TIME-DEPENDENT OPTIMIZED EFFECTIVE POTENTIAL IN THE LINEAR RESPONSE REGIME

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TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

Time-dependent density functional theory of spin-polarized systems is based on the fact [1, 2] that the exact time-dependent spin densities $n_\sigma(\mathbf{r}t) = \langle \Psi(t) | \hat{n}_\sigma(\mathbf{r}) | \Psi(t) \rangle$ of an interacting many-particle system subject to time-dependent potentials $v_{\text{ext}\,\sigma}(\mathbf{r}t)$ can be calculated from the orbitals of an auxiliary noninteracting system, i. e.

$$n_\sigma(\mathbf{r}t) = \sum_j^{N_\sigma} |\phi_{j\sigma}(\mathbf{r}t)|^2 \quad . \tag{1}$$

The orbitals $\phi_{j\sigma}(\mathbf{r}t)$ satisfy the time-dependent Kohn-Sham equations (atomic units are used throughout)

$$i\,(\partial/\partial t)\,\phi_{j\sigma}(\mathbf{r}t) = \left(-\nabla^2/2 + v_\sigma(\mathbf{r}t)\right)\phi_{j\sigma}(\mathbf{r}t) \quad , \quad j = 1,\,\ldots\,,N_\sigma \tag{2}$$

with suitable initial conditions $\phi_{j\sigma}(\mathbf{r}t_0)$ chosen to represent the spin densities $n_{0\,\sigma}(\mathbf{r}) = \langle \Psi_0 | \hat{n}_\sigma(\mathbf{r}) | \Psi_0 \rangle$ of the initial (many-body) state Ψ_0 at time $t = t_0$. The time-dependent local effective potential in Eq. (2) is given by the sum of the external potential, the Hartree-potential and the time-dependent exchange-correlation (xc) potential

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

with the total density $n(\mathbf{r}t) = \sum_\sigma n_\sigma(\mathbf{r}t)$. To date, most applications of the time-dependent Kohn-Sham scheme (1) – (3) fall in the linear response regime (see e.g. [3] for a recent review). In this limit, one considers electronic systems subject to external potentials of the form

$$v_{\text{ext}\,\sigma}(\mathbf{r}t) = \begin{cases} v_{0\,\sigma}(\mathbf{r}) & ; \quad t \le t_0 \\ v_{0\,\sigma}(\mathbf{r}) + v_{1\,\sigma}(\mathbf{r}t) & ; \quad t > t_0 \end{cases} \tag{4}$$

where $v_{0\,\sigma}(\mathbf{r})$ denotes the static external potential of the unperturbed system (e. g. a nuclear Coulomb potential plus a static magnetic field that couples to the electronic

spin only) and $v_{1\,\sigma}(\mathbf{r}t)$ is a time-dependent perturbation. We assume that at times $t \leq t_0$ the system is in the ground state corresponding to $v_{0\,\sigma}(\mathbf{r})$. In this case, the time-dependent density is a functional of the external potential alone also at $t = t_0$ and the full 1-1 correspondence

$$\{v_{\text{ext}\,\sigma}(\mathbf{r}t)\} \quad \overset{1-1}{\longleftrightarrow} \quad \{n_\sigma(\mathbf{r}t)\} \tag{5}$$

is guaranteed for the interacting system [1, 2]. This 1-1 mapping can be established for any particle-particle interaction, in particular also for vanishing particle-particle interaction. Consequently, the time-dependent density $n(\mathbf{r}t)$ uniquely determines the time-dependent effective potential (3) as well:

$$\{v_\sigma(\mathbf{r}t)\} \quad \overset{1-1}{\longleftrightarrow} \quad \{n_\sigma(\mathbf{r}t)\} \quad . \tag{6}$$

Combining (5) and (6) we see that the time-dependent external potential $v_{\text{ext}\,\sigma}(\mathbf{r}t)$ and the effective potential $v_\sigma(\mathbf{r}t)$ are also in 1-1 correspondence:

$$\{v_\sigma(\mathbf{r}t)\} \quad \overset{1-1}{\longleftrightarrow} \quad \{v_{\text{ext}\,\sigma}(\mathbf{r}t)\} \quad . \tag{7}$$

The above statements can be used to establish a relation between the density-density response function of the noninteracting (Kohn-Sham) system

$$\chi_{\text{s}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') = \left.\frac{\delta n_\sigma(\mathbf{r}t)}{\delta v_{\sigma'}(\mathbf{r}'t')}\right|_{v[n_0]} \tag{8}$$

and the density-density response function of the interacting electron system

$$\chi_{\sigma\sigma'}(\mathbf{r}, t, \mathbf{r}', t') = \left.\frac{\delta n_\sigma(\mathbf{r}, t)}{\delta v_{\text{ext}\,\sigma'}(\mathbf{r}', t')}\right|_{v_0} = \sum_\nu \int d^3x \int d\tau \left.\frac{\delta n_\sigma(\mathbf{r}, t)}{\delta v_\nu(\mathbf{x}, \tau)}\frac{\delta v_\nu(\mathbf{x}, \tau)}{\delta v_{\text{ext}\,\sigma'}(\mathbf{r}', t')}\right|_{n_0} \quad . \tag{9}$$

Obviously, they are connected via the functional derivative

$$\left.\frac{\delta v_\sigma(\mathbf{r}, t)}{\delta v_{\text{ext}\,\sigma'}(\mathbf{r}', t')}\right|_{n_0} = \delta_{\sigma\sigma'}\delta(\mathbf{r} - \mathbf{r}')\,\delta(t - t')$$

$$+ \sum_\nu \int d^3x \int d\tau \left(\frac{\delta(t - \tau)}{|\mathbf{r} - \mathbf{x}|} + \frac{\delta v_{\text{xc}\,\sigma}(\mathbf{r}, t)}{\delta n_\nu(\mathbf{x}, \tau)}\right) \frac{\delta n_\nu(\mathbf{x}, \tau)}{\delta v_{\text{ext}\,\sigma'}(\mathbf{r}', t')} \quad . \tag{10}$$

of the map (7) by the Dyson-type relation

$$\chi_{\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') = \chi_{\text{s}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') + \sum_{\nu\nu'} \int d^3x \int d\tau \int d^3x' \int d\tau' \, \chi_{\text{s}\,\sigma\nu}(\mathbf{r}, t, \mathbf{x}, \tau)$$

$$\times \left(\frac{\delta(\tau - \tau')}{|\mathbf{x} - \mathbf{x}'|} + f_{\text{xc}\,\nu\nu'}(\mathbf{x}, \tau, \mathbf{x}', \tau')\right) \chi_{\nu'\sigma'}(\mathbf{x}', \tau', \mathbf{r}', t') , \tag{11}$$

where the so-called time-dependent exchange-correlation kernel

$$f_{\text{xc}\,\sigma\sigma'}(\mathbf{r}, t, \mathbf{r}', t') := \left.\frac{\delta v_{\text{xc}\,\sigma}(\mathbf{r}, t)}{\delta n_{\sigma'}(\mathbf{r}', t')}\right|_{n_0} \tag{12}$$

is a functional of the ground-state spin densities $\{n_{0\,\sigma}(\mathbf{r})\}$. Eqs. (11) and (12) constitute an exact representation of the linear density response of the interacting system. A detailed discussion of its formal properties and of applications can be found in [3].

In the following, we are going to describe an approach to the construction of $f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r}t,\mathbf{r}',t')$ based on the recently proposed [4] time-dependent version of the so-called optimized potential (OEP). This method leads to $v_{\mathrm{xc}\,\sigma}$ as a function of $(\mathbf{r}t)$ via solution of an integral equation rather than to $v_{\mathrm{xc}\,\sigma}$ as an explicit functional of the spin densities. The definition (12) can therefore not be applied directly. It turns out however that the central equation (11) holds for a quantity $f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r},t,\mathbf{r}',t')$ defined through an integral equation which is quite analogous to - though more complicated than - the integral equation for the OEP.

THE TIME-DEPENDENT OPTIMIZED EFFECTIVE POTENTIAL

For stationary systems, a given expression for the total energy $E[\varphi_{j\sigma}]$ of an N-electron system as a functional of a set of spin orbitals $\{\varphi_{j\sigma}(\mathbf{r})\}$ (e. g. the Hartree-Fock total energy functional in the exchange-only case) is the starting point for the construction of the OEP [5, 6]. Then, the variationally best $local$ effective potential is determined for each spin orientation such that, when inserted in a stationary single-particle Schrödinger equation, it yields the set of $N = \sum_\sigma N_\sigma$ eigenfunctions (corresponding to the N_σ lowest eigenvalues) that minimize $E[\varphi_{j\sigma}]$. Although built from orbitals, this scheme is in fact a true density functional method, since, by virtue of the theorems of Hohenberg and Kohn and Kohn and Sham, the computed orbitals are functionals of the density.

In practice, the full OEP scheme is computationally considerably more demanding than traditional density functional schemes since it requires the numerical solution of an integral equation for each $v_{\mathrm{xc}\,\sigma}(\mathbf{r})$. There exists, however, an approximate OEP scheme, recently proposed by Krieger, Li and Iafrate (KLI) [7, 8], which is numerically as easy to handle as the ordinary Kohn-Sham scheme. This simplified OEP has been applied very successfully to the calculation of atomic properties [9, 10, 11].

In order to derive a time-dependent generalization of the OEP we consider an N-electron system subject to a potential of the form (4) which, for all times up until t_0, has been in the ground state associated with the static external potential $v_{0\sigma}(\mathbf{r})$. We assume that the corresponding stationary OEP problem has been solved for that system, i. e. a local effective potential for each spin orientation and a set of N spin orbitals $\{\varphi_{j\sigma}\}$ (with energy eigenvalues $\varepsilon_{j\sigma}$) minimizing a given energy functional $E[\varphi_{j\sigma}]$ are assumed to be known. Our goal is to determine the time evolution of the system under the influence of the total external potential $v_{\mathrm{ext}\sigma}(\mathbf{r}t) = v_{0\sigma}(\mathbf{r}) + v_{1\sigma}(\mathbf{r}t)$ from t_0 up until an arbitrary later time t_1. Note that in this section we do not linearize with respect to $v_1(\mathbf{r}t)$ but develop the full time-dependent theory. The construction of an optimized local effective potential starts with the quantum mechanical action

$$A[\phi_{j\sigma}] = \sum_\sigma \sum_j^{N_\sigma} \int_{-\infty}^{t_1} dt \int d^3r \; \phi_{j\sigma}^*(\mathbf{r}t) \left(i\,\partial/\partial t + \nabla^2/2 \right) \phi_{j\sigma}(\mathbf{r}t)$$

$$-\sum_\sigma \int_{-\infty}^{t_1} dt \int d^3r \; n_\sigma(\mathbf{r}t) v_{\mathrm{ext}\sigma}(\mathbf{r}t) - \frac{1}{2}\int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \; \frac{n(\mathbf{r}t)n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} - A_{\mathrm{xc}}[\phi_{j\sigma}] \quad (13)$$

written as a functional of $N = \sum_\sigma N_\sigma$ time-dependent spin orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$. In the following we will not refer to any specific approximation for the exchange-correlation functional $A_{\mathrm{xc}}[\phi_{j\sigma}]$. We mention however, that in an exchange-only theory A_{xc} would be replaced by the time-dependent Hartree-Fock (TDHF) expression

$$A_{\mathrm{x}} = -(1/2)\sum_\sigma \sum_{i,j}^{N_\sigma} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \; \phi_{i\sigma}^*(\mathbf{r}'t)\phi_{j\sigma}(\mathbf{r}'t)\phi_{i\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}t) \,/\, |\mathbf{r}-\mathbf{r}'| \quad . \quad (14)$$

The orbitals are solutions of the time-dependent Schrödinger equation (2) with the initial condition $\phi_{j\sigma}(\mathbf{r}t) = \varphi_{j\sigma}(\mathbf{r})\exp[-i\varepsilon_{j\sigma}(t-t_0)]$ for $-\infty < t \le t_0$. The local effective potential $v_\sigma(\mathbf{r}t)$ has to be determined in such a way that the $\{\phi_{j\sigma}(\mathbf{r}t)\}$, resulting from Eq. (2), render the total action functional $A[\phi_{j\sigma}]$ stationary. Therefore, we have to solve the following variational problem:

$$\frac{\delta A[\phi_{j\sigma}]}{\delta v_\sigma(\mathbf{r}t)} = \sum_{\sigma'} \int_{-\infty}^{+\infty} dt' \int d^3 r' \sum_{j}^{N_{\sigma'}} \left(\frac{\delta A[\phi_{j\sigma}]}{\delta \phi_{j\sigma'}(\mathbf{r}'t')} \frac{\delta \phi_{j\sigma'}(\mathbf{r}'t')}{\delta v_\sigma(\mathbf{r}t)} + \frac{\delta A[\phi_{j\sigma}]}{\delta \phi_{j\sigma'}^*(\mathbf{r}'t')} \frac{\delta \phi_{j\sigma'}^*(\mathbf{r}'t')}{\delta v_\sigma(\mathbf{r}t)} \right) = 0 \ . \tag{15}$$

In order to compute the functional derivative $\delta A / \delta \phi_{j\sigma}$, the first term of Eq. (13) has to be integrated by parts with respect to the time coordinate. We impose the usual boundary condition on $\phi_{j\sigma}(\mathbf{r}t)$ at $t = t_1$, i. e. $\delta \phi_{j\sigma}(\mathbf{r}t_1) = 0$, thus obtaining a zero boundary contribution. The other boundary contribution at $t = -\infty$ vanishes, too, because the action functional (13), in order to be well-defined, is to be calculated by introducing the usual factor $\exp(\eta t)$ in the integrand and taking $\lim_{\eta \to 0^+}$ after the integration. Then, substituting Eq. (3) and making use of the fact that $\phi_{j\sigma}^*$ solves the complex conjugate of the Schrödinger equation (2), we find

$$\frac{\delta A[\phi_{j\sigma}]}{\delta \phi_{j\sigma}(\mathbf{r}'t')} = [v_{\mathrm{xc}\,\sigma}(\mathbf{r}'t') - u_{\mathrm{xc}j\sigma}(\mathbf{r}'t')]\,\phi_{j\sigma}^*(\mathbf{r}'t')\,\theta(t_1 - t') \quad , \tag{16}$$

where

$$u_{\mathrm{xc}j\sigma}(\mathbf{r}t) = \frac{1}{\phi_{j\sigma}^*(\mathbf{r}t)} \frac{\delta A_{\mathrm{xc}}[\phi_{j\sigma}]}{\delta \phi_{j\sigma}(\mathbf{r}t)} \tag{17}$$

and $\theta(x)$ denotes the usual step function (1 for $x > 0$, 0 for $x < 0$). An analogous expression is obtained for $\delta A / \delta \phi_{j\sigma}^*$ which, for all reasonable (i. e. real) functionals $A[\phi_{j\sigma}]$, is the complex conjugate of (16).

In order to evaluate $\delta A / \delta v_\sigma$ from Eq. (15), we further need the functional derivatives $\delta \phi_{j\sigma} / \delta v_\sigma$ and $\delta \phi_{j\sigma}^* / \delta v_\sigma$. To this end, we consider the orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$ 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 $\delta v_\sigma(\mathbf{r}t)$ and let it evolve *backwards* in time. The corresponding perturbed wave functions $\phi_{j\sigma}'(\mathbf{r}t)$ are determined by the backward Schrödinger equation

$$i\,(\partial/\partial t)\,\phi_{j\sigma}'(\mathbf{r}t) = \left(-\nabla^2/2 + v_\sigma(\mathbf{r}t) + \delta v_\sigma(\mathbf{r}t)\right)\phi_{j\sigma}'(\mathbf{r}t) \quad , \quad j = 1, \ldots, N_\sigma \tag{18}$$

with the initial condition $\phi_{j\sigma}'(\mathbf{r}t_1) = \phi_{j\sigma}(\mathbf{r}t_1)$. The resulting first-order correction to the wave function $\phi_{j\sigma}(\mathbf{r}t)$ under the influence of $\delta v_\sigma(\mathbf{r}t)$ is given by

$$\delta \phi_{j\sigma}(\mathbf{r}t) = i \sum_{k=1}^{\infty} \int_{t}^{t_1} dt' \int d^3 r' \, \phi_{k\sigma}^*(\mathbf{r}'t')\delta v_\sigma(\mathbf{r}'t')\phi_{j\sigma}(\mathbf{r}'t')\phi_{k\sigma}(\mathbf{r}t) \ . \tag{19}$$

from which we can read off the desired functional derivative

$$\frac{\delta \phi_{j\sigma'}^{bw}(\mathbf{r}'t')}{\delta v_\sigma(\mathbf{r}t)} = i\delta_{\sigma\sigma'} \sum_{k=1}^{\infty} \phi_{k\sigma}^*(\mathbf{r}t)\phi_{j\sigma}(\mathbf{r}t)\phi_{k\sigma}(\mathbf{r}'t')\,\theta(t_1 - t)\,\theta(t - t') \quad . \tag{20}$$

Once again, $\delta \phi_{j\sigma'}^* / \delta v_\sigma$ leads to the complex conjugate expression. We can now insert (16) and (20) in the variational equation (15), and the result is the time-dependent OEP (TDOEP) integral equation for the local exchange-correlation potential $v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)$:

$$\int_{-\infty}^{t_1} dt' \int d^3 r' \left(iK_\sigma(\mathbf{r}t, \mathbf{r}'t') \sum_{j}^{N_\sigma} \phi_{j\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}'t') [v_{\mathrm{xc}\,\sigma}(\mathbf{r}'t') - u_{\mathrm{xc}j\sigma}(\mathbf{r}'t')] + c.c. \right) = 0 \ . \tag{21}$$

4

The kernel $K_\sigma(\mathbf{r}t, \mathbf{r}'t') = \sum_{k=1}^\infty \phi_{k\sigma}^*(\mathbf{r}t)\phi_{k\sigma}(\mathbf{r}'t')\theta(t-t')$ can be identified with the Green's function of the system, which satisfies the differential equation

$$\left[i\,\partial/\partial t' - \left(-\nabla'^2/2 + v_\sigma(\mathbf{r}'t')\right)\right]K_\sigma(\mathbf{r}t, \mathbf{r}'t') = -i\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \qquad (22)$$

with the initial condition $K_\sigma(\mathbf{r}t, \mathbf{r}'t') = 0$ for $t' > t$. The TDOEP scheme is now complete: the integral equation (21) has to be solved for $v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)$ in combination with the Schrödinger equation (2) and the differential equation (22) for $K_\sigma(\mathbf{r}t, \mathbf{r}'t')$, both with the appropriate initial conditions. It is easy to show that in the time interval $[-\infty, t_1]$ the exchange-correlation potential $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$ is unique up to within an additive, purely time-dependent function $c(t)$ (as expected in view of the Runge-Gross theorem). Also it can be demonstrated [12] that for time-independent external potentials ($v_{1\sigma}(\mathbf{r}t) \equiv 0$) the TDOEP reduces to the stationary OEP.

The implementation of the full TDOEP scheme is an extremely demanding task. It is therefore highly desirable to construct approximations of $v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)$ which are *explicit* functionals of the orbitals $\{\phi_{j\sigma}\}$, thereby avoiding the need to solve the integral equation numerically. With similar manipulations as developed by KLI for the stationary case [8, 9] one can derive the so-called TDKLI expression [4]

$$\begin{aligned}
\tilde{v}_{\mathrm{xc}\,\sigma}(\mathbf{r}t) = {} & \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t) \frac{1}{2}\left(u_{\mathrm{xc}j\sigma}(\mathbf{r}t) + u_{\mathrm{xc}j\sigma}^*(\mathbf{r}t)\right) \\
& + \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t) \left[\bar{\tilde{v}}_{\mathrm{xc}j\sigma}(t) - \frac{1}{2}\left(\bar{u}_{\mathrm{xc}j\sigma}(t) + \bar{u}_{\mathrm{xc}j\sigma}^*(t)\right)\right] \\
& + \frac{i}{4n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} \nabla^2 n_{j\sigma}(\mathbf{r}t) \int_{-\infty}^t dt' \left(\bar{u}_{\mathrm{xc}j\sigma}(t') - \bar{u}_{\mathrm{xc}j\sigma}^*(t')\right) .
\end{aligned} \qquad (23)$$

The tilde indicates that this is only an approximate solution of the TDOEP equation (21) and the overbar is a shorthand notation for the orbital average, i.e. $\bar{\tilde{v}}_{\mathrm{xc}j\sigma}(t) = \int d^3r\, n_{j\sigma}(\mathbf{r}t)\tilde{v}_{\mathrm{xc}j\sigma}\mathbf{r}(t)$. The last term of Eq. (23) vanishes identically for a large class of exchange-correlation functionals A_{xc} including all functionals depending on $\{\phi_{j\sigma}\}$ only through the combinations $\phi_{j\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}'t')$ (such as the TDHF functional, Eq. (14)). Eq. (23) is still an integral equation for $\tilde{v}_{\mathrm{xc}\sigma}$. In contrast to the full TDOEP equation it can be solved analytically [7]: Multiplying Eq. (23) by $n_{k\sigma}(\mathbf{r}t)$ and integrating over all space yields

$$\bar{\tilde{v}}_{\mathrm{xc}k\sigma}(t) = \bar{w}_{\mathrm{xc}k\sigma}(t) + \sum_j^{N_\sigma} M_{kj\sigma}(t)\bar{\tilde{v}}_{\mathrm{xc}j\sigma}(t) \quad , \qquad (24)$$

where

$$\begin{aligned}
w_{\mathrm{xc}\,\sigma}(\mathbf{r}t) = {} & \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t) \frac{1}{2}\left(u_{\mathrm{xc}j\sigma}(\mathbf{r}t) + u_{\mathrm{xc}j\sigma}^*(\mathbf{r}t)\right) \\
& - \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t) \left[\frac{1}{2}\left(\bar{u}_{\mathrm{xc}j\sigma}(t) + \bar{u}_{\mathrm{xc}j\sigma}^*(t)\right)\right] \\
& + \frac{i}{4n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} \nabla^2 n_{j\sigma}(\mathbf{r}t) \int_{-\infty}^t dt' \left(\bar{u}_{\mathrm{xc}j\sigma}(t') - \bar{u}_{\mathrm{xc}j\sigma}^*(t')\right)
\end{aligned} \qquad (25)$$

and

$$M_{kj\sigma}(t) = \int d^3r\, \frac{n_{k\sigma}(\mathbf{r}t)n_{j\sigma}(\mathbf{r}t)}{n_\sigma(\mathbf{r}t)} \quad . \qquad (26)$$

Solving Eq. (24) for $\bar{\tilde{v}}_{\mathrm{xc}j\sigma}(t)$ requires inversion of the $N_\sigma \times N_\sigma$ matrix $A_{kj\sigma}(t) = \delta_{kj} - M_{kj\sigma}(t)$ and leads to

$$\bar{\tilde{v}}_{\mathrm{xc}j\sigma}(t) = \sum_k^{N_\sigma} \left(A_\sigma^{-1}(t) \right)_{jk} \overline{w}_{\mathrm{xc}k\sigma}(t) \quad . \tag{27}$$

When Eq. (27) is substituted into Eq. (23), one obtains $\tilde{v}_{\mathrm{xc}\sigma}(\mathbf{r}t)$ as an explicit functional of the orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$. The TDKLI scheme has been applied successfully to the nonperturbative description of atoms [13, 14, 15] and clusters [16] in strong laser pulses.

THE EXCHANGE CORRELATION KERNEL WITHIN THE TDOEP

In the previous section we presented the TDOEP scheme as a method to treat a time-dependent interacting many particle system nonperturbatively. We now discuss the linear density response to the time-dependent part of the external potential in the TDOEP, and show how it is related to the TDDFT linear response formalism. Note that to recover the Dyson-type equation (11) we have to establish an equation of the form

$$\left. \frac{\delta v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)}{\delta v_{\mathrm{ext}\,\sigma'}(\mathbf{r}'t')} \right|_{v^{(0)}} = \sum_\nu \int d^3y \int d\tau\, f_{\mathrm{xc}\,\sigma\nu}(\mathbf{r}t, \mathbf{y}\tau) \chi_{\nu\sigma'}(\mathbf{y}\tau, \mathbf{r}'t') \tag{28}$$

where

$$\chi_{\nu\sigma'}(\mathbf{y}\tau, \mathbf{r}'t') = \frac{\delta n_\sigma(\mathbf{y}\tau)}{\delta v_{\mathrm{ext}\,\sigma'}(\mathbf{r}'t')} \quad . \tag{29}$$

Within the TDOEP scheme the exchange-correlation potential does not depend explicitly on the spin densities n_σ. The density-dependence is only implicit through the orbitals. Therefore the evaluation of the functional derivative $\delta v_{\mathrm{xc}}/\delta v_{\mathrm{ext'}}$ is more complicated than in ordinary TDDFT. The integral equation (21) does not even define $v_{\mathrm{xc}\,\sigma}$ as an explicit functional of only the occupied orbitals $\{\phi_{j\sigma}; j = 1 \ldots N_\sigma\}$ but contains the Greens function $K_\sigma(\mathbf{r}t, \mathbf{r}'t')$. For the moment we therefore imagine $v_{\mathrm{xc}\,\sigma}$ to be a functional of all orbitals $\{\phi_{j\sigma}\}$. By applying the chain rule for functional derivatives on the left hand side of Eq. (28) several times we obtain

$$\frac{\delta v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)}{\delta v_{\mathrm{ext}\,\sigma'}(\mathbf{r}'t')} = \sum_{\nu\nu'\tilde{\nu}} \int d^3y \int d\tau \int d^3y' \int d\tau' \int d^3\tilde{y} \int d\tilde{\tau}$$

$$\times \sum_m \left(\frac{\delta v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)}{\delta\phi_{m\nu}(\mathbf{y}\tau)} \frac{\delta\phi_{m\nu}(\mathbf{y}\tau)}{\delta v_{\nu'}(\mathbf{y}'\tau')} + \frac{\delta v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)}{\delta\phi_{m\nu}^*(\mathbf{y}\tau)} \frac{\delta\phi_{m\nu}^*(\mathbf{y}\tau)}{\delta v_{\nu'}(\mathbf{y}'\tau')} \right) \frac{\delta v_{\nu'}(\mathbf{y}'\tau')}{\delta n_{\tilde{\nu}}(\tilde{\mathbf{y}}\tilde{\tau})} \frac{\delta n_{\tilde{\nu}}(\tilde{\mathbf{y}}\tilde{\tau})}{\delta v_{\mathrm{ext}\,\sigma'}(\mathbf{r}'t')} \quad . \tag{30}$$

Comparison of (30) and (28) yields the following representation for the exchange-correlation kernel

$$f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') = \left[\sum_{\nu\nu'} \int d^3y \int d\tau \int d^3y' \int d\tau' \right.$$

$$\times \sum_m \left(\frac{\delta v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)}{\delta\phi_{m\nu}(\mathbf{y}\tau)} \frac{\delta\phi_{m\nu}(\mathbf{y}\tau)}{\delta v_{\nu'}(\mathbf{y}'\tau')} + \frac{\delta v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)}{\delta\phi_{m\nu}^*(\mathbf{y}\tau)} \frac{\delta\phi_{m\nu}^*(\mathbf{y}\tau)}{\delta v_{\nu'}(\mathbf{y}'\tau')} \right) \left. \frac{\delta v_{\nu'}(\mathbf{y}'\tau')}{\delta n_{\sigma'}(\mathbf{r}'t')} \right]_{\phi_{j\sigma}(t) = \phi_{j\sigma}^{(0)}(t)} \quad . \tag{31}$$

Here the functional derivatives $\delta\phi_{j\sigma'}/\delta v_\sigma$ and $\delta v_{\sigma'}/\delta n_\sigma$ refer to the mappings

$$v_\sigma \longrightarrow \{\phi_{j\sigma}\} \tag{32}$$

$$v_\sigma \longleftrightarrow \{n_{j\sigma}\} \tag{33}$$

defined by solution of the Schrödinger equation (2) for $t > t_0$ under the initial condition $\phi_{j\sigma}^{(0)}(\mathbf{r}t_0) = \varphi_{j\sigma}(\mathbf{r})$. The correspondence (33) between potentials and spin densities

is one-to-one by the Runge-Gross theorem. The left hand side of Eq. (31) is to be evaluated at the stationary orbitals $\phi_{j\sigma}^{(0)}(\mathbf{r}t) = \varphi_{j\sigma}(\mathbf{r})e^{-\epsilon_{j\sigma}(t-t_0)}$ corresponding to $v(\mathbf{r}t) = v^{(0)}(\mathbf{r})$ for all times. For $\delta\phi_{j\sigma'}/\delta v_\sigma$ we obtain from first-order perturbation theory

$$\frac{\delta\phi_{j\sigma}(\mathbf{r}t)}{\delta v_{\sigma'}(\mathbf{r}'t')} = -i\delta_{\sigma\sigma'}\ \phi_{j\sigma}(\mathbf{r}'t')\sum_k \phi_{k\sigma}(\mathbf{r}t)\phi_{k\sigma}^*(\mathbf{r}'t')\theta(t-t') \quad , \tag{34}$$

and for $\delta\phi_{j\sigma'}^*/\delta v_\sigma$ the complex conjugate. The derivative $\delta v_{\sigma'}/\delta n_\sigma$ is the inverse of the noninteracting density-density response function

$$\tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r}t,\mathbf{r}'t') = \frac{\delta n_\sigma(\mathbf{r}t)}{\delta v_{\sigma'}(\mathbf{r}'t')}$$

$$= -i\theta(t-t')\delta_{\sigma\sigma'}\sum_{j,k}(\ f_{k\sigma} - f_{j\sigma}\ )\ \phi_{j\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}'t')\phi_{k\sigma}(\mathbf{r}'t')\phi_{k\sigma}^*(\mathbf{r}t) \tag{35}$$

($\tilde{\chi}_{\mathrm{s}}$ reduces to χ_{s} of (8) after inserting the stationary orbitals $\phi^{(0)}(t)$; the $f_{j\sigma}$ are occupation factors). Thus multiplying Eq. (31) with $\tilde{\chi}_{\mathrm{s}\sigma'\tilde{\sigma}}(\mathbf{r}'t',\tilde{\mathbf{r}}\tilde{t})$ from the right and integrating over $\mathbf{r}'t'$ yields the following integral equation for the exchange-correlation kernel

$$\int dt' \int d^3r'\ \left\{ -i\sum_m \left(\ f_{m\sigma'}\, f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r}t,\mathbf{r}'t') - g_{\mathrm{xc}\,\sigma\sigma'}^{(m)}(\mathbf{r}t,\mathbf{r}'t')\ \right) \right.$$

$$\left. \times \left[\ \phi_{m\sigma'}(\mathbf{y}\tau)\phi_{m\sigma'}^*(\mathbf{r}'t')\sum_k \phi_{k\sigma'}(\mathbf{r}'t')\phi_{k\sigma'}^*(\mathbf{y}\tau)\theta(t'-\tau)\ \right]_{\phi_{j\sigma}(t)=\phi_{j\sigma}^{(0)}(t)} + c.c. \right\} = 0\ . \tag{36}$$

where we used the abbreviation

$$g_{\mathrm{xc}\,\sigma\sigma'}^{(m)}(\mathbf{r}t,\mathbf{r}'t') = \left[\ \frac{1}{\phi_{m\sigma'}^*(\mathbf{r}'t')}\frac{\delta v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)}{\delta\phi_{m\sigma'}(\mathbf{r}'t')}\ \right]_{\phi_{j\sigma}(t)=\phi_{j\sigma}^{(0)}(t)} . \tag{37}$$

We emphasize that Eq.(36) is by no means restricted to the TDOEP but defines the xc-kernel in any scheme involving a representation of a local xc-potential as a functional of the orbitals rather than the spin densities. We observe that Eq.(36) is formally identical with the integral equation for the time-dependent OEP xc-potential (21) with $v_{\mathrm{xc}\,\sigma}(\mathbf{r}'t')$ and $u_{\mathrm{xc}\,j\sigma}(\mathbf{r}'t')$ replaced by $f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r}t,\mathbf{r}'t')$ and $g_{\mathrm{xc}\,\sigma\sigma'}^{(j)}(\mathbf{r}t,\mathbf{r}'t')$, respectively. Consequently it can be treated by the same approximation methods once the quantity $g_{\mathrm{xc}}^{(j)}$ has been obtained from a functional $v_{\mathrm{xc}}[\{\phi_{j\sigma}\}]$.

Within the full TDOEP scheme one can still not evaluate the derivatives in (37) directly because one has only an implicit knowledge of the functional form of $v_{\mathrm{xc}}[\{\phi_{j\sigma}\}]$. An exact procedure to overcome this difficulty is presented in the appendix and can be outlined as follows: Acting with $\delta/\delta\phi_{j\sigma}$ on Eq. (21) one generates a system of integral equations for the derivatives $\delta v_{\mathrm{xc}}/\delta\phi_{j\sigma}$ of the xc-potential. These relations can be combined with Eq. (37) to a single integral equation defining f_{xc} in terms of derivatives $\delta A_{\mathrm{xc}}/\delta\phi_{j\sigma}$ and $\delta^2 A_{\mathrm{xc}}/\delta\phi_{j\sigma}\delta\phi_{j'\sigma'}$ of the xc-part of the action functional.

For practical calculations, however, it is desirable to devise a sufficiently simple analytic approximation of f_{xc}. To this end we consider the expression

$$v_{\mathrm{xc}\,\sigma}^{\mathrm{appr}}(\mathbf{r}t) = \sum_j^{N_\sigma} \frac{|\psi_{j\sigma}(\mathbf{r}t)|^2}{2n_\sigma(\mathbf{r}t)}\left[u'_{\mathrm{xc}\,j\sigma}(\mathbf{r}t) + u'^*_{\mathrm{xc}\,j\sigma}(\mathbf{r}t) \right] \tag{38}$$

as an approximate solution to (21), which means that we keep only the first term on the right hand side of Eq. (23). In the static exchange-only case this procedure leads

to the so-called Slater approximation [17]. Now we apply the same approximation to (36), i.e., we set

$$f_{\text{xc}\,\sigma\sigma'}^{\text{appr}}(\mathbf{y}\tau, \mathbf{r}'t') = \sum_j \frac{|\varphi_{j\sigma'}(\mathbf{r})|^2}{2n_{0\,\sigma'}(\mathbf{r})} \left[g_{\text{xc}\,\sigma\sigma'}^{(j)}(\mathbf{y}\tau, \mathbf{r}'t') + c.c. \right] \qquad (39)$$

and use the explicit analytical form (38) to evaluate (37). In the TD x-only approximation defined by (14) this scheme yields the compact expression

$$f_{\text{x}\,\sigma\sigma'}^{\text{appr}}(\mathbf{r}t, \mathbf{r}'t') = -\,\delta(t - t')\,\delta_{\sigma\sigma'} \frac{\left| \sum_k f_{k\sigma}\varphi_{k\sigma}(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}') \right|^2}{|\mathbf{r} - \mathbf{r}'|\, n_{0\,\sigma}(\mathbf{r})\, n_{0\,\sigma}(\mathbf{r}')} \,. \qquad (40)$$

We remark that in general the Fourier transform of the xc-kernel defined by Eq. (36) is frequency-dependent (even in the TD x-only case), a feature which is not accounted for in the present treatment of this equation. However, for the special case of a two-electron system treated within TD x-only theory, Eqs. (40) and (38) are the *exact* solutions of the respective integral equations, as is easily checked.

CALCULATION OF EXCITATION ENERGIES

The traditional Hohenberg-Kohn theorem guarantees that every observable of a stationary physical system can be expressed in terms of its ground-state density. In principle, this is also true for the set of excited-state energies: Knowledge of the external potential, which is a unique functional of the ground-state density, allows the calculation of any excited state and its energy. In practise, however, the description of excited states within stationary density-functional theory is a notoriously difficult subject [18 – 33]. In particular, the Kohn-Sham eigenvalues, introduced as purely mathematical constructs into density-functional theory, cannot simply be interpreted as excited-state energies.

In this section we shall discuss a different approach to the calculation of excitation energies which is based on time-dependent density functional theory in the linear response regime [34, 35]. Similar ideas were recently proposed by Casida and coworkers [36] on the basis of the one-particle density matrix.

Since the response functions (8) and (9) as well as the xc kernel (12) are functionals of the ground-state density only, this approach represents a way of explicitly constructing functionals for excitation energies in terms of ground state properties.

To calculate excitation energies from time-dependent density functional theory we use the fact that the frequency-dependent linear density response of a finite system exhibits discrete poles at the true excitation energies of the unperturbed system. Taking the Dyson-type equation (11) for the interacting density-density response function, the exact linear density response can be written as the linear density response of a noninteracting (Kohn-Sham) system to an effective perturbation. The fundamental idea is to use this formally exact representation of the linear density response to calculate the shifts of the Kohn-Sham orbital eigenvalue differences (which are the poles of the Kohn-Sham response function) toward the true excitation energies (which are the poles of the interacting response function).

Inserting the Fourier transform (with respect to time) of relation (11) into the equation

$$n_{1\sigma}(\mathbf{r}, \omega) = \sum_\nu \int d^3y\, \chi_{\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) v_{1\nu}(\mathbf{y}, \omega) \qquad (41)$$

for the frequency-dependent linear (spin) density response, one obtains the response equation

$$n_{1\sigma}(\mathbf{r}, \omega) = \sum_{\nu} \int d^3y \, \chi_{s\,\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) v_{s\,1\nu}(\mathbf{y}, \omega) \tag{42}$$

of non-interacting particles subject to the effective perturbation

$$v_{s\,1\nu}(\mathbf{y}, \omega) = v_{1\nu}(\mathbf{y}, \omega) + \sum_{\nu'} \int d^3y' \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\,\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) n_{1\nu'}(\mathbf{y}', \omega). \tag{43}$$

Equations (42) and (43) have to be solved self-consistently for the frequency-dependent linear spin density response $n_{1\sigma}(\mathbf{r}, \omega)$.

The response-function χ_s of the Kohn-Sham system can be expressed in terms of the unperturbed static Kohn-Sham spin orbitals $\varphi_{j\sigma}$ as

$$\chi_{s\,\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) = \delta_{\sigma\sigma'} \sum_{j,k} (f_{k\sigma} - f_{j\sigma}) \frac{\varphi_{j\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{\omega - (\epsilon_{j\sigma} - \epsilon_{k\sigma}) + i\eta} \tag{44}$$

where $f_{k\sigma}$, $f_{j\sigma}$ are occupation factors (1 or 0). The summations in (44) run over all unperturbed Kohn-Sham orbitals, including the continuum states.

Note that the equations (42) and (43) are valid not only in the conventional formulation but also in the OEP formulation of time-dependent density functional theory, where the same Dyson-type relation (11) holds true as has been demonstrated in the previous section. In particular, one can employ approximate exchange-correlation kernels in Eq. (43) which were derived in the framework of the TDOEP.

In order to calculate the shifts from the KS single-particle energy differences towards the true excitation energies Ω of the interacting system, we rewrite Eq. (42) together with Eq. (43) as

$$\sum_{\nu'} \int d^3y' \left(\delta_{\sigma\nu'} \delta(\mathbf{r} - \mathbf{y}') - \sum_{\nu} \int d^3y \, \chi_{s\,\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) \right.$$
$$\times \left. \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\,\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) \right) n_{1\nu'}(\mathbf{y}', \omega)$$
$$= \sum_{\nu} \int d^3y \, \chi_{s\,\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) v_{1\nu}(\mathbf{y}, \omega). \tag{45}$$

In general, the true excitation energies Ω are not identical with the Kohn-Sham excitation energies $\epsilon_{j\sigma} - \epsilon_{k\sigma}$. Therefore, the right-hand side of Eq. (45) remains finite for $\omega \to \Omega$. Since, on the other hand, the exact spin-density response $n_{1\sigma}$, has poles at the true excitation energies Ω, the integral operator acting on $n_{1\sigma}$ on the left-hand side of Eq. (45) cannot be invertible for $\omega \to \Omega$ (Assuming the existence of the inverse operator, its action on both sides of Eq. (45) results in a finite right-hand side for $\omega \to \Omega$. This leads to a contradiction since $n_{1\sigma}$, remaining on the left-hand side, has a pole at $\omega = \Omega$).

Consequently, the true excitation energies Ω are characterized as those frequencies where the eigenvalues of the integral operator acting on the spin-density vector in Eq. (45) vanish. Integrating out the delta-function in Eq. (45), the true excitation energies Ω are those frequencies, where the eigenvalues $\lambda(\omega)$ of

$$\sum_{\nu'} \int d^3y' \sum_{\nu} \int d^3y \, \chi_{s\,\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\,\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) \gamma_{\nu'}(\mathbf{y}', \omega) =$$
$$\lambda(\omega) \gamma_{\sigma}(\mathbf{r}, \omega) \tag{46}$$

satisfy

$$\lambda(\Omega) = 1 \,. \tag{47}$$

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

To facilitate the notation, we 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 $(k\sigma \to j\sigma)$. Moreover, we define

$$\Phi_{q\sigma}(\mathbf{r}) := \phi_{k\sigma}(\mathbf{r})^* \phi_{j\sigma}(\mathbf{r}) \,, \tag{48}$$

$$\alpha_{q\sigma} := f_{k\sigma} - f_{j\sigma} \tag{49}$$

and set

$$\xi_{q\sigma}(\omega) := \sum_{\nu'} \int d^3y' \int d^3y \, \Phi_{q\sigma}(\mathbf{y})^* \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{\text{xc}\,\sigma\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) \gamma_{\nu'}(\mathbf{y}', \omega) \,. \tag{50}$$

Using these definitions, Eq. (46) can be recast into

$$\sum_q \frac{\alpha_{q\sigma} \Phi_{q\sigma}(\mathbf{r})}{\omega - \omega_{q\sigma} + i\eta} \xi_{q\sigma}(\omega) = \lambda(\omega) \gamma_\sigma(\mathbf{r}, \omega) \,. \tag{51}$$

Solving this equation for $\gamma_\sigma(\mathbf{r}, \omega)$ and reinserting the result on the right-hand side of Eq. (50) we arrive at

$$\sum_{\sigma'} \sum_{q'} \frac{M_{q\sigma\,q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} \xi_{q'\sigma'}(\omega) = \lambda(\omega) \xi_{q\sigma}(\omega) \,, \tag{52}$$

where we have introduced the matrix elements

$$M_{q\sigma\,q'\sigma'}(\omega) = \alpha_{q'\sigma'} \int d^3r \int d^3r' \, \Phi^*_{q\sigma}(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) \right) \Phi_{q'\sigma'}(\mathbf{r}') \,. \tag{53}$$

Note that the summation in Eq. (52) extends over an infinite number of single-particle transitions $q'\sigma'$ between occupied and unoccupied Kohn-Sham orbitals, so that up to this point, no approximations have been made.

In order to actually calculate the excitation spectrum, the eigenvalue problem (52) has to be truncated in one way or another. One possibility is to expand all quantities in Eq. (52) about one particular KS-orbital energy difference $\omega_{p\tau}$ [34, 35]. The true excitation energies Ω are then determined by the solution of

$$\lambda(\Omega) = \frac{A(\omega_{p\tau})}{\Omega - \omega_{p\tau}} + B(\omega_{p\tau}) + \ldots = 1 \tag{54}$$

For non-degenerate single-particle poles $\omega_{p\tau}$, the coefficients in Eq. (54) are given by

$$A(\omega_{p\tau}) = M_{p\tau\,p\tau}(\omega_{p\tau}) \tag{55}$$

and

$$B(\omega_{p\tau}) = \left. \frac{dM_{p\tau p\tau}}{d\omega} \right|_{\omega_{p\tau}} + \frac{1}{M_{p\tau p\tau}(\omega_{p\tau})} \sum_{q'\sigma' \neq p\tau} \frac{M_{p\tau\,q'\sigma'}(\omega_{p\tau}) M_{q'\sigma'\,p\tau}(\omega_{p\tau})}{\omega_{p\tau} - \omega_{q'\sigma'} + i\eta} \,. \tag{56}$$

If the pole $\omega_{p\tau}$ is $\wp$-fold degenerate, $\omega_{p_1\tau_1} = \omega_{p_2\tau_2} = \ldots = \omega_{p_\wp\tau_\wp} \equiv \omega_0$, the lowest-order coefficient A in Eq. (54) is determined by a $\wp$-dimensional matrix equation

$$\sum_{k=1}^{\wp} M_{p_i\tau_i\,p_k\tau_k}(\omega_0) \xi^{(n)}_{p_k\tau_k} = A_n(\omega_0) \xi^{(n)}_{p_i\tau_i} \,, \quad i = 1 \ldots \wp \,, \tag{57}$$

10

leading to $\wp$ different coefficients $A_1 \ldots A_\wp$, in general. For excitation energies Ω close to ω_0, the lowest-order term of the above Laurent expansion will dominate the series. In this single pole approximation (SPA), Eq. (54) reduces to

$$\lambda_n(\Omega) \approx \frac{A_n(\omega_0)}{\Omega - \omega_0} = 1 \,. \tag{58}$$

The condition (47) and its complex conjugate, $\lambda^*(\Omega) = 1$, finally lead to to a simple (approximate) expression for the exact excitation energies.

$$\Omega_n \approx \omega_0 + \Re A_n(\omega_0) \,. \tag{59}$$

For closed-shell systems, every Kohn-Sham orbital eigenvalue is degenerate with respect to spin, i.e. the spin multiplet structure is absent in the bare Kohn-Sham eigenvalue spectrum. Within the SPA, the dominant terms in the corrections to the Kohn-Sham eigenvalues towards the true multiplet energies naturally emerge from the solution of the (2×2) eigenvalue problem

$$\sum_{\sigma'=\uparrow,\downarrow} M_{p\sigma p\sigma'}(\omega_0)\xi_{p\sigma'}(\omega_0) = A\xi_{p\sigma}(\omega_0) \,. \tag{60}$$

Then, the resulting excitation energies are:

$$\Omega_{1,2} = \omega_0 + \Re \left\{ M_{p\uparrow p\uparrow} \pm M_{p\uparrow p\downarrow} \right\} \,. \tag{61}$$

Using the explicit form of the matrix elements (53) one finds

$$\Omega_1 = \omega_0 + 2\Re \int d^3r \int d^3r' \, \Phi_p^*(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'; \omega_0) \right) \Phi_p(\mathbf{r}') \tag{62}$$

$$\Omega_2 = \omega_0 + 2\Re \int d^3r \int d^3r' \, \Phi_p^*(\mathbf{r})\mu_0^2 G_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'; \omega_0)\Phi_p(\mathbf{r}') \tag{63}$$

where, since we are dealing with spin saturated systems, we have dropped the spin-index of $\Phi_{p\sigma}$ for simplicity. The xc-kernels appearing in Eqs. (62) and (63) are given by

$$f_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{4} \sum_{\sigma,\sigma'=\pm1} f_{\mathrm{xc}\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) \tag{64}$$

$$G_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{4\mu_0^2} \sum_{\sigma,\sigma'=\pm1} (\sigma \cdot \sigma')f_{\mathrm{xc}\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) \,. \tag{65}$$

The latter kernel, G_{xc}, is responsible for the exchange and correlation effects in the Kohn-Sham equation for the linear response of the frequency-dependent magnetization density $m(\mathbf{r}, \omega)$ [2]. The fact that the magnetization density response naturally involves spin-flip processes suggests that Ω_2 can be attributed to spin triplet excitation energies of many-electron systems. The corresponding spin singlet excitation energies, on the other hand, are given by Ω_1.

Apart from the explicit calculation of the dominant contributions to the shifts of the Kohn-Sham eigenvalue differences towards the true excitation energies, one can, in principle, solve Eq. (52) directly. At the frequencies $\omega = \Omega$ Eq. (52) can be written as

$$\sum_{q'\sigma'} \left(M_{q\sigma q'\sigma'}(\Omega) + \delta_{q\sigma q'\sigma'}\omega_{q\sigma} \right) \beta_{q'\sigma'}(\Omega) = \Omega\beta_{q\sigma}(\Omega) \,, \tag{66}$$

where we have introduced

$$\beta_{q\sigma}(\Omega) := \xi_{q\sigma}(\Omega)/(\Omega - \omega_{q\sigma}) . \tag{67}$$

Hence, the exact excitation energies Ω are the exact solutions of the nonlinear matrix-equation (66). Truncation of the infinite-dimensional matrix in Eq. (66) amounts to the approximation of $\chi^{(0)}$ by a finite sum

$$\chi^{(0)}(\mathbf{r}, \mathbf{r}', \omega) \approx \sum_{\sigma=\uparrow\downarrow} \sum_{q}^{Q} \alpha_q \frac{\Phi_q(\mathbf{r})\Phi_q(\mathbf{r}')}{\omega - \omega_{q\sigma}} . \tag{68}$$

Thus, instead of expanding about a single pole, we explicitly take into account several poles of the noninteracting response function. Taking the adiabatic approximation for the xc-kernels, the matrix elements $M_{q\sigma\,q'\sigma'}$ become real and frequency independent, and the excitation energies Ω are then given as the eigenvalues of the $(Q \times Q)$ matrix $M_{q\sigma\,q'\sigma'}(\Omega = 0) + \delta_{q\sigma\,q'\sigma'}\omega_{q\sigma}$.

Results for the He Atom

In this section we report numerical results for excitation energies of the He atom using the above formalism of time-dependent density functional theory. The scheme generally involves three different types of approximations: (i) In the calculation of the KS orbital energies one employs some approximation of the static xc potential v_{xc}. (ii) The xc kernel f_{xc} needs to be approximated. (iii) The infinite-dimensional eigenvalue problem (52) (or, equivalently, (66)) must be truncated in one way or another. The aim of the present work is to investigate the effects due to the approximations (ii) and (iii). In order to eliminate the errors (i) associated with the approximation for the ground-state KS potential we employ the *exact* xc potential of the He atom [37]. Table 1 shows the excitation energies of neutral helium, calculated in the single-pole approximation (SPA) (Eqs. (62) and (63)) and obtained from the truncated matrix equation (66) in comparison with results of the nonrelativistic variational calculation of Kono and Hattori [38] (column 8). The matrix equation (66) was solved using $N = 34$ unoccupied Kohn-Sham orbitals of s or p symmetry. For each symmetry class the resulting dimension of the (fully coupled but truncated) matrix in Eq. (66) is $(4N \times 4N)$ (due to the spin-degeneracy of the KS orbitals of Helium and the fact that the frequency dependent Kohn-Sham response function is symmetric in the complex plane with respect to the imaginary axis).

The excitation energies resulting from equation (66) are listed in column 5 for f_{xc}^{ALDA}, the so called adiabatic local density approximation for the exchange-correlation kernel [39], where the parametrization of Vosko, Wilk and Nusair [40] has been used for the correlation energy per particle. In column 7 we list the excitation energies obtained with the TDOEP kernel f_{x-only}^{appr} (Eq. (40)).

Within the accuracy of the figures given in the table, the results are converged with respect to variations of the dimension of the matrix in Eq. (66). Hence, the remaining difference between the results of the variational calculation [38] given in column 8 and the values obtained from our TDDFT formalism (column 5 and 7) is entirely due to the approximations in the xc kernels.

As also noted by Umrigar [41], it is a remarkable fact that for the exact Kohn-Sham potential of Helium, the Kohn-Sham excitation energies $\epsilon_j - \epsilon_k$, denoted $\Delta\omega_{KS}$ (column 3), are already very close to the exact spectrum, with $\Delta\omega_{KS}$ lying always between the singlet and the triplet energies. Hence, our method yields correspondingly small corrections towards singlet and triplet energies.

Table 1. Comparison of the excitation energies of neutral helium, calculated from the exact xc potential by using approximate xc kernels. All values are in Hartrees.

State	$k \to j$	$\Delta\omega_{\mathrm{KS}}$	ALDA (xc)		TDOEP (x-only)		exact[b]
			SPA	full[a]	SPA	full[a]	
2^3S	$1s \to 2s$	0.7460	0.7357	0.7351	0.7232	0.7207	0.7285
2^1S			0.7718	0.7678	0.7687	0.7659	0.7578
3^3S	$1s \to 3s$	0.8392	0.8366	0.8368	0.8337	0.8343	0.8350
3^1S			0.8458	0.8461	0.8448	0.8450	0.8425
4^3S	$1s \to 4s$	0.8688	0.8678	0.8679	0.8667	0.8671	0.8672
4^1S			0.8714	0.8719	0.8710	0.8713	0.8701
5^3S	$1s \to 5s$	0.8819	0.8814	0.8815	0.8808	0.8811	0.8811
5^1S			0.8832	0.8835	0.8830	0.8832	0.8825
6^3S	$1s \to 6s$	0.8888	0.8885	0.8885	0.8882	0.8883	0.8883
6^1S			0.8895	0.8898	0.8894	0.8896	0.8892
7^3S	$1s \to 7s$	0.8929	0.8927	0.8927	0.8925	0.8926	0.8926
7^1S			0.8933	0.8935	0.8932	0.8934	0.8931
8^3S	$1s \to 8s$	0.8955	0.8954	0.8954	0.8952	0.8953	0.8953
8^1S			0.8958	0.8959	0.8957	0.8958	0.8956
9^3S	$1s \to 9s$	0.8972	0.8972	0.8972	0.8971	0.8971	0.8971
9^1S			0.8975	0.8976	0.8974	0.8975	0.8974
2^3P	$1s \to 2p$	0.7772	0.7702	0.7698	0.7693	0.7688	0.7706
2^1P			0.7764	0.7764	0.7850	0.7844	0.7799
3^3P	$1s \to 3p$	0.8476	0.8456	0.8457	0.8453	0.8453	0.8456
3^1P			0.8483	0.8483	0.8500	0.8501	0.8486
4^3P	$1s \to 4p$	0.8722	0.8714	0.8715	0.8712	0.8713	0.8714
4^1P			0.8726	0.8726	0.8732	0.8733	0.8727
5^3P	$1s \to 5p$	0.8836	0.8832	0.8832	0.8831	0.8831	0.8832
5^1P			0.8838	0.8838	0.8841	0.8842	0.8838
6^3P	$1s \to 6p$	0.8898	0.8895	0.8895	0.8895	0.8895	0.8895
6^1P			0.8899	0.8899	0.8901	0.8901	0.8899
7^3P	$1s \to 7p$	0.8935	0.8933	0.8933	0.8933	0.8933	0.8933
7^1P			0.8935	0.8936	0.8937	0.8937	0.8936
8^3P	$1s \to 8p$	0.8959	0.8958	0.8958	0.8958	0.8958	0.8958
8^1P			0.8959	0.8959	0.8960	0.8960	0.8959
9^3P	$1s \to 9p$	0.8975	0.8975	0.8975	0.8974	0.8975	0.8975
9^1P			0.8976	0.8976	0.8976	0.8976	0.8976
Mean abs. dev.[c]			0.0011	0.0010	0.0010	0.0010	
Mean percentage error			0.15%	0.13%	0.13%	0.13%	

[a]Using the lowest 34 unoccupied orbitals of s and p symmetry, respectively.
[b]Nonrelativistic variational calculation [38].
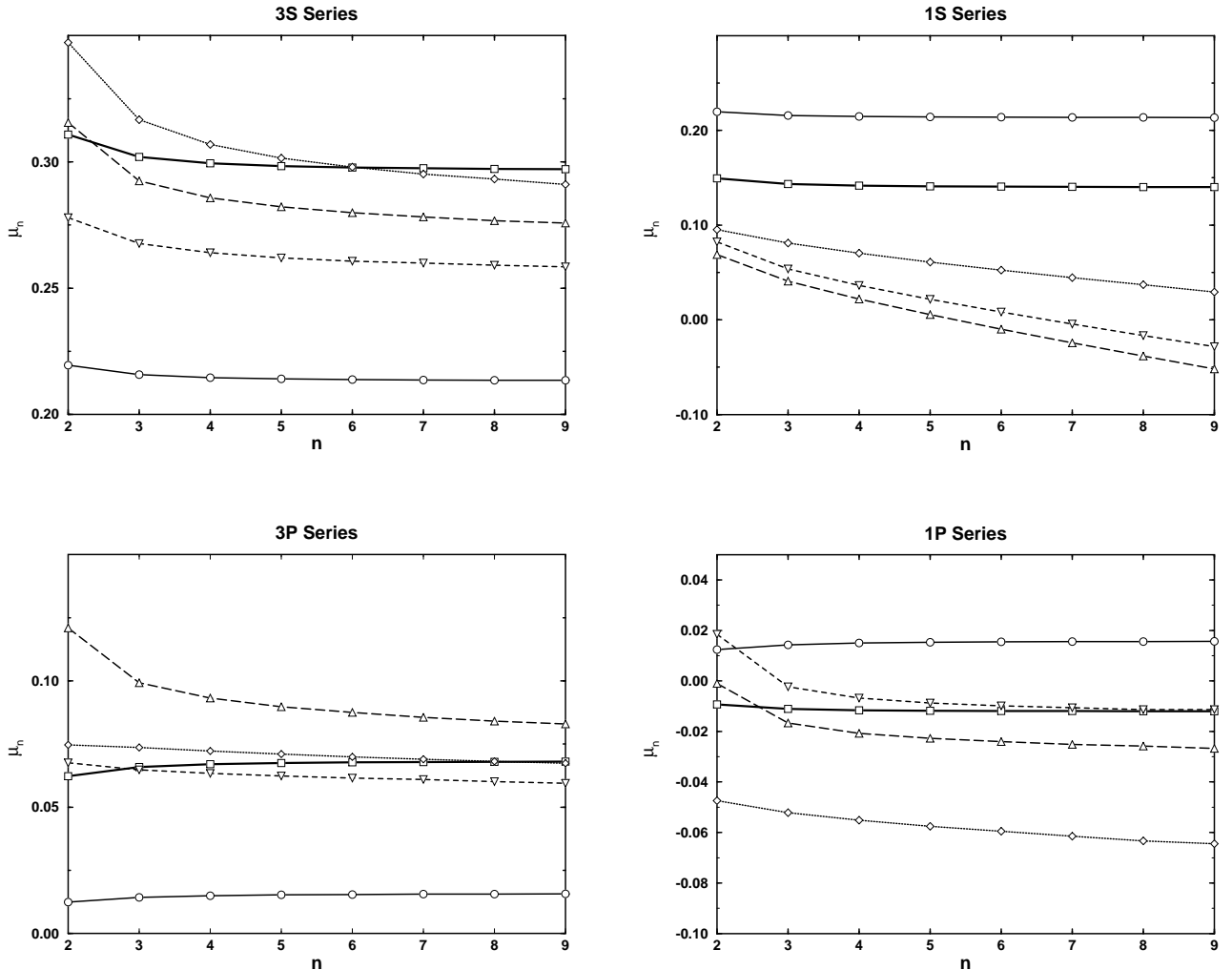[c]Mean value of the absolute deviations from the exact values.

Figure 1. Quantum defects μ_n of the S and P series in Helium, calculated from the exact Kohn-Sham potential of Helium using various approximations for the exchange correlation kernel (triangles up: $f_{\mathrm{x-only}}^{\mathrm{ALDA}}$, triangles down: $f_{\mathrm{xc}}^{\mathrm{ALDA}}$ using the parametrization of Ref. [40], diamonds: $f_{\mathrm{x-only}}^{\mathrm{TDOEP}}$ (Eq. 40)) in comparison with the values of a variational calculation (squares). The circles denote the quantum defects of the uncorrected Kohn-Sham eigenvalues.

Comparing the results of the single-pole approximation (SPA) in columns 4 and 6 to the solutions of the "full" matrix equations in columns 5 and 7, respectively, we see that there is very little change (from a few hundredth of a percent to at most one half percent) in the resulting excitation energies. Thus we conclude that in helium the single-pole approximation gives the dominant correction to the Kohn-Sham excitation spectrum.

Figure 1 shows the quantum defects obtained from the calculated excitation energies. Except for the $1P$ series, the results for the quantum defects obtained with the (x-only) TDOEP kernel (40) are closest to the exact values. Since expression (40) is the exact solution of the integral equation (36) for two-electron systems in the x-only limit, the remaining difference between the TDOEP results and the exact values can be attributed to the lack of correlation terms in $f_{\mathrm{x-only}}^{TDOEP}$. Their explicit incorporation (within ALDA) into f_{xc} reduces the singlet-triplet splitting, as can be seen from Table 2.

Table 2. Singlet-triplet separations in neutral helium calculated from the exact xc potential by using various approximate xc kernels. Calculated from Eq. (0.65), using the lowest 34 unoccupied orbitals of s and p symmetry. All values are in mHartrees.

State	ALDA xc[a]	ALDA x-only	TDOEP x-only	exact[b]
$2S$	32.7	42.2	45.2	29.3
$3S$	9.4	11.1	10.8	7.4
$4S$	4.0	4.7	4.3	2.9
$5S$	2.1	2.4	2.2	1.4
$6S$	1.3	1.4	1.2	0.8
$7S$	0.8	0.9	0.8	0.5
$8S$	0.6	0.6	0.5	0.3
$9S$	0.4	0.5	0.4	0.2
$2P$	6.6	16.7	15.6	9.3
$3P$	2.6	4.5	4.7	2.9
$4P$	1.1	1.8	2.0	1.3
$5P$	0.6	0.9	1.0	0.6
$6P$	0.3	0.5	0.6	0.4
$7P$	0.2	0.3	0.4	0.2
$8P$	0.1	0.2	0.3	0.2
$9P$	0.1	0.2	0.2	0.1
dev.[c]	0.7	2.0	2.0	

[a]Including correlation contributions in the form of Vosko, Wilk and Nusair [40].
[b]Taken from Ref. [38]
[c]Mean absolute deviation from the exact values

The TDOEP scheme offers a starting point for the construction of an approximate xc kernel, which is *not* based on the homogeneous electron gas. Work along the lines of improving the TDOEP kernels by the inclusion of suitable correlation contributions is in progress.

On the other hand, we agree with the authors of Ref. [42] that the inaccuracies introduced by *approximate* ground-state exchange-correlation *potentials* can be substantial. In the LDA and in the popular GGAs for instance, the highest occupied orbital eigenvalue is in error by about a factor of two, due to spurious self-interaction. There may be error cancellations for the lower Kohn-Sham eigenvalue differences, but in general one should not expect to get a reliable (Kohn-Sham) spectrum in LDA and GGAs, because the respective potentials have the wrong behavior for large r. In addition, this causes the number of (unoccupied) bound KS states to be *finite*. It is very unlikely that these defects will be cured by better approximations of f_{xc} alone, since the terms containing f_{xc} only give corrections to the underlying Kohn-Sham eigenvalue spectrum. Hence, the quantitiative calculation of excitation energies heavily depends on the accuracy of the ground-state potential employed.

APPENDIX
The TDOEP integral equation for the exchange-correlation kernel

Within the TDOEP the functional derivatives $\delta v_{\mathrm{xc}}/\delta\phi_{j\sigma}$ in (37) have to be extracted from the integral equation for the potential (21). To this end we rewrite the latter as

$$
\sum_{\sigma'} \int dt' \int d^3 r' \left\{ \tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') v_{xc\,\sigma'}(\mathbf{r}'t') \right.
$$
$$
\left. -i\,\delta_{\sigma\sigma'} \sum_{j,l} \left(u_{xc\,j\sigma'}(\mathbf{r}'t') - u^*_{xc\,l\sigma'}(\mathbf{r}'t') \right) \phi_{j\sigma'}(\mathbf{r}t)\phi^*_{j\sigma'}(\mathbf{r}'t') \; \phi_{l\sigma'}(\mathbf{r}'t')\phi^*_{l\sigma'}(\mathbf{r}t)\theta(t-t') \right\} = 0,
$$
(69)

where the functions $\tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}$ are defined in (35). We now act with $\delta/\delta\phi_{m\nu'}$ on Eq. (69) which yields a system of coupled integral equations

$$
\sum_{\sigma'} \int dt' \int d^3 r' \; \tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') \frac{\delta v_{xc\,\sigma'}(\mathbf{r}'t')}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')} =
$$
$$
\sum_{\sigma'} \int dt' \int d^3 r' \left(\frac{\delta}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')} \left\{ +i\,\delta_{\sigma\sigma'} \sum_{j,l} \left(u_{xc\,j\sigma'}(\mathbf{r}'t') - u^*_{xc\,l\sigma'}(\mathbf{r}'t') \right) \right. \right.
$$
$$
\left. \left. \times \; \phi_{j\sigma'}(\mathbf{r}t)\phi^*_{j\sigma'}(\mathbf{r}'t') \; \phi_{l\sigma'}(\mathbf{r}'t')\phi^*_{l\sigma'}(\mathbf{r}t)\theta(t-t') \right\} - \frac{\delta\tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t')}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')} v_{xc\,\sigma'}(\mathbf{r}'t') \right) . \quad (70)
$$

and similarly for $\delta/\delta\phi^*_{m\nu'}$. To make use of Eq. (70) we transform the integral equation (36) for f_{xc} by acting with $\tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}$ from the left

$$
\sum_{\sigma'\nu'} \int dt' \int d^3 r' \int d\tau' \int d^3 y' \; \tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') f^{OEP}_{xc\,\sigma'\nu'}(\mathbf{r}'t', \mathbf{y}'\tau')\tilde{\chi}_{\mathrm{s}\,\nu',\nu}(\mathbf{y}'\tau', \mathbf{y}\tau)
$$
$$
= \sum_{\sigma'\nu'} \int dt' \int d^3 r' \int d\tau' \int d^3 y' \; \sum_m \tilde{\chi}_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t')
$$
$$
\times \left[\frac{\delta v_{xc\,\sigma'}(\mathbf{r}'t')}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')} \frac{\delta\phi_{m\nu'}(\mathbf{y}'\tau')}{\delta v_\nu(\mathbf{y}\tau)} + \frac{\delta v_{xc\,\sigma'}(\mathbf{r}'t')}{\delta\phi^*_{m\nu'}(\mathbf{y}'\tau')} \frac{\delta\phi^*_{m\nu'}(\mathbf{y}'\tau')}{\delta v_\nu(\mathbf{y}\tau)} \right] .
$$
(71)

The functional derivatives $\delta\phi_{j\sigma'}/\delta v_\sigma$ are given by (34). Now we can insert (70) in (71) and obtain

$$\sum_{\sigma'\nu'}\int dt'\int d^3r'\int d\tau'\int d^3y'\;\chi^{(0)}_{\sigma\sigma'}(\mathbf{r}t,\mathbf{r}'t')f^{OEP}_{xc\,\sigma'\nu'}(\mathbf{r}'t',\mathbf{y}'\tau')\chi^{(0)}_{\nu',\nu}(\mathbf{y}'\tau',\mathbf{y}\tau)$$

$$=\sum_{\sigma'\nu'}\int dt'\int d^3r'\int d\tau'\int d^3y'\;\sum_{m}\Bigg[$$

$$\Bigg\{\Bigg(+i\delta_{\sigma\sigma'}\frac{\delta}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')}\sum_{j,l}\Big(u_{xc\,j\sigma'}(\mathbf{r}'t')-u^*_{xc\,l\sigma'}(\mathbf{r}'t')\Big)\,\phi_{j\sigma'}(\mathbf{r}t)\phi^*_{j\sigma'}(\mathbf{r}'t')$$

$$\times\;\phi_{l\sigma'}(\mathbf{r}'t')\phi^*_{l\sigma'}(\mathbf{r}t)\theta(t-t')\Bigg)-\frac{\delta\tilde{\chi}_{s\,\sigma\sigma'}(\mathbf{r}t,\mathbf{r}'t')}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')}v_{xc\,\sigma'}(\mathbf{r}'t')\Bigg\}\frac{\delta\phi_{m\nu'}(\mathbf{y}'\tau')}{\delta v_\nu(\mathbf{y}\tau)}$$

$$+\Bigg\{\Bigg(+i\delta_{\sigma\sigma'}\frac{\delta}{\delta\phi^*_{m\nu'}(\mathbf{y}'\tau')}\sum_{j,l}\Big(u_{xc\,j\sigma'}(\mathbf{r}'t')-u^*_{xc\,l\sigma'}(\mathbf{r}'t')\Big)\,\phi_{j\sigma'}(\mathbf{r}t)\phi^*_{j\sigma'}(\mathbf{r}'t')$$

$$\times\;\phi_{l\sigma'}(\mathbf{r}'t')\phi^*_{l\sigma'}(\mathbf{r}t)\theta(t-t')\Bigg)-\frac{\delta\tilde{\chi}_{s\,\sigma\sigma'}(\mathbf{r}t,\mathbf{r}'t')}{\delta\phi^*_{m\nu'}(\mathbf{y}'\tau')}v_{xc\,\sigma'}(\mathbf{r}'t')\Bigg\}\frac{\delta\phi^*_{m\nu'}(\mathbf{y}'\tau')}{\delta v_\nu(\mathbf{y}\tau)}\;\Bigg]_{\phi_{j\sigma}(t)=\phi^{(0)}_{j\sigma}(t)}.$$

$$(72)$$

Eq. (72) is whithin the OEP an exact equation defining the exchange-correlation kernel in terms of functional derivatives of the action functional A_{xc}. After performing the functional derivatives and inserting the stationary orbitals it takes the following form:

$$\sum_{\sigma'\nu'}\int dt'\int d^3r'\int d\tau'\int d^3y'\;\chi^{(0)}_{\sigma\sigma'}(\mathbf{r}t,\mathbf{r}'t')f^{OEP}_{xc\,\sigma'\nu'}(\mathbf{r}'t',\mathbf{y}'\tau')\chi^{(0)}_{\nu',\nu}(\mathbf{y}'\tau',\mathbf{y}\tau)$$

$$=\sum_{\sigma'\nu'}\delta_{\sigma\sigma'}\delta_{\nu'\nu}\int dt'\int d^3r'\int d\tau'\int d^3y'\;\theta(t-t')\theta(\tau'-\tau)\sum_{jlmk}\Bigg[$$

$$\Bigg\{\frac{1}{\phi^*_{j\sigma'}(\mathbf{r}'t')}\left(\frac{1}{\phi^*_{m\nu'}(\mathbf{y}'\tau')}\frac{\delta}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')}-\frac{1}{\phi_{k\nu'}(\mathbf{y}'\tau')}\frac{\delta}{\delta\phi^*_{k\nu'}(\mathbf{y}'\tau')}\right)\frac{\delta A_{xc}[\{\phi_{j\sigma}\}]}{\delta\phi_{j\sigma'}(\mathbf{r}'t')}-$$

$$\frac{1}{\phi_{l\sigma'}(\mathbf{r}'t')}\left(\frac{1}{\phi^*_{m\nu'}(\mathbf{y}'\tau')}\frac{\delta}{\delta\phi_{m\nu'}(\mathbf{y}'\tau')}-\frac{1}{\phi_{k\nu'}(\mathbf{y}'\tau')}\frac{\delta}{\delta\phi^*_{k\nu'}(\mathbf{y}'\tau')}\right)\frac{\delta A_{xc}[\{\phi_{j\sigma}\}]}{\delta\phi^*_{l\sigma'}(\mathbf{r}'t')}\Bigg\}$$

$$\times\;\tilde{F}_{\sigma'\,jl}(\mathbf{r}t,\mathbf{r}'t')\tilde{F}^*_{\nu'\,mk}(\mathbf{y}'\tau',\mathbf{y}\tau)\;\Bigg]_{\phi_{j\sigma}(t)=\phi^{(0)}_{j\sigma}(t)}$$

$$-\,i\theta(t-\tau)\delta_{\sigma\nu}\sum_{jlmk}\varphi_{j\sigma}(\mathbf{r})\varphi^*_{l\sigma}(\mathbf{r})\varphi_{m\sigma}(\mathbf{y})\varphi^*_{k\sigma}(\mathbf{y}\int d^3r'\Bigg\{$$

$$e^{-i(\epsilon_{k\sigma}-\epsilon_{m\sigma})(t-\tau)}\left(\frac{\delta_{jk}\,\varphi^*_{m\sigma}(\mathbf{r}')\varphi_{l\sigma}(\mathbf{r}')}{\epsilon_{l\sigma}-\epsilon_{m\sigma}+i\eta}\left[\Big(f_{m\sigma}-f_{k\sigma}\Big)v^{(0)}_{xc\,\sigma}(\mathbf{r}')-u^{(0)}_{xc\,m\sigma}(\mathbf{r}')\right]\right.$$

$$\left.-\frac{\delta_{lm}\varphi^*_{j\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r}')}{\epsilon_{k\sigma}-\epsilon_{j\sigma}+i\eta}\left[\Big(f_{m\sigma}-f_{k\sigma}\Big)v^{(0)}_{xc\,\sigma}(\mathbf{r}')+u^{(0)\,*}_{xc\,k\sigma}(\mathbf{r}')\right]\right)$$

$$+e^{-i(\epsilon_{j\sigma}-\epsilon_{l\sigma})(t-\tau)}\left(\frac{\delta_{jk}\,\varphi^*_{m\sigma}(\mathbf{r}')\varphi_{l\sigma}(\mathbf{r}')}{\epsilon_{l\sigma}-\epsilon_{m\sigma}+i\eta}\left[\Big(f_{j\sigma}-f_{l\sigma}\Big)v^{(0)}_{xc\,\sigma}(\mathbf{r}')+u^{(0)\,*}_{xc\,l\sigma}(\mathbf{r}')\right]\right.$$

$$\left.-\frac{\delta_{lm}\varphi^*_{j\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r}')}{\epsilon_{k\sigma}-\epsilon_{j\sigma}+i\eta}\left[\Big(f_{j\sigma}-f_{l\sigma}\Big)v^{(0)}_{xc\,\sigma}(\mathbf{r}')-u^{(0)}_{xc\,j\sigma}(\mathbf{r}')\right]\right)\Bigg\}.$$

$$(73)$$

where

$$\tilde{F}_{\sigma'\,jl}(\mathbf{r}t,\mathbf{r}'t')=\phi_{j\sigma'}(\mathbf{r}t)\phi^*_{j\sigma'}(\mathbf{r}'t')\phi_{l\sigma'}(\mathbf{r}'t')\phi^*_{l\sigma'}(\mathbf{r}t)\;.\tag{74}$$

Some simplicfication of this equation can be achieved for action functionals depending on the orbitals only through the spin density matrices $\Gamma_\sigma(\mathbf{r}t,\mathbf{r}'t') = \sum_j f_{j\sigma}\phi_{j\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}'t')$. In this case the OEP integral equations (21) for the stationary xc-potential and the exchange-correlation kernel $f_{\mathrm{xc}\,\sigma\sigma'}$, respectively, read as follows:

$$\int dt' \int d^3r' \int d^3z'\, \kappa_\sigma^{(0)}(\mathbf{r}t;\mathbf{r}',\mathbf{z}',t') \left(v_{xc\,\sigma}^{(0)}(\mathbf{r}'t')\delta(\mathbf{r}'-\mathbf{z}') - \left.\frac{\delta A_{xc}}{\delta\Gamma_\sigma(\mathbf{z}',\mathbf{r}';t')}\right|_{\phi^{(0)}} \right) = 0.$$

(75)

and

$$\int dt' \int d\tau' \int d^3r' \int d^3z \int d^3y' \int d^3z'\, \kappa_\sigma^{(0)}(\mathbf{r}t;\mathbf{z},\mathbf{r}',t')\, \kappa_\nu^{(0)\,\dagger}(\mathbf{z}',\mathbf{y}',\tau';\mathbf{y}\tau)$$

$$\times \left[f_{xc\,\sigma\nu}^{OEP}(\mathbf{r}'t',\mathbf{y}'\tau')\delta(\mathbf{z}-\mathbf{r}')\delta(\mathbf{z}'-\mathbf{y}') - \left.\frac{\delta^2 A_{xc}}{\delta\Gamma_\nu(\mathbf{y}',\mathbf{z}';\tau')\delta\Gamma_\sigma(\mathbf{r}',\mathbf{z};t')}\right|_{\phi_{j\sigma}(t)=\phi_{j\sigma}^{(0)}(t)} \right]$$

$$= -i\,\theta(t-\tau)\delta_{\sigma\nu} \sum_{jlmk} \varphi_{j\sigma}(\mathbf{r})\varphi_{l\sigma}^*(\mathbf{r})\varphi_{m\sigma}(\mathbf{y})\varphi_{k\sigma}^*(\mathbf{y})$$

$$\times \left\{ \left(\left(f_{m\sigma}-f_{k\sigma} \right) e^{-i(\epsilon_{k\sigma}-\epsilon_{m\sigma})(t-\tau)} + \left(f_{j\sigma}-f_{l\sigma} \right) e^{-i(\epsilon_{j\sigma}-\epsilon_{l\sigma})(t-\tau)} \right) \right.$$

$$\times \left(\frac{\delta_{jk}}{\epsilon_{l\sigma}-\epsilon_{m\sigma}+i\eta} < \varphi_{m\sigma} \mid v_{xc\,\sigma}^{(0)} - \left.\frac{\delta A_{xc}}{\delta\Gamma_\sigma}\right|_{\phi^{(0)}} \mid \varphi_{l\sigma} > \right.$$

$$\left.\left. - \frac{\delta_{lm}}{\epsilon_{k\sigma}-\epsilon_{j\sigma}+i\eta} < \varphi_{j\sigma} \mid v_{xc\,\sigma}^{(0)} - \left.\frac{\delta A_{xc}}{\delta\Gamma_\sigma}\right|_{\phi^{(0)}} \mid \varphi_{k\sigma} > \right) \right\}.$$

(76)

Here

$$\kappa_\sigma^{(0)}(\mathbf{r}t;\mathbf{z},\mathbf{r}',t') = i\sum_{jl} \left(f_{j\sigma}-f_{l\sigma} \right) \varphi_{j\sigma}(\mathbf{r})\varphi_{j\sigma}^*(\mathbf{z})\,\varphi_{l\sigma}(\mathbf{r}')\varphi_{l\sigma}^*(\mathbf{r})e^{-i(\epsilon_{j\sigma}-\epsilon_{l\sigma})(t-t')}\theta(t-t')$$

(77)

describes the density response of a noninteracting system to a nonlocal perturbation,

$$\kappa_\nu^{(0)\,\dagger}(\mathbf{z}',\mathbf{y}',\tau';\mathbf{y}\tau) =$$
$$-i\sum_{mk} \left(f_{m\sigma}-f_{k\sigma} \right) \varphi_{m\nu}^*(\mathbf{z}')\varphi_{m\nu}(\mathbf{y})\,\varphi_{k\nu}^*(\mathbf{y})\varphi_{k\nu}(\mathbf{y}')e^{-i(\epsilon_{k\nu}-\epsilon_{m\nu})(\tau'-\tau)}\theta(\tau'-\tau). \qquad (78)$$

is its adjoint and we adopted the notation

$$< \varphi_{j\sigma} \mid v_{xc\,\sigma}^{(0)} - \left.\frac{\delta A_{xc}}{\delta\Gamma_\sigma}\right|_{\phi^{(0)}} \mid \varphi_{l\sigma} >$$

$$= \int d^3r' \int d^3y'\, \varphi_{j\sigma}^*(\mathbf{y}') \left(v_{xc\,\sigma}^{(0)}(\mathbf{r}')\delta(\mathbf{r}'-\mathbf{y}') - \left.\frac{\delta A_{xc}}{\delta\Gamma_\sigma(\mathbf{r}',\mathbf{y}')}\right|_{\phi^{(0)}} \right) \varphi_{l\sigma}(\mathbf{r}'). \qquad (79)$$

We remark that the KLI approximation scheme amounts to replacing κ^0 by

$$\kappa_\sigma^{(0)\,\mathrm{KLI}}(\mathbf{r}t;\mathbf{r}',\mathbf{z}',t') = i\sum_{jk} \left(f_{j\sigma}+f_{k\sigma}-2\delta_{j\,k}f_{j\sigma} \right) \varphi_{j\sigma}(\mathbf{r})\varphi_{j\sigma}^*(\mathbf{r})\,\varphi_{k\sigma}(\mathbf{z}')\varphi_{k\sigma}^*(\mathbf{r})\delta(t-t') \quad (80)$$

and that the approximation (38) corresponds to skip here the term $-2\delta_{j\,k}f_{j\sigma}$. These manipulations can also be applied on the lhs of the integral equation (76). One is also tempted to neglect the rhs of Eq. (76) because the here entering combination of matrix elements (79) should be forced to be small by Eq. (75). In this way one gets fully analytic approximations for $f_{\mathrm{xc}\,\sigma\sigma'}$. The resulting expressions are however still quite complicated. In the applications discussed in this paper they perform also not better than the simple formula (39).

18

Acknowledgments

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