ORBITAL FUNCTIONALS IN STATIC AND TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

E.K.U. Gross, T. Kreibich, M. Lein, and M. Petersilka

Institut für Theoretische Physik
Universität Würzburg
Am Hubland
D-97074 Würzburg
Germany

INTRODUCTION

Density functional theory (DFT) is among the most powerful quantum mechanical methods for calculating the electronic structure of atoms, molecules and solids [1, 2, 3]. In this introduction we present a brief overview of DFT, putting particular emphasis on the appearance of orbital functionals. To describe the electronic many-body system, we have to deal with the Hamiltonian

$$\hat{H} = \hat{T} + \hat{W}_{\text{Clb}} + \hat{V} \tag{1}$$

where

$$\hat{T} = \sum_{i=1}^{N} \Big(-\frac{\hbar^2}{2m} \nabla_i^2 \Big) \tag{2}$$

denotes the kinetic-energy operator,

$$\hat{W}_{\text{Clb}} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{3}$$

represents the Coulomb interaction between the electrons, and

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i) \tag{4}$$

contains all external potentials acting on the electrons, typically the Coulomb potentials of the nuclei.

Modern DFT is based on the celebrated theorem of Hohenberg and Kohn (HK) [4] which, for systems with nondegenerate ground states, may be summarized by the following three statements:

1. The ground-state density n uniquely determines the ground-state wave function $\Psi[n]$ as well as the external potential $v = v[n]$ (up to within an irrelevant additive constant). As a consequence, any observable of a static many-particle system is a functional of its ground-state density.

2. The total-energy functional
$$E_{v_0}[n] := \langle\Psi[n]|\hat{T} + \hat{W}_{\mathrm{Clb}} + \hat{V}_0|\Psi[n]\rangle \tag{5}$$
of a particular physical system characterized by the external potential v_0 is equal to the exact ground-state energy E_0 if and only if the exact ground-state density n_0 is inserted. For all other densities $n \neq n_0$, the inequality
$$E_0 < E_{v_0}[n] \tag{6}$$
holds. Consequently, the exact ground-state density n_0 and the exact ground-state energy E_0 can be determined by solving the Euler-Lagrange equation
$$\frac{\delta}{\delta n(\mathbf{r})} E_{v_0}[n] = 0. \tag{7}$$

3. The functional
$$F[n] := \langle\Psi[n]|\hat{T} + \hat{W}_{\mathrm{Clb}}|\Psi[n]\rangle \tag{8}$$
is universal in the sense that it is independent of the external potential v_0 of the particular system considered, i.e. it has the same functional form for all systems with a fixed particle-particle interaction ($\hat{W}_{\mathrm{Clb}}$ in our case).

The Hohenberg-Kohn theorem can be viewed as an *exact* reformulation of quantum mechanics, only using the one-particle electronic density instead of the much more complicated many-body wave function. In practice, however, one has to resort to approximations for the functional $F[n]$. A systematic way for constructing such approximations arises from an expansion of $F[n]$ in powers of the Coulomb-coupling constant e^2:
$$F[n] = F^{(0)}[n] + e^2 F^{(1)}[n] + e^4 F^{(2)}[n] + ... \tag{9}$$
Here, the zeroth-order term is given by the kinetic energy of non-interacting particles,
$$F^{(0)}[n] = T_{\mathrm{s}}[n]\,. \tag{10}$$
In first order one obtains the Hartree- and exchange-energy functionals,
$$e^2 F^{(1)}[n] = \frac{e^2}{2}\int d^3r \int d^3r'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{x}}[n]\,, \tag{11}$$
and the remaining terms define the correlation-energy functional,
$$\sum_{i=2}^{\infty}(e^2)^i F^{(i)}[n] =: E_{\mathrm{c}}[n]\,. \tag{12}$$
Using this decomposition, the HK total-energy functional (5) can be written as
$$E_{v_0}[n] = T_{\mathrm{s}}[n] + \int d^3r\, n(\mathbf{r})v_0(\mathbf{r}) + \frac{e^2}{2}\int d^3r \int d^3r'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{xc}}[n]\,, \tag{13}$$

where E_x and E_c have been merged, yielding the so-called exchange-correlation functional E_xc.

Eq. (13) contains two non-trivial density functionals: the non-interacting kinetic-energy functional $T_\mathrm{s}[n]$ and the exchange-correlation-energy functional $E_\mathrm{xc}[n]$. In historical retrospective we may identify three generations of density functional schemes which may be classified according to the level of approximations used for the universal functionals $T_\mathrm{s}[n]$ and $E_\mathrm{xc}[n]$.

In the *first generation* of DFT, *explicitly* density-dependent functionals were used to approximate both $T_\mathrm{s}[n]$ and $E_\mathrm{xc}[n]$. The simplest approximation of this kind is the Thomas-Fermi model, where $E_\mathrm{xc}[n]$ is neglected completely and $T_\mathrm{s}[n]$ is approximated by

$$T_\mathrm{s}^\mathrm{TF}[n] = \frac{3}{10}\left(3\pi^2\right)^{2/3}\frac{\hbar^2}{m}\int d^3r\, n(\mathbf{r})^{5/3}\,. \tag{14}$$

For functionals of this type the HK variational principle (7) can be used directly, leading to equations of the Thomas-Fermi type. As these equations only contain one basic variable, namely the density $n(\mathbf{r})$ of the system, they are readily solved numerically. The results obtained in this way, however, are generally of only moderate accuracy.

The major advance of the *second generation* of DFT which was introduced by Kohn and Sham [5] lies in the use of the *exact* functional for the kinetic energy of non-interacting particles:

$$T_\mathrm{s}^\mathrm{exact}[n] = \sum_{\substack{i=1\\ \text{lowest } \varepsilon_i}}^{N} \int d^3r\, \varphi_i^*[n](\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\varphi_i[n](\mathbf{r})\,, \tag{15}$$

where $\{\varphi_i\}$ are suitably chosen single-particle orbitals (see below).

Although the expression (15) depends explicitly on single-particle orbitals, it is indeed a functional of the density. This can be seen by applying the HK theorem to a system of non-interacting particles: Since the proof of the HK theorem does not depend on the particular form of the particle-particle interaction, it is valid for *any* given interaction $\hat{W}$, in particular also for $\hat{W} \equiv 0$, i.e. for non-interacting systems described by Hamiltonians of the form

$$\hat{H}_\mathrm{s} = \hat{T} + \hat{V}_\mathrm{s}. \tag{16}$$

Hence the potential $v_\mathrm{s}(\mathbf{r})$ is uniquely determined by the ground-state density:

$$v_\mathrm{s}(\mathbf{r}) = v_\mathrm{s}[n](\mathbf{r}). \tag{17}$$

As a consequence, all single-particle orbitals satisfying the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_\mathrm{s}[n](\mathbf{r})\right)\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r}) \tag{18}$$

are functionals of the density as well:

$$\varphi_j(\mathbf{r}) = \varphi_j[n](\mathbf{r}). \tag{19}$$

Therefore, *any* functional depending explicitly on the set of single-particle orbitals – like the expression (15) for the kinetic energy – is an (implicit) functional of the density, provided the orbitals come from a local (i.e. multiplicative) potential.

Treating the kinetic-energy functional exactly, the total-energy functional employed in the second generation of DFT becomes:

$$E_{v_0}^{\mathrm{KS}}[n] = T_{\mathrm{s}}^{\mathrm{exact}}[n] + \int d^3r\, v_0(\mathbf{r})n(\mathbf{r}) + \frac{e^2}{2}\int d^3r \int d^3r'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{xc}}[n]\,, \tag{20}$$

where only the xc energy has to be approximated.

In order to calculate the minimizing density of the energy functional (20), we now determine the potential v_{s} of the non-interacting system (16) in such a way that it yields the correct ground-state density of the interacting many-body system:

$$n(\mathbf{r}) = \sum_{\substack{i=1 \\ \text{lowest } \varepsilon_i}}^{N} |\varphi_i(\mathbf{r})|^2\,, \tag{21}$$

where the orbitals satisfy the single-particle Schrödinger equation (18). If such a system exists, the local effective potential $v_{\mathrm{s}}[n]$ is uniquely determined and can be obtained from the HK variational principle: Plugging Eq. (20) into Euler equation (7) and using Eq. (18), we obtain

$$v_{\mathrm{s}}[n](\mathbf{r}) = v_0(\mathbf{r}) + e^2\int d^3r'\, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\mathrm{xc}}[n](\mathbf{r}) \tag{22}$$

where we have defined the xc potential as

$$v_{\mathrm{xc}}[n](\mathbf{r}) := \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}. \tag{23}$$

The single-particle Schrödinger equation (18), together with the effective potential (22) and the prescription for calculating the density (21) are known as Kohn-Sham equations. In practice, these equations have to be solved self-consistently employing approximate but explicitly density-dependent functionals for $E_{\mathrm{xc}}[n]$. The simplest and surprisingly successful approximation is the well-known local-density approximation (LDA):

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int d^3r\, n(\mathbf{r})\epsilon_{\mathrm{xc}}(n(\mathbf{r}))\,, \tag{24}$$

where $\epsilon_{\mathrm{xc}}(n)$ is the known xc energy per particle of the homogeneous electron gas of constant density n. More recently, density-gradient-dependent approximations – the so-called generalized gradient approximations (GGAs),

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int d^3r\, n(\mathbf{r})\epsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \ldots)\,, \tag{25}$$

have become increasingly popular and give excellent results for a wide range of atomic, molecular and solid-state systems.

Finally, in the *third generation of DFT*, one employs, in addition to the *exact* expression for T_{s}, also the *exact* expression for the exchange energy, given by

$$E_{\mathrm{x}}^{\mathrm{exact}}[n] = -\frac{e^2}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{j,k=1}^{N_\sigma}\int d^3r \int d^3r'\, \frac{\varphi_{j\sigma}^*(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{26}$$

Only the correlation part of $E_{\mathrm{xc}}[n]$ needs to be approximated in this approach. In contrast to the conventional second-generation KS scheme, the third generation allows for the treatment of explicitly orbital-dependent functionals for E_{c} as well, giving more flexibility in the construction of such approximations. Therefore, this scheme naturally lends itself for the use of correlation-energy functionals derived from many-body-perturbation theory. There the correlation energy is given as the sum of all higher-order diagrams in terms of the non-interacting Greens function, which itself is a simple functional of single-particle orbitals.

The central equation in the third generation of DFT is still the KS equation (18). The difference between the second and the third generation lies in the level of approximation to the xc energy. As a consequence of the orbital dependence of E_{xc} in the third generation of DFT the calculation of $v_{\mathrm{xc}}[n](\mathbf{r})$ from Eq. (23) is somewhat more complicated. It has to be determined from an integral equation, known as the optimized effective potential (OEP) equation [6, 7]. The OEP integral equation as well as a semi-analytical method of approximately solving it will be discussed in the following section, along with a selection of numerical results.

THE OEP METHOD

Derivation of the OEP integral equation

We are going to derive the OEP equations for the spin-dependent version of DFT [8, 9], where the basic variables are the spin-up and spin-down densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, respectively. They are obtained by self-consistently solving the single-particle Schrödinger equations (atomic units are used from now on)

$$\left(-\frac{\nabla^2}{2}+v_{\mathrm{s}\,\sigma}[n_\uparrow,n_\downarrow](\mathbf{r})\right)\varphi_{j\sigma}(\mathbf{r})=\varepsilon_{j\sigma}\varphi_{j\sigma}(\mathbf{r})\,,\qquad j=1,\ldots N_\sigma\,,\qquad \sigma=\uparrow,\downarrow \tag{27}$$

where

$$n_\sigma(\mathbf{r})=\sum_{i=1}^{N_\sigma}|\varphi_{i\sigma}(\mathbf{r})|^2. \tag{28}$$

The Kohn-Sham potentials $v_{\mathrm{s}\,\sigma}(\mathbf{r})$ may be written in the usual way as

$$v_{\mathrm{s}\,\sigma}(\mathbf{r})=v_0(\mathbf{r})+\int d^3r'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+v_{\mathrm{xc}\,\sigma}(\mathbf{r}), \tag{29}$$

where

$$n(\mathbf{r})=\sum_{\sigma=\uparrow,\downarrow}n_\sigma(\mathbf{r})\,, \tag{30}$$

and

$$v_{\mathrm{xc}\,\sigma}(\mathbf{r}):=\frac{\delta E_{\mathrm{xc}}\left[n_\uparrow,n_\downarrow\right]}{\delta n_\sigma(\mathbf{r})}. \tag{31}$$

If the xc-energy functional is now given as an explicit (approximate) functional of spin orbitals and therefore only an *implicit* functional of the spin densities $n_\uparrow$ and $n_\downarrow$,

$$E_{\mathrm{xc}}^{\mathrm{OEP}}=E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]\,, \tag{32}$$

the evaluation of the functional derivative in Eq. (31) is somewhat more complicated. In order to calculate the xc potentials, we use the chain rule for functional derivatives to obtain

$$
\begin{aligned}
v_{\mathrm{xc}\,\sigma}^{\mathrm{OEP}}(\mathbf{r}) &= \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}\left[\{\varphi_{j\tau}\}\right]}{\delta n_\sigma(\mathbf{r})} \\
&= \sum_{\alpha=\uparrow,\downarrow} \sum_{\beta=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int d^3r' \int d^3r'' \left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}\left[\{\varphi_{j\tau}\}\right]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta v_{\mathrm{s}\,\beta}(\mathbf{r}'')} + \mathrm{c.c.} \right) \frac{\delta v_{\mathrm{s}\,\beta}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})}\,.
\end{aligned}
\tag{33}
$$

The last term on the right-hand side is the inverse χ_{s}^{-1} of the static density response function of a system of non-interacting particles

$$
\chi_{\mathrm{s}\,\alpha\beta}\left(\mathbf{r},\mathbf{r}'\right) := \frac{\delta n_\alpha(\mathbf{r})}{\delta v_{\mathrm{s}\,\beta}(\mathbf{r}')}. \tag{34}
$$

This quantity is diagonal with respect to the spin variables so that Eq. (33) reduces to

$$
v_{\mathrm{xc}\,\sigma}^{\mathrm{OEP}}(\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int d^3r' \int d^3r'' \left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}\left[\{\varphi_{j\tau}\}\right]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r}'')} + \mathrm{c.c.} \right) \chi_{\mathrm{s}\,\sigma}^{-1}\left(\mathbf{r}'',\mathbf{r}\right). \tag{35}
$$

Acting with the response operator (34) on both sides of Eq. (35) one obtains

$$
\int d^3r'\; v_{\mathrm{xc}\,\sigma}^{\mathrm{OEP}}(\mathbf{r}')\chi_{\mathrm{s}\,\sigma}\left(\mathbf{r}',\mathbf{r}\right) = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int d^3r'\; \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}\left[\{\varphi_{j\tau}\}\right]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r})} + \mathrm{c.c.} \tag{36}
$$

To further evaluate this equation, we note that the first functional derivative on the right-hand side of Eq. (36) is readily computed once an explicit expression for $E_{\mathrm{xc}}^{\mathrm{OEP}}$ in terms of single-particle orbitals is given. The remaining functional derivative on the right-hand side of Eq. (36) can be exactly calculated by first-order perturbation theory. This yields

$$
\frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r})} = \delta_{\alpha,\sigma} \sum_{\substack{k=1\\k\neq i}}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r}')\varphi_{k\sigma}^*(\mathbf{r})}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}} \varphi_{i\sigma}(\mathbf{r}). \tag{37}
$$

Using this equation, the response function

$$
\chi_{\mathrm{s}\,\alpha\beta}\left(\mathbf{r},\mathbf{r}'\right) = \frac{\delta}{\delta v_{\mathrm{s}\,\beta}(\mathbf{r}')} \left(\sum_{i=1}^{N_\alpha} \varphi_{i\alpha}^*(\mathbf{r})\varphi_{i\alpha}(\mathbf{r}) \right) \tag{38}
$$

is readily expressed in terms of the orbitals as

$$
\chi_{\mathrm{s}\,\sigma}\left(\mathbf{r},\mathbf{r}'\right) = \sum_{i=1}^{N_\sigma} \sum_{\substack{k=1\\k\neq i}}^{\infty} \frac{\varphi_{i\sigma}^*(\mathbf{r})\varphi_{k\sigma}(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{i\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}} + \mathrm{c.c.} \tag{39}
$$

Inserting (37) and (39) in Eq. (36), we obtain the standard form of the OEP integral equation:

$$
\sum_{i=1}^{N_\sigma} \int d^3r' \varphi_{i\sigma}^*(\mathbf{r}') \left(v_{\mathrm{xc}\,\sigma}^{\mathrm{OEP}}(\mathbf{r}') - u_{\mathrm{xc}i\sigma}(\mathbf{r}') \right) G_{\mathrm{s}i\sigma}\left(\mathbf{r}',\mathbf{r}\right) \varphi_{i\sigma}(\mathbf{r}) + \mathrm{c.c.} = 0 \tag{40}
$$

where

$$u_{\mathrm{xc}i\sigma}(\mathbf{r}) := \frac{1}{\varphi^*_{i\sigma}(\mathbf{r})} \frac{\delta E^{\mathrm{OEP}}_{\mathrm{xc}}\left[\{\varphi_{j\tau}\}\right]}{\delta \varphi_{i\sigma}(\mathbf{r})} \tag{41}$$

and

$$G_{\mathrm{s}i\sigma}\left(\mathbf{r},\mathbf{r}'\right) := \sum_{\substack{k=1\\k\neq i}}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r})\varphi^*_{k\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}}. \tag{42}$$

This integral equation has to be solved simultaneously with the KS equation (27).

The derivation of the OEP integral equation (40) described here was given by Shaginyan [10] and by Görling and Levy [11]. It is important to note that the same expression results [6, 7, 12, 13, 14, 15] if one demands that the local single-particle potential appearing in Eq. (27) be the *optimized* one yielding orbitals minimizing the total-energy functional, i.e., that

$$\left.\frac{\delta E^{\mathrm{OEP}}_{v_0}}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r})}\right|_{v_{\mathrm{s}\,\sigma}=v^{\mathrm{OEP}}} = 0. \tag{43}$$

This equation is the historical origin [6] of the name *optimized effective potential.* The name might be somewhat misleading, since *no additional* optimization for the potential is used. Indeed, as was first pointed out by Perdew and co-workers [16, 17], Eq. (43) is equivalent to the HK variational principle. This is most easily seen by applying the functional chain rule to Eq. (43) yielding

$$0 = \frac{\delta E^{\mathrm{OEP}}_{v_0}}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r})} = \sum_{\alpha} \int d^3r' \, \frac{\delta E^{\mathrm{OEP}}_{v_0}}{\delta n_\alpha(\mathbf{r}')} \frac{\delta n_\alpha(\mathbf{r}')}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r})}. \tag{44}$$

Once again, the last term on the right-hand side of Eq. (44) can be identified with the static KS response function (34). Hence, acting with the inverse response operator on Eq. (44) leads to the HK variational principle

$$0 = \frac{\delta E^{\mathrm{OEP}}_{v_0}}{\delta n_\sigma(\mathbf{r})}. \tag{45}$$

Approximation of Krieger, Li, and Iafrate

The OEP method discussed in the preceding paragraph opens up a way for using orbital-dependent functionals within the KS scheme. However, as a price to pay, one has to solve an integral equation self-consistently with the KS equation. Due to the rather large computational effort involved in this scheme, it has not been used extensively. Indeed, full solutions of the OEP integral equation have been achieved so far only for systems of high symmetry such as spherical atoms [13, 7, 18, 19, 20]. For solids, further numerical simplifications have been employed, such as the atomic sphere approximation [21, 22, 23, 24] or the use of pseudopotentials for the core electrons [25]. Clearly, practical applications of the OEP scheme to a greater variety of systems require some simplification.

Krieger, Li, and Iafrate (KLI) have suggested an approximation leading to a highly accurate but numerically tractable scheme preserving many important properties of the exact OEP method [13, 26, 21, 27, 28, 18, 19, 12, 29]. It is most easily derived by replacing the energy denominator of the Greens function (42) by a single constant, i.e.

$$G_{\mathrm{s}i\sigma}(\mathbf{r}',\mathbf{r}) \approx \frac{1}{\Delta\varepsilon}\left(\delta(\mathbf{r}'-\mathbf{r}) - \varphi_{i\sigma}(\mathbf{r})'\varphi^*_{i\sigma}(\mathbf{r})\right) . \tag{46}$$

Substituting this into the OEP integral equation (40) leads to an approximate equation, known as the KLI approximation:

$$v^{\mathrm{KLI}}_{\mathrm{xc}\,\sigma}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \left[u_{\mathrm{xc}i\sigma}(\mathbf{r}) + (\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \bar{u}_{\mathrm{xc}i\sigma})\right] + c.c. \tag{47}$$

where $\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma}$ is defined as

$$\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} := \int d^3r \varphi^*_{i\sigma}(\mathbf{r}) v^{\mathrm{KLI}}_{\mathrm{xc}\,\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \,. \tag{48}$$

In contrast to the full OEP equation (40), the KLI equation, still being an integral equation, can be solved explicitly in terms of the orbitals $\{\varphi_{i\sigma}\}$: Multiplying Eq. (47) by $|\varphi_{j\sigma}(\mathbf{r})|^2$ and integrating over space yields

$$\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}j\sigma} = \bar{v}^{\mathrm{S}}_{\mathrm{xc}j\sigma} + \sum_{i=1}^{N_\sigma - 1} N_{ji\sigma} \left(\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \frac{1}{2} \left(\bar{u}_{\mathrm{xc}i\sigma} + \bar{u}^*_{\mathrm{xc}i\sigma} \right) \right) , \tag{49}$$

where

$$\bar{v}^{\mathrm{S}}_{\mathrm{xc}j\sigma} := \int d^3r \, \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \frac{1}{2} \left(u_{\mathrm{xc}i\sigma}(\mathbf{r}) + u^*_{\mathrm{xc}i\sigma}(\mathbf{r}) \right) \tag{50}$$

and

$$N_{ji\sigma} := \int d^3r \, \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{n_\sigma(\mathbf{r})}. \tag{51}$$

The term corresponding to the highest occupied orbital $\varphi_{N_\sigma \sigma}$ has been excluded from the sum in Eq. (49) because $\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}N_\sigma\sigma} = \bar{u}_{\mathrm{xc}N_\sigma\sigma}$ [13]. The remaining unknown constants $(\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \bar{u}_{\mathrm{xc}i\sigma})$ are determined by the linear equation

$$\sum_{i=1}^{N_\sigma - 1} (\delta_{ji} - N_{ji\sigma}) \left(\bar{v}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \frac{1}{2} \left(\bar{u}_{\mathrm{xc}i\sigma} + \bar{u}^*_{\mathrm{xc}i\sigma} \right) \right) = \left(\bar{v}^{\mathrm{S}}_{\mathrm{xc}j\sigma} - \frac{1}{2} \left(\bar{u}_{\mathrm{xc}j\sigma} + \bar{u}^*_{\mathrm{xc}j\sigma} \right) \right) \tag{52}$$

with $j = 1, \dots N_\sigma - 1$. Solving Eq. (52) and substituting the result into Eq. (47), we obtain an explicitly orbital dependent functional. The approximation (46) might appear rather crude. However, it can be justified by a much more rigorous derivation, showing that the KLI equation can be interpreted as a mean-field type approximation [13, 12].

We finally mention that the OEP and KLI methods have recently been generalized to relativistic situations [30, 31, 32], which arise e.g. in the treatment of heavier systems.

Rigorous properties of the OEP and KLI methods

To conclude this section, we summarize some exact properties of the OEP and KLI methods.

1. No spurious self-interactions

   Since both the OEP and the KLI method are constructed to deal with orbital-dependent functionals, one can employ xc-energy functionals – like the expression for the exact exchange-energy functional – which exactly cancel the spurious self-interaction contained in the Hartree term.

Table 1. Various self-consistently calculated x-only results for the Ar atom. All values in atomic units.

	OEP	KLI	B88	xPW91	xLDA
E_{tot}	-526.8122	-526.8105	-526.7998	-526.7710	-524.5174
ε_{1s}	-114.4524	-114.4279	-114.1890	-114.1887	-113.7159
ε_{2s}	-11.1534	-11.1820	-10.7911	-10.7932	-10.7299
ε_{2p}	-8.7339	-8.7911	-8.4107	-8.4141	-8.3782
ε_{3s}	-1.0993	-1.0942	-0.8459	-0.8481	-0.8328
ε_{3p}	-0.5908	-0.5893	-0.3418	-0.3441	-0.3338
ε_{4s}	-0.1607	-0.1616	-0.0102	-0.0122	-0.0014
$< r^2 >$	1.4465	1.4467	1.4791	1.4876	1.4889
$< r^{-1} >$	3.8736	3.8738	3.8731	3.8729	3.8648
$n(0)$	3839.7	3832.6	3847.3	3847.0	3818.7

2. Asymptotics

   If the exact expression for the exchange energy is used, both the OEP and the KLI potential fall of as $-1/r$ as $r \to \infty$ (for finite systems) [13, 33], thus reflecting the proper cancelation of self-interaction errors. One has to emphasize that this holds true for all orbitals (i.e. for the occupied as well as the unoccupied orbitals) because the KS potential is the same for all orbitals. In contrast, the Hartree-Fock (HF) potential falls off like $-1/r$ only for the occupied, but *not* for the unoccupied orbitals, leading to much too weakly bound virtual HF orbitals. As a consequence, the OEP orbitals and orbital energies can serve as a much better starting point for the calculation of excited state properties.

3. Derivative discontinuities

   If one considers the exact xc potential as a function of the particle number N, it exhibits discontinuities at integer values of N [34]. This has important consequences for the values of band gaps in insulators of semi-conductors (for a detailed description see e.g. [2]). Neither the LDA nor the GGAs can reproduce these discontinuities. To date, the OEP and the KLI potential are the only known approximations of $v_{\text{xc}}(\mathbf{r})$ reproducing this feature.

Selected results

We begin with a comparison of x-only results. The x-only limit of the xc-energy functional is given by the exact Fock term, Eq. (26). As explained in the preceding section, the OEP method then provides the corresponding exchange potential $v_{\text{x}}^{\text{exact}}(\mathbf{r})$ and therefore represents the exact implementation of x-only DFT. Consequently it provides a benchmark for testing approximate exchange-energy functionals employed within the Kohn-Sham scheme. In Table 1 we show, as a typical example, various results for the argon atom obtained with different x-only methods. Besides the OEP and KLI methods employing the exact exchange-energy functional (26) described above, we also list results from conventional KS-DFT obtained with the approximations due to Becke (B88) [35], Perdew and Wang (PW91) [36], and from the well-known x-only LDA approximation. The KLI results given in the second column of Table 1 clearly demonstrate the high quality of the KLI approximation as all results differ only slightly from the exact OEP ones. For all standard DFT methods, the disagreement is much more pronounced, especially for the highest occupied orbital energies and even more so for the unoccupied ones. As already mentioned, the reason for this lies in the

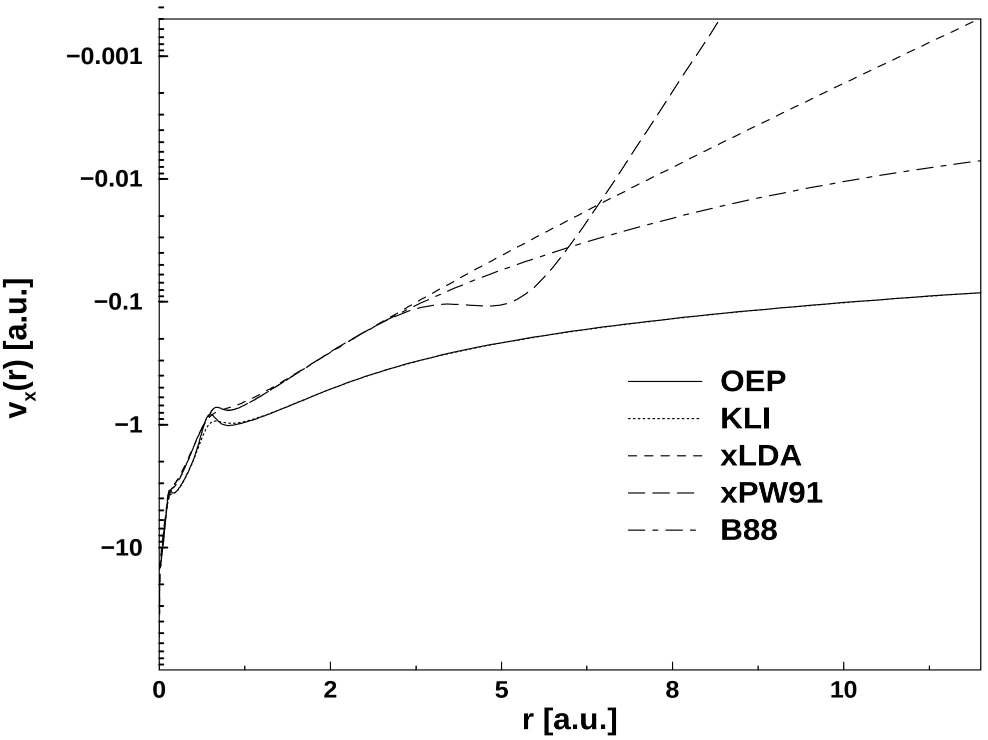

Figure 1. Exchange potentials $v_{\mathrm{x}}(r)$ for Ar from various self-consistent x-only calculations in the valence region.

asymptotic behavior of the corresponding exchange potentials: While both the OEP and the KLI potential yield the correct $-1/r$ decay for large r and therefore become indistinguishable in this region, the potentials derived from the conventional density-dependent approximations fall off much too rapidly as can be seen from Figure 1.

If one aims at the description of heavier elements one should take relativistic effects into account. As shown in Ref. [37, 31, 32], the derivation based on relativistic DFT (for the case of vanishing external magnetic fields) leads to the same expressions for the OEP integral equation (40) and the KLI approximation (47), only with the KS spin orbitals replaced by relativistic KS spinors. Fully relativistic calculations then yield results similar to the non-relativistic case: The data obtained from the relativistic x-only OEP and KLI methods agree closely with each other, while the relativistic LDA [38, 39] and GGA [40] approximations yield larger errors. This becomes evident from Table 2, where we list the relativistic contribution to the total energy, i.e. the difference between the total energy obtained from fully relativistic and non-relativistic calculations: The second column of Table 2 shows that the relativistic version of the KLI method introduces almost no additional errors, thus maintaining the quality of the non-relativistic KLI approximation. In contrast, the conventional density-dependent approximations – in addition to the deviations already known from the non-relativistic case – are not able to reproduce the effects induced by relativity with the same degree of accuracy.

The inclusion of correlation effects into the OEP scheme is straightforward, as already indicated in the introduction. As we will demonstrate in this section, the correlation-energy functional developed by Colle and Salvetti (CS) [41, 42] is well suited for atomic systems. This functional has been obtained through a series of approximations starting from a Jastrow-type ansatz for the correlated total wave function . It

Table 2. Relativistic Contribution to the total energy calculated from various self-consistent x-only approximations. $\bar{\Delta}$ denotes the mean absolute deviation and $\bar{\delta}$ the average relative deviation (in 0.1 percent) from the exact ROEP values. All numbers in atomic units. Taken from [31].

	ROEP	RKLI	RB88	xRLDA
He	0.000	0.000	0.000	0.000
Be	0.003	0.003	0.003	0.002
Ne	0.145	0.145	0.145	0.138
Mg	0.320	0.320	0.321	0.308
Ar	1.867	1.867	1.867	1.821
Ca	2.953	2.953	2.952	2.888
Zn	16.770	16.770	16.779	16.555
Kr	36.820	36.820	36.822	36.432
Sr	46.553	46.553	46.552	46.092
Pd	106.526	106.526	106.526	105.715
Cd	128.243	128.243	128.243	127.323
Xe	214.858	214.858	214.825	213.522
Ba	252.222	252.221	252.176	250.725
Yb	676.551	676.549	676.590	673.785
Hg	1240.513	1240.511	1240.543	1236.349
Rn	1736.144	1736.142	1736.151	1730.890
Ra	1934.770	1934.768	1934.781	1929.116
No	3953.155	3953.151	3953.979	3944.569
$\bar{\Delta}$		0.001	0.056	1.788
$\bar{\delta}$		0.009	1.14	33.7

Table 3. Total absolute ground-state energies for first-row atoms from various self-consistent calculations. Quantum chemistry (QC) values from [45]. $\bar{\Delta}$ denotes the mean absolute deviation from the exact non-relativistic values [46]. All numbers in Hartrees. Taken from [15] and modified.

	KLICS	xcLDA	BLYP	PW91	QC	exact
He	2.9033	2.8346	2.9071	2.9000	2.9049	2.9037
Li	7.4829	7.3433	7.4827	7.4742	7.4743	7.4781
Be	14.6651	14.4465	14.6615	14.6479	14.6657	14.6674
B	24.6564	24.3525	24.6458	24.6299	24.6515	24.6539
C	37.8490	37.4683	37.8430	37.8265	37.8421	37.8450
N	54.5905	54.1344	54.5932	54.5787	54.5854	54.5893
O	75.0717	74.5248	75.0786	75.0543	75.0613	75.067
F	99.7302	99.1112	99.7581	99.7316	99.7268	99.734
Ne	128.9202	128.2299	128.9730	128.9466	128.9277	128.939
$\bar{\Delta}$	0.0047	0.3813	0.0108	0.0114	0.0045	

may be written in spin-polarized form as [43]

$$\begin{aligned} E_{\mathrm{c}}^{\mathrm{CS}}[\{\varphi_{j\tau}\}] = & - ab \int d^3r \; \gamma(\mathbf{r})\xi(\mathbf{r}) \left[\sum_{\sigma} n_{\sigma}(\mathbf{r}) \sum_{i} |\nabla \varphi_{i\sigma}(\mathbf{r})|^2 \; - \; \frac{1}{4} |\nabla n(\mathbf{r})|^2 \right. \\ & \left. - \frac{1}{4} \sum_{\sigma} n_{\sigma}(\mathbf{r}) \triangle n_{\sigma}(\mathbf{r}) \; + \; \frac{1}{4} n(\mathbf{r}) \triangle n(\mathbf{r}) \right] \\ & - a \int d^3r \; \gamma(\mathbf{r}) \frac{n(\mathbf{r})}{\eta(\mathbf{r})}, \end{aligned} \tag{53}$$

where

$$\gamma(\mathbf{r}) = 4 \, \frac{n_{\uparrow}(\mathbf{r}) n_{\downarrow}(\mathbf{r})}{n(\mathbf{r})^2}, \tag{54}$$

$$\eta(\mathbf{r}) = 1 + d \, n(\mathbf{r})^{-\frac{1}{3}}, \tag{55}$$

$$\xi(\mathbf{r}) = \frac{n(\mathbf{r})^{-\frac{5}{3}} e^{-cn(\mathbf{r})^{-\frac{1}{3}}}}{\eta(\mathbf{r})}. \tag{56}$$

The constants a, b, c, and d are given by

$$\begin{aligned} a &= 0.04918, \quad & b &= 0.132, \\ c &= 0.2533, \quad & d &= 0.349. \end{aligned}$$

In Table 3 we compare total ground state energies of first-row atoms calculated self-consistently with various approximations. The first column, headed KLICS, shows the results from the KLI method employing the exact exchange-energy functional (26) plus the CS correlation-energy functional, while the next columns show conventional KS results. The latter were obtained with an LDA functional using the parametrization of the correlation energy of a homogeneous electron gas by Perdew and Wang [44]; the x-energy functional due to Becke [35] combined with the c-energy functional of Lee, Yang, and Parr [43], denoted as BLYP; and the generalized gradient approximation due to Perdew and Wang [36], referred to as PW91. The quantum chemistry values, headed QC, are from a highly accurate complete basis set quadratic CI calculation using atomic pair natural orbitals [45]. The exact non-relativistic energies, i.e. the experimental values with relativistic effects subtracted, have been taken from [46]. The mean absolute deviations of the calculated from the exact values, denoted by $\bar{\Delta}$, clearly show that the KLICS approach is significantly more accurate than the conventional KS methods and almost as accurate as the traditional QC scheme. We emphasize that the numerical effort involved in the KLICS scheme for atoms is only slightly higher than in the LDA and GGA schemes.

Apart from total energies, the highest occupied orbital energies, which should be equal to the exact ionization potential in an exact implementation of DFT, are much closer to the experimental ionization potentials in the KLICS scheme than in the conventional KS approaches. This is shown in Table 4: All the numbers of the conventional KS calculations are off by about 100%, which can be traced back to the wrong asymptotic behavior of the xc-potentials in these approximations. Again, only the KLICS approximation provides the correct $-1/r$ decay for $r \to \infty$, which results in much more reliable predictions for quantities depending strongly on this region of space. As shown here, this is of crucial importance for the ionization potential, but it also becomes important, when excitation energies are calculated from DFT, as we will show later.

Table 4. Ionization potentials from the highest occupied orbital energy of neutral atoms. $\bar{\Delta}$ denotes the mean absolute deviation from the experimental values, taken from [49]. All values in Hartrees. Taken from [15] and modified.

	KLICS	xcLDA	BLYP	PW91	experiment
He	0.945	0.570	0.585	0.583	0.903
Li	0.200	0.116	0.111	0.119	0.198
Be	0.329	0.206	0.201	0.207	0.343
B	0.328	0.151	0.143	0.149	0.305
C	0.448	0.228	0.218	0.226	0.414
N	0.579	0.309	0.297	0.308	0.534
O	0.559	0.272	0.266	0.267	0.500
F	0.714	0.384	0.376	0.379	0.640
Ne	0.884	0.498	0.491	0.494	0.792
Na	0.189	0.113	0.106	0.113	0.189
Mg	0.273	0.175	0.168	0.174	0.281
Al	0.222	0.111	0.102	0.112	0.220
Si	0.306	0.170	0.160	0.171	0.300
P	0.399	0.231	0.219	0.233	0.385
S	0.404	0.228	0.219	0.222	0.381
Cl	0.506	0.305	0.295	0.301	0.477
Ar	0.619	0.382	0.373	0.380	0.579
$\bar{\Delta}$	0.030	0.176	0.183	0.177	

Table 5. Calculated bond lengths of the closed-shell-first-row dimers and hydrides. HF values taken from [50]. Experimental values from [51] except where noted. All values in atomic units. Taken from [48].

	KLICS	PW91	xcLDA	HF	experiment
H_2	1.378	1.414	1.446	1.379	1.401[a]
Li_2	5.086	5.153	5.120	5.304	5.051
Be_2	-[b]	4.588	4.522	-	4.63[c]
C_2	2.306	2.367	2.354	-	2.3481
N_2	1.998	2.079	2.068	2.037	2.074
F_2	2.465	2.669	2.615	2.542	2.6682
LiH	2.971	3.030	3.030	3.092	3.0154
BH	2.274	2.356	2.373	-	2.3289
FH	1.684	1.756	1.761	1.722	1.7325

[a] Exact value from [52].

[b] There is no local minimum in the electronic potential curve.

[c] From [53].

The feasibility of the KLI approximation for more complex systems has been shown recently [47, 48, 32] by x-only and KLICS calculations for diatomic molecules. To this end, we have implemented these approaches in our fully numerical basis-set-free code for diatomic molecules. For comparison, we have also performed calculations employing the conventional LDA [44] and the PW91 functional for E_{xc}.

In Table 5 we display results for the bond lengths. It is apparent that the KLICS scheme leads to equilibrium distances which are generally too short, an effect present

Table 6. Absolute total ground-state energies of the closed-shell-first-row dimers and hydrides calculated at the bond lengths given in Table 5. Estimates for exact values calculated using dissociation energies from Table 7 and nonrelativistic, infinite nuclear mass atomic ground-state energies from [54]. All numbers in atomic units. Taken from [48].

	KLICS	PW91	xcLDA	exact
H_2	1.171444	1.170693	1.137692	1.174448[a]
Li_2	14.9982	14.9819	14.7245	14.9954
Be_2	29.3197[b]	29.3118	28.9136	29.3385
C_2	75.7736	75.8922	75.2041	75.922
N_2	109.4683	109.5449	108.6959	109.5424
F_2	199.4377	199.5699	198.3486	199.5299
LiH	8.0723	8.0625	7.9189	8.0705
BH	25.2857	25.2688	24.9770	25.29
FH	100.4241	100.4715	99.8490	100.4596

[a] Exact value from [52].

[b] Calculated at the experimental bond length 4.63 a.u.

in the HF approximation as well. Most notable is the fact that the potential energy curve of Be_2 displays no local minimum in this approximation. Good agreement with experiment is found only for Li_2. Except for this molecule, the PW91 values are clearly superior.

Total absolute ground-state energies calculated at the bond lengths given in Table 5 are shown in Table 6. For the lighter molecules H_2, Li_2, Be_2, LiH, and BH the KLICS and PW91 results are of the same good quality, yielding errors of a few mHartrees. For the heavier molecules, however, the KLICS results are worse. Being the simplest approximation, it is not surprising that the LDA gives values for the total energies which show the largest errors.

Apart from H_2 and LiH, the dissociation energies obtained within the KLICS approach are disappointing, as may be seen in Table 7. In most cases, the magnitude is underestimated considerably and for Be_2 and F_2 even the wrong sign is obtained. Since the corresponding *atomic* ground-state energies given in the previous section are of excellent quality, the error must be due to correlation effects present in molecules only. In particular, the left-right correlation error [56] well-known in HF theory also occurs in DFT when the exact Fock expression (26) for E_x is employed. Apparently, this error is not sufficiently corrected for by the CS functional. The LDA and PW91 results are clearly much better, the latter reducing the over-binding tendencies of the former.

In the asymptotic region, however, the KLICS xc potential is of better quality than the conventional xc potentials: In Table 8 we list the absolute values of the highest occupied molecular orbital energies, which, in *exact* DFT, should be identical with the ionization potentials of the systems under consideration. It is evident that the conventional KS approaches represented by the LDA and PW91 functionals yield results which are typically 40 percent too high, while the KLICS values are much closer to the experimental results. As for atomic systems, this fact may be traced back to the correct asymptotic behavior of the KLICS xc potential for large r.

Table 7. Dissociation energies of the closed-shell-first-row dimers and hydrides calculated at the bond lengths given in Table 5. HF values taken from [50]. All numbers in mHartrees. Taken from [48].

	KLICS	PW91	xcLDA	HF	experiment
H_2	171.444	167.665	180.270	121.0	174.475[b]
Li_2	32.4	33.5	37.9	3.5	39.3[c]
Be_2	-10.5[a]	15.9	20.6	-	3.8[c]
C_2	75.6	239.2	267.5	-	232[d]
N_2	287.3	387.5	427.1	167.5	364.0[d]
F_2	-22.7	106.7	126.2	-54.7	62.1[d]
LiH	89.4	86.8	96.9	48.4	92.4[d]
BH	129.3	137.4	145.8	-	135[e]
FH	193.9	238.4	259.1	130.8	225.7[e]

[a] Calculated at the experimental bond length 4.63 a.u.
[b] Exact value from [52].
[c] From [53].
[d] From [51].
[e] From [55].

Table 8. Absolute values for the highest occupied orbital energies of the closed-shell-first-row dimers and hydrides calculated at the bond lengths given in Table 5. Experimental values are the ionization potentials taken from [51]. All numbers in atomic units. Taken from [48].

	KLICS	PW91	xcLDA	experiment
H_2	0.621563	0.382656	0.373092	0.5669
Li_2	0.1974	0.1187	0.1187	0.18
Be_2	0.2560[a]	0.1678	0.1660	-
C_2	0.4844	0.2942	0.2987	0.4465
N_2	0.6643	0.3804	0.3826	0.5726
F_2	0.6790	0.3512	0.3497	0.5764
LiH	0.3237	0.1621	0.1612	0.283[b]
BH	0.3692	0.2058	0.2041	0.359
FH	0.6803	0.3567	0.3594	0.5894

[a] Calculated at the experimental bond length 4.63 a.u.
[b] From [57].

Density functional theory can be generalized to allow for the description of time-dependent many-particle systems [58, 59, 60, 61]. An atom being placed in the focus of a laser field constitutes an example of such a time-dependent system. Owing to rapid experimental progress in the field of laser physics, femto-second laser pulses of very high intensity have become available in recent years. The electric field produced in such pulses can reach or even exceed the strength of the static nuclear Coulomb field as experienced by an electron on the lowest Bohr orbit. If an atomic system is placed in the focus of such a pulse, one observes a wealth of new phenomena [62, 63, 64] which cannot be explained by traditional perturbation theory. In principle, the solution of the fully interacting time-dependent Schrödinger equation is required. The aim of a density-functional description in this intensity regime is to "replace" the solution of the full time-dependent Schrödinger equation by the solution of time-dependent Kohn-Sham equations.

Traditional spectroscopy, on the other hand, mainly aims at the interaction of low-intensity laser fields with matter, in order to probe properties of the undisturbed system. Theoretical descriptions in this intensity regime are typically based on the calculation of the linear density response $n_1(\mathbf{r}, t)$ to a weak external perturbation

$$v_1(\mathbf{r}, t) = \mathcal{E} z \cos(\omega t) \tag{57}$$

describing an electric dipole field of amplitude $\mathcal{E}$ and frequency ω, linearly polarized along the z-direction. The dynamical polarizability then follows from

$$\alpha(\omega) = -\frac{1}{\mathcal{E}} \int d^3r \, z \, n_1(\mathbf{r}, \omega) \, . \tag{58}$$

This quantity is directly related to the photo-absorption cross section $\sigma(\omega)$ via

$$\sigma(\omega) = -\frac{4\pi\omega}{c} \Im \alpha(\omega) \, . \tag{59}$$

Time-dependent Hohenberg-Kohn-Sham formalism

In contrast to the ground-state formalism [4], where the existence proof relies on the Rayleigh-Ritz principle for the energy, the proof for time-dependent systems [58] is based directly on the Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi(t) = \hat{H}(t) \Psi(t) \tag{60}$$

where

$$\hat{H}(t) = \hat{T} + \hat{W}_{\mathrm{Clb}} + \hat{V}(t) \, . \tag{61}$$

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

$$\Psi(t_0) = \Psi_0 \tag{62}$$

under the influence of different external potentials of the form

$$\hat{V}(t) = \sum_{i=1}^{N} v(\mathbf{r}_i, t) \, . \tag{63}$$

Following the proof first given by Runge and Gross [58], one can formulate the following Hohenberg-Kohn-type theorem: The densities $n(\mathbf{r},t)$ and $n'(\mathbf{r},t)$ evolving from a common initial state $\Psi_0 = \Psi(t_0)$ under the influence of two potentials $v(\mathbf{r},t)$ and $v'(\mathbf{r},t)$ are always different provided that the potentials differ by more than a purely time-dependent ($\mathbf{r}$-independent) function:

$$v(\mathbf{r},t) \neq v'(\mathbf{r},t) + c(t)\,.^{*} \tag{64}$$

To prove this theorem, the potentials v and v' are required to be expandable in Taylor series about the initial time t_0. The condition (64) then guarantees that there exists some (lowest-order) k where the Taylor coefficients $v_k(\mathbf{r}) = \partial^k/\partial t^k v(\mathbf{r},t)\big|_{t_0}$ and $v'_k(\mathbf{r}) = \partial^k/\partial t^k v'(\mathbf{r},t)\big|_{t_0}$ differ by more than a constant. Using the equation of motion for the expectation value of the paramagnetic current density operator and the continuity equation, one arrives at the central equation of the proof:

$$\left(\frac{\partial}{\partial t}\right)^{k+2} (n(\mathbf{r},t) - n'(\mathbf{r}t))\Bigg|_{t=t_0} = \nabla\cdot(n(\mathbf{r},t_0)\nabla(v_k(\mathbf{r}) - v'_k(\mathbf{r}))\ . \tag{65}$$

It can be shown that the right-hand side of (65) cannot vanish identically. Hence the densities $n(\mathbf{r},t)$ and $n'(\mathbf{r},t)$ will become different infinitesimally later than t_0. The detailed proof and the formulation of precise conditions for the external potentials can be found in [59]. An extension of the Runge-Gross proof to the spin-dependent situation was formulated by Liu and Vosko [65].

Note that the right-hand side of Eq. (65) is linear in $v_k(\mathbf{r}) - v'_k(\mathbf{r})$. 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 ensures the invertibility of time-dependent linear response operators.

The uniqueness of the external potential reproducing a v-representable density (i.e. a density evolving out of a given initial state under the influence of an external potential v) can be established for *any fixed* particle-particle interaction, in particular also for $\hat{W}_{\text{Clb}} \equiv 0$ (this can be seen from Equation (65), in which the the particle-particle interaction does not occur). Hence, given a non-interacting v-representable density $n(\mathbf{r},t)$, the potential $v_{\text{s}}[n](\mathbf{r},t)$ leading to this density in a non-interacting system is uniquely determined. Assuming that the density of the interacting system of interest is simultaneously non-interacting v-representable, it can be obtained from

$$n(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2 \tag{66}$$

with orbitals $\phi_{j\sigma}(\mathbf{r},t)$ satisfying the time-dependent Kohn-Sham equation

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_{\text{s}}[n](\mathbf{r},t)\right)\phi_j(\mathbf{r},t) \quad . \tag{67}$$

Usually, the single-particle potential v_{s} is written as

$$v_{\text{s}}[n](\mathbf{r},t) = v(\mathbf{r},t) + \int d^3r'\,\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r},t)\,, \tag{68}$$

where $v(\mathbf{r},t)$ is the external time-dependent field. Equation (68) *defines* the time-dependent xc potential. In practice, this quantity has to be approximated.

---

[*] In analogy to the ground-state formalism, where the potentials are required to differ by more than a constant, the condition (64) ensures that the resulting wave functions $\Psi(t)$ and $\Psi'(t)$ differ by more than just a purely time-dependent phase factor.

One has to emphasize that the time-dependent Kohn-Sham (TDKS) scheme does *not* follow from a variational principle, but rather from the basic 1-1 mapping (applied to non-interacting particles) and the assumption of non-interacting v-representability.

Like in static DFT, the great advantage of the time-dependent Kohn Sham scheme lies in its computational simplicity compared to other methods such as time-dependent Hartree-Fock or time-dependent configuration interaction [66–73]. In contrast to time-dependent Hartree-Fock, the effective single-particle potential v_s is a *local* potential, i.e., a multiplicative operator in configuration space.

It is important to keep in mind that in the time-dependent case the 1–1 correspondence between potentials and densities can be established only for a *fixed* initial many-body state Ψ_0. Consequently, $v[n]$ and $v_{\mathrm{xc}}[n]$ implicitly depend on the initial many-body wave function and on the initial Kohn-Sham Slater determinant. However, for a large class of systems, namely those where both Ψ_0 and the initial KS Slater determinant are non-degenerate ground states, the Kohn-Sham potential is indeed a functional of the density *alone*. This is because any non-degenerate ground state Ψ_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.

Approximations of the time-dependent exchange-correlation potential

Adiabatic Local Density Approximation The simplest possible approximation of the time-dependent xc potential is the so-called *time-dependent* or *"adiabatic" local density approximation* (ALDA) [59]. It was first introduced in semiconductor physics by T. Ando [74] and later, for finite systems, by Zangwill and Soven [75]. The ALDA employs the functional form of the static LDA with a time-dependent density:

$$v_{\mathrm{xc}}^{\mathrm{ALDA}}[n](\mathbf{r},t) = v_{\mathrm{xc}}^{\mathrm{hom}}(n(\mathbf{r},t)) = \frac{d}{d\rho}\left(\rho\epsilon_{\mathrm{xc}}^{\mathrm{hom}}(\rho)\right)\Big|_{\rho=n(\mathbf{r},t)} . \tag{69}$$

Here $\epsilon_{\mathrm{xc}}^{\mathrm{hom}}$ is the xc energy per particle of the homogeneous electron gas. Parameterizations of this quantity can be found in [76, 44]. By its very definition, the ALDA can be expected to be a good approximation only for nearly homogeneous densities, i.e., for functions $n(\mathbf{r},t)$ that are slowly varying both spatially and temporally. It will turn out, however, that the ALDA gives rather accurate results even for rapidly varying densities.

Time-Dependent Optimized Effective Potential Like in the stationary case, the optimized effective potential method offers a viable route to go beyond the local density approximation. In particular, it offers a clear cut way to construct self-interaction-free functionals. In order to derive a time-dependent generalization [77] of the OEP we consider an N-electron system subject to a potential of the form

$$v_{\mathrm{ext}\,\sigma}(\mathbf{r},t) = \begin{cases} v_{0\sigma}(\mathbf{r}) & ; \quad t < t_0 \\ v_{0\sigma}(\mathbf{r}) + v_{1\sigma}(\mathbf{r},t) & ; \quad t \geq t_0 \end{cases} \tag{70}$$

For all times until t_0, the system 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 until an arbitrary later time t_1. The construction of the optimized local effective potential starts with the quantum mechanical action

$$A[\phi_{j\sigma}] = \sum_{\sigma}\sum_{j}^{N_\sigma}\int_{-\infty}^{t_1} dt \int d^3r\, \phi^*_{j\sigma}(\mathbf{r}t)\left(i\,\partial/\partial t + \nabla^2/2\right)\phi_{j\sigma}(\mathbf{r}t)$$
$$-\sum_{\sigma}\int_{-\infty}^{t_1} dt \int d^3r\, n_\sigma(\mathbf{r}t) v_{\mathrm{ext}\,\sigma}(\mathbf{r}t) - \frac{1}{2}\int_{-\infty}^{t_1} dt \int d^3r \int d^3r'\, \frac{n(\mathbf{r}t)n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} - A_{\mathrm{xc}}[\phi_{j\sigma}] \quad (71)$$

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 expression [78]

$$A_{\mathrm{x}} = -\frac{1}{2}\sum_{\sigma}\sum_{i,j}^{N_\sigma}\int_{-\infty}^{t_1} dt \int d^3r \int d^3r'\, \phi^*_{i\sigma}(\mathbf{r}'t)\phi_{j\sigma}(\mathbf{r}'t)\phi_{i\sigma}(\mathbf{r}t)\phi^*_{j\sigma}(\mathbf{r}t) \,/\, |\mathbf{r}-\mathbf{r}'| \quad . \qquad (72)$$

The orbitals are solutions of the spin-dependent TDKS equation

$$i\frac{\partial}{\partial t}\phi_{j\sigma}(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_{\mathrm{s}\sigma}[n](\mathbf{r},t)\right)\phi_{j\sigma}(\mathbf{r},t) \quad . \qquad (73)$$

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 $v_{\mathrm{s}\,\sigma}(\mathbf{r}t)$ has to be determined in such a way that the $\{\phi_{j\sigma}(\mathbf{r}t)\}$, resulting from Eq. (67), render the total action functional $A[\phi_{j\sigma}]$ stationary. Therefore, we have to solve the following variational problem:

$$\frac{\delta A[\phi_{j\sigma}]}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r}t)} = \sum_{\sigma'}\int_{-\infty}^{+\infty} dt' \int d^3r' \sum_{j}^{N_{\sigma'}}\left(\frac{\delta A[\phi_{j\sigma}]}{\delta\phi_{j\sigma'}(\mathbf{r}'t')}\frac{\delta\phi_{j\sigma'}(\mathbf{r}'t')}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r}t)} + \frac{\delta A[\phi_{j\sigma}]}{\delta\phi^*_{j\sigma'}(\mathbf{r}'t')}\frac{\delta\phi^*_{j\sigma'}(\mathbf{r}'t')}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r}t)}\right) = 0\,. \qquad (74)$$

The functional derivative of A with respect to the orbitals is given by

$$\frac{\delta A[\phi_{j\sigma}]}{\delta\phi_{j\sigma}(\mathbf{r}'t')} = \left[v_{\mathrm{xc}\,\sigma}(\mathbf{r}'t') - u_{\mathrm{xc}\,j\sigma}(\mathbf{r}'t')\right]\phi^*_{j\sigma}(\mathbf{r}'t')\,\theta(t_1 - t')\,, \qquad (75)$$

with the abbreviation

$$u_{\mathrm{xc}\,j\sigma}(\mathbf{r}t) = \frac{1}{\phi^*_{j\sigma}(\mathbf{r}t)}\frac{\delta A_{\mathrm{xc}}[\phi_{j\sigma}]}{\delta\phi_{j\sigma}(\mathbf{r}t)}\,. \qquad (76)$$

$\theta(x)$ denotes the usual step function (1 for $x > 0$, 0 for $x < 0$). The functional derivative $\delta A/\delta\phi^*_{j\sigma}$ is just the complex conjugate of expression (75). From first-order perturbation theory, we can read off the functional derivative

$$\frac{\delta\phi_{j\sigma'}(\mathbf{r}'t')}{\delta v_{\mathrm{s}\,\sigma}(\mathbf{r}t)} = i\delta_{\sigma\sigma'}\sum_{k=1}^{\infty}\phi^*_{k\sigma}(\mathbf{r}t)\phi_{j\sigma}(\mathbf{r}t)\phi_{k\sigma}(\mathbf{r}'t')\,\theta(t_1 - t)\,\theta(t - t') \qquad (77)$$

and the complex conjugate expression for $\delta\phi^*_{j\sigma'}/\delta v_{\mathrm{s}\,\sigma}$. Insertion of Eqs. (75) and (77) in the variational equation (74) results in the time-dependent OEP (TDOEP) integral equation for the local exchange-correlation potential $v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)$:

$$\int_{-\infty}^{t_1} dt' \int d^3r' \left(iK_\sigma(\mathbf{r}t,\mathbf{r}'t')\sum_{j}^{N_\sigma}\phi_{j\sigma}(\mathbf{r}t)\phi^*_{j\sigma}(\mathbf{r}'t')\left[v_{\mathrm{xc}\,\sigma}(\mathbf{r}'t') - u_{\mathrm{xc}\,j\sigma}(\mathbf{r}'t')\right] + c.c.\right) = 0\,. \qquad (78)$$

The kernel $K_\sigma(\mathbf{r}t, \mathbf{r}'t') = \sum_{k=1}^{\infty} \phi^*_{k\sigma}(\mathbf{r}t)\phi_{k\sigma}(\mathbf{r}'t')\, \theta(t-t')$ is identical with the Green's function of the system.

The TDOEP scheme is now complete: the integral equation (78) has to be solved for $v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)$ simultaneously with the Kohn-Sham equation (73).

Clearly, the full TDOEP scheme is computationally extremely demanding. It is therefore highly desirable to construct approximations of $v_{\mathrm{xc}\,\sigma}(\mathbf{r}t)$ which are *explicit* functionals of the orbitals $\{\phi_{j\sigma}\}$. Similar manipulations to those developed by KLI for the stationary case [79, 12], lead to the so-called TDKLI expression [77]

$$\begin{aligned}
\tilde{v}_{\mathrm{xc}\,\sigma}(\mathbf{r}t) &= \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)\, \frac{1}{2}\left(u_{\mathrm{xc}\,j\sigma}(\mathbf{r}t) + u^*_{\mathrm{xc}\,j\sigma}(\mathbf{r}t)\right) \\
&+ \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t) \left[\overline{\tilde{v}}_{\mathrm{xc}\,j\sigma}(t) - \frac{1}{2}\left(\overline{u}_{\mathrm{xc}\,j\sigma}(t) + \overline{u}^*_{\mathrm{xc}\,j\sigma}(t)\right)\right] \\
&+ \frac{i}{4n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} \nabla^2 n_{j\sigma}(\mathbf{r}t) \int_{-\infty}^{t} dt' \left(\overline{u}_{\mathrm{xc}\,j\sigma}(t') - \overline{u}^*_{\mathrm{xc}\,j\sigma}(t')\right) \, . \qquad (79)
\end{aligned}$$

The tilde indicates that this is only an approximate solution of the TDOEP equation (78) and the over-bar is a shorthand notation for the orbital average, i.e. $\overline{\tilde{v}}_{\mathrm{xc}\,j\sigma}(t) = \int d^3r\, n_{j\sigma}(\mathbf{r},t)\tilde{v}_{\mathrm{xc}\,\sigma}(\mathbf{r},t)$. The last term of Eq. (79) vanishes identically for a large class of exchange-correlation functionals A_{xc}. This includes all functionals which depend on $\{\phi_{j\sigma}\}$ only through the combinations $\phi_{j\sigma}(\mathbf{r},t)\phi^*_{j\sigma}(\mathbf{r}',t)$ (such as the exact x-only functional, Eq. (72)). Eq. (79) is still an integral equation for $\tilde{v}_{\mathrm{xc}\,\sigma}$. In contrast to the full TDOEP equation it can be solved analytically [80]: Multiplying Eq. (79) by $n_{k\sigma}(\mathbf{r}t)$ and integrating over all space yields

$$\overline{\tilde{v}}_{\mathrm{xc}\,k\sigma}(t) = \overline{w}_{\mathrm{xc}\,k\sigma}(t) + \sum_j^{N_\sigma} N_{kj\sigma}(t)\overline{\tilde{v}}_{\mathrm{xc}\,j\sigma}(t)\, , \qquad (80)$$

where

$$\begin{aligned}
w_{\mathrm{xc}\,\sigma}(\mathbf{r}t) &= \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)\, \frac{1}{2}\left(u_{\mathrm{xc}\,j\sigma}(\mathbf{r}t) + u^*_{\mathrm{xc}\,j\sigma}(\mathbf{r}t)\right) \\
&- \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t) \left[\frac{1}{2}\left(\overline{u}_{\mathrm{xc}\,j\sigma}(t) + \overline{u}^*_{\mathrm{xc}\,j\sigma}(t)\right)\right] \\
&+ \frac{i}{4n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} \nabla^2 n_{j\sigma}(\mathbf{r}t) \int_{-\infty}^{t} dt' \left(\overline{u}_{\mathrm{xc}\,j\sigma}(t') - \overline{u}^*_{\mathrm{xc}\,j\sigma}(t')\right) \qquad (81)
\end{aligned}$$

and

$$N_{kj\sigma}(t) = \int d^3r\, \frac{n_{k\sigma}(\mathbf{r}t)n_{j\sigma}(\mathbf{r}t)}{n_\sigma(\mathbf{r}t)} \quad . \qquad (82)$$

The solution of Eq. (80) for $\overline{\tilde{v}}_{\mathrm{xc}\,j\sigma}(t)$ requires inversion of the $N_\sigma \times N_\sigma$ matrix $A_{kj\sigma}(t) = \delta_{kj} - N_{kj\sigma}(t)$ and leads to

$$\overline{\tilde{v}}_{\mathrm{xc}\,j\sigma}(t) = \sum_k^{N_\sigma} \left(A^{-1}_\sigma(t)\right)_{jk} \overline{w}_{\mathrm{xc}\,k\sigma}(t) \quad . \qquad (83)$$

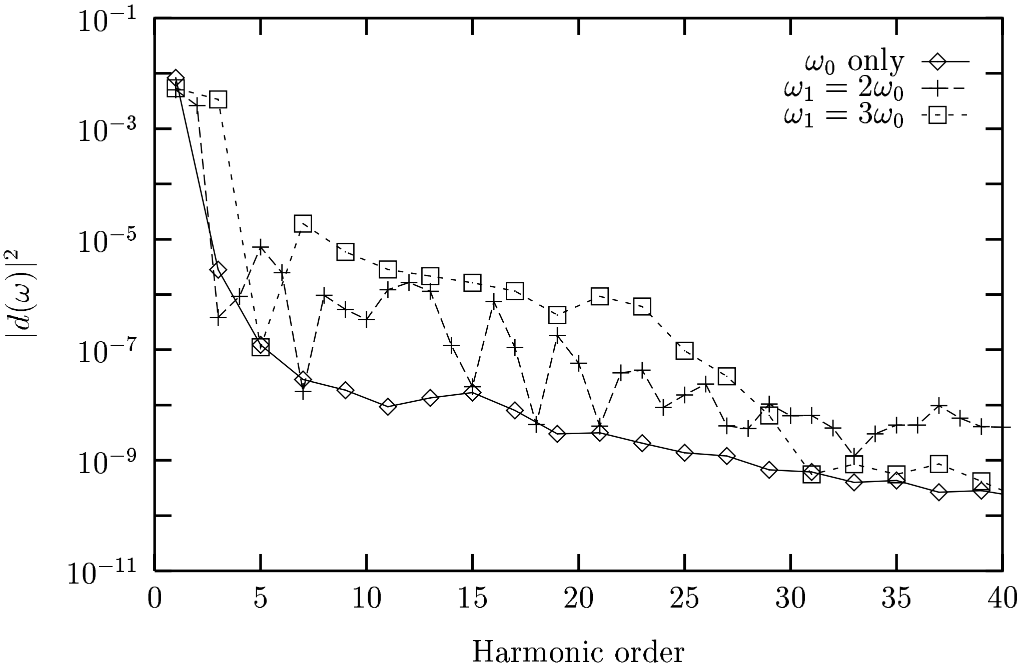

Figure 2. Harmonic spectra of helium resulting from a one–color calculation and from two two–color calculations. One of the latter includes the second and the other includes the third harmonic in addition to the fundamental frequency. The laser parameters used are $\lambda = 616$ nm and $I = 7.0 \times 10^{14}$ W/cm^2.

By substitution of Eq. (83) into Eq. (79), $\tilde{v}_{\mathrm{xc}\,\sigma}(\mathbf{r}t)$ is obtained as an explicit functional of the orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$.

The TDOEP scheme has been successfully applied to the non-perturbative description of atoms [81, 82, 83] and clusters [84, 85, 86] in strong laser pulses. In Fig. 2 we show the harmonic generation spectrum of the He atom in a two-color laser pulse [87].

Time-dependent Kohn-Sham equations in the linear-response regime

If the external field intensity is low, it is sufficient to consider only changes of the time-dependent density which are *linear* in the applied field. Within the framework of time-dependent density-functional theory, a formally exact representation of the linear spin-density response $n_{1\sigma}(\mathbf{r}, t)$ of interacting electrons can be derived [88] in terms of the response function χ_s of the corresponding (non-interacting) Kohn-Sham system:

$$n_{1\,\sigma}(\mathbf{r}, t) = \sum_{\sigma'} \int dt' \int d^3r'\, \chi_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r}, t, \mathbf{r}', t')\, v_{\mathrm{s},1\,\sigma'}(\mathbf{r}', t')\,. \tag{84}$$

$v_{\mathrm{s},1}$ is the linearized time-dependent KS potential

$$\begin{aligned} v_{\mathrm{s},1\,\sigma}(\mathbf{r}, t) \, &= v_{1\sigma}(\mathbf{r}, t) + \sum_{\sigma'} \int d^3r'\, \frac{n_{1\sigma'}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \\ &+ \sum_{\sigma'} \int d^3r' \int dt'\, f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r}, t, \mathbf{r}', t')\, n_{1\sigma'}(\mathbf{r}', t')\,. \end{aligned} \tag{85}$$

It contains the external perturbation $v_{1\sigma}$ and the Hartree- and exchange-correlation contributions to first order in the perturbing potential $v_{1\sigma}$. The so-called time-dependent xc kernel

$$f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r},t,\mathbf{r}',t') := \left.\frac{\delta v_{\mathrm{xc}\,\sigma}[n_\uparrow,n_\downarrow](\mathbf{r},t)}{\delta n_{\sigma'}(\mathbf{r}',t')}\right|_{n_{0\uparrow},n_{0\downarrow}} \tag{86}$$

is a functional of the initial ground-state densities. Combining Eqs. (84) and (85) and taking the Fourier transform with respect to time, the *exact* frequency-dependent linear density response is seen to be

$$\begin{aligned} n_{1\sigma}(\mathbf{r},\omega) &= \sum_\nu \int d^3y\,\chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r},\mathbf{y};\omega)v_{1\nu}(\mathbf{y},\omega) \\ &+ \sum_{\nu\nu'}\int d^3y\int d^3y'\chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r},\mathbf{y};\omega)\left(\frac{1}{|\mathbf{y}-\mathbf{y}'|}+f_{\mathrm{xc}\,\nu\nu'}[n_0](\mathbf{y},\mathbf{y}';\omega)\right)n_{1\nu'}(\mathbf{y}',\omega)\,. \end{aligned} \tag{87}$$

The Kohn-Sham response function χ_{s} is readily expressed in terms of the static unperturbed Kohn-Sham orbitals $\varphi_{k\sigma}$:

$$\chi_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) = \delta_{\sigma\sigma'}\sum_{j,k}(f_{k\sigma}-f_{j\sigma})\frac{\varphi_{j\sigma}(\mathbf{r})\varphi^*_{k\sigma}(\mathbf{r})\varphi^*_{j\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r}')}{\omega-(\epsilon_{j\sigma}-\epsilon_{k\sigma})+i\eta}\,. \tag{88}$$

Here, $(f_{k\sigma}, f_{j\sigma})$ are the occupation numbers (0 or 1) of the KS orbitals. The summation in (88) ranges over both occupied and unoccupied orbitals, including the continuum states.

The exchange-correlation kernel f_{xc}, given by Eq. (86), comprises all dynamical exchange and correlation effects to first order in the perturbing potential. For spin-unpolarized ground states, the spin-dependent exchange-correlation kernel has the form

$$f_{\mathrm{xc}\uparrow\uparrow} = f_{\mathrm{xc}\downarrow\downarrow} = f_{\mathrm{xc}} + \mu_0^2 G_{\mathrm{xc}} \tag{89}$$

$$f_{\mathrm{xc}\uparrow\downarrow} = f_{\mathrm{xc}\downarrow\uparrow} = f_{\mathrm{xc}} - \mu_0^2 G_{\mathrm{xc}} \tag{90}$$

(μ_0 denotes the Bohr magneton). In practice, $f_{\mathrm{xc}\sigma\sigma'}$ is of course only approximately known. Again, the simplest possible approximation is the spin-dependent version of the adiabatic local density approximation (69). For spin-unpolarized ground states, this leads to

$$\begin{aligned} f_{\mathrm{xc}}^{\mathrm{ALDA}}(\mathbf{r},\mathbf{r}';\omega) &= \delta(\mathbf{r}-\mathbf{r}')\,\frac{d^2}{d\rho}\left.\left(\rho\epsilon_{\mathrm{xc}}^{\mathrm{hom}}(\rho,\zeta=0)\right)\right|_{\rho=n_0(\mathbf{r})} \\ &= \delta(\mathbf{r}-\mathbf{r}')\,\left.f_{\mathrm{xc}}^{\mathrm{hom}}(\rho,\zeta=0,q=0,\omega=0)\right|_{\rho=n_0(\mathbf{r})} \end{aligned} \tag{91}$$

and

$$G_{\mathrm{xc}}^{\mathrm{ALDA}}(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}')\left.\frac{\alpha_{\mathrm{xc}}(\rho)}{\mu_0^2\rho}\right|_{\rho=n_0(\mathbf{r})}, \tag{92}$$

where

$$\alpha_{\mathrm{xc}} = \left.\frac{\delta^2}{\delta\zeta^2}\left(\epsilon_{\mathrm{xc}}^{\mathrm{hom}}(\rho,\zeta)\right)\right|_{\zeta=0} \tag{93}$$

is the exchange-correlation contribution to the spin-stiffness (ζ stands for the relative spin polarization). Most notably, the Fourier transforms (91) and (92) of the time-dependent response kernels in the ALDA have no frequency dependence at all. Beyond this adiabatic limit, frequency-dependent approximations of the xc kernel have been obtained [89, 90, 91, 92]. We finally mention an explicitly orbital-dependent approximation of the xc kernel,

$$f^{\mathrm{PGG}}_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r},\mathbf{r}') = -\delta_{\sigma\sigma'} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \frac{\left|\sum_k f_{k\sigma}\,\varphi_{k\sigma}(\mathbf{r})\varphi^*_{k\sigma}(\mathbf{r}')\right|^2}{n_\sigma(\mathbf{r})n_\sigma(\mathbf{r}')} \,. \tag{94}$$

which Petersilka, Gossmann, and Gross (PGG) have obtained from a linearization of the TDOEP equation [88, 93] using the x-only functional (72).

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 practice, however, the description of excited states within stationary density-functional theory is a notoriously difficult subject [94–105]. 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 chapter a different approach [88, 106] to the calculation of excitation energies is presented which is based on time-dependent density functional theory in the linear response regime. The formalism has been successfully applied to the calculation of molecular excitation spectra [107–114].

In the standard linear response formalism, the full response function

$$\chi_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) = \lim_{\delta\to 0^+} \sum_m \left(\frac{\langle\psi_0|\hat{n}_\sigma(\mathbf{r})|\psi_m\rangle\langle\psi_m|\hat{n}_{\sigma'}(\mathbf{r}')|\psi_0\rangle}{\omega-(E_m-E_0)+i\delta} - \frac{\langle\psi_0|\hat{n}_{\sigma'}(\mathbf{r}')|\psi_m\rangle\langle\psi_m|\hat{n}_\sigma(\mathbf{r})|\psi_0\rangle}{\omega+(E_m-E_0)+i\delta} \right) . \tag{95}$$

is formally constructed from the exact many-body eigenfunctions and energies

$$H(t_0)|\Psi_m\rangle = E_m|\Psi_m\rangle \tag{96}$$

of the full static many-body Hamiltonian $H(t_0)$ at t_0. It is obvious from Eq. (95) that the frequency-dependent linear density response has poles at the exact excitation energies $\Omega = E_m - E_0$.

The key idea of a density functional calculation of excitation energies is to start from a particular KS excitation energy $\epsilon_{j\sigma} - \epsilon_{k\sigma}$ (which are the poles of the Kohn-Sham response function (88)) and to use the formally exact representation (87) of the linear density response to calculate the shifts of the Kohn-Sham excitation energies towards the true excitation energies Ω.

To calculate these shifts, we rewrite Eq. (87) as a linear integral equation for the frequency dependent linear density response:

$$\sum_{\nu'} \int\! d^3y' \left[\delta_{\sigma\nu'}\delta(\mathbf{r}-\mathbf{y}') - \sum_\nu \int\! d^3y \chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r},\mathbf{y};\omega) \left(\frac{1}{|\mathbf{y}-\mathbf{y}'|} + f_{\mathrm{xc}\,\nu\nu'}(\mathbf{y},\mathbf{y}';\omega) \right) \right] n_{1\nu'}(\mathbf{y}',\omega)$$
$$= \sum_\nu \int d^3y\, \chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r},\mathbf{y};\omega) v_{1\nu}(\mathbf{y},\omega) \,. \tag{97}$$

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. (97) 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. (97) cannot be invertible for $\omega \to \Omega$.

Consequently, the true excitation energies Ω are characterized as those frequencies where the integral operator acting on the spin-density vector in Eq. (97) becomes non-invertible, i.e. has vanishing eigenvalues. Hence, the true excitation energies Ω are those frequencies where the eigenvalues $\lambda(\omega)$ of

$$\sum_{\nu'} \int d^3y' \sum_{\nu} \int d^3y \, \chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r},\mathbf{y};\omega) \left(\frac{1}{|\mathbf{y}-\mathbf{y}'|} + f_{\mathrm{xc}\,\nu\nu'}(\mathbf{y},\mathbf{y}';\omega) \right) \gamma_{\nu'}(\mathbf{y}',\omega) = \\ = \lambda(\omega)\gamma_\sigma(\mathbf{r},\omega) \tag{98}$$

satisfy

$$\lambda(\Omega) = 1\,. \tag{99}$$

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

$$\Phi_{q\sigma}(\mathbf{r}) := \varphi^*_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) \tag{100}$$

and set

$$\xi_{q\sigma}(\omega) := \sum_{\nu'} \int d^3y' \int d^3y \, \Phi_{q\sigma}(\mathbf{y})^* \left(\frac{1}{|\mathbf{y}-\mathbf{y}'|} + f_{\mathrm{xc}\,\sigma\nu'}(\mathbf{y},\mathbf{y}';\omega) \right) \gamma_{\nu'}(\mathbf{y}',\omega)\,. \tag{101}$$

Using these definitions, we arrive at [106]

$$\sum_{\sigma'} \sum_{q'} \frac{M_{q\sigma\, q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} \xi_{q'\sigma'}(\omega) = \lambda(\omega)\xi_{q\sigma}(\omega)\,, \tag{102}$$

where we have introduced the matrix elements

$$M_{q\sigma\, q'\sigma'}(\omega) = \alpha_{q'\sigma'} \int d^3r \int d^3r' \, \Phi^*_{q\sigma}(\mathbf{r}) \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) \right) \Phi_{q'\sigma'}(\mathbf{r}')\,. \tag{103}$$

So far, no approximations have been made.

In order to actually calculate the excitation spectrum, the eigenvalue problem (102) has to be truncated in one way or another. For finite systems, where we encounter well separated poles of the linear density response due to the discrete level structure, one possibility is to expand all quantities in Eq. (102) about one particular KS-orbital energy difference $\omega_{p\tau}$ [88, 106]. The true excitation energies Ω are then determined by the solution of

$$\lambda(\Omega) = \frac{A(\omega_{p\tau})}{\Omega - \omega_{p\tau}} + B(\omega_{p\tau}) + \ldots = 1 \tag{104}$$

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

$$A(\omega_{p\tau}) = M_{p\tau\, p\tau}(\omega_{p\tau}) \tag{105}$$

and

$$B(\omega_{p\tau}) = \left.\frac{dM_{p\tau p\tau}}{d\omega}\right|_{\omega_{p\tau}} + \frac{1}{M_{p\tau p\tau}(\omega_{p\tau})} \sum_{q'\sigma' \neq p\tau} \frac{M_{p\tau\, q'\sigma'}(\omega_{p\tau}) M_{q'\sigma'\, p\tau}(\omega_{p\tau})}{\omega_{p\tau} - \omega_{q'\sigma'} + i\eta} \,. \tag{106}$$

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. (104) is determined by a $\wp$-dimensional matrix equation

$$\sum_{k=1}^{\wp} M_{p_i\tau_i\, p_k\tau_k}(\omega_0) \xi^{(n)}_{p_k\tau_k} = A_n(\omega_0) \xi^{(n)}_{p_i\tau_i} \,, \quad i = 1 \ldots \wp \,, \tag{107}$$

leading to $\wp$ different coefficients $A_1 \ldots A_\wp$. 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. (**??**) reduces to

$$\lambda_n(\Omega) \approx \frac{A_n(\omega_0)}{\Omega - \omega_0} = 1 \,. \tag{108}$$

The condition (99) and its complex conjugate, $\lambda^*(\Omega) = 1$, finally lead to to a simple (approximate) expression for the excitation energies.

$$\Omega_n \approx \omega_0 + \Re A_n(\omega_0) \,. \tag{109}$$

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

$$\sum_{\sigma' = \uparrow,\downarrow} M_{p\sigma p\sigma'}(\omega_0) \xi_{p\sigma'}(\omega_0) = A \xi_{p\sigma}(\omega_0) \,. \tag{110}$$

Then, the resulting excitation energies are:

$$\Omega_{1,2} = \omega_0 + \Re \left\{ M_{p\uparrow p\uparrow} \pm M_{p\uparrow p\downarrow} \right\} \,. \tag{111}$$

Using the explicit form of the matrix elements (103) one finds[†]

$$\Omega_1 = \omega_0 + 2\Re \int d^3r \int d^3r'\, \Phi^*_p(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'; \omega_0) \right) \Phi_p(\mathbf{r}') \tag{112}$$

$$\Omega_2 = \omega_0 + 2\Re \int d^3r \int d^3r'\, \Phi^*_p(\mathbf{r}) \mu_0^2 G_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'; \omega_0) \Phi_p(\mathbf{r}') \,. \tag{113}$$

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 $m(\mathbf{r}, \omega)$ [65]. 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. Hence the spin-multiplet structure, originally absent in the bare Kohn-Sham eigenvalue spectrum, is recovered.

[†] Since we are dealing with spin saturated systems, we have dropped the spin-index of $\Phi_{p\sigma}$ for simplicity.

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 also solve Eq. (102) directly. At the frequencies $\omega = \Omega$, Eq. (102) can be written as

$$\sum_{q'\sigma'} \left(M_{q\sigma\, q'\sigma'}(\Omega) + \delta_{q\sigma\, q'\sigma'}\omega_{q\sigma} \right) \beta_{q'\sigma'}(\Omega) = \Omega \beta_{q\sigma}(\Omega) \,, \tag{114}$$

where we have introduced

$$\beta_{q\sigma}(\Omega) := \xi_{q\sigma}(\Omega)/(\Omega - \omega_{q\sigma}) \,. \tag{115}$$

Hence, the exact excitation energies Ω are the exact solutions of the nonlinear matrix-equation (114). Truncation of the infinite-dimensional matrix in Eq. (114) amounts to the approximation of $\chi^{(0)}$ by a finite sum

$$\chi^{(0)}(\mathbf{r}, \mathbf{r}', \omega) \approx \sum_{\sigma=\uparrow\downarrow} \sum_{q}^{Q} \alpha_q \frac{\Phi_q(\mathbf{r})\Phi_q(\mathbf{r}')}{\omega - \omega_{q\sigma}} \,. \tag{116}$$

Thus, instead of expanding about a single pole, we explicitly take into account several poles of the noninteracting response function. Using the ALDA 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 $M_{q\sigma\, q'\sigma'}(\Omega = 0) + \delta_{q\sigma, q'\sigma'}\omega_{q\sigma}$.

The scheme developed above involves three different types of approximations:

1. In the calculation of the Kohn-Sham orbitals $\varphi_k(\mathbf{r})$ and their eigenvalues ϵ_k, one employs some approximation of the static xc potential v_{xc}.
2. Given the stationary Kohn-Sham orbitals and the ground state density, the functional form of the xc kernel $f_{\mathrm{xc}\,\sigma\sigma'}$ needs to be approximated in order to calculate the matrix elements defined in Eq. (103).
3. Once the matrix elements are obtained, the infinite-dimensional eigenvalue problem (102) (or, equivalently, (114)) must be truncated in one way or another.

Results for atoms and molecules As a first application of the method, we have calculated the lowest excitation energies of the alkaline earth elements and the zinc series. The values listed in Table 9 are from a calculation using the KLI-x-only approximation for the static xc potential and the adiabatic local density approximation for the xc kernels. Apparently, the KS-eigenvalue differences alone do not resolve singlet-triplet splittings, but are always located in between the experimentally measured singlet and triplet excitation energies. The multiplet structure, however, is already obtained within the SPA, i.e. by adding the lowest order correction terms given by Eqs. (112) and (113). The experimentally measured excitations are quite well reproduced.

In addition to spin-multiplet splittings, large splittings of spatial multiplets are observed in molecules. In Table 10, the excitation energies of the CO molecule are given. The stationary KS orbitals and eigenvalues were calculated using the LDA for exchange and correlation. For the functional form of the xc kernels the ALDA was used. Again, the single-pole approximation gives the dominant corrections of the Kohn-Sham eigenvalue differences towards the experimentally measured energies. The results from a solution of Eq. (114) are listed in the column headed “full”. Here we have coupled all occupied and the lowest 9 unoccupied molecular orbitals. In general, this leads to a

Table 9. The lowest S→P excitation energies of the alkaline earths, calculated from the x-only KLI potential. The experimental values (first column) [115] are compared with results calculated in SPA from Eq. (112) for the singlet and from Eq. (113) for the triplet using the ALDA (91, 92) for the xc kernel. For comparison, the ordinary LDA-Δ_{SCF} values are given in the third column. The Kohn-Sham orbital-energy differences ω_{KS} are shown in the last column (All values in atomic units).

Atom	State	Expt.	SPA	Δ_{SCF}	ω_{KS}	Atom	State	Expt.	SPA	Δ_{SCF}	ω_{KS}
Be	$^1P_1$	0.194	0.199	0.166	0.130	Zn	$^1P_1$	0.213	0.209	0.202	0.157
	$^3P_0$	0.100					$^3P_0$	0.147			
	$^3P_1$	0.100	0.098	0.091	0.130		$^3P_1$	0.148	0.140	0.158	0.157
	$^3P_2$	0.100					$^3P_2$	0.150			
Mg	$^1P_1$	0.160	0.165	0.150	0.117	Sr	$^1P_1$	0.099	0.106	0.096	0.071
	$^3P_0$	0.100					$^3P_0$	0.065			
	$^3P_1$	0.100	0.098	0.103	0.117		$^3P_1$	0.066	0.059	0.068	0.071
	$^3P_2$	0.100					$^3P_2$	0.068			
Ca	$^1P_1$	0.108	0.118	0.106	0.079	Cd	$^1P_1$	0.199	0.185	0.173	0.135
	$^3P_0$	0.069					$^3P_0$	0.137			
	$^3P_1$	0.070	0.065	0.072	0.079		$^3P_1$	0.140	0.120	0.136	0.135
	$^3P_2$	0.070					$^3P_2$	0.145			

Table 10. Excitation energies for CO from an xcLDA–calculation at $R = 2.1322$ a.u. The LDA was employed for v_{xc} and the ALDA for the xc kernels. ω_{KS} denotes the KS orbital energy difference. All numbers in mHartrees.

State		ω_{KS}	SPA	full[a]	exp[b]
A $^1\Pi$	$5\sigma \rightarrow 2\pi$	252.3	326.8	310.2	312.7
a $^3\Pi$			223.8	221.4	232.3
B $^1\Sigma^+$	$5\sigma \rightarrow 6\sigma$	333.2	338.9	338.0	396.2
b $^3\Sigma^+$			331.5	331.6	382.2
I $^1\Sigma^-$	$1\pi \rightarrow 2\pi$	362.6	362.6	362.6	363.1
e $^3\Sigma^-$			362.6	362.6	363.1
a′ $^3\Sigma^+$			318.1	314.9	312.7
D $^1\Delta$			381.2	380.7	375.9
d $^3\Delta$			340.4	339.6	344.0
c $^3\Pi$	$4\sigma \rightarrow 2\pi$	438.8	420.4	420.2	424.5
E $^1\Pi$	$1\pi \rightarrow 6\sigma$	443.6	443.5	443.5	423.7

[a] Neglecting continuum states.
[b] From [116].

more refined approximation of the spectrum, since more configurations are taken into account. However, the differences with respect to the SPA are usually small, especially for the triplet states.

Considering the computational simplicity of the approach, the quality of the results is very promising. This opens up the road towards a reliable calculation of spectra for larger systems, like clusters and large molecules. Since the present scheme is mainly concerned with the calculation of corrections to the Kohn-Sham eigenvalue spectrum, it has to be stressed, however, that a quantitative calculation of excitation energies substantially depends on the accuracy of the ground state xc potential employed. In the LDA and in the popular GGAs for instance, which are not free of spurious self-interaction effects, the highest occupied orbital eigenvalues are in error by about a factor of two. Cancellation of self-interaction errors has been observed for lower excited states [111, 112, 114], but, in general, a resulting excitation spectrum which is accurate for all states can only be expected if self-interaction free xc potentials are used. The development of orbital functionals should offer a viable route in this direction.

VAN DER WAALS INTERACTIONS

Van der Waals (vdW) forces are caused by correlations between distant electronic fluctuations. In an intuitive picture, the origin of the vdW energy can be understood as follows: Consider a system consisting of two neutral subsystems A and B at a distance R and suppose an electric dipole moment is spontaneously created in one of the subsystems. As a consequence, a second dipole is induced in the other subsystem. The interaction between the two dipole moments creates the vdW energy. According to this argument, the R^{-3} decay of dipole fields enters twice so that the asymptotic behavior of the vdW energy is

$$E_{\mathrm{vdW}} \simeq -\frac{C_6}{R^6} \quad \text{for} \quad R \to \infty \tag{117}$$

with the vdW coefficient C_6. (The R^{-6} behavior only applies to finite subsystems; for extended subsystems such as metal surfaces one obtains different power laws.)

The subject can be treated rigorously by applying second-order perturbation theory. This leads to the Zaremba-Kohn formula [117]

$$E_{\mathrm{vdW}} = -\frac{1}{2\pi} \int\limits_A d^3x\, d^3x' \int\limits_B d^3r\, d^3r' \int\limits_0^\infty du\, \frac{\chi^A(\mathbf{x},\mathbf{x}';iu)\, \chi^B(\mathbf{r},\mathbf{r}';iu)}{|\mathbf{x}-\mathbf{r}| \quad |\mathbf{x}'-\mathbf{r}'|}\,, \tag{118}$$

which expresses the vdW energy in terms of the imaginary-frequency response functions χ^A and χ^B of the isolated and unperturbed subsystems A and B. Through a multipole expansion of Eq. (118) one recovers the asymptotic behavior (117) with the vdW coefficient now given by

$$C_6 = \frac{1}{2\pi} \sum_{i,j=1}^{3} (1-\delta_{3i})(1-3\delta_{3j}) \int\limits_0^\infty du\, \alpha_{ij}^A(iu)\, \alpha_{ij}^B(iu)\,, \tag{119}$$

where the 3-axis is chosen to point from A to B and, for each subsystem, α_{ij} is the polarizability tensor (i.e. the tensorial generalization of Eq. (58)):

$$\alpha_{ij}(\omega) = -\int d^3r\, d^3r'\, r_i r_j'\, \chi(\mathbf{r},\mathbf{r}';\omega) = -\frac{1}{\mathcal{E}} \int d^3r\, r_i\, n_1(\mathbf{r},\omega)_j\,. \tag{120}$$

Here $n_1(\mathbf{r},\omega)_j$ is the linear density response to the perturbation $v_1(\mathbf{r}t) = \mathcal{E} r_j \cos(\omega t)$.

TDDFT provides a very efficient way of calculating the C_6 coefficients: Given an approximation for the xc kernel, Eqs. (87) and (88) can be used to determine the density responses $n_1(\mathbf{r},\omega)_j$ which, by Eqs. (119) and (120) give the vdW coefficients. With this method, van Gisbergen et al [118, 119] have obtained vdW coefficients for a large variety of molecules in rather good agreement with experiment.

In the present section, however, we want to go beyond the asymptotic limit: Our goal is to construct a functional for the xc energy that yields accurate total energies *and* has the correct asymptotic behavior (117). In other words, we want a "seamless" scheme which gives reliable results at any subsystem separation and is still applicable in the case of overlapping subsystems.

Static DFT, as a matter of principle, yields the exact ground-state energy, including long-range vdW contributions. The commonly used approximate functionals such as the LDA and the GGAs, however, are not able to reproduce vdW forces, at least not the asymptotic R^{-6} behavior.

Several suggestions have been made for the treatment of vdW interactions in DFT [120, 121, 122, 123, 124]. Yet, there has been only one seamless calculation so far, performed by Dobson and Wang [125]. It follows the concept of [123] and deals with a jellium slab situation. In the case of atoms and molecules there is no functional that has been shown to provide both vdW coefficients and total correlation energies accurately. The scheme proposed by Kohn, Meir, and Makarov [124] should in principle be capable of this, but its computational implementation appears to be rather demanding.

Here, we suggest an approximation for the correlation-energy functional which will prove to describe the vdW limit correctly. The derivation is based on the adiabatic connection formula and on TDDFT. Numerical results will be presented for total correlation energies as well as vdW coefficients.

Construction of a correlation-energy functional containing the vdW energy

Since the HK theorem is valid for any particle-particle interaction, we can apply it to a system with arbitrary Coulomb coupling constant λ. Thus for each value of λ between 0 and 1 there exists a uniquely determined external potential that reproduces the spin densities of the fully interacting system. (In the special case $\lambda = 0$ this potential is equal to the KS potential.) The adiabatic connection formula expresses the xc energy as an integral over the coupling constant (see e.g. [122]):

$$E_{\mathrm{xc}} = -\frac{1}{2}\int_0^1 d\lambda \int d^3r\, d^3r'\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\{\left[\frac{1}{\pi}\int_0^\infty du \sum_{\sigma\sigma'} \chi^{(\lambda)}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';iu)\right] + n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right\} . \tag{121}$$

Here, $\chi^{(\lambda)}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';iu)$ denotes the spin-density response function at coupling strength λ and imaginary frequency iu. The exact exchange energy is obtained from Eq. (121) if $\chi^{(\lambda)}_{\sigma\sigma'}$ is replaced by the KS reponse function $\chi_{\mathrm{s}\,\sigma\sigma'}$. Hence, the correlation energy $E_{\mathrm{c}} = E_{\mathrm{xc}} - E_{\mathrm{x}}$ is given by

$$E_{\mathrm{c}} = -\frac{1}{2\pi}\int_0^1 d\lambda \int d^3r\, d^3r'\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty du \sum_{\sigma\sigma'}\left[\chi^{(\lambda)}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';iu) - \chi_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r},\mathbf{r}';iu)\right] . \tag{122}$$

$\chi^{(\lambda)}_{\sigma\sigma'}$ is related to the KS reponse function $\chi_{\mathrm{s}\,\sigma\sigma'}$ by a Dyson-type equation involving the λ-dependent xc kernel $f^{(\lambda)}_{\mathrm{xc}}$:

$$\begin{aligned}\chi^{(\lambda)}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) &= \chi_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) + \\ &+\sum_{\nu\nu'}\int d^3x\, d^3x'\, \chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r},\mathbf{x};\omega)\left[\frac{\lambda}{|\mathbf{x}-\mathbf{x}'|}+f^{(\lambda)}_{\mathrm{xc}\,\nu\nu'}(\mathbf{x},\mathbf{x}';\omega)\right]\chi^{(\lambda)}_{\nu'\sigma'}(\mathbf{x}',\mathbf{r}';\omega)\,.\end{aligned} \tag{123}$$

Substituting (123) into (122) leads to

$$\begin{aligned}E_{\mathrm{c}} = -\frac{1}{2\pi}\int_0^1 d\lambda \int d^3r\, d^3r'\, d^3x\, d^3x'\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty du \\ \sum_{\nu\nu'\sigma\sigma'}\chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r},\mathbf{x};iu)\left[\frac{\lambda}{|\mathbf{x}-\mathbf{x}'|}+f^{(\lambda)}_{\mathrm{xc}\,\nu\nu'}(\mathbf{x},\mathbf{x}';iu)\right]\chi^{(\lambda)}_{\nu'\sigma'}(\mathbf{x}',\mathbf{r}';iu)\,.\end{aligned} \tag{124}$$

Eq.(124) is the starting point for our construction of an approximate correlation-energy functional. To this end, the xc kernel is approximated by the simple orbital-dependent formula suggested by Petersilka, Gossmann, and Gross [88, 93], given in Eq. (94). The λ-dependent version of it is linear in λ. Further, we approximate the interacting response function on the right-hand side of Eq. (124) by the non-interacting response function:

$$\chi^{(\lambda)}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) \simeq \chi_{\mathrm{s}\,\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega)\,. \tag{125}$$

Then the integrations over λ and u in Eq. (124) can be done analytically. The resulting orbital functional reads as follows:

$$\begin{aligned}E^{\chi_{\mathrm{s}}}_{\mathrm{c}} = -\frac{1}{2}\sum_{\substack{jkmn\\ \sigma\sigma'}} f_{jk\sigma}f_{mn\sigma'}\int d^3r\, d^3r'\, d^3x\, d^3x' \\ \frac{1}{|\mathbf{r}-\mathbf{r}'|}\, f_{\mathrm{hxc}\,\sigma\sigma'}(\mathbf{x},\mathbf{x}')\frac{Z_{jk\sigma}(\mathbf{r},\mathbf{x})Z_{mn\sigma'}(\mathbf{x}',\mathbf{r}')}{\omega_{j\sigma,k\sigma}+\omega_{m\sigma',n\sigma'}}\,.\end{aligned} \tag{126}$$

Here

$$Z_{jk\sigma}(\mathbf{r},\mathbf{r}') = \varphi^*_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')\varphi^*_{j\sigma}(\mathbf{r}')\,, \tag{127}$$

$$\omega_{j\sigma,k\sigma} = \epsilon_{j\sigma}-\epsilon_{k\sigma}\,, \tag{128}$$

$$f_{jk\sigma} = f_{k\sigma}(1-f_{j\sigma})\,, \tag{129}$$

and

$$f_{\mathrm{hxc}\,\sigma\sigma'}(\mathbf{x},\mathbf{x}') = \frac{1}{|\mathbf{x}-\mathbf{x}'|}+f^{\mathrm{PGG}}_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{x},\mathbf{x}')\,. \tag{130}$$

Apparently, Eq. (126) is similar to second-order perturbation theory. This means that we can expect reasonable results for finite systems. On the other hand, the functional will diverge if it is applied to the uniform electron gas; i.e., it will fail for bulk metals.

In the case of two non-overlapping subsystems A and B at distance $R\to\infty$, the correlation energy (126) consists of a constant part (equal to the correlation energies of

Table 11. VdW coefficients C_6.[a]

Atoms	x-KLI	KLICS	LDA-SIC-KLI	empirical
He-He	1.664	1.639	1.594	1.458
He-Ne	3.490	3.424	3.495	3.029
Ne-Ne	7.447	7.284	7.761	6.383
Ar-Ar	128.5	124.4	133.2	64.30
Kr-Kr	282.4	271.3	290.0	129.6
Xe-Xe	730.7	697.1	734.6	285.9
Li-Li	1460	1313	1423	1390
Li-Na	1689	1453	1485	1450
Na-Na	1957	1614	1560	1510
K-K	6665	5265	4662	3890 ± 20
Rb-Rb	9624	7505	6347	4870 ± 70
H-He	3.022	2.995	2.948	2.82 ± 0.02
H-Ne	6.060	5.976	6.227	5.71 ± 0.07
H-Li	67.99	64.96	67.22	66.4 ± 0.5
H-Na	81.14	75.43	74.50	71.8 ± 0.3

[a] Coefficients calculated from Eq. (131), first three rows, are compared with empirical numbers. Hydrogen wave functions were calculated from the exact potential, all other wave functions from x-only-KLI, KLICS, or LDA-SIC-KLI potentials as indicated. Empirical C_6 values from [127] and [128]. Empirical values of the alkali atoms are accurate to 3 digits if no uncertainty is indicated. All numbers in atomic units.

the isolated subsystems) and a vdW part. A multipole expansion of the latter shows that it exhibits the correct R^{-6} dependence with the vdW coefficient

$$C_6^{\chi_\mathrm{s}} = \sum_{i=1}^{3}(1+3\delta_{3i}) \sum_{\substack{jkmn\\ \sigma\sigma'}} f_{jk\sigma} f_{mn\sigma'} \frac{\left|\langle k\sigma|r_i|j\sigma\rangle^{(A)}\right|^2 \left|\langle n\sigma'|r_i|m\sigma'\rangle^{(B)}\right|^2}{\omega_{j\sigma,k\sigma} + \omega_{m\sigma',n\sigma'}}\,, \tag{131}$$

which, in the numerator, involves dipole-operator matrix elements of the isolated subsystems. We note that the xc kernel has dropped out. This is due to the fact that $f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega)$ goes to zero much faster than the Coulomb interaction for $|\mathbf{r}'-\mathbf{r}| \to \infty$.

Görling and Levy have derived Eq. (131) by applying perturbation theory to the vdW energy directly [126]. This shows that, as far as the C_6 coefficients are concerned, our approximation is exactly equivalent to second-order perturbation theory.

Results

Table 11 shows the resulting vdW coefficients for combinations of rare-gas atoms, alkali atoms, and hydrogen. The hydrogen wave functions were calculated from the exact potential. For the rare-gas and alkali atoms we used x-only-KLI, Colle-Salvetti-KLI (KLICS), and LDA-SIC-KLI orbitals, as indicated. (LDA-SIC is LDA with self-interaction correction [129].) We conclude that the agreement with the empirical values is very good for light atoms (H, He, Li, Ne, Na), but becomes worse for heavier elements. Compared to the rare gases, the alkali atoms are more sensitive to what kind of KS orbitals we insert.

The response of a hydrogen atom is given by the non-interacting response function without approximation. Therefore, Eq. (131) is *exact* in the case of two vdW-interacting hydrogen atoms. Indeed, the calculated C_6(H-H) of 6.499 a.u. (not shown in Table 11) equals the empirical value [128] of (6.49 ± 0.02) a.u.

Table 12. Atomic correlation energies from various approximations.[a]

Atom	$E_c^{\chi_s}$	LDA	LDA-SIC-KLI	KLICS	PW91	exact/empirical
He	-0.048	-0.111	-0.0582	-0.0416	-0.0450	-0.0421
Be	-0.13	-0.224	-0.1169	-0.0934	-0.0942	-0.0962
Ne	-0.41	-0.739	-0.4283	-0.3757	-0.3784	-0.394
Ar	-0.67	-1.423	-0.8330	-0.7435	-0.7687	-0.72

[a]The χ_s approximation (126) using the PGG xc kernel (94), first row, is compared with self-consistent DFT results and with exact DFT correlation energies for He, Be, Ne [130, 131] and the conventional quantum-chemical correlation energy for Ar [54]. All numbers in Hartrees.

Table 13. Total atomic ground-state energies from various approximations.[a]

Atom	E^{χ_s}	LDA	LDA-SIC-KLI	KLICS	PW91	exact/empirical
He	-2.910	-2.835	-2.920	-2.903	-2.900	-2.9037
Be	-14.71	-14.446	-14.695	-14.665	-14.648	-14.6674
Ne	-128.96	-128.230	-129.287	-128.920	-128.947	-128.939
Ar	-527.48	-525.940	-528.432	-527.553	-527.539	-527.604
$\bar{\delta}(\%)$	0.14	1.19	0.29	0.016	0.070	

[a]Total energies obtained from the χ_s approximation using the PGG xc kernel are compared with self-consistent DFT results and exact/empirical values [46, 2]. $\bar{\delta}$ denotes the mean relative deviation from the exact/empirical values. All energies in Hartrees.

In Table 12 we present correlation energies for He, Be, Ne, and Ar. Here, we have evaluated Eq. (126) with x-only-KLI wave functions. We compare our results with self-consistent DFT correlation energies following from well-known functionals (LDA, LDA-SIC, KLICS, PW91). Further we compare with the exact DFT correlation energies of He, Be, and Ne [130, 131] and with a semi-empirical value [54] for the quantum-chemical correlation energy of Ar. (This quantity is defined by $E_c^{\mathrm{QC}} = E - E^{\mathrm{HF}}$ and should be very close to the DFT correlation energy; cf. [132].)

By adding the "χ_s correlation energy" to the x-only-KLI energy we obtain the total ground-state energies shown in Table 13. Again we compare with self-consistent DFT calculations and with exact/empirical reference values.

From Tables 12 and 13 we infer that our approximation is performing better than LDA and LDA-SIC. Especially the correlation energies of the rare-gas atoms are described accurately. However, the energies produced by the Colle-Salvetti and the PW91 functionals are still closer to the reference values.

To summarize, we have introduced a correlation-energy functional which reproduces the correct asymptotic R^{-6} behavior of the vdW interaction. This functional was then used to calculate atomic correlation energies and vdW coefficients. The numerical results for the vdW coefficients of light atoms and the energies of noble-gas atoms are quite satisfactory. In view of this, the present approach appears to be a promising starting point for further refinement.

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