

DENSITY FUNCTIONAL THEORY OF TIME-DEPENDENT SYSTEMS

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1 Introduction

The response of an interacting many-particle system to a time-dependent external field can usually be treated within linear response theory. Due to rapid experimental progress in the field of laser physics, however, ultra-short laser pulses of very high intensity have become available in recent years. The electric field produced in such pulses can reach the strength of the electric field caused by atomic nuclei. If an atomic system is placed in the focus of such a laser pulse one observes a wealth of new phenomena [1] which cannot be explained by traditional perturbation theory. The non-perturbative quantum mechanical description of interacting particles moving in a very strong time-dependent external field therefore has become a prominent problem of theoretical physics. In principle, it requires a full solution of the time-dependent Schrödinger equation for the interacting many-body system, which is an exceedingly difficult task. In view of the success of density functional methods in the treatment of stationary many-body systems and in view of their numerical simplicity, a time-dependent version of density functional theory appears highly desirable, both within and beyond the regime of linear response.

The first steps towards a time-dependent Kohn-Sham (KS) scheme were taken by Peuckert [2] and by Zangwill and Soven [3]. 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 LDA, i. e.

$$v_{xc}(\mathbf{r}t) = \left. \frac{de_{xc}^{hom}(n)}{dn} \right|_{n=n(\mathbf{r}t)} \quad , \quad (2)$$

where $e_{xc}^{hom}(n)$ is the xc energy per volume of the homogeneous electron gas. This approximation can be expected to be good only if the time dependence of $n(\mathbf{r}t)$ is sufficiently slow. In practice, however, it gave quite good results even for the case of rather rapid time dependence.

The approach of Zangwill and Soven is valid *under the assumption* that a time-dependent KS theorem exists. Significant steps towards a rigorous foundation of time-dependent density functional theory were taken by Deb and Ghosh [4]–[7] and by Bartolotti [8]–[11] who formulated and explored Hohenberg-Kohn (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 formulation covering essentially all time-dependent potentials of interest was given by Runge and Gross [12]. A detailed description of the time-dependent density functional formalism will be presented in section 2. The central result is a set of time-dependent KS 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.

To date, most applications of the formalism fall in the regime of linear response. The linear response limit of time-dependent density functional theory will be discussed in section 3. After that, in section 4, we shall present a new method [13] of constructing approximations of the time-dependent xc potential *beyond* the linear response regime. This method can be viewed as the time-dependent counterpart of the so-called optimized potential method [14]–[29].

2 Formal Framework

In this section we deal with many-electron systems moving in an explicitly time-dependent potential

$$\hat{V}(t) = \sum_{\sigma=\uparrow\downarrow} \int d^3r v(\mathbf{r}t) \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \quad . \quad (3)$$

The total Hamiltonian is given by

$$\hat{H}(t) = \hat{T} + \hat{U} + \hat{V}(t) \quad , \quad (4)$$

where \hat{T} is the kinetic energy of the electrons

$$\hat{T} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \hat{\psi}_\sigma(\mathbf{r}) \quad (5)$$

and \hat{U} is the mutual Coulomb interaction

$$\hat{U} = \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3r \int d^3r' \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) \quad (6)$$

(atomic units are used throughout). The number of electrons, N , is fixed.

Ordinary time-independent density functional theory is based on the existence of an exact mapping between densities and external potentials. In the ground state formalism, 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 existence proof for a 1-1 mapping between time-dependent potentials and time-dependent densities, first given by Runge and Gross [12], is somewhat more involved and will briefly be indicated below. Starting from the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Phi(t) = \hat{H}(t) \Phi(t) \quad (7)$$

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

$$\Phi(t_0) = \Phi_0 \quad (8)$$

under the influence of different external potentials $v(\mathbf{r}t)$. For each fixed initial state Φ_0 , formal solution of the Schrödinger equation (7) defines a map

$$\mathcal{A} : v(\mathbf{r}t) \longrightarrow \Phi(t) \quad (9)$$

between the external potentials and the corresponding time-dependent many-particle wave functions and a second map

$$\mathcal{B} : \Phi(t) \longrightarrow n(\mathbf{r}t) = \langle \Phi(t) | \hat{n}(\mathbf{r}) | \Phi(t) \rangle \quad (10)$$

between the many-particle wave functions and the time-dependent densities. The aim is to prove invertibility of the complete map

$$\mathcal{G} : v(\mathbf{r}t) \longrightarrow n(\mathbf{r}t) \quad (11)$$

In the following we shall demonstrate that if the potentials $v(\mathbf{r}t)$ are required to be expandable in a Taylor series with respect to the time coordinate around the initial time t_0 , then the map \mathcal{G} is indeed invertible up to within an additive, merely time-dependent function in the potential. In other words, two densities $n(\mathbf{r}t)$ and $n'(\mathbf{r}t)$ evolving from a common initial state Φ_0 under the influence of the potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ are always different provided that the potentials differ by more than a purely time-dependent function:

$$v(\mathbf{r}t) \neq v'(\mathbf{r}t) + c(t) \quad (12)$$

Using the condition that the potentials v and v' can be expanded in a Taylor series,

$$v(\mathbf{r}t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(\mathbf{r})(t - t_0)^k \quad (13)$$

$$v'(\mathbf{r}t) = \sum_{k=0}^{\infty} \frac{1}{k!} v'_k(\mathbf{r})(t - t_0)^k \quad , \quad (14)$$

Eq. (12) 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

$$v_k(\mathbf{r}) - v'_k(\mathbf{r}) = \left. \frac{\partial^k}{\partial t^k} (v(\mathbf{r}t) - v'(\mathbf{r}t)) \right|_{t=t_0} \neq \text{const.} \quad (15)$$

To demonstrate the 1-1 correspondence we prove in a first step that the current densities

$$\mathbf{j}(\mathbf{r}t) = \langle \Phi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi(t) \rangle \quad (16)$$

and

$$\mathbf{j}'(\mathbf{r}t) = \langle \Phi'(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi'(t) \rangle \quad (17)$$

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

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \sum_{\sigma=\uparrow\downarrow} \left(\hat{\psi}_\sigma^\dagger(\mathbf{r}) (\nabla \hat{\psi}_\sigma(\mathbf{r})) - (\nabla \hat{\psi}_\sigma^\dagger(\mathbf{r})) \hat{\psi}_\sigma(\mathbf{r}) \right) \quad (18)$$

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 $\hat{Q}(t)$,

$$\frac{\partial}{\partial t} \langle \Phi(t) | \hat{Q}(t) | \Phi(t) \rangle = \langle \Phi(t) | \left(\frac{\partial \hat{Q}}{\partial t} - i[\hat{Q}(t), \hat{H}(t)] \right) | \Phi(t) \rangle \quad , \quad (19)$$

we obtain for the current densities:

$$\frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}t) = \frac{\partial}{\partial t} \langle \Phi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi(t) \rangle = -i \langle \Phi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Phi(t) \rangle \quad (20)$$

$$\frac{\partial}{\partial t} \mathbf{j}'(\mathbf{r}t) = \frac{\partial}{\partial t} \langle \Phi'(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi'(t) \rangle = -i \langle \Phi'(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}'(t)] | \Phi'(t) \rangle \quad . \quad (21)$$

Since Φ and Φ' evolve from the same initial state

$$\Phi(t_0) = \Phi'(t_0) = \Phi_0 \quad (22)$$

we can write

$$\begin{aligned} \left. \frac{\partial}{\partial t} (\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)) \right|_{t=t_0} &= -i \langle \Phi_0 | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Phi_0 \rangle \\ &= -n_0(\mathbf{r}) \nabla (v(\mathbf{r}t_0) - v'(\mathbf{r}t_0)) \end{aligned} \quad (23)$$

with the initial density

$$n_0(\mathbf{r}) = \langle \Phi_0 | \hat{n}(\mathbf{r}) | \Phi_0 \rangle \quad . \quad (24)$$

If the condition (15) is satisfied for $k = 0$ the right-hand side of (23) cannot vanish identically and \mathbf{j} and \mathbf{j}' will become different infinitesimally later than t_0 . If (15) holds for some finite $k > 0$ we use Eq. (19) ($k + 1$) times and obtain after some algebra:

$$\left(\frac{\partial}{\partial t} \right)^{k+1} (\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)) \Big|_{t=t_0} = -n_0(\mathbf{r}) \nabla w_k(\mathbf{r}) \neq 0 \quad (25)$$

with

$$w_k(\mathbf{r}) = \left(\frac{\partial}{\partial t} \right)^k (v(\mathbf{r}t) - v'(\mathbf{r}t)) \Big|_{t=t_0} \quad . \quad (26)$$

Once again, we conclude that

$$\mathbf{j}(\mathbf{r}t) \neq \mathbf{j}'(\mathbf{r}t) \quad (27)$$

provided that (15) holds for v and v' . To prove the corresponding statement for the densities we use the continuity equation

$$\frac{\partial}{\partial t} (n(\mathbf{r}t) - n'(\mathbf{r}t)) = -\nabla \cdot (\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)) \quad (28)$$

and calculate the $(k+1)$ th time derivative of Eq. (28) at $t = t_0$:

$$\left(\frac{\partial}{\partial t} \right)^{k+2} (n(\mathbf{r}t) - n'(\mathbf{r}t)) \Big|_{t=t_0} = \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) \quad . \quad (29)$$

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. (29) cannot vanish identically. This is done by reductio ad absurdum: Assume

$$\nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) \equiv 0 \quad (30)$$

and evaluate the integral

$$\begin{aligned} & \int d^3r n_0(\mathbf{r}) [\nabla w_k(\mathbf{r})]^2 \\ &= - \int d^3r w_k(\mathbf{r}) \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) + \oint d\mathbf{S} \cdot (n_0(\mathbf{r}) w_k(\mathbf{r}) \nabla w_k(\mathbf{r})) \quad , \quad (31) \end{aligned}$$

where we have used Green's theorem. The first integral on the right-hand side of (31) vanishes by assumption. For physically reasonable potentials (i. e. potentials arising from normalizable external charge densities), the surface integral vanishes as well [30]. Since the integrand on the left-hand side is non-negative one concludes that

$$n_0(\mathbf{r}) [\nabla w_k(\mathbf{r})]^2 \equiv 0 \quad (32)$$

in contradiction to $w_k(\mathbf{r}) \neq \text{const.}$ This completes the proof of the theorem.

We note in passing that the right-hand side of Eq. (29) 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 3 because it ensures the invertibility of linear response operators.

Having established the existence of the inverse map

$$\mathcal{G}^{-1} : n(\mathbf{r}t) \longrightarrow v(\mathbf{r}t) + c(t) \quad , \quad (33)$$

subsequent application of the map \mathcal{A} tells us that the many-particle wave function is a functional of the time-dependent density, unique up to within a purely time-dependent phase $\alpha(t)$:

$$\Phi(t) = e^{-i\alpha(t)} \Psi[n](t) \quad . \quad (34)$$

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

$$Q[n](t) = \langle \Psi[n](t) | \hat{Q}(t) | \Psi[n](t) \rangle \quad . \quad (35)$$

The ambiguity in the phase cancels out. As a particular example, the right-hand side of Eq. (20) can be considered as a density functional which depends parametrically on \mathbf{r} and t :

$$\mathbf{P}[n](\mathbf{r}t) \equiv -i\langle\Psi[n](t)|\hat{\mathbf{j}}(\mathbf{r}),\hat{H}(t)|\Psi[n](t)\rangle \quad . \quad (36)$$

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

$$\frac{\partial}{\partial t}n(\mathbf{r}t) = -\nabla\cdot\mathbf{j}(\mathbf{r}t) \quad (37)$$

$$\frac{\partial}{\partial t}\mathbf{j}(\mathbf{r}t) = \mathbf{P}[n](\mathbf{r}t) \quad . \quad (38)$$

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

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 v_s exists for 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

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

As usual, 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. The second term on the right-hand side of Eq. (41) is the time-dependent Hartree potential while the third term is the xc potential which, in practice, 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 configuration interaction [31]–[36].

There is an important difference between the ordinary ground state density functional theory and the time-dependent formalism developed above: the 1–1 correspondence between potentials and densities can be established only for a *fixed* initial many-body state Φ_0 . Consequently, the functional $\mathbf{P}[n]$ implicitly depends on Φ_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 Φ_0 . In general, there exist infinitely many Slater determinants reproducing a given density [37, 38].

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 for all times. 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 Φ_0 . One has to emphasize, however, that for a large class of systems, namely those where both Φ_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 Φ_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.

The functionals $\mathbf{P}[n]$, $v_s[n]$, $v_{xc}[n]$ are well-defined only for v -representable densities, i. e. for densities that come from some time-dependent potential satisfying Eq. (13). Moreover, the derivation of the time-dependent KS scheme requires the assumption of non-interacting v -representability of the interacting density. In view of this, a Levy-Lieb-type [39, 40, 41] 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 [42, 43].

Besides these mathematical generalizations, a number of extensions of the time-dependent density functional formalism to physically different situations have been developed. Those include spin-polarized systems [44], multicomponent systems [45], time-dependent ensembles [46, 47], external vector potentials [43, 48] as well as superconducting systems [49].

3 Frequency-dependent Linear Response

In this section we shall consider the density response of an N -electron system being initially, i. e. at times $t \leq t_0$, in its ground state. In this case, the initial density $n_0(\mathbf{r})$ can be calculated from the ordinary ground state KS equations

$$\left(-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + \int d^3r' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n_0](\mathbf{r}) \right) \varphi_j^{(0)}(\mathbf{r}) = \varepsilon_j \varphi_j^{(0)}(\mathbf{r}) \quad (42)$$

$$n_0(\mathbf{r}) = \sum_{\text{lowest } N} |\varphi_j^{(0)}(\mathbf{r})|^2 \quad . \quad (43)$$

At $t = t_0$ a perturbation is switched on so that the total potential is given by

$$v(\mathbf{r}t) = v_0(\mathbf{r}) + v_1(\mathbf{r}t) \quad (44)$$

$$v_1(\mathbf{r}t) = 0 \quad \text{for } t \leq t_0 \quad . \quad (45)$$

The objective is to calculate the linear density response $n_1(\mathbf{r}t)$ to the perturbation $v_1(\mathbf{r}t)$. Conventionally, n_1 is computed from the full linear response function χ as

$$n_1(\mathbf{r}t) = \int_{t_0}^{\infty} dt' \int d^3r' \chi(\mathbf{r}t, \mathbf{r}'t') v_1(\mathbf{r}'t') \quad . \quad (46)$$

Since the time-dependent KS equations (39)–(41) provide a formally exact way of calculating the time-dependent density, we can compute the exact density response $n_1(\mathbf{r}t)$ as the response of the non-interacting KS system:

$$n_1(\mathbf{r}t) = \int_{t_0}^{\infty} dt' \int d^3r' \chi_s(\mathbf{r}t, \mathbf{r}'t') v_s^{(1)}(\mathbf{r}'t') \quad , \quad (47)$$

where $v_s^{(1)}$ is the effective time-dependent potential evaluated *to first order* in the perturbing potential, i. e.

$$v_s^{(1)}(\mathbf{r}t) = v_1(\mathbf{r}t) + \int d^3r' \frac{n_1(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + \int dt' \int d^3r' f_{xc}[n_0](\mathbf{r}t, \mathbf{r}'t') n_1(\mathbf{r}'t') \quad . \quad (48)$$

Here the exchange-correlation kernel f_{xc} is given by the functional derivative of v_{xc} ,

$$f_{xc}[n_0](\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta v_{xc}[n](\mathbf{r}t)}{\delta n(\mathbf{r}'t')} \right|_{n=n_0} , \quad (49)$$

evaluated at the initial ground state density n_0 .

While the full response function χ is very hard to calculate, the non-interacting KS response function can be computed relatively easily. In terms of the static initial KS orbitals $\varphi_j^{(0)}$ (Eq. (42)), the Fourier transform of $\chi_s(\mathbf{r}t, \mathbf{r}'t')$ with respect to $(t - t')$ can be expressed as

$$\chi_s(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_{k,j} (f_k - f_j) \delta_{\sigma_k \sigma_j} \frac{\varphi_k^{(0)*}(\mathbf{r}) \varphi_j^{(0)}(\mathbf{r}) \varphi_j^{(0)*}(\mathbf{r}') \varphi_k^{(0)}(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta} , \quad (50)$$

where f_k, f_j are the usual Fermi occupation factors and σ_k denotes the spin orientation of the k th orbital.

Eqs. (47) and (48) constitute the KS equations for the linear density response. They provide a formally exact self-consistent scheme to calculate the density response $n_1(\mathbf{r}t)$.

For practical applications one has to find approximations for the exchange-correlation kernel f_{xc} . To this end, it is useful to express f_{xc} in terms of the full response function χ . An exact representation of f_{xc} is readily obtained by solving Eq. (46) for v_1 and inserting the result in Eq. (48). Eq. (47) then yields

$$f_{xc}[n_0](\mathbf{r}t, \mathbf{r}'t') = \chi_s^{-1}[n_0](\mathbf{r}t, \mathbf{r}'t') - \chi^{-1}[n_0](\mathbf{r}t, \mathbf{r}'t') - \frac{\delta(t - t')}{|\mathbf{r} - \mathbf{r}'|} , \quad (51)$$

where χ_s^{-1} and χ^{-1} stand for the kernels of the corresponding inverse integral operators whose existence on the set of densities specified by Eqs. (45) and (46) follows from Eq. (29), as discussed above. 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 [50, 51].

Due to causality, $f_{xc}(\mathbf{r}t, \mathbf{r}'t')$ vanishes for $t' > t$, i. e., f_{xc} is not symmetric with respect to an interchange of $(\mathbf{r}t)$ with $(\mathbf{r}'t')$. Consequently, $f_{xc}(\mathbf{r}t, \mathbf{r}'t')$ cannot be [52] a second functional derivative $\delta^2 F_{xc}[n]/\delta n(\mathbf{r}t)\delta n(\mathbf{r}'t')$. 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, in contrast to the static case. We mention that v_{xc} can be written as a functional derivative within certain approximations that are local in time, such as the one given by Eq. (2).

Eq. (51) shows that f_{xc} depends on the time arguments only through the difference $(t - t')$ so that we can work with the Fourier transform $f_{xc}[n_0](\mathbf{r}, \mathbf{r}'; \omega)$ as well.

Once again, the most straightforward approximation for f_{xc} is the LDA where the *functional* $f_{xc}[n_0]$ is replaced by the corresponding *function* $f_{xc}^{hom}(n_0)$ of the homogeneous electron gas, evaluated at the initial density $n_0(\mathbf{r})$ of the actual inhomogeneous system:

$$f_{xc}^{LDA}[n_0](\mathbf{r}, \mathbf{r}'; \omega) := f_{xc}^{hom}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega) \quad . \quad (52)$$

The LDA of non-local quantities, such as response functions, always involves some ambiguity [53, 54] 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 $f_{xc} \rightarrow f_{xc}^{hom}$ we now make the assumption that *both* $n_0(\mathbf{r})$ and $n_1(\mathbf{r}\omega)$ are slowly varying on the length scale given by the range of $f_{xc}^{hom}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega)$. In this “double” local density limit, the change in the xc potential can be calculated as

$$v_{xc}^{(1)}(\mathbf{r}\omega) = n_1(\mathbf{r}\omega) \int d^3r' f_{xc}^{hom}(n_0(\mathbf{r}), |\mathbf{r} - \mathbf{r}'|; \omega) \quad . \quad (53)$$

In terms of the Fourier transform of f_{xc}^{hom} with respect to $(\mathbf{r} - \mathbf{r}')$, Eq. (53) amounts to the approximation [55]

$$f_{xc}[n_0](\mathbf{r}, \mathbf{r}'; \omega) \longrightarrow \delta(\mathbf{r} - \mathbf{r}') f_{xc}^{hom}(n_0(\mathbf{r}), q = 0; \omega) \quad . \quad (54)$$

This approximation requires the xc kernel of the homogeneous electron gas as input. In order to investigate this quantity we consider Eq. (51) in the homogeneous case. Fourier transformation with respect to $(\mathbf{r} - \mathbf{r}')$ and $(t - t')$ leads to

$$f_{xc}^{hom}(n_0, q; \omega) = \frac{1}{\chi_s^{hom}(n_0, q; \omega)} - \frac{1}{\chi^{hom}(n_0, q; \omega)} - \frac{4\pi}{q^2} \quad . \quad (55)$$

The response function χ_s^{hom} of a non-interacting homogeneous system is of course well-known: χ_s^{hom} is identical with the Lindhard function.

Eq. (55) shows that the response function χ^{hom} of the homogeneous electron gas uniquely determines the xc kernel f_{xc}^{hom} and thus f_{xc}^{LDA} . Unfortunately, χ^{hom} is not known exactly. However, some exact features of χ^{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 [56]

$$\lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = 0) = \frac{d^2}{dn^2}(e_{xc}^{hom}(n)) \equiv f_0(n) \quad , \quad (56)$$

where, as before, $e_{xc}^{hom}(n)$ denotes the exchange-correlation energy per volume of the homogeneous electron gas.

2. The third-frequency-moment sum rule leads to [57]

$$\begin{aligned} & \lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = \infty) \\ &= -\frac{4}{5} n^{2/3} \frac{d}{dn} \left(\frac{e_{xc}^{hom}(n)}{n^{5/3}} \right) + 6n^{1/3} \frac{d}{dn} \left(\frac{e_{xc}^{hom}(n)}{n^{4/3}} \right) \equiv f_\infty(n) \quad . \quad (57) \end{aligned}$$

3. According to the best estimates [58, 59] of e_{xc}^{hom} , the following relation holds for all densities:

$$f_0(n) < f_\infty(n) < 0 \quad . \quad (58)$$

4. The short-wavelength behavior is given by [60]

$$\lim_{q \rightarrow \infty} f_{xc}^{hom}(q, \omega) = -\frac{2}{3} \cdot \frac{4\pi}{q^2} (1 - g(0)) \quad , \quad (59)$$

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

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

$$\text{Re} f_{xc}^{hom}(q, \omega) = \text{Re} f_{xc}^{hom}(q, -\omega) \quad (60)$$

$$\text{Im} f_{xc}^{hom}(q, \omega) = -\text{Im} f_{xc}^{hom}(q, -\omega) \quad (61)$$

6. $f_{xc}^{hom}(q, \omega)$ is an analytic function of ω in the upper half of the complex ω -plane and approaches a real function $f_\infty(q)$ for $\omega \rightarrow \infty$ [61]. Therefore, the function $f_{xc}^{hom}(q, \omega) - f_\infty(q)$ satisfies standard Kramers-Kronig relations:

$$\text{Re} f_{xc}^{hom}(q, \omega) - f_\infty(q) = \mathbf{P} \int \frac{d\omega'}{\pi} \frac{\text{Im} f_{xc}^{hom}(q, \omega')}{\omega' - \omega} \quad (62)$$

$$\text{Im} f_{xc}^{hom}(q, \omega) = -\mathbf{P} \int \frac{d\omega'}{\pi} \frac{\text{Re} f_{xc}^{hom}(q, \omega') - f_\infty(q)}{\omega' - \omega} \quad (63)$$

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

$$\lim_{\omega \rightarrow \infty} \text{Im} f_{xc}^{hom}(q, \omega) = -\frac{c}{\omega^{3/2}} \quad (64)$$

for any $q < \infty$ [62]. A second-order perturbation expansion [62, 63] of the irreducible polarization propagator leads to the high-density limit

$$c = \frac{23\pi}{15} \quad (65)$$

8. In the same limit, the real part of f_{xc}^{hom} behaves like [55]

$$\lim_{\omega \rightarrow \infty} \text{Re} f_{xc}^{hom}(q, \omega) = f_\infty(q) + \frac{c}{\omega^{3/2}} \quad (66)$$

Since $c > 0$, the infinite-frequency value f_∞ is approached from above. This implies, in view of the relation (58), that $\text{Re} f_{xc}^{hom}(q=0, \omega)$ cannot grow monotonically from f_0 to f_∞ .

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 [62, 64, 65].

The approximation (2) employed by Zangwill and Soven leads, by virtue of Eq. (49), to the following approximation for f_{xc} :

$$f_{xc}^{ZS}[n_0](\mathbf{r}t, \mathbf{r}'t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}') \left. \frac{d^2 e_{xc}^{hom}(n)}{dn^2} \right|_{n=n_0(\mathbf{r})} \quad (67)$$

Comparison with (56) shows that

$$f_{xc}^{ZS}[n_0](\mathbf{r}t, \mathbf{r}'t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}') f_{xc}^{hom}(n_0(\mathbf{r}), q=0; \omega=0) \quad (68)$$

In other words, Zangwill and Soven employed the static ($\omega=0$) response of the homogeneous electron gas. Gross and Kohn [30, 55] went beyond this limit by explicitly including the frequency dependence of f_{xc}^{hom} in Eq. (54). Taking into account the exact

high- and low-frequency limits, Gross and Kohn proposed the following parametrization:

$$Im f_{xc}^{hom}(q=0, \omega) = \frac{a(n)\omega}{(1+b(n)\omega^2)^{5/4}} \quad , \quad (69)$$

where

$$a(n) = -c(\gamma/c)^{5/3}(f_\infty(n) - f_0(n))^{5/3} \quad (70)$$

$$b(n) = (\gamma/c)^{4/3}(f_\infty(n) - f_0(n))^{4/3} \quad (71)$$

$$\gamma = \frac{(\Gamma(1/4))^2}{4\sqrt{2\pi}} \quad . \quad (72)$$

f_0 , f_∞ , and c are given by Eqs. (56), (57), and (65), respectively. Using the Kramers-Kronig relation (62), the real part can be expressed as

$$\begin{aligned} & Re f_{xc}^{hom}(q=0, \omega) \\ &= f_\infty + \frac{a}{\pi s^2} \sqrt{\frac{8}{b}} \left[2E\left(\frac{1}{\sqrt{2}}\right) - \frac{1+s}{2} \Pi\left(\frac{1-s}{2}, \frac{1}{\sqrt{2}}\right) \right. \\ & \left. - \frac{1-s}{2} \Pi\left(\frac{1+s}{2}, \frac{1}{\sqrt{2}}\right) \right] \quad , \quad s^2 = 1 + b\omega^2 \quad . \quad (73) \end{aligned}$$

E and Π are complete elliptic integrals of the second and third kind in the standard notation of Byrd and Friedman [66].

Figs. 1 and 2 show the real and imaginary part of f_{xc}^{hom} as calculated from (69) and (73). 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 ω becomes less pronounced for higher densities. In the extreme high-density limit, the difference between f_0 and f_∞ tends to zero. One finds the exact result

$$f_\infty - f_0 \sim r_s^2 \quad \text{for } r_s \rightarrow 0 \quad . \quad (74)$$

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

We finally mention that an extension of the parametrization (69) to non-vanishing q was given by Dabrowski [67]. The spin-dependent case was treated by Liu [68]. A similar interpolation for the exchange-correlation kernel of the 2-dimensional electron gas has been derived by Holas and Singwi [62].

The time-dependent KS scheme defined by Eqs. (47) and (48) has turned out to be remarkably successful. It has been applied to the photo-response of atoms [3, 69, 70] and molecules [71, 72], metallic [73]–[79] and semiconductor surfaces [80], bulk semiconductors [81] and metal clusters [82]–[85]. As an example for the quality of the results we show, in Fig. 3, the photoabsorption cross section of xenon. A comprehensive review of applications is given in the book by Mahan and Subbaswamy [87].

For finite systems, the Fourier transform of the linear density response (46) has poles at the true excitation energies of the interacting many-body system. Since Eq. (47) is an *exact* representation of the linear density response it can be exploited for the calculation of excitation energies. On the basis of Eq. (47), a simple additive correction to the poles of χ_s , i. e. to the KS single-particle excitation energies, has recently been proposed [88].

Fig. 1. Real part of the parametrization for $f_{xc}^{hom}(q = 0, \omega)$
(from [57])

Fig. 2. Imaginary part of the parametrization for
 $f_{xc}^{hom}(q = 0, \omega)$ (from [57])

Fig. 3. Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold (from [3]). Solid line: self-consistent time-dependent KS calculation; dash-dot line: self-consistent time-dependent Hartree calculation ($f_{xc} \equiv 0$); dashed line: independent particle result (Hartree and exchange-correlation kernels neglected); crosses: experimental data from [86].

4 Time-dependent Optimized Effective Potential

In the last section an approximation of the xc functional was derived within the regime of linear response; in other words, an approximate expression for the first-order coefficient f_{xc} of the functional Taylor expansion of $v_{xc}[n]$ about n_0 has been determined. *Beyond* the realm of linear response theory, the only approximation of v_{xc} used until today is the adiabatic approximation given by Eq. (2). In the following, a new approach to the construction of $v_{xc}(\mathbf{r}t)$ will be developed [13] which can be viewed as a time-dependent version of the so-called optimized potential method (OPM). The approach leads to v_{xc} as a function of $(\mathbf{r}t)$ rather than to v_{xc} as an explicit functional of the density. The OPM of stationary systems [14, 15] takes as starting point a given expression for the total energy $E[\varphi_1 \dots \varphi_N]$ of an N -electron system as a functional of a set of single-particle orbitals $\{\varphi_j(\mathbf{r})\}$ (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 $E[\varphi_1 \dots \varphi_N]$. In practice, the full OPM scheme is computationally quite involved since it requires the numerical solution of an integral equation for $v_{xc}(\mathbf{r})$. 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 [15]–[20]. There exists, however, an approximate OPM scheme, recently proposed by Krieger, Li, and Iafrate (KLI) [21]–[29], 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.

In order to derive 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 $\{\varphi_j\}$ (with energy eigenvalues ε_j) minimizing a given energy functional $E[\varphi_1 \dots \varphi_N]$ 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

$$A[\phi_1 \dots \phi_N] = \sum_j^N \int_{-\infty}^{t_1} dt \int d^3r \phi_j^*(\mathbf{r}t) \left(i \frac{\partial}{\partial t} + \frac{\nabla^2}{2} \right) \phi_j(\mathbf{r}t) - \int_{-\infty}^{t_1} dt \int d^3r n(\mathbf{r}t) v(\mathbf{r}t) - \frac{1}{2} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{n(\mathbf{r}t) n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} - A_{xc}[\phi_1 \dots \phi_N] \quad (75)$$

written as a functional of N time-dependent single-particle orbitals $\{\phi_j(\mathbf{r}t)\}$ where $n(\mathbf{r}t) = \sum_j^N |\phi_j(\mathbf{r}t)|^2$. In the following no specific approximation is used for the exchange-correlation functional $A_{xc}[\phi_1 \dots \phi_N]$, but we mention that in an exchange-only theory A_{xc} would be replaced by the time-dependent Hartree-Fock expression

$$A_x^{\text{HF}} = -\frac{1}{2} \sum_{i,j}^N \delta_{\sigma_i \sigma_j} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{\phi_i^*(\mathbf{r}'t) \phi_j(\mathbf{r}'t) \phi_i(\mathbf{r}t) \phi_j^*(\mathbf{r}t)}{|\mathbf{r} - \mathbf{r}'|} \quad (76)$$

(σ_j denotes the spin orientation of the j th orbital). The orbitals are solutions of the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \phi_j(\mathbf{r}t) = \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}t) \right) \phi_j(\mathbf{r}t) \quad , \quad j = 1, \dots, N \quad , \quad (77)$$

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

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + v_{\text{H}}(\mathbf{r}t) + v_{xc}(\mathbf{r}t) \quad , \quad (78)$$

where $v_{\text{H}}(\mathbf{r}t) = \int d^3r' n(\mathbf{r}'t) / |\mathbf{r} - \mathbf{r}'|$ denotes the time-dependent Hartree potential. The total potential $v_s(\mathbf{r}t)$ has to be determined in such a way that the $\{\phi_j(\mathbf{r}t)\}$, resulting from Eq. (77), render the total action functional $A[\phi_1 \dots \phi_N]$ stationary. Therefore, we have to solve the following variational problem:

$$\frac{\delta A[\phi_1 \dots \phi_N]}{\delta v_s(\mathbf{r}t)} = \sum_j^N \int_{-\infty}^{+\infty} dt' \int d^3r' \left(\frac{\delta A[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}'t')} \frac{\delta \phi_j(\mathbf{r}'t')}{\delta v_s(\mathbf{r}t)} + \frac{\delta A[\phi_1 \dots \phi_N]}{\delta \phi_j^*(\mathbf{r}'t')} \frac{\delta \phi_j^*(\mathbf{r}'t')}{\delta v_s(\mathbf{r}t)} \right) = 0 \quad . \quad (79)$$

We first compute the functional derivatives $\delta A / \delta \phi_j$ and $\delta A / \delta \phi_j^*$: defining

$$u_{xcj}(\mathbf{r}t) = \frac{1}{\phi_j^*(\mathbf{r}t)} \frac{\delta A_{xc}[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}t)} \quad , \quad (80)$$

we obtain

$$\frac{\delta A[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}'t')} = \left[-i \frac{\partial}{\partial t'} - \left(-\frac{\nabla'^2}{2} + v(\mathbf{r}'t') + v_H(\mathbf{r}'t') + u_{xcj}(\mathbf{r}'t') \right) \right] \phi_j^*(\mathbf{r}'t') \theta(t_1 - t') \quad (81)$$

and an analogous expression for $\delta A/\delta \phi_j^*$ which, for all reasonable (i. e. real) functionals $A[\phi_1 \dots \phi_N]$, is the complex conjugate of (81). $\theta(x)$ denotes the usual step function (1 for $x > 0$, 0 for $x < 0$). To arrive at Eq. (81) the first term of Eq. (75) has to be integrated by parts with respect to the time coordinate. We impose the usual boundary condition on $\phi_j(\mathbf{r}t)$ at $t = t_1$, i. e. $\delta \phi_j(\mathbf{r}t_1) = 0$, thus obtaining a zero boundary contribution. The other boundary contribution at $t = -\infty$ vanishes, too, because the action functional (75), 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. (78) into (81) and making use of the fact that ϕ_j^* solves the complex conjugate of the Schrödinger equation (77), we find

$$\frac{A[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}'t')} = [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j^*(\mathbf{r}'t') \theta(t_1 - t') \quad . \quad (82)$$

In order to evaluate $\delta A/\delta v_s$ from Eq. (79), we further need the functional derivatives $\delta \phi_j/\delta v_s$ and $\delta \phi_j^*/\delta v_s$. The stationary OPM eigenfunctions $\{\varphi_j(\mathbf{r}), j = 1, \dots, \infty\}$ form a complete orthonormal set, and so do the time-evolved states $\{\phi_j(\mathbf{r}t), j = 1, \dots, \infty\}$ for any time $t \in [-\infty, t_1]$, and we denote this set by Φ_t . Now consider Φ_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 $\phi'_j(\mathbf{r}t)$ are determined by the backward Schrödinger equation

$$i \frac{\partial}{\partial t} \phi'_j(\mathbf{r}t) = \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}t) + \delta v_s(\mathbf{r}t) \right) \phi'_j(\mathbf{r}t) \quad , \quad j = 1, \dots, N \quad (83)$$

with the initial condition $\phi'_j(\mathbf{r}t_1) = \phi_j(\mathbf{r}t_1)$. 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 $\phi'_j(\mathbf{r}t)$ in terms of the set Φ_t ,

$$\phi'_j(\mathbf{r}t) = \sum_{k=1}^{\infty} c_{jk}(t) \phi_k(\mathbf{r}t) \quad , \quad (84)$$

and insert this expansion in (83), utilizing Eq. (77). The resulting equation

$$i \sum_{k=1}^{\infty} \dot{c}_{jk}(t) \phi_k(\mathbf{r}t) = \sum_{k=1}^{\infty} c_{jk}(t) \delta v_s(\mathbf{r}t) \phi_k(\mathbf{r}t) \quad (85)$$

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

$$\dot{c}_{jl}(t) = \frac{1}{i} \sum_{k=1}^{\infty} c_{jk}(t) \int d^3r \phi_l^*(\mathbf{r}t) \delta v_s(\mathbf{r}t) \phi_k(\mathbf{r}t) \quad . \quad (86)$$

We now make the usual ansatz for a perturbation expansion,

$$c_{jk}(t) = c_{jk}^{(0)}(t) + c_{jk}^{(1)}(t) + \dots \quad (87)$$

and collect corresponding orders on each side of Eq. (86). This yields

$$\begin{aligned} \dot{c}_{jl}^{(0)}(t) &= 0 \\ \dot{c}_{jl}^{(1)}(t) &= \frac{1}{i} \sum_{k=1}^{\infty} c_{jk}^{(0)}(t) \int d^3r \phi_l^*(\mathbf{r}t) \delta v_s(\mathbf{r}t) \phi_k(\mathbf{r}t) \\ &\vdots \end{aligned} \quad (88)$$

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

$$c_{jl}^{(1)}(t) = \frac{1}{i} \int_{t_1}^t dt' \int d^3r \phi_l^*(\mathbf{r}t') \delta v_s(\mathbf{r}t') \phi_j(\mathbf{r}t') \quad . \quad (89)$$

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

$$\delta \phi_j(\mathbf{r}t) = \sum_{k=1}^{\infty} c_{jk}^{(1)}(t) \phi_k(\mathbf{r}t) = i \sum_{k=1}^{\infty} \int_t^{t_1} dt' \int d^3r' \phi_k^*(\mathbf{r}'t') \delta v_s(\mathbf{r}'t') \phi_j(\mathbf{r}'t') \phi_k(\mathbf{r}t) \quad . \quad (90)$$

Therefore, the desired functional derivative is

$$\frac{\delta \phi_j(\mathbf{r}'t')}{\delta v_s(\mathbf{r}t)} = i \sum_{k=1}^{\infty} \phi_k^*(\mathbf{r}t) \phi_j(\mathbf{r}t) \phi_k(\mathbf{r}'t') \theta(t_1 - t) \theta(t - t') \quad . \quad (91)$$

Once again, $\delta \phi_j^*/\delta v_s$ leads to the complex conjugate expression. We can now insert (82) and (91) in the variational equation (79), and the result is the time-dependent OPM (TDOPM) integral equation for the local exchange-correlation potential $v_{xc}(\mathbf{r}t)$:

$$i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3r' [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}'t') K(\mathbf{r}t, \mathbf{r}'t') + c.c. = 0 \quad . \quad (92)$$

The kernel

$$K(\mathbf{r}t, \mathbf{r}'t') = \sum_{k=1}^{\infty} \phi_k^*(\mathbf{r}t) \phi_k(\mathbf{r}'t') \theta(t - t') \quad (93)$$

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

$$\left[i \frac{\partial}{\partial t'} - \left(-\frac{\nabla'^2}{2} + v_s(\mathbf{r}'t') \right) \right] K(\mathbf{r}t, \mathbf{r}'t') = -i \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (94)$$

with the initial condition $K(\mathbf{r}t, \mathbf{r}'t') = 0$ for $t' > t$. The TDOPM scheme is now complete: the integral equation (92) has to be solved for $v_{xc}(\mathbf{r}t)$ in combination with the Schrödinger equation (77) and the differential equation (94) 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. (92) in the following way (using the fact that v_{xc} is real):

$$\begin{aligned} & i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3 r' [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}'t') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \phi_k^*(\mathbf{r}t) \phi_k(\mathbf{r}'t') \theta(t - t') + c.c. \\ & = i \sum_j^N \phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}t) \int_{-\infty}^t dt' \int d^3 r' (u_{xcj}(\mathbf{r}'t') - u_{xcj}^*(\mathbf{r}'t')) \phi_j(\mathbf{r}'t') \phi_j^*(\mathbf{r}'t') \quad . \quad (95) \end{aligned}$$

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

$$A_{xc}[\phi_1 \dots \phi_N] \longrightarrow \int_{-\infty}^{t_1} dt' E_{xc}[\phi_1(t') \dots \phi_N(t')] \quad , \quad (96)$$

where $E_{xc}[\varphi_1 \dots \varphi_N]$ is the corresponding ground state exchange-correlation energy functional. Definition (80) then yields

$$u_{xcj}^{static}(\mathbf{r}t) = \left[\frac{1}{\tilde{\varphi}_j^*(\mathbf{r})} \frac{\delta E_{xc}[\tilde{\varphi}_1 \dots \tilde{\varphi}_N]}{\delta \tilde{\varphi}_j(\mathbf{r})} \right]_{\tilde{\varphi}_j(\mathbf{r}) = \varphi_j(\mathbf{r}) e^{-i\varepsilon_j(t-t_0)}} \quad . \quad (97)$$

We assume that the value of $E_{xc}[\varphi_1 \dots \varphi_N]$ remains unchanged if the arguments $\{\varphi_j(\mathbf{r})\}$ are multiplied by phase factors $e^{i\alpha_j}$. If this is the case, we can use the identity

$$\phi_j(\mathbf{r}t) = \sqrt{\phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}t)} \frac{\phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}_0 t)}{|\phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}_0 t)|} e^{i \arg(\phi_j(\mathbf{r}_0 t))} \quad (98)$$

(where \mathbf{r}_0 is an arbitrary reference point) and write E_{xc} in Eq. (96) as a functional of the combinations $\phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}'t)$. Then it is not difficult to show that u_{xcj}^{static} is independent of time and that the right-hand side of (95) is zero. We therefore obtain

$$\begin{aligned} & i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3 r' [v_{xc}(\mathbf{r}') - u_{xcj}^{static}(\mathbf{r}')] \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \varphi_k^*(\mathbf{r}) \varphi_k(\mathbf{r}') e^{-i(\varepsilon_j - \varepsilon_k)(t-t')} \theta(t - t') \\ & + c.c. = 0 \quad . \quad (99) \end{aligned}$$

Performing the integration over t' we find the stationary OPM integral equation [15]

$$\lim_{\eta \rightarrow 0^+} \sum_j^N \int d^3 r' [v_{xc}(\mathbf{r}') - u_{xcj}^{static}(\mathbf{r}')] \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\varphi_k^*(\mathbf{r}) \varphi_k(\mathbf{r}')}{\varepsilon_j - \varepsilon_k - i\eta} + c.c. = 0 \quad . \quad (100)$$

The derivation of Eq. (100) shows that in order to recover the static limit from the time-dependent formalism one had to extend the time integral in Eq. (75) 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. (92) similar to the one proposed by KLI in the

stationary case [26, 29]. This will lead to an alternative but still exact form of the TDOPM scheme which allows one to construct approximations of $v_{xc}(\mathbf{rt})$ which are *explicit* functionals of the orbitals $\{\phi_j\}$, thereby avoiding the need to solve the integral equation. Following Refs. [26] and [29], we define

$$p_j(\mathbf{rt}) = \frac{-i}{\phi_j^*(\mathbf{rt})} \int_{-\infty}^{t_1} dt' \int d^3r' [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j^*(\mathbf{r}'t') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \phi_k^*(\mathbf{rt}) \phi_k(\mathbf{r}'t') \theta(t - t') \quad (101)$$

and

$$\bar{u}_{xcj}(t) = \int d^3r n_j(\mathbf{rt}) u_{xcj}(\mathbf{rt}) \quad (102)$$

where $n_j(\mathbf{rt}) = |\phi_j(\mathbf{rt})|^2$. Eq. (95) can then be written as

$$\sum_j^N n_j(\mathbf{rt}) p_j(\mathbf{rt}) + c.c. = -i \sum_j^N n_j(\mathbf{rt}) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \quad , \quad (103)$$

and it is easy to show that

$$\int d^3r n_j(\mathbf{rt}) p_j(\mathbf{rt}) = 0 \quad . \quad (104)$$

Evaluating $\phi_j(\mathbf{rt})[-i \partial/\partial t + \nabla^2/2 - v_s(\mathbf{rt})]\phi_j^*(\mathbf{rt})p_j(\mathbf{rt})$ we find after some straightforward algebra that $p_j(\mathbf{rt})$ satisfies the following differential equation:

$$\begin{aligned} \frac{1}{2} \nabla \cdot (n_j(\mathbf{rt}) \nabla p_j(\mathbf{rt})) - i n_j(\mathbf{rt}) \frac{\partial}{\partial t} p_j(\mathbf{rt}) - i \mathbf{J}_j(\mathbf{rt}) \cdot \nabla p_j(\mathbf{rt}) \\ = -n_j(\mathbf{rt}) [v_{xc}(\mathbf{rt}) - u_{xcj}(\mathbf{rt}) - (\bar{v}_{xcj}(t) - \bar{u}_{xcj}(t))] \end{aligned} \quad (105)$$

with the current density $\mathbf{J}_j(\mathbf{rt}) = (2i)^{-1} (\phi_j^*(\mathbf{rt}) \nabla \phi_j(\mathbf{rt}) - \phi_j(\mathbf{rt}) \nabla \phi_j^*(\mathbf{rt}))$ and $\bar{v}_{xcj}(t) = \int d^3r n_j(\mathbf{rt}) v_{xc}(\mathbf{rt})$. Finally, operating with ∇^2 on Eq. (103) and using Eq. (105) we find

$$\begin{aligned} v_{xc}(\mathbf{rt}) &= \frac{1}{n(\mathbf{rt})} \sum_j^N n_j(\mathbf{rt}) \frac{1}{2} (u'_{xcj}(\mathbf{rt}) + u'^*_{xcj}(\mathbf{rt})) \\ &+ \frac{1}{n(\mathbf{rt})} \sum_j^N n_j(\mathbf{rt}) \left[\bar{v}_{xcj}(t) - \frac{1}{2} (\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t)) \right] \\ &+ \frac{i}{4n(\mathbf{rt})} \sum_j^N \nabla^2 n_j(\mathbf{rt}) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \end{aligned} \quad (106)$$

where

$$u'_{xcj}(\mathbf{rt}) = u_{xcj}(\mathbf{rt}) + \frac{1}{n_j(\mathbf{rt})} \left[\frac{1}{2} \nabla \cdot (p_j(\mathbf{rt}) \nabla n_j(\mathbf{rt})) + i n_j(\mathbf{rt}) \frac{\partial}{\partial t} p_j(\mathbf{rt}) + i \mathbf{J}_j(\mathbf{rt}) \cdot \nabla p_j(\mathbf{rt}) \right]. \quad (107)$$

Eqs. (106) and (107) together with the differential equation (105) for $p_j(\mathbf{rt})$ and the condition (104) (which can be used to fix the constant left undetermined by Eq. (105)) represent an exact alternative formulation of the TDOPM scheme. The advantage of Eq. (106) lies in the fact that it is a very convenient starting point for constructing approximations of $v_{xc}(\mathbf{rt})$ as explicit functionals of the $\{\phi_j(\mathbf{rt})\}$: it is only necessary to approximate $p_j(\mathbf{rt})$ in Eq. (107) by a suitably chosen functional of the orbitals. We can then readily solve Eq. (106) *analytically* for $v_{xc}(\mathbf{rt})$, as we shall show below.

We expect an *approximate* potential $\tilde{v}_{xc}(\mathbf{rt})$ defined in this way to be close to the exact $v_{xc}(\mathbf{rt})$. 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. (107) we obtain

$$\begin{aligned} \bar{u}'_{xcj}(t) - \bar{u}_{xcj}(t) = \\ \frac{1}{2} \int d^3r \nabla \cdot (p_j(\mathbf{rt}) \nabla n_j(\mathbf{rt})) + i \int d^3r \left[n_j(\mathbf{rt}) \frac{\partial}{\partial t} p_j(\mathbf{rt}) + \mathbf{J}_j(\mathbf{rt}) \cdot \nabla p_j(\mathbf{rt}) \right] . \end{aligned} \quad (108)$$

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 $-\nabla \cdot \mathbf{J}_j(\mathbf{rt})$ by $\partial n_j(\mathbf{rt})/\partial t$. Hence we find

$$\bar{u}'_{xcj}(t) - \bar{u}_{xcj}(t) = i \frac{\partial}{\partial t} \int d^3r n_j(\mathbf{rt}) p_j(\mathbf{rt}) = 0 \quad , \quad (109)$$

where the last equality follows from Eq. (104).

The simplest approximation is obtained by replacing p_j by its average value, i. e. by setting $p_j(\mathbf{rt}) \equiv 0$. The resulting approximate potential \tilde{v}_{xc} is determined by the equation

$$\begin{aligned} \tilde{v}_{xc}(\mathbf{rt}) &= \frac{1}{n(\mathbf{rt})} \sum_j^N n_j(\mathbf{rt}) \frac{1}{2} (u_{xcj}(\mathbf{rt}) + u_{xcj}^*(\mathbf{rt})) \\ &+ \frac{1}{n(\mathbf{rt})} \sum_j^N n_j(\mathbf{rt}) \left[\bar{v}_{xcj}(t) - \frac{1}{2} (\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t)) \right] \\ &+ \frac{i}{4n(\mathbf{rt})} \sum_j^N \nabla^2 n_j(\mathbf{rt}) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \quad . \end{aligned} \quad (110)$$

This equation is still an integral equation for \tilde{v}_{xc} . It can, however, be solved analytically [25]: multiplying Eq. (110) by $n_k(\mathbf{rt})$ and integrating over all space yields

$$\bar{v}_{xck}(t) = \bar{w}_{xck}(t) + \sum_j^N M_{kj}(t) \bar{v}_{xcj}(t) \quad , \quad (111)$$

where we have defined

$$\begin{aligned} w_{xc}(\mathbf{rt}) &= \frac{1}{n(\mathbf{rt})} \sum_j^N n_j(\mathbf{rt}) \frac{1}{2} (u_{xcj}(\mathbf{rt}) + u_{xcj}^*(\mathbf{rt})) \\ &- \frac{1}{n(\mathbf{rt})} \sum_j^N n_j(\mathbf{rt}) \frac{1}{2} (\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t)) \\ &+ \frac{i}{4n(\mathbf{rt})} \sum_j^N \nabla^2 n_j(\mathbf{rt}) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \end{aligned} \quad (112)$$

and

$$M_{kj}(t) = \int d^3r \frac{n_k(\mathbf{rt}) n_j(\mathbf{rt})}{n(\mathbf{rt})} \quad . \quad (113)$$

Solving Eq. (111) for $\bar{v}_{xcj}(t)$ requires inversion of the $N \times N$ matrix

$$A_{kj}(t) = \delta_{kj} - M_{kj}(t) \quad (114)$$

and leads to

$$\bar{v}_{xcj}(t) = \sum_k^N \left(A^{-1}(t) \right)_{jk} \bar{w}_{xck}(t) \quad . \quad (115)$$

When Eq. (115) is substituted into Eq. (110), one obtains $\tilde{v}_{xc}(\mathbf{r}t)$ as an explicit functional of the orbitals $\{\phi_j(\mathbf{r}t)\}$. As the exact $v_{xc}(\mathbf{r}t)$ which follows from Eq. (92), $\tilde{v}_{xc}(\mathbf{r}t)$ is determined by Eq. (110) only up to within a purely time-dependent function $c(t)$.

The last term of Eqs. (110) and (112) vanishes identically for a large class of exchange-correlation functionals A_{xc} . This class includes all functionals depending on $\{\phi_j\}$ only through the combinations $\phi_j(\mathbf{r}t)\phi_j^*(\mathbf{r}'t)$ (such as the time-dependent Hartree-Fock functional, Eq. (76)).

Eq. (110) combined with the Schrödinger equation (77) represents a time-dependent scheme which is numerically much less involved than, e. g. , the time-dependent Hartree-Fock method. On the basis of the experience with the stationary KLI scheme we expect a very small loss of accuracy compared with time-dependent Hartree-Fock. Atomic systems subject to intense laser pulses are currently being studied with this method.

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