$  law just quoted is replaced [229] by  $R^{-7}$ . This retarded form takes over whenever  $R \gg c/\omega$ , where  $\omega$  is a characteristic response or fluctuation frequency of the electronic systems. We will consider only the non-retarded case here).

From the work of Casimir, Lifshitz, London and many others [229] we know that the perturbation expression for the dispersion interaction between separated

| Atom | State   | $\Omega_{\text{exp}}$ | $\Omega^{\text{LDA}}$ | $\Omega(\Delta_{\text{SCF}})$ | $\omega_0^{\text{LDA}}$ |
|------|---------|-----------------------|-----------------------|-------------------------------|-------------------------|
| Be   | $^1P_1$ | 0.388                 | 0.399                 | 0.331                         | 0.257                   |
|      | $^3P_0$ | 0.200                 |                       |                               |                         |
|      | $^3P_1$ | 0.200                 | 0.192                 | 0.181                         | 0.257                   |
|      | $^3P_2$ | 0.200                 |                       |                               |                         |
| Mg   | $^1P_1$ | 0.319                 | 0.351                 | 0.299                         | 0.249                   |
|      | $^3P_0$ | 0.199                 |                       |                               |                         |
|      | $^3P_1$ | 0.199                 | 0.209                 | 0.206                         | 0.249                   |
|      | $^3P_2$ | 0.200                 |                       |                               |                         |
| Ca   | $^1P_1$ | 0.216                 | 0.263                 | 0.211                         | 0.176                   |
|      | $^3P_0$ | 0.138                 |                       |                               |                         |
|      | $^3P_1$ | 0.139                 | 0.145                 | 0.144                         | 0.176                   |
|      | $^3P_2$ | 0.140                 |                       |                               |                         |
| Zn   | $^1P_1$ | 0.426                 | 0.477                 | 0.403                         | 0.352                   |
|      | $^3P_0$ | 0.294                 |                       |                               |                         |
|      | $^3P_1$ | 0.296                 | 0.314                 | 0.316                         | 0.352                   |
|      | $^3P_2$ | 0.300                 |                       |                               |                         |
| Sr   | $^1P_1$ | 0.198                 | 0.241                 | 0.193                         | 0.163                   |
|      | $^3P_0$ | 0.130                 |                       |                               |                         |
|      | $^3P_1$ | 0.132                 | 0.136                 | 0.135                         | 0.163                   |
|      | $^3P_2$ | 0.136                 |                       |                               |                         |
| Cd   | $^1P_1$ | 0.398                 | 0.427                 | 0.346                         | 0.303                   |
|      | $^3P_0$ | 0.274                 |                       |                               |                         |
|      | $^3P_1$ | 0.279                 | 0.269                 | 0.272                         | 0.303                   |
|      | $^3P_2$ | 0.290                 |                       |                               |                         |

Table 1: The lowest  $S \rightarrow P$  excitation energies of various atoms. The experimental values (first column) [226] are compared with results calculated from Eq. (362) for the singlet and from Eq. (363) for the triplet (second column) and with ordinary  $\Delta_{\text{SCF}}$  values (third column). The LDA was employed for  $v_{\text{xc}}$  and the ALDA for the  $\text{xc}$  kernels. The corresponding Kohn-Sham orbital-energy differences  $\omega_0$  are shown in the last column (All values in rydbergs).

| Atom | State   | $\Omega_{\text{exp}}$ | $\Omega^{\text{OPM}}$ | $\Omega(\Delta_{\text{SCF}})$ | $\omega_0^{\text{OPM}}$ |
|------|---------|-----------------------|-----------------------|-------------------------------|-------------------------|
| Be   | $^1P_1$ | 0.388                 | 0.392                 | 0.331                         | 0.259                   |
|      | $^3P_0$ | 0.200                 |                       |                               |                         |
|      | $^3P_1$ | 0.200                 | 0.138                 | 0.181                         | 0.259                   |
|      | $^3P_2$ | 0.200                 |                       |                               |                         |
| Mg   | $^1P_1$ | 0.319                 | 0.327                 | 0.299                         | 0.234                   |
|      | $^3P_0$ | 0.199                 |                       |                               |                         |
|      | $^3P_1$ | 0.199                 | 0.151                 | 0.206                         | 0.234                   |
|      | $^3P_2$ | 0.200                 |                       |                               |                         |
| Ca   | $^1P_1$ | 0.216                 | 0.234                 | 0.211                         | 0.157                   |
|      | $^3P_0$ | 0.138                 |                       |                               |                         |
|      | $^3P_1$ | 0.139                 | 0.090                 | 0.144                         | 0.157                   |
|      | $^3P_2$ | 0.140                 |                       |                               |                         |
| Zn   | $^1P_1$ | 0.426                 | 0.422                 | 0.403                         | 0.314                   |
|      | $^3P_0$ | 0.294                 |                       |                               |                         |
|      | $^3P_1$ | 0.296                 | 0.250                 | 0.316                         | 0.314                   |
|      | $^3P_2$ | 0.300                 |                       |                               |                         |
| Sr   | $^1P_1$ | 0.198                 | 0.210                 | 0.193                         | 0.141                   |
|      | $^3P_0$ | 0.130                 |                       |                               |                         |
|      | $^3P_1$ | 0.132                 | 0.081                 | 0.135                         | 0.141                   |
|      | $^3P_2$ | 0.136                 |                       |                               |                         |
| Cd   | $^1P_1$ | 0.398                 | 0.376                 | 0.346                         | 0.269                   |
|      | $^3P_0$ | 0.274                 |                       |                               |                         |
|      | $^3P_1$ | 0.279                 | 0.211                 | 0.272                         | 0.269                   |
|      | $^3P_2$ | 0.290                 |                       |                               |                         |

Table 2: The lowest  $S \rightarrow P$  excitation energies of various atoms. The experimental values (first column) [226] are compared with results calculated from Eq. (362) for the singlet and from Eq. (363) for the triplet (second column) and with ordinary  $\Delta_{\text{SCF}}$  values (third column). The optimized effective potential was used for  $v_{\text{xc}}$  and the approximate OPM kernel (325) for  $f_{\text{xc}}$  and  $G_{\text{xc}}$ . The corresponding Kohn-Sham orbital-energy differences  $\omega_0$  are shown in the last column (All values in rydbergs).

| Atom | State   | $\Omega_{\text{exp}}$ | $\Omega^{\text{OPM+ALDA}}$ | $\Omega(\Delta_{\text{SCF}})$ | $\omega_0^{\text{OPM}}$ |
|------|---------|-----------------------|----------------------------|-------------------------------|-------------------------|
| Be   | $^1P_1$ | 0.388                 | 0.398                      | 0.331                         | 0.259                   |
|      | $^3P_0$ | 0.200                 |                            |                               |                         |
|      | $^3P_1$ | 0.200                 | 0.196                      | 0.181                         | 0.259                   |
|      | $^3P_2$ | 0.200                 |                            |                               |                         |
| Mg   | $^1P_1$ | 0.319                 | 0.329                      | 0.299                         | 0.234                   |
|      | $^3P_0$ | 0.199                 |                            |                               |                         |
|      | $^3P_1$ | 0.199                 | 0.196                      | 0.206                         | 0.234                   |
|      | $^3P_2$ | 0.200                 |                            |                               |                         |
| Ca   | $^1P_1$ | 0.216                 | 0.236                      | 0.211                         | 0.157                   |
|      | $^3P_0$ | 0.138                 |                            |                               |                         |
|      | $^3P_1$ | 0.139                 | 0.129                      | 0.144                         | 0.157                   |
|      | $^3P_2$ | 0.140                 |                            |                               |                         |
| Zn   | $^1P_1$ | 0.426                 | 0.417                      | 0.403                         | 0.314                   |
|      | $^3P_0$ | 0.294                 |                            |                               |                         |
|      | $^3P_1$ | 0.296                 | 0.280                      | 0.316                         | 0.314                   |
|      | $^3P_2$ | 0.300                 |                            |                               |                         |
| Sr   | $^1P_1$ | 0.198                 | 0.211                      | 0.193                         | 0.141                   |
|      | $^3P_0$ | 0.130                 |                            |                               |                         |
|      | $^3P_1$ | 0.132                 | 0.117                      | 0.135                         | 0.141                   |
|      | $^3P_2$ | 0.136                 |                            |                               |                         |
| Cd   | $^1P_1$ | 0.398                 | 0.370                      | 0.346                         | 0.269                   |
|      | $^3P_0$ | 0.274                 |                            |                               |                         |
|      | $^3P_1$ | 0.279                 | 0.239                      | 0.272                         | 0.269                   |
|      | $^3P_2$ | 0.290                 |                            |                               |                         |

Table 3: The lowest  $S \rightarrow P$  excitation energies of various atoms. The experimental values (first column) [226] are compared with results calculated from Eq. (362) for the singlet and from Eq. (363) for the triplet (second column) and with ordinary  $\Delta_{\text{SCF}}$  values (third column). The optimized effective potential was used for  $v_{\text{xc}}$  and the ALDA for the xc kernels. The corresponding Kohn-Sham orbital-energy differences  $\omega_0$  are shown in the last column (All values in rydbergs).

systems can be related to the electric polarizabilities of the interacting species, and also to the correlation of fluctuating electric multipoles on the two systems. In the Present TDDFT context, a useful polarizability form for the second-order dispersion interaction was given by Zaremba and Kohn [231] who derived it directly from second-order perturbation theory:

$$E^{(2)} = -\frac{1}{2\pi} \int d^3 r_1 \int d^3 r_2 \int d^3 r'_1 \int d^3 r'_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{1}{|\mathbf{r}'_1 - \mathbf{r}'_2|} \times \int_0^\infty du \chi_a(\mathbf{r}_1, \mathbf{r}'_1, iu) \chi_b(\mathbf{r}_2, \mathbf{r}'_2, iu). \quad (368)$$

Here  $\chi_a(\mathbf{r}, \mathbf{r}', \omega)$  and  $\chi_b(\mathbf{r}, \mathbf{r}', \omega)$  are the exact density-density response functions (157) of each separate system in the absence of the other.  $\chi_a$  is defined by the linear density response  $n_{1a}(\mathbf{r}) \exp(iu)$  of the electrons in system a to an externally applied electron potential energy perturbation  $V_1^{ext}(\mathbf{r}) e^{iu}$ :

$$n_{1a}(\mathbf{r}) = \int d^3 r' \chi_a(\mathbf{r}, \mathbf{r}', iu) V_1^{ext}(\mathbf{r}') \quad (369)$$

and similarly for  $\chi_b$ . It is important to note that  $\chi_a$  includes the electron-electron interaction amongst the electrons of system a to all orders, and similarly for  $\chi_b$ . (Note also that, unlike Ref. [231], we have referred the space arguments of  $\chi_a$  and  $\chi_b$  in (368) to a common origin.)

The expression (368) is more general than the familiar asymptotic  $R^{-6}$  form. It applies to neutral quantal systems of any shape (not necessarily spherical) provided that  $R$  is still large enough that the electron densities do not overlap and that the inter-system Coulomb interaction can be treated in second order. We can recover the  $R^{-6}$  form by assuming that  $R \gg A, B$  where  $A$  and  $B$  are the spatial dimensions of the two systems. Then one can expand the Coulomb interactions in (368) in multipoles. The lowest nonvanishing term gives, with the "3" axis chosen along  $\mathbf{R}$ ,

$$E^{(2)}(R) \sim \frac{-1}{2\pi} \sum_{i,j=1}^3 \frac{(1-3\delta_{3i})(1-3\delta_{3j})}{R^6} \int_0^\infty du \alpha_{ij}^{(a)}(iu) \alpha_{ij}^{(b)}(iu), \quad R \gg A, B \quad (370)$$

where, for each system

$$\alpha_{ij}(\omega) = \int d^3 r \int d^3 r' (r_i - X_i)(r'_j - X_j) \chi(\mathbf{r}, \mathbf{r}', \omega) \quad (371)$$

is the dipole polarizability tensor and  $\mathbf{X}$  is the centre of electronic charge of the system. When the polarizabilities are isotropic so that  $\alpha_{ij} = \alpha \delta_{ij}$ , (370) reduces to the more familiar London form [229]

$$E^{(2)}(R) \sim \frac{-3}{\pi R^6} \int_0^\infty du \alpha^{(a)}(iu) \alpha^{(b)}(iu). \quad (372)$$

Van Gisbergen, Snijders and Baerends [232] have evaluated a formula equivalent to (370) for diatomic and polyatomic molecules, using the ALDA to obtain the  $\{\alpha_{ij}\}$ . They find that, for the *isotropic* part of the vdW interaction, ALDA gives errors of similar size (but mostly opposite sign) to time-dependent Hartree Fock theory (except for the smallest atoms). This was achieved with much less computational effort than in the time-dependent Hartree Fock approach. The isotropic vdW coefficients, like the static and dynamic polarizabilities, were found to be somewhat too large. For the *anisotropic* part of the interaction, they found that ALDA compares favourably with both Hartree-Fock and Many-Body Perturbation Theory. Since

the ALDA contains unphysical orbital self-interaction, one can speculate that the use of self-interaction corrected (SIC) functionals might further improve the accuracy of the method employed in Ref. [232]. These unphysical self-interactions cause orbitals to “see” an incorrectly large charge from the other electrons, causing orbitals to be too spatially extended and hence too polarizable. This presumably has effects mainly at the isotropic level. Furthermore, SIC phenomena are known to be strongest for small systems with highly localized orbitals. Both of these considerations can be expected to cause difficulties in the very cases where van Gisbergen, Snijders and Baerends observed the least favourable ALDA results in comparison with other methods. This SIC explanation gains further support from the work of Pacheco and Ekardt [166] on alkali metal microclusters. Their static and dynamic SIC terms [233] were found to have significant effects on the polarizability and vdW interaction for small clusters and even, to a lesser degree, for quite large ones.

Van Gisbergen *et al.* [232] commented that their numerical method could accommodate more sophisticated forms of TDDFT than simply the ALDA, and in particular, considering temporal and spatial nonlocality in the xc kernel, they felt that the latter might be the more important.

Before leaving the discussion of vdW interactions in non-overlapping systems, we mention that the exact second-order dispersion formula (368) can be used [234] to derive a class of approximate vdW expressions for the groundstate energy as an explicit but highly nonlocal functional of the groundstate density. The idea is to make a direct local density approximation for the interacting susceptibilities  $\chi_a$  and  $\chi_b$  in (368). Extreme care is needed, however, to ensure one does not violate the charge conservation condition

$$\int d^3r \chi(\mathbf{r}, \mathbf{r}', \omega) = 0 \quad (373)$$

or the reciprocity condition

$$\chi(\mathbf{r}, \mathbf{r}', iu) = \chi(\mathbf{r}', \mathbf{r}, -iu) \text{ for real } u. \quad (374)$$

An *Ansatz* satisfying these conditions and based on the simplest, pressure-free hydrodynamic analysis of the uniform electron gas was given in [234]:

$$\chi_{local}^{inhom}(\mathbf{r}, \mathbf{r}', \omega) = \nabla_r \cdot \nabla_{r'} \left[ \frac{n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')}{\omega^2 - \omega_p^2(n(\mathbf{r}))} \right] \quad (375)$$

When this is substituted into (368) for each of  $\chi_a$  and  $\chi_b$  one obtains

$$E^{(2)} = -\frac{3}{32\pi^2} \int d^3r_1 \int d^3r_2 \frac{1}{r_{12}^6} \frac{\omega_1\omega_2}{(\omega_1 + \omega_2)} \quad (376)$$

where  $\omega_1 = \omega_{p1} = (4\pi n_a(\mathbf{r}_1)/m)^{1/2}$  is the local plasma frequency at an arbitrary point  $\mathbf{r}_1$  inside system a, and similarly for  $\omega_2$ . Equation (376) constitutes a very nonlocal groundstate density functional, and it clearly provides a systematic basis for the much-used [229] simple notion of pairwise addition of  $R^{-6}$  vdW contributions. It is interesting that the integrand in (376) is proportional to the *harmonic mean*,  $\omega_1\omega_2/(\omega_1 + \omega_2)$ , of the two local plasma frequencies. The same formula (376) was very recently postulated [235] by Andersson, Langreth and Lundqvist on different grounds. They obtained (376) by examining limiting cases and so modifying a somewhat similar formula previously postulated by Rapcewicz and Ashcroft [236] on the basis of diagrammatic arguments. The Rapcewicz-Ashcroft formula differs from (376) only in the replacement of  $\omega_1 + \omega_2$  by  $2\sqrt{\omega_1\omega_2}$  on the denominator of (376). It was shown in [236] and [235] that these simple formulae give quite good

answers for the isotropic  $R^{-6}$  dispersion coefficient for various atomic pairs, provided that one uses an appropriate cutoff in the low-density tails of the electron distributions.

The derivation of (376) given in [234] promises to be extendable to more sophisticated local approximations for  $\chi_a$  and  $\chi_b$  in (368), based perhaps on hydrodynamics with the inclusion of pressure (Thomas-Fermi hydrodynamics [112]) or of pressure plus density gradient (Thomas-Fermi-Weizsäcker hydrodynamics [237]). With suitable care to satisfy the constraints (373) and (374), one may thereby hope to obtain a more accurate extension of (376) involving gradients of the groundstate density and, possibly, having less dependence on spatial cutoffs.

(ii) *vdW interactions in closely juxtaposed or overlapping systems*: The work of van Gisbergen *et al.* [232] and Pacheco and Ekardt [166], discussed in the previous section, shows that TDDFT, at least in the form of the ALDA, can represent the state of the art in evaluating van der Waals interactions in *well-separated* systems that are too large for methods such as the Configuration Interaction approach. What of more general cases where the electron clouds *overlap* or where no large separation exists? To study this for large systems, we seek a density functional approach, but first we need to appreciate the origin of the vdW force in terms of correlation physics.

In essence, dispersion forces arise from the correlation between dynamic charge density fluctuations in two different systems or in distant parts of one system. The difficulty [228] in describing vdW forces in the static LDA or gradient approaches is therefore not surprising since in a highly inhomogeneous system (exemplified by, but not limited to, a pair of separated subsystems) these correlations may be quite different from those in the uniform or near-uniform electron gas upon which the LDA and the various gradient approximations are based.

The previous section applied only to well-separated subsystems. The necessary correlations between distant fluctuations were generated by the application of second-order perturbation theory, and the TDLDA aspect of the calculation was not called upon to produce the vdW correlations directly. For overlapping systems (and for some closely juxtaposed systems), low-order perturbation theory in the Coulomb potential is not appropriate. The present section will outline an approach, currently under development, which does generate such long-ranged correlations in a natural fashion by the solution of a highly nonlocal real-space screening integral equation. Nevertheless, local density approximations are made wherever possible for the independent-electron susceptibility  $\chi_s$  and the exchange-correlation kernel  $f_{xc}$ , neither of which needs to be long-ranged in order to generate the basic long-ranged vdW correlations.

The starting point for the proposed new approach is an exact formula [238], [239], based on the adiabatic connection formula and the zero-temperature fluctuation-dissipation theorem, relating the groundstate xc energy to the interacting susceptibility  $\chi$ :

$$E_{xc} = -\frac{1}{2} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left[ \left( \frac{1}{\pi} \int_0^\infty du \chi(\lambda, \mathbf{r}, \mathbf{r}', iu) \right) + n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \right] \quad (377)$$

Here  $\chi(\lambda, \mathbf{r}, \mathbf{r}', \omega)$  is the interacting susceptibility defined as before but with a reduced Coulomb interaction  $\lambda/r$  acting between electrons. It was shown in Ref. [234] that *the charge conservation condition (373) for  $\chi$  implies xc hole normalization*. Use of the independent-electron Kohn-Sham susceptibility  $\chi_s = \chi(\lambda = 0, \mathbf{r}, \mathbf{r}', iu)$  rather than  $\chi(\lambda, \mathbf{r}, \mathbf{r}', iu)$  in (377) yields the exact exchange energy. Subtraction of this exchange energy expression from the above xc energy yields the correlation

energy

$$E_c = -\frac{1}{2\pi} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_0^\infty du \left( \chi(\lambda, \mathbf{r}, \mathbf{r}', iu) - \chi_s(\mathbf{r}, \mathbf{r}', iu) \right). \quad (378)$$

Equation (378) is required to produce the dispersion interactions under study. Petersilka, Gossmann and Gross [69] have shown that  $\chi$  and  $\chi_s$  are related exactly by a Dyson-type equation involving the dynamic nonlocal xc kernel  $f_{xc}$  as well as the Coulomb kernel (cf. Equation (152)):

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi_s(\mathbf{r}, \mathbf{r}', \omega) + \int d^3x \int d^3x' \chi_s(\mathbf{r}, \mathbf{x}, \omega) \left( \frac{1}{|\mathbf{x} - \mathbf{x}'|} + f_{xc}(\mathbf{x}, \mathbf{x}', \omega) \right) \chi(\mathbf{x}', \mathbf{r}', \omega) \quad (379)$$

Equations (377) and (379) are of course exact provided that  $f_{xc}$  is exact, and so they contain *inter alia* the exact vdW interaction. Consider first a homogeneous electron gas. If  $f_{xc}$  is arbitrarily set to zero, and (379) is Fourier-transformed with use of the convolution theorem, (379) is then seen to be the equation for the RPA response function  $\chi$  in terms of the bare (dynamic Kohn-Sham-Lindhard) response  $\chi_s$ . Again with the assumption  $f_{xc} = 0$ , but with the homogeneous assumption removed, (377) and (379) merely represent the inhomogeneous generalization of the well-known RPA groundstate correlation energy of the homogeneous electron gas. This case of zero  $f_{xc}$  already has some rather useful properties with respect to the vdW interaction. It has been shown in detail [239] that, when the correlation energy recipe (377), (379) with  $f_{xc} = 0$  is applied to an arbitrary pair of widely-separated systems, the Zaremba-Kohn second-order vdW energy expression (368) is reproduced, with the following exception: the susceptibilities  $\chi_a$  and  $\chi_b$  are the approximate RPA-interacting susceptibilities of each system, rather than including the exact interactions within each subsystem. Thus the full inhomogeneous RPA correlation energy already contains the essence of the vdW interaction, and will produce an  $R^{-6}$  dependence in the appropriate limit. An examination of the detailed proof in [239] further shows that the long-ranged vdW interaction achieved in the RPA does NOT arise because of any long-ranged behaviour of the independent-electron susceptibility  $\chi_s$  (indeed  $\chi_s$  is not normally long-ranged). Rather, the long range of the vdW interaction comes from the long range of the Coulomb interaction in the screening equation (379). Thus a local density approximation for  $\chi_s$  will not spoil the vdW properties, but may slightly alter the interacting susceptibilities  $\chi_a$  and  $\chi_b$  in the asymptotic form (368). Furthermore the reintroduction of  $f_{xc}$  within a local approximation can also be seen, from the working of Ref. [239], to maintain the form (368) in the separated limit, but the individual susceptibilities  $\chi_a$  and  $\chi_b$  will now involve  $f_{xc}$  and hence will be closer to the required interacting susceptibilities.

To summarize the previous paragraph: If we make short-ranged local-density or gradient approximations for  $\chi_s$  and  $f_{xc}$  in the exact groundstate energy scheme (377), (379), we obtain an approximate and highly nonlocal prescription for the groundstate correlation energy, with the groundstate density  $n(\mathbf{r})$  as the only input. This scheme is expected to produce a rather good approximation to the long-ranged vdW dispersion interaction between widely separated subsystems, a result due principally to the retention, in full, of the nonlocal coulomb kernel in the real-space screening integral equation (379).

What is now required is a sufficient set of constraints on the kernel  $f_{xc}$  so that the *short-ranged* aspects of the groundstate correlation energy are also reproduced by (377), (379) at a level of approximation comparable, say, to the groundstate LDA or GGA. If this can be achieved, we will have a "seamless" scheme, equally reasonable for chemically bonded systems, metals etc., and also for fully or partly subdivided systems at all separations. This should allow investigation of the intermediate region of interaction where both short-ranged and long-ranged correlations are significant,



even for systems too large for traditionally accurate methods such as CI or Møller-Plesset perturbation theory. (Recall that wavefunctions are not needed for the present scheme, only groundstate densities, so that one may perform "real-space quantum chemistry" without basis-set problems).

The details of this scheme are currently being worked out. Although it aims for a groundstate energy functional, it depends heavily on time-dependent density functional theory in the sense that the properties of the *dynamic* TDDFT xc kernel  $f_{xc}(\mathbf{r}, \mathbf{r}', iu)$  for inhomogeneous systems are of the essence. Further details of some constraints to be obeyed by  $f_{xc}$  are discussed in Ref. [239]. Some supporting evidence for the utility of a local approximation for  $\chi_s$  in a highly inhomogeneous system are given in [113]. Current indications are that, for jellium slab situations where the inhomogeneity is only one-dimensional, the complete scheme (377), (379) (even with the exact Kohn-Sham  $\chi_s$  but with a local approximation for  $f_{xc}$ ) can be computed on a single-processor 1- MFlop workstation in  $10^2$  hours or less. With Monte Carlo methods for the integrations in (377), and/or faster or parallel machines, more involved geometries should be tractable.

## 8 Applications beyond the perturbative regime: Atoms in strong femto-second laser pulses

Owing to rapid experimental progress in the field of laser physics, ultra-short laser pulses of very high intensity have become available in recent years. The electric field produced in such pulses can reach or even exceed the strength of the static nuclear Coulomb field. If an atomic system is placed in the focus of such a laser pulse one observes a wealth of new phenomena [240] which cannot be explained by perturbation theory. In this case a non-perturbative treatment, i.e., the solution of the full TDKS equations (39) – (41) is mandatory. The total *external* potential seen by the electrons is given by

$$v(\mathbf{r}, t) = -\frac{Z}{r} + E_0 f(t) z \sin(\omega_0 t) \quad (380)$$

where  $Z$  is the nuclear charge. The second term on the right-hand side of Eq. (380) is the potential due to the laser field in dipole approximation, written in the length form. Since the wavelength of currently used lasers is almost always very large compared to any characteristic length associated with an atomic system, the dipole approximation turns out to be very good in practice [241].  $E_0$  denotes the peak electric field strength and  $f(t)$  characterizes the envelope function of the pulse which, in the calculations described below, is linearly ramped to its peak value over the first 10 cycles and then held constant. The field is assumed to be polarized along the  $z$ -direction.

In the following, we compare the results of a TDCLI calculation using the approximate potential (313) with an ALDA calculation using the potential (186), both for the exchange-only case [242, 243]. The numerical procedure [244] to solve the TDKS equations is similar to the one developed by Kulander [245, 246], who solved the time-dependent Schrödinger equation for hydrogen and the time-dependent Hartree equation for helium in a laser pulse. The spin orbitals are expressed in cylindrical coordinates and, due to the linear polarization of the field, the spin as well as the angular part of the orbitals are preserved. Consequently, a fully three-dimensional treatment only requires a two-dimensional grid for the numerical integration. In the following, the time-dependent orbitals will always be characterized by the indices indicating the *initial* state of the respective orbital; e.g.,  $\varphi_{2s}(\mathbf{r}, t)$  describes an electron which initially was in a 2s spin orbital:  $\varphi_{2s}(\mathbf{r}, t = 0) = \phi_{2s}(\mathbf{r})$ . The integration of the single-particle equations is performed using a finite-difference

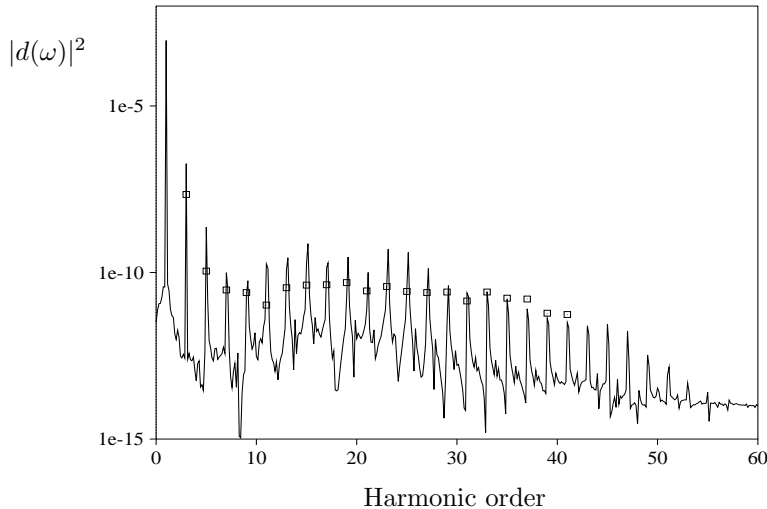


Figure 4: *Harmonic spectrum for He at  $\lambda = 616$  nm and  $I = 3.5 \times 10^{14}$  W/cm<sup>2</sup>. The squares represent experimental data taken from Ref. [248] normalized to the value of the 33rd harmonic of the calculated spectrum. The experiment was performed with a peak intensity of  $1.4 \times 10^{14}$  W/cm<sup>2</sup>.*

representation of the kinetic energy operator. A Crank-Nicholson technique is employed for the (unitary) time propagation of the orbitals.

Once a numerical solution of the TDKS equations has been obtained, the resulting time-dependent density is sufficient to calculate any desired observable of the system. Some quantities are easily calculated while others (such as ATI spectra) are harder to extract from the density. But, as demonstrated in section 2, *all* physical observables can be calculated from the density, in principle. In the following we shall describe the calculation of two different quantities, namely the *harmonic spectrum* and the *ionization yields*.

To obtain the harmonic spectrum, we calculate the induced dipole moment

$$d(t) = \int d^3r z n(\mathbf{r}, t) \quad (381)$$

which is then Fourier transformed over the last 5 cycles of the constant-intensity interval. The square of the resulting Fourier transform,  $|d(\omega)|^2$ , has been shown [247] to be proportional to the experimentally observed harmonic distribution to within a very good approximation. Figure 4 shows the result of a simulation for the helium atom at a laser wavelength of  $\lambda = 616$  nm and peak intensity of  $I = 3.5 \times 10^{14}$  W/cm<sup>2</sup>. The calculation was made with the TDKLI scheme which, for two electrons in the x-only limit, reduces to the ordinary time-dependent Hartree method. One observes peaks in the energy-resolved photon spectrum at odd multiples of the external laser frequency. From perturbation theory one would expect an exponential decrease of the peak intensities. Figure 4, however, shows a plateau of peak intensities up until roughly the 47th harmonic. This plateau is a typical nonlinear phenomenon. The squares in Fig. 4 indicate experimental results [248] obtained with the same laser frequency at an intensity of  $1.4 \times 10^{14}$  W/cm<sup>2</sup>. Various calculations were performed with different peak intensities, but the best agreement with the experiment was achieved in the calculation for  $I = 3.5 \times 10^{14}$  W/cm<sup>2</sup> shown in Fig. 4. The discrepancy between this intensity and the experimental intensity of  $1.4 \times 10^{14}$  W/cm<sup>2</sup> might be due to the uncertainty of the experimentally determined peak intensity which can be as high as a factor of two.

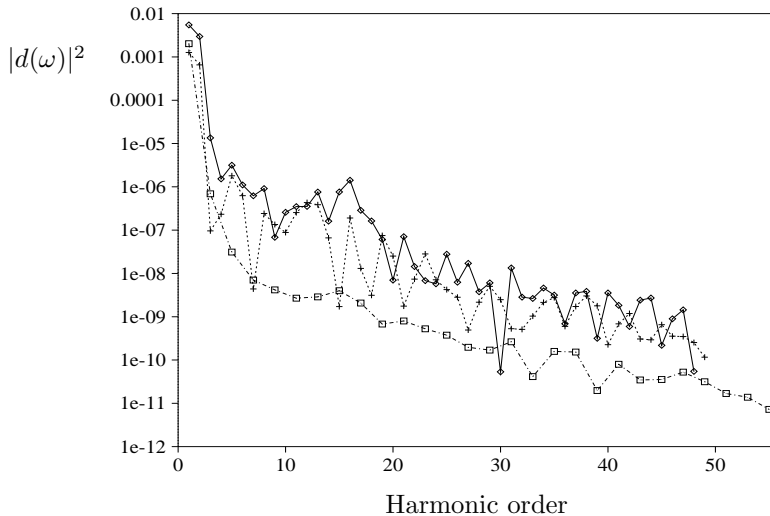


Figure 5: Harmonic distribution for He in a two-colour laser field. The two wavelengths are 616 nm and 308 nm, and the intensity is  $3.5 \times 10^{14}$  W/cm<sup>2</sup> for both of them. Crosses are the results for  $\varphi = 0$  and diamonds denote the values obtained with phase shift  $\varphi = 0.7\pi$ . For comparison, the squares indicate the harmonic distribution for He in a one-colour field with  $\lambda = 616$  nm and  $I = 7 \times 10^{14}$  W/cm<sup>2</sup>.

The harmonic generation of helium in a strong two-color laser field has also been studied [243, 108]. The two lasers with frequencies  $\omega_0$  and  $2\omega_0$ , respectively, are operated with the same peak intensity and a constant relative phase difference  $\varphi$ . This results in a total external potential of the form

$$v(\mathbf{r}, t) = -\frac{Z}{r} + E_0 f(t) z [\sin(\omega_0 t) + \sin(2\omega_0 t + \varphi)] \quad (382)$$

where both fields are linearly polarized along the  $z$ -axis.

Calculated harmonic distributions induced by a two-colour field with different relative phases are shown in Fig. 5. To avoid overcrowding, only the calculated peak intensities are plotted and connected with straight lines. The fundamental wavelength is again 616 nm and the intensity is  $3.5 \times 10^{14}$  W/cm<sup>2</sup> for both frequency components. We also show the one-colour spectrum for  $\lambda = 616$  nm calculated with the *same* total intensity as the two-colour field, i. e.  $I = 7 \times 10^{14}$  W/cm<sup>2</sup>. In the two-colour spectrum, harmonics at all higher multiples (including even multiples) of the fundamental frequency  $\omega_0$  occur due to nonlinear mixing processes of the two fields [249]. Most of the harmonics produced by the two-colour field in the plateau region are one to two orders of magnitude more intense than those obtained in the one-colour calculation although the total intensity of the external laser field is the same in all cases. Similar results have recently been found for hydrogen in a two-colour field [250]. One possible reason for this remarkable enhancement is that in a two-colour field one specific high-order harmonic can be generated by a large number of different mixing processes [249].

In order to simulate ionization, the grid contains an absorbing boundary to remove the flux of electrons leaving the nucleus. When some portion of the wave function propagates to the outer edges of the grid it is absorbed. We assume this flux corresponds to the ionized part of the wave function. Strictly speaking, such a criterion is meaningful only after long times when the respective contributions have propagated very far away from the nucleus. For the wave lengths considered here, a cylindrical grid of  $20 \times 60$  a.u. was found to be sufficient. As time proceeds, more

and more electrons will be removed from the atom and, accordingly, the norm of the TDKS orbitals taken over the finite volume of the grid,

$$N_{j\sigma}(t) = \int_{\text{finite volume}} d^3r |\varphi_{j\sigma}(\mathbf{r}, t)|^2, \quad (383)$$

decreases with time.

Figure 6 compares the results of a TDKLI and an ALDA calculation [243] for Ne exposed to a laser field with wavelength  $\lambda = 248$  nm and intensity  $I = 3 \times 10^{15}$  W/cm<sup>2</sup>. Figure 6 shows the norm (383) of those orbitals which were initially in the Ne 2s, 2p<sub>0</sub> and 2p<sub>1</sub> states. The 1s electrons have been frozen, i.e., only the 2s and 2p electrons are propagated by solving the TDKS equations, whereas the time evolution of the 1s electrons is given by

$$\varphi_{1s}(\mathbf{r}, t) = \phi_{1s}(\mathbf{r}) e^{-i\epsilon_{1s}(t-t_0)}. \quad (384)$$

As expected, among the Ne 2s, 2p<sub>0</sub> and 2p<sub>1</sub> orbitals, the 2s orbital is the least ionized one because it is initially more strongly bound (by roughly a factor of 2) than the 2p orbitals. A little surprising at first sight, the 2p<sub>0</sub> and 2p<sub>1</sub> orbitals differ by about an order of magnitude in their degree of ionization (60% for the 2p<sub>0</sub> orbital compared to only 4.75% for the 2p<sub>1</sub> orbital within TDKLI, and 56% for the 2p<sub>0</sub> compared to 7.7% for the 2p<sub>1</sub> orbital within the ALDA). This difference has been observed before by Kulander [251, 252] for the case of xenon (in a single-active-electron calculation). It is due to the fact that the 2p<sub>0</sub> orbital is oriented along the polarization direction of the laser field, which makes it easier for the electrons to escape the nuclear attraction than for the case of the 2p<sub>1</sub> orbital, which is oriented perpendicularly to the field polarization.

To explain the difference between the results obtained within the TDKLI and ALDA schemes shown in Fig. 6, we observe that the initial 2s and 2p<sub>0</sub>, 2p<sub>1</sub> orbital energies in LDA differ quite considerably from those obtained with the KLI method: It takes 5 photons to ionize the 2p orbitals in KLI compared to only 3 photons in LDA. Similarly, it takes 11 photons to ionize the 2s orbital in KLI and only 9 in LDA. The difference between the curves in Fig. 6A and C is thus hardly surprising. On the other hand, it seems quite unexpected that the ALDA and TDKLI curves cross in Fig. 6B so that the ALDA curve comes to lie *above* the TDKLI curve. This behaviour can be attributed to the fact that the other orbitals are ionized much more strongly in ALDA than in TDKLI, so that their electron density near the nucleus (and therefore their screening of the nuclear charge) is decreased. This makes it more difficult for the 2p<sub>0</sub> electrons to escape within the ALDA scheme.

Figure 6 clearly shows the superiority of the TDKLI approach over the ALDA. The spurious self-interaction present in the ALDA causes the orbitals to be too weakly bound and hence the ALDA is not reliable in the calculation of ionization.

The probabilities of finding neutral, singly, doubly, etc. ionized atoms at time  $t$  are readily expressed in terms of the norms (383). For instance, in the case of helium, one has

$$N_{1s\uparrow}(t) = N_{1s\downarrow}(t) = \int_{\text{finite volume}} d^3r \frac{n(\mathbf{r}, t)}{2} \equiv N_{1s}(t), \quad (385)$$

and the probabilities for neutral, singly and doubly charged helium are

$$P^0(t) = N_{1s}(t)^2 \quad (386)$$

$$P^{+1}(t) = 2N_{1s}(t)(1 - N_{1s}(t)) \quad (387)$$

$$P^{+2}(t) = (1 - N_{1s}(t))^2. \quad (388)$$

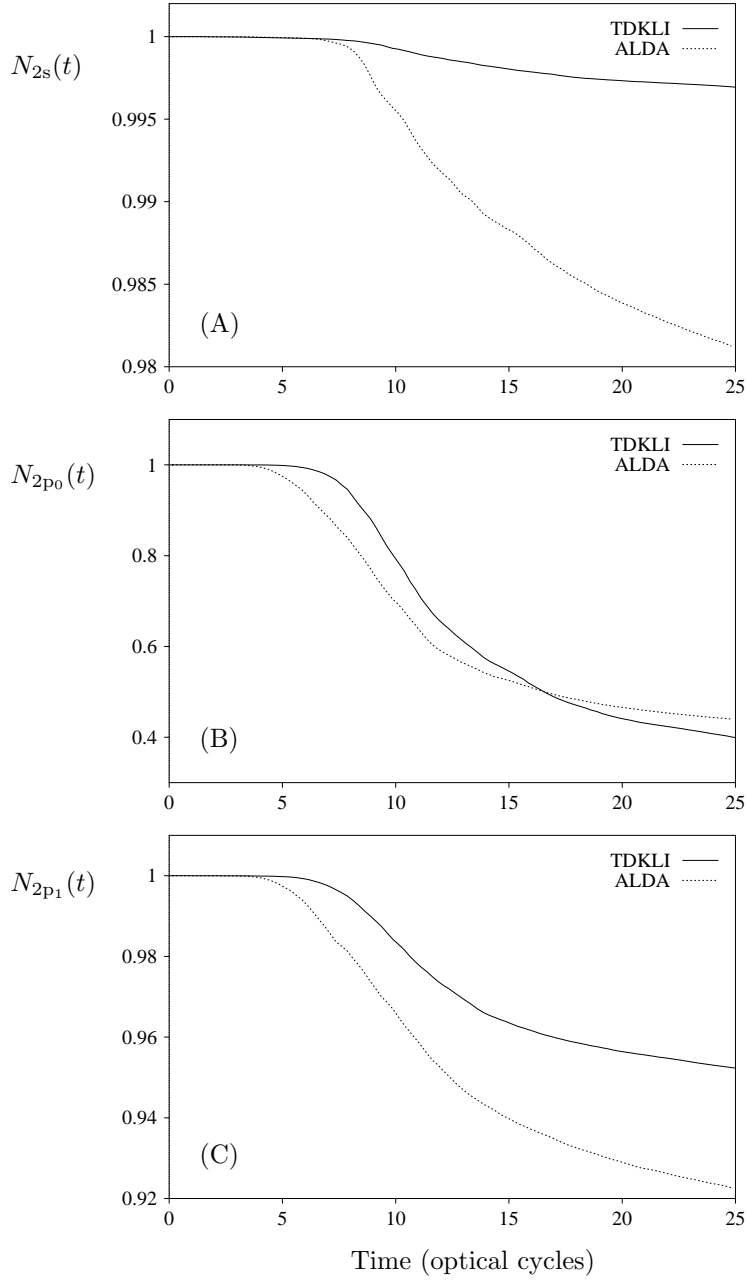


Figure 6: Time evolution of the norm of the Ne 2s orbital (A), the Ne 2p<sub>0</sub> orbital (B) and the Ne 2p<sub>1</sub> orbital (C), calculated in the x-only TDKLI and ALDA schemes. Laser parameters:  $\lambda = 248$  nm,  $I = 3 \times 10^{15}$  W/cm<sup>2</sup>, linear ramp over the first 10 cycles. One optical cycle corresponds to 0.82 femtoseconds.

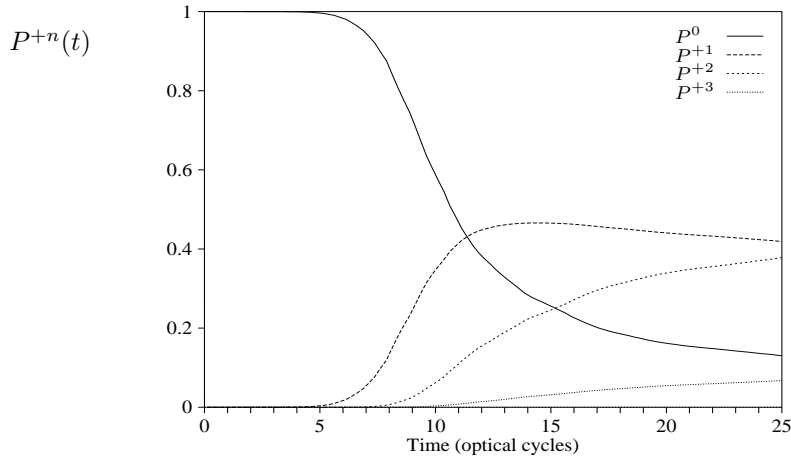


Figure 7: Population of the differently charged states of Ne. Laser parameters as in Fig. 6 ( $\lambda = 248$  nm,  $I = 3 \times 10^{15}$  W/cm<sup>2</sup>, linear ramp over the first 10 cycles).

For many-electron atoms similar combinatorial considerations [244] are performed to determine the probabilities for the various charged ions. Figure 7 shows the probabilities of finding neutral, singly, doubly and triply charged Ne as calculated from the norms of Fig. 6.

These probabilities as a function of time cannot be compared directly with experiment. This is because the laser focus, in addition to the temporal pulse shape, has a *spatial* intensity profile due to which not all atoms in the laser focus experience the same intensity. Hence a realistic calculation of ion yields requires many runs at various peak intensities. Work along these lines remains an important field for the future. In this way one might be able to understand the structures in the strong field ionization spectra of He [253] which have been the subject of heated discussions in recent years.

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