Optimized Effective Potential for Atoms and Molecules

T. GRABO, T. KREIBICH and E. K. U. GROSS
Institut für Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.

Abstract. We describe the optimized effective potential method of density functional theory and the semi-analytical approximation due to Krieger, Li and Iafrate. Results for atomic and molecular systems including correlation contributions are presented and compared with conventional Kohn–Sham methods. The combination of the exact exchange energy functional with the correlation energy functional of Colle and Salvetti works extremely well for atomic systems, while further improvement is required for molecular systems.

1. Introduction

Density functional heory (DFT) is a powerful quantum mechanical method for calculating the electronic structure of atoms, molecules and solids [1–3]. The success of DFT hinges on the availability of good approximations for the total-energy functional. In this article we shall describe a particular approach to the construction of such approximations which involves explicitly orbital-dependent functionals. In order to describe the nature of this approach we will first briefly review the foundations of DFT.

We are concerned with Coulomb systems described by Hamiltonians of the type

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

where (atomic units are used throughout this article)

$$\hat{T} = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 \right) \tag{2}$$

denotes the kinetic energy operator,

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

represents the Coulomb interaction between the particles, and

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

contains all external potentials of the system, typically the Coulomb potentials of the nuclei.

Modern DFT is based on the celebrated theorem of Hohenberg and Kohn (HK) [4] which may be summarized by the following three statements:

1. The ground-state density ρ uniquely determines the external potential $v = v[\rho]$ as well as the ground-state wave function $\Psi[\rho]$. As a consequence, any observable of a static many-particle system is a functional of its ground-state density.

2. The total-energy functional

$$E_{v_0}[\rho] := \langle \Psi[\rho] | \hat{T} + \hat{W}_{\mathrm{Clb}} + \hat{V}_0 | \Psi[\rho] \rangle \tag{5}$$

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 ρ_0 is inserted. For all other densities $\rho \neq \rho_0$ the inequality

$$E_0 < E_{v_0}[\rho] \tag{6}$$

holds. Consequently, the exact ground-state density ρ_0 and the exact ground-state energy E_0 can be determined by solving the Euler–Lagrange equation

$$\frac{\delta}{\delta \rho(\mathbf{r})} E_{v_0}[\rho] = 0. \tag{7}$$

3. The functional

$$F[\rho] := \langle \Psi[\rho] | \hat{T} + \hat{W}_{\mathrm{Clb}} | \Psi[\rho] \rangle \tag{8}$$

is universal in the sense that it is independent of the external potential v_0 of the particular system considered, i.e. it is of the same functional form for all systems with a fixed particle-particle interaction ($\hat{W}_{\mathrm{Clb}}$ in our case).

The proof of the HK theorem does not depend on the particular form of the particle–particle interaction. It is valid for *any* given particle–particle interaction $\hat{W}$, in particular also for $\hat{W} \equiv 0$, i.e. for non-interacting systems described by Hamiltonians of the form

$$\hat{H}_S = \hat{T} + \hat{V}_S. \tag{9}$$

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

$$V_S(\mathbf{r}) = V_S[\rho](\mathbf{r}). \tag{10}$$

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

$$\left(-\frac{\nabla^2}{2} + V_S[\rho](\mathbf{r})\right)\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r}) \tag{11}$$

are functionals of the density as well:

$$\varphi_j(\mathbf{r}) = \varphi_j[\rho](\mathbf{r}). \tag{12}$$

The HK total-energy functional of non-interacting particles is given by

$$E_S[\rho] = T_S[\rho] + \int d^3r \; \rho(\mathbf{r}) V_S(\mathbf{r}) \tag{13}$$

where $T_S[\rho]$ is the kinetic-energy functional of non-interacting particles:

$$T_S[\rho] = \sum_{\substack{i=1\\ \text{lowest}\,\varepsilon_i}}^{N} \int d^3r\,\varphi_i^*[\rho](\mathbf{r})\left(-\frac{\nabla^2}{2}\right)\varphi_i[\rho](\mathbf{r}). \tag{14}$$

We emphasize that the quantity (14) really represents a *functional of the density*: functional means that we can assign a unique number $T_S[\rho]$ to any function $\rho(\mathbf{r})$. This is done by first calculating that actual potential $V_S(\mathbf{r})$ which uniquely corresponds to $\rho(\mathbf{r})$. Several numerical schemes have been devised to achieve this task [5–10]. Then we take this potential, solve the Schrödinger Equation (11) with it to obtain a set of orbitals $\{\varphi_j(\mathbf{r})\}$ and use those to calculate the number T_S by evaluating the right-hand side of Equation (14). As a matter of fact, by the same chain of arguments, *any orbital functional is an (implicit) functional of the density*, provided the orbitals come from a local, i.e. multiplicative potential.

Returning to the *interacting* system of interest we now define the so-called exchange-correlation (xc) energy functional by

$$E_{xc}[\rho] := F[\rho] - \frac{1}{2}\int d^3r \int d^3r'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - T_S[\rho]. \tag{15}$$

The HK total-energy functional (5) can then be written as

$$E_{v_0}[\rho] = T_S[\rho] + \int d^3r \; v_0(\mathbf{r})\rho(\mathbf{r})$$
$$+ \frac{1}{2}\int d^3r \int d^3r'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho]. \tag{16}$$

In historical retrospect we may identify three generations of density functional schemes which may be classified according to the level of approximations used for the universal functionals $T_S[\rho]$ and $E_{xc}[\rho]$.

In what we call the *first generation of DFT, explicitly* density-dependent functionals are used to approximate both $T_S[\rho]$ and $E_{\text{xc}}[\rho]$. For example, the simplest and historically first approximation of this kind is the Thomas–Fermi model, where $E_{\text{xc}}[\rho]$ is neglected completely and $T_S[\rho]$ is approximated by

$$T_S^{\text{TF}}[\rho] = \frac{3}{10}(3\pi^2)^{2/3} \int \mathrm{d}^3 r \rho(\mathbf{r})^{5/3} \tag{17}$$

yielding

$$
\begin{aligned}
E_{v_0}^{\text{TF}}[\rho] &= \frac{3}{10}(3\pi^2)^{2/3} \int \mathrm{d}^3 r \rho(\mathbf{r})^{5/3} + \int \mathrm{d}^3 r \, v(\mathbf{r})\, \rho(\mathbf{r}) \\
&\quad + \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\end{aligned}
\tag{18}
$$

as approximate expression for the total-energy functional. 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 $\rho(\mathbf{r})$ of the system, they are readily solved numerically. The results obtained in this way, however, are generally of moderate quality.

The *second generation* of DFT employs the *exact* functional (14) for the non-interacting kinetic energy and an approximate density functional for the xc energy:

$$
\begin{aligned}
E_{v_0}^{\text{KS}}[\rho] &= T_S^{\text{exact}}[\rho] + \int \mathrm{d}^3 r \, v_0(\mathbf{r})\rho(\mathbf{r}) + \\
&\quad + \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho].
\end{aligned}
\tag{19}
$$

This total-energy expression leads to the Kohn–Sham (KS) version of DFT [11] as will be shown in the following. Plugging Equation (19) into the variational principle (7) yields

$$
0 = \frac{\delta T_S^{\text{exact}}[\rho]}{\delta\rho(\mathbf{r})} + v_0(\mathbf{r}) + \int \mathrm{d}^3 r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}.
\tag{20}
$$

The variation of the non-interacting kinetic energy functional is given by

$$
\begin{aligned}
\delta T_S^{\text{exact}}[\rho] &= \delta \sum_{i=1}^{N} \left\langle \varphi_i[\rho] \left| -\frac{\nabla^2}{2} \right| \varphi_i[\rho] \right\rangle \\
&= \delta \left[\sum_{i=1}^{N} \varepsilon_i[\rho] - \int \mathrm{d}^3 r' V_S[\rho](\mathbf{r}')\rho(\mathbf{r}') \right]
\end{aligned}
\tag{21}
$$

where the one-particle Equation (11) has been used. Since the HK theorem ensures the one-to-one correspondence between the density and the one-particle potential, a variation $\delta\rho$ of the former will result in a variation δV_S of the latter. Therefore, the variation of the one-particle energies ε_i can be calculated using first-order perturbation theory yielding

$$\delta\varepsilon_i = \langle\varphi_i[\rho]|\delta V_S[\rho]|\varphi_i[\rho]\rangle. \tag{22}$$

Using this result in (21) gives

$$\delta T_S^{\text{exact}}[\rho] = -\int d^3r \quad \rho \quad ' \quad] \quad V \quad (\quad _S \quad \mathbf{r} \quad [\quad ' \tag{23}) \quad \delta \quad \rho$$

which, combined with Equation (20) leads to

$$V_S[\rho](\mathbf{r}) = v_0(\quad d^3r \frac{\rho}{|\mathbf{r}-\mathbf{r}'|}')+ V_{\text{xc}}[\rho](\mathbf{r})+ \quad (\quad \int \mathbf{r} \quad ' \tag{24})$$

where we have defined the xc potential as

$$V_{\text{xc}}[\rho](\mathbf{r}):=\frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}. \tag{25}$$

Being the HK variational equation of the *interacting* system, Equation (20) determines the exact ground-state density of the interacting system. Since Equation (24), on the other hand, is equivalent to Equation (20), the density

$$\rho(\mathbf{r}) = \sum_{\substack{i=1 \\ N \text{ lowest } \varepsilon_i}}^{N} |\varphi_i(\mathbf{r})|^2 \tag{26}$$

resulting from the solution of the Schrödinger Equation (11) with the potential (24) must be identical with the ground-state density of the *interacting* system of interest. Equations (11), (24), (25) and (26) are known as Kohn–Sham equations. In practice, these equations have to be solved self-consistently employing approximate but explicitly density-dependent functionals for $E_{\text{xc}}[\rho]$. The resulting scheme is still easy to solve numerically and – especially for sophisticated density-gradient-dependent approximations of $E_{\text{xc}}[\rho]$ – gives excellent results for a wide range of atomic, molecular and solid-state systems [2,12].

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

$$E_{\text{x}}^{\text{exact}}[\rho] = -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{j,k=1}^{N_\sigma}\int d^3r\int d^3r'\frac{\varphi_{j\sigma}^*(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{27}$$

Only the correlation part of $E_{xc}[\rho]$ 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.

The central equation in the third generation of DFT is still the KS Equation (11). The difference between the second and third generations 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 $V_{xc}[\rho](\mathbf{r})$ from Equation (25) is somewhat more complicated. A detailed derivation will be given in the following section for the spin-dependent version of DFT. The result is an integral equation determining the xc potential. This integral equation, known as the optimized effective potential (OEP) equation, is very hard to solve numerically. To avoid a full-scale numerical solution, Krieger, Li and Iafrate (KLI) [13–21] have devised a semi-analytical scheme for solving the OEP integral equation approximately. This scheme is described in the subsequent section. After that, some rigorous properties of the OEP and KLI solutions will be briefly discussed and finally numerical results for atomic and molecular systems will be presented.

We finally mention that a time-dependent generalization of the OEP has recently been developed [22] to deal with explicitly time-dependent situations such as atoms in strong laser pulses [23]. In the linear-response regime this method has led to a rather successful procedure [24] to calculate excitation energies from the poles of the frequency-dependent density response. Time-dependent applications of this kind will not be discussed in the present article. The interested reader is referred to a recent review of time-dependent DFT [25].

2. The OEP Method

2.1. DERIVATION OF THE OEP EQUATIONS

We are going to derive the OEP equations for the spin-dependent version of DFT [26, 27], where the basic variables are the spin-up and spin-down densities $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, respectively. They are obtained by self-consistently solving the single-particle Schrödinger equations

$$\left(-\frac{\nabla^2}{2} + V_{S\sigma}[\rho_\uparrow, \rho_\downarrow](\mathbf{r})\right)\varphi_{j\sigma}(\mathbf{r}) = \varepsilon_{j\sigma}\varphi_{j\sigma}(\mathbf{r}) \quad j = 1, \ldots, N_\sigma$$

$$\sigma = \uparrow, \downarrow \tag{28}$$

where

$$\rho_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \tag{29}$$

For convenience we shall assume in the following that infinitesimal symmetry-breaking terms have been added to the external potential to remove any possible degeneracies.

The KS orbitals can then be labeled such that

$$\varepsilon_{1\sigma} < \varepsilon_{2\sigma} < \cdots < \cdots < \cdots_{N_\sigma\sigma} \tag{30}$$

The Kohn–Sham potentials $V_{S\sigma}(\mathbf{r})$ may be written in the usual way as

$$V_{S\sigma}(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_{\mathrm{xc}\sigma}(\mathbf{r}), \tag{31}$$

$$\rho(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \rho_\sigma(\mathbf{r}) \tag{32}$$

where

$$V_{\mathrm{xc}\sigma}(\mathbf{r}) := \frac{\delta E_{\mathrm{xc}}[\rho_\uparrow, \rho_\downarrow]}{\delta\rho_\sigma(\mathbf{r})}. \tag{33}$$

The starting point of the OEP method is the total-energy functional

$$
\begin{aligned}
E_{v_0}^{\mathrm{OEP}}[\rho_\uparrow, \rho_\downarrow] &= \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma} \int d^3r \, \varphi_{i\sigma}^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\varphi_{i\sigma}(\mathbf{r}) \\
&\quad + \int d^3r \, v_0(\mathbf{r})\rho(\mathbf{r}) \\
&\quad + \frac{1}{2}\int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad + E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]
\end{aligned}
\tag{34}
$$

where, in contrast to ordinary spin DFT, the xc energy is an *explicit* (approximate) functional of spin orbitals and therefore only an *implicit* functional of the spin densities $\rho_\uparrow$ and $\rho_\downarrow$. In order to calculate the xc potentials from Equation (33) we use the chain rule for functional derivatives to obtain

$$
\begin{aligned}
V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}) &= \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]}{\delta\rho_\sigma(\mathbf{r})} \\
&= \sum_{\alpha=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha} \int d^3r' \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta\rho_\sigma(\mathbf{r})} + \text{c.c.}
\end{aligned}
\tag{35}
$$

and, by applying the functional chain rule once more,

$$
\begin{aligned}
V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r}) = & \sum_{\alpha=\uparrow,\downarrow} \sum_{\beta=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \mathrm{d}^3 r' \int \mathrm{d}^3 r'' \times \\
& \times \left(\frac{\delta E_{\text{xc}}^{\text{OEP}}[\{\varphi_{j\tau}\}]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\beta}(\mathbf{r}'')} + \text{c.c.} \right) \frac{\delta V_{S\beta}(\mathbf{r}'')}{\delta \rho_\sigma(\mathbf{r})}.
\end{aligned} \tag{36}
$$

The last term on the right-hand side is readily identified with the inverse $\chi_S^{-1}(\mathbf{r}, \mathbf{r}')$ of the density response function of a system of non-interacting particles

$$
\chi_{S\alpha,\beta}(\mathbf{r}, \mathbf{r}') := \frac{\delta \rho_\alpha(\mathbf{r})}{\delta V_{S\beta}(\mathbf{r}')}. \tag{37}
$$

This quantity is diagonal with respect to the spin variables so that Equation (36) reduces to

$$
\begin{aligned}
V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r}) = & \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \mathrm{d}^3 r' \int \mathrm{d}^3 r'' \times \\
& \times \left(\frac{\delta E_{\text{xc}}^{\text{OEP}}[\{\varphi_{j\tau}\}]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r}'')} + \text{c.c.} \right) \chi_{S\sigma}^{-1}(\mathbf{r}'', \mathbf{r}).
\end{aligned} \tag{38}
$$

Acting with the response operator (37) on both sides of Equation (38) one obtains

$$
\int \mathrm{d}^3 r' V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r}') \chi_{S\sigma}(\mathbf{r}', \mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int \mathrm{d}^3 r \frac{\delta E_{\text{xc}}^{\text{OEP}}[\{\varphi_{j\tau}\}]}{\delta \varphi_{i\alpha}(\mathbf{r}')} \frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r})} + \text{c.c.} \tag{39}
$$

Finally, the second functional derivative on the right-hand side of Equation (39) is calculated using first-order perturbation theory. This yields

$$
\frac{\delta \varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r})} = \delta_{\alpha,\sigma} \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r}') \varphi_{k\sigma}^*(\mathbf{r})}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \varphi_{i\sigma}(\mathbf{r}). \tag{40}
$$

Using this equation, the response function

$$
\chi_{S\alpha,\beta}(\mathbf{r}, \mathbf{r}') = \frac{\delta}{\delta V_{S\beta}(\mathbf{r}')} \left(\sum_{i=1}^{N_\alpha} \varphi_{i\alpha}^*(\mathbf{r}) \varphi_{i\alpha}(\mathbf{r}) \right) \tag{41}
$$

is readily expressed in terms of the orbitals as

$$
\chi_{S\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_\sigma} \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{i\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} + \text{c.c.} \tag{42}
$$

Inserting (40) and (42) in Equation (39), we obtain the standard form of the OEP integral equation:

$$\sum_{i=1}^{N_\sigma} \int \mathrm{d}^3 r' (V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}') - u_{\mathrm{xc}i\sigma}(\mathbf{r}')) G_{Si\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') + \mathrm{c.c.} = 0 \quad (43)$$

where

$$u_{\mathrm{xc}i\sigma}(\mathbf{r}) := \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]}{\delta \varphi_{i\sigma}(\mathbf{r})} \quad (44)$$

and

$$G_{Si\sigma}(\mathbf{r}, \mathbf{r}') := \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}}. \quad (45)$$

The derivation of the OEP integral Equation (43) described here was first given by Görling and Levy [28, 29]. It is important to note that the same expression results [15, 30–32] if one demands that the local one-particle potential appearing in Equation (28) be the *optimized* one yielding orbitals minimizing the total-energy functional (34), i.e. that

$$\left. \frac{\delta E_{v_0}^{\mathrm{OEP}}}{\delta V_{S\sigma}(\mathbf{r})} \right|_{V_{S\sigma} = V_\sigma^{\mathrm{OEP}}} = 0. \quad (46)$$

This equation is the historical origin [30] of the name *optimized effective potential*. As was first pointed out by Perdew and co-workers [33, 34], Equation (46) is equivalent to the HK variational principle. This is most easily seen by applying the functional chain rule to Equation (46) yielding

$$0 = \frac{\delta E_{v_0}^{\mathrm{OEP}}}{\delta V_{S\sigma}(\mathbf{r})} = \sum_\alpha \int \mathrm{d}^3 r' \frac{\delta E_{v_0}^{\mathrm{OEP}}}{\delta \rho_\alpha(\mathbf{r}')} \frac{\delta \rho_\alpha(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r})}. \quad (47)$$

Once again, the last term on the right-hand side of Equation (47) can be identified with the KS response function (37). Hence, acting with the inverse response operator on Equation (47) leads to the HK variational principle

$$0 = \frac{\delta E_{v_0}^{\mathrm{OEP}}}{\delta \rho_\sigma(\mathbf{r})}. \quad (48)$$

2.2. APPROXIMATION OF KRIEGER, LI AND IAFRATE

In order to use the OEP method derived in the last section we have to solve Equation (43) for the xc potential $V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}$. Unfortunately, there is no known analytic solution for

$V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}$ depending explicitly on the set of single-particle orbitals $\{\varphi_{i\sigma}\}$. Furthermore, Equation (43) is not in a form that allows for successive approximations of the xc potential. Thus, we need to solve the full integral equation numerically, which is a rather demanding task and has been achieved so far only for systems of high symmetry such as spherical atoms [15, 18, 19, 31, 35] and for solids within the linear muffin tin orbitals atomic sphere approximation [36–38].

However, Krieger, Li and Iafrate [13–21] recently proposed a transformation of Equation (43) that leads to an alternative but still exact form of the OEP equation which lends itself as a starting point for a highly accurate approximation of the OEP potential. Defining

$$
\begin{aligned}
\psi_{i\sigma}^*(\mathbf{r}) \; &:= \; \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\int \mathrm{d}^3 r' \varphi_{i\sigma}^*(\mathbf{r}')(V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}') - u_{\mathrm{xci}\sigma}(\mathbf{r}'))\varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \varphi_{k\sigma}^*(\mathbf{r}) \\
&= \; \int \mathrm{d}^3 r' \, \varphi_\sigma^*(\mathbf{r}') (V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}') - u_{\mathrm{xci}\sigma}(\mathbf{r}')) G_{Si\sigma}(\mathbf{r}', \mathbf{r}),
\end{aligned}
\tag{49}
$$

the OEP integral Equation (43) can be rewritten as

$$
\sum_{i=1}^{N_\sigma} \psi_{i\sigma}^*(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) + \mathrm{c.c.} = 0.
\tag{50}
$$

Since the KS orbitals $\{\varphi_{i\sigma}\}$ span an orthonormal set we readily conclude from equation (49) that the function $\psi_{i\sigma}(\mathbf{r})$ is orthogonal to $\varphi_{i\sigma}(\mathbf{r})$:

$$
\int \mathrm{d}^3 r \psi_{i\sigma}^*(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) = 0.
\tag{51}
$$

The quantity $G_{Si\sigma}(\mathbf{r}', \mathbf{r})$ given by Equation (45) is the Green's function of the KS equation projected onto the subspace orthogonal to $\varphi_{i\sigma}(\mathbf{r})$, i.e., it satisfies the equation

$$
(\hat{h}_{S\sigma}(\mathbf{r}) - \varepsilon_{i\sigma}) G_{Si\sigma}(\mathbf{r}', \mathbf{r}) = -[\delta(\mathbf{r}' - \mathbf{r}) - \varphi_{i\sigma}(\mathbf{r}')\varphi_{i\sigma}^*(\mathbf{r})]
\tag{52}
$$

where $\hat{h}_{S\sigma}(\mathbf{r})$ is a shorthand notation for the KS Hamiltonian

$$
\hat{h}_{S\sigma}(\mathbf{r}) := \frac{\nabla^2}{2} + V_{S\sigma}[\rho_\uparrow, \rho_\downarrow](\mathbf{r}).
\tag{53}
$$

Using Equation (52), we can act with the operator $(\hat{h}_{S\sigma} - \varepsilon_{i\sigma})$ on Equation (49), leading to

$$
(\hat{h}_{S\sigma}(\mathbf{r}) - \varepsilon_{i\sigma})\psi_{i\sigma}^*(\mathbf{r}) = -[V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}) - u_{\mathrm{xci}\sigma}(\mathbf{r}) - (\bar{V}_{\mathrm{xci}\sigma} - \bar{u}_{\mathrm{xci}\sigma})]\varphi_{i\sigma}^*(\mathbf{r})
\tag{54}
$$

where $\bar{V}_{\mathrm{xc}i\sigma}$ denotes the average of $V_{\mathrm{xc}\sigma}(\mathbf{r})$ with respect to the ith orbital, i.e.

$$\bar{V}_{\mathrm{xc}i\sigma} := \int \mathrm{d}^3 r \varphi_{i\sigma}^*(\mathbf{r}) V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \tag{55}$$

and

$$\bar{u}_{\mathrm{xc}i\sigma} := \int \mathrm{d}^3 r \varphi_{i\sigma}^*(\mathbf{r}) u_{\mathrm{xc}i\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}). \tag{56}$$

Using the KS Equation (28), we can solve Equation (54) for $V_{S\sigma}(\mathbf{r})\psi_{i\sigma}^*(\mathbf{r})$:

$$V_{S\sigma}(\mathbf{r})\psi_{i\sigma}^*(\mathbf{r}) = -[V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}) - u_{\mathrm{xc}i\sigma}(\mathbf{r}) - (\bar{V}_{\mathrm{xc}i\sigma} - \bar{u}_{\mathrm{xc}i\sigma})]\varphi_{i\sigma}^*(\mathbf{r}) +$$
$$+ \left(\frac{\nabla^2}{2} + \quad {}_i \quad \varepsilon \quad {}_\sigma \quad {}_i \quad (\quad {}_\sigma \quad \mathbf{r} \tag{57} \right) \quad) \quad \psi \quad . \quad {}^*$$

The differential Equation (54) has the structure of a KS equation with an additional inhomogeneity term. Equation (54) plus the boundary condition that $\psi_{i\sigma}^*(\mathbf{r})$ tends to zero as $r \to \infty$ uniquely determines $\psi_{i\sigma}^*(\mathbf{r})$. We can prove this statement by assuming that there are two independent solutions $\psi_{i\sigma,1}^*(\mathbf{r})$ and $\psi_{i\sigma,2}^*(\mathbf{r})$ of Equation (54). Then the difference between these two solutions, $\Psi_{i\sigma}^*(\mathbf{r}) := \psi_{i\sigma,1}^*(\mathbf{r}) - \psi_{i\sigma,2}^*(\mathbf{r})$, satisfies the homogeneous KS equation

$$(\hat{h}_{S\sigma} - \varepsilon_{i\sigma})\Psi_{i\sigma}^*(\mathbf{r}) = 0, \tag{58}$$

which has a unique solution

$$\Psi_{i\sigma}^*(\mathbf{r}) = \varphi_{i\sigma}^*(\mathbf{r}), \tag{59}$$

if the above boundary condition is fulfilled. However, this solution leads to a contradiction with the orthogonality relation (51) so that $\Psi_{i\sigma}^*(\mathbf{r})$ can only be the trivial solution of Equation (58),

$$\Psi_{i\sigma}^*(\mathbf{r}) \equiv 0. \tag{60}$$

This completes the proof.

At this point it is useful to attach some physical meaning to the quantity $\psi_{i\sigma}$: from Equation (49) it is obvious that $\psi_{i\sigma}$ is the usual first-order shift in the wavefunction caused by the perturbing potential $\delta V_{i\sigma} = V_{\mathrm{xc}\sigma}^{\mathrm{OEP}} - u_{\mathrm{xc}i\sigma}$. This fact also motivates the boundary condition assumed above. In x-only theory, $u_{\mathrm{x}i\sigma}$ is the local, orbital-dependent HF exchange potential so that $\psi_{i\sigma}$ is the first order shift of the KS wavefunction towards the HF wavefunction. One has to realize, however, that the first-order change of the orbital dependent potential $u_{\mathrm{x}i\sigma}[\{\varphi_{i\sigma}\}]$ has been neglected. This change can be expected to be small compared to $\delta V_{i\sigma}$ [20].

Having found an equation satisfied by $\psi^*_{i\sigma}(\mathbf{r})$ in which $V^{\text{OEP}}_{\text{xc}\sigma}(\mathbf{r})$ shows up explicitly, we may use this identity to further transform the OEP Equation (50). To this end we multiply Equation (50) by the KS potential $V_{S\sigma}(\mathbf{r})$

$$\sum_{i=1}^{N_\sigma} V_{S\sigma}(\mathbf{r})[\ldots]\psi^*\varphi + \text{c.c.} = 0 \tag{61}$$

and employ Equation (57) to obtain

$$0 = \sum_{i=1}^{N_\sigma}\left\{[V^{\text{OEP}}_{\text{xc}\sigma}(\mathbf{r}) - u_{\mathbf{x}ci\sigma}(\mathbf{r}) - (\bar{V}_{\mathbf{x}ci\sigma} - \bar{u}_{\mathbf{x}ci\sigma})]\varphi^*_{i\sigma}(\mathbf{r}) - \right.$$
$$\left. - \left(\frac{\nabla^2}{2} + \varepsilon_{i\sigma}\right)\psi^*_{i\sigma}(\mathbf{r})\right\}\varphi_{i\sigma}(\mathbf{r}) + \text{c.c.} \tag{62}$$

Solving this equation for $V^{\text{OEP}}_{\text{xc}\sigma}$ yields

$$V^{\text{OEP}}_{\text{xc}\sigma}(\mathbf{r}) = \frac{1}{2\rho_\sigma(\mathbf{r})}\sum_{i=1}^{N_\sigma}\left\{|\varphi_{i\sigma}(\mathbf{r})|^2[u_{\text{xc}i\sigma}(\mathbf{r}) + (\bar{V}_{\text{xc}i\sigma} - \bar{u}_{\text{xc}i\sigma})] + \right.$$
$$\left. + \left(\frac{\nabla^2}{2}\psi^*_{i\sigma}(\mathbf{r}) + \varepsilon_{i\sigma}\psi^*_{i\sigma}(\mathbf{r})\right)\varphi_{i\sigma}(\mathbf{r})\right\} + \text{c.c.} \tag{63}$$

The second term in the curly brackets may be rewritten by using the KS and the OEP equation again, leading to

$$\sum_{i=1}^{N_\sigma}\left(\frac{\nabla^2}{2}\psi^*_{i\sigma}(\mathbf{r}) + \varepsilon_{i\sigma}\psi^*_{i\sigma}(\mathbf{r})\right)\varphi_{i\sigma}(\mathbf{r}) + \text{c.c.}$$
$$= \sum_{i=1}^{N_\sigma}\left[\left(\frac{\nabla^2}{2}\psi^*_{i\sigma}(\mathbf{r})\right)\varphi_{i\sigma}(\mathbf{r}) - \psi^*_{i\sigma}(\mathbf{r})\left(\frac{\nabla^2}{2}\varphi_{i\sigma}(\mathbf{r})\right)\right] + \text{c.c.}$$
$$= -\sum_{i=1}^{N_\sigma}\nabla\cdot(\psi^*_{i\sigma}(\mathbf{r})\nabla\varphi_{i\sigma}(\mathbf{r})) + \text{c.c.} \tag{64}$$

In this way Equation (63) may be written as

$$V^{\text{OEP}}_{\text{xc}\sigma}(\mathbf{r}) = \frac{1}{2\rho_\sigma(\mathbf{r})}\sum_{i=1}^{N_\sigma}|\varphi|^2[v_{\text{xc}i\sigma}(\mathbf{r}) + (\bar{V}_{\text{xc}i\sigma} - \bar{u}_{\text{xc}i\sigma})] + \text{c.c.} \tag{65}$$

with

$$v_{\text{xci}\sigma}(\mathbf{r}) = u_{\text{xci}\sigma}(\mathbf{r}) - \frac{1}{|\varphi_{i\sigma}(\mathbf{r})|^2} \nabla \cdot (\psi_{i\sigma}^*(\mathbf{r}) \nabla \varphi_{i\sigma}(\mathbf{r})). \tag{66}$$

Equation (65) is an exact transformation of the original OEP integral Equation (43). The advantage of Equation (65), although still being an integral equation, lies in the fact that it may serve as a starting point for constructing approximations of $V_{\text{xc}\sigma}^{\text{OEP}}$: We only need to approximate $\psi_{i\sigma}^*$ in Equation (66) by a suitable functional of the orbitals.

The simplest possible approximation is obtained by completely neglecting the terms involving $\psi_{i\sigma}^*$, i.e. by replacing $v_{\text{xci}\sigma}$ by $u_{\text{xci}\sigma}$. At first sight, this approximation might appear rather crude. It can be interpreted, however, as a mean-field approximation in the sense that the neglected terms averaged over the ground-state spin density $\rho_\sigma(\mathbf{r})$ vanish. To demonstrate this, we investigate the quantity

$$\int d^3 r \nabla \cdot \frac{1}{2} \sum_{i=1}^{N_\sigma} (\psi_{i\sigma}^*(\mathbf{r}) \nabla \varphi_{i\sigma}(\mathbf{r})) \tag{67}$$

which amounts to the difference between the exact $V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r})$ and the approximated xc potential averaged over $\rho_\sigma(\mathbf{r})$. By virtue of the divergence theorem, the integral can be transformed to a surface integral. The latter vanishes because $\psi_{i\sigma}^*(\mathbf{r})$ and $\varphi_{i\sigma}(\mathbf{r})$ decrease exponentially for $r \to \infty$ [15]. Hence, the neglected terms have zero average value. The resulting equation, known as the KLI approximation, is given by

$$V_{\text{xc}\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 [u_{\text{xci}\sigma}(\mathbf{r}) + (\bar{V}_{\text{xci}\sigma}^{\text{KLI}} - \bar{u}_{\text{xci}\sigma})] + \text{c.c.} \tag{68}$$

which has proved to be an excellent approximation to the full xc potential $V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r})$ [15, 18, 19]. We immediately recognize that this form is very similar to the Slater potential.

In contrast to the full OEP Equation (43), the KLI equation, still being an integral equation, can be solved explicitly in terms of the orbitals $\{\varphi_{i\sigma}\}$: multiplying Equation (68) by $|\varphi_{j\sigma}(\mathbf{r})|^2$ and integrating over space yields

$$\bar{V}_{\text{xcj}\sigma}^{\text{KLI}} = \bar{V}_{\text{xcj}\sigma}^{S} + \sum_{i=1}^{N_\sigma-1} M_{ji} V_{\text{xci}\sigma}^{\text{KLI}} \left(-\frac{1}{2}(\bar{u}_{\text{xci}\sigma} + \bar{u}_{\text{xci}\sigma}^*)\right), \tag{69}$$

where

$$\bar{V}_{\text{xcj}\sigma}^{S} := \int d^3 r \frac{\phi_{j\sigma}^2(\mathbf{r})}{\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \frac{1}{2}(u_{\text{xci}\sigma}(\mathbf{r}) + u_{\text{xci}\sigma}^*(\mathbf{r})) \tag{70}$$

and

$$M_{ji\sigma} := \int d^3r \frac{\varphi_{j\sigma}(\mathbf{r})|\varphi_{i\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})}.$$
(71)

The term corresponding to the highest occupied orbital $\varphi_{N_\sigma\sigma}$ has been excluded from the sum in Equation (69) because $\bar{V}_{\mathrm{xc}N_\sigma\sigma} = \bar{u}_{\mathrm{xc}N_\sigma\sigma}$ [15]. The remaining unknown constants $(\bar{V}_{\mathrm{xc}i\sigma}^{\mathrm{KLI}} - \frac{1}{2}(\bar{u}_{\mathrm{xc}i\sigma} + \bar{u}_{\mathrm{xc}i\sigma}^*))$ are determined by the linear equation

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

$$= \left(\bar{V}_{\mathrm{xc}j\sigma}^S - \frac{1}{2}(\bar{u}_{\mathrm{xc}j\sigma} + \bar{u}_{\mathrm{xc}j\sigma}^*) \right),$$
(72)

with $j = 1, \ldots, N_\sigma - 1$. Solving Equation (72) and substituting the result into Equation (68), we obtain an explicitly orbital dependent functional.

We note that the KLI Equation (68) can also be obtained by a less rigorous derivation, namely by approximating the energy denominator in the Green's function (52) by a single constant as was first suggested by Sharp and Horton [30] and further elaborated by Krieger, Li, and Iafrate [13, 15].

Numerical calculations [15, 18, 19] for atomic systems neglecting correlation effects have shown that the KLI approximation gives excellent results which deviate only by a few ppm from the much more involved exact solutions of the full OEP integral Equation (43). Results for diatomic molecules [39] appear to be of similar quality. Examples will be presented in Section 3.

2.3. RIGOROUS PROPERTIES OF THE OEP AND KLI POTENTIALS

To conclude this section we will describe (without proof) some exact properties of the OEP method and the KLI approximation.

- *Asymptotics*: for finite systems, both the full OEP and the KLI potential fall off as $-1/r$ for $r \to \infty$ [15] if the exact expression (27) for the exchange-energy functional is employed.
- *Freedom of self-interaction*: if the employed xc-energy functional cancels the self-interaction of the Hartree term, this property is preserved by the KLI approximation. Thus x-only OEP and x-only KLI schemes are self-interaction free. It has to be noted, however, that the inclusion of an LDA-correlation-energy functional might introduce a self-interaction error again.
- *Derivative discontinuities*: an important property of the *exact* xc energy is that it exhibits derivative discontinuities as a function of particle number N at integer values of N. This has important consequences for the values of band gaps in insulators and semiconductors (for a detailed description see e.g. [2]):

Table I. 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
$\langle r^2 \rangle$	1.4465	1.4467	1.4791	1.4876	1.4889
$\langle r^{-1} \rangle$	3.8736	3.8738	3.8731	3.8729	3.8648
$\rho(0)$	3839.7	3832.6	3847.3	3847.0	3818.7

The correct value E^g of the gap is obtained by adding the discontinuity Δ_{xc} of the xc potential to the KS gap, i.e., $E^g = E^g_{\text{KS}} + \Delta_{\text{xc}}$. Neither the LDA nor GGAs reproduce this discontinuity. To date, the OEP and the KLI potential are the only known approximations of $V_{\text{xc}}(\mathbf{r})$ that reproduce this property of the exact xc potential [15].

3. Selected Results

3.1. ATOMIC SYSTEMS

We begin with a comparison of x-only results. In an x-only world, the OEP represents the *exact* KS potential of DFT and can therefore serve as a standard to compare approximations with.

In Table I we show as a typical example various results for the argon atom obtained with different x-only methods. Besides the exact OEP and KLI methods employing the exact exchange energy functional (27) described above, we also list results from conventional KS-DFT obtained with the x-energy-functional approximations due to Becke (B88) [40], Perdew and Wang (PW91) [41] and from the well-known x-only LDA approximation. The KLI results given in the second column of Table I 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.

Extensive calculations for atoms [32, 39, 42] have shown that a suitable correlation-energy functional to be combined with the exact exchange energy functional in the KLI scheme is the one developed by Colle and Salvetti (CS) [43, 44]. It is given by

$$E_c^{\mathrm{CS}}[\{\varphi_{i\sigma}\}]$$

$$= -ab \int \mathrm{d}^3 r \gamma(\mathbf{r})\xi(\mathbf{r}) \times$$

$$\times \left[\sum_\sigma \rho_\sigma(\mathbf{r}) \sum_i |\nabla\varphi_{i\sigma}(\mathbf{r})|^2 - \frac{1}{4}|\nabla\rho(\mathbf{r})|^2 - \right.$$

$$\left. -\frac{1}{4}\sum_\sigma \rho_\sigma(\mathbf{r})\Delta\rho_\sigma(\mathbf{r}) + \frac{1}{4}\rho(\mathbf{r})\Delta\rho(\mathbf{r}) \right] -$$

$$-a \int \mathrm{d}^3 r \gamma(\mathbf{r})\frac{\rho(\mathbf{r})}{\eta(\mathbf{r})}, \tag{73}$$

where

$$\gamma(\mathbf{r}) = 4\frac{\rho_\uparrow(\mathbf{r})\rho_\downarrow(\mathbf{r})}{\rho(\mathbf{r})^2}, \tag{74}$$

$$\eta(\mathbf{r}) = 1 + \qquad {}^{1/3}, \quad d \qquad\qquad \rho \qquad\qquad (\qquad\qquad \mathbf{r} \tag{75} \qquad) \qquad\qquad {}^-$$

$$\xi(\mathbf{r}) = \frac{\rho(\mathbf{r})^{-5/3}\exp[-c\rho(\mathbf{r})^{-1/3}]}{\eta(\mathbf{r})}. \tag{76}$$

The values of constants a, b, c and d are $a = 0.04918$, $b = 0.132$, $c = 0.2533$, $d = 0.349$.

In Table II 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 (27) plus the CS-correlation energy functional, while the next columns show conventional KS results. The latter were obtained with an LDA functional using the parametrisation of the correlation energy of a homogeneous electron gas by Perdew and Wang [47]; the x-energy functional due to Becke [40] combined with the c-energy functional of Lee, Yang and Parr [48], denoted as BLYP; and the generalized gradient approximation due to Perdew and Wang [41], referred to as PW91. The quantum chemistry values, headed QC, are based on configuration interaction calculations [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 $\bar{\Delta}$, are about the same for the KLICS and QC approaches, while they are about twice as high for the GGAs and about a factor of 80 higher in the LDA. We emphasize that the numerical effort involved in the KLICS scheme for atoms is only slightly higher than in the LDA and GGA schemes.

Table II. 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 [32] 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	

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 III: all the conventional KS calculations are inadequate, the numbers are off by about 100% due to the wrong asymptotic behaviour of the xc-potentials in these approximations. Only the KLICS scheme results in a potential with the correct $-1/r$ decay for large r.

3.2. RESULTS FOR DIATOMIC MOLECULES

The feasibility of the KLI approximation for more complex systems has been demonstrated recently [39] by x-only calculations on diatomic molecules. Some x-only results for the N_2 molecule are shown in Table IV. Among all the density functional approaches the KLI scheme yields results closest to the HF values. In principle, the density functional results should not be compared with HF but rather with exact x-only OEP values. For molecules, however, the latter are not available yet. From atomic results [18, 19] it is expected that HF and exact x-only OEP values will agree closely for total energies while the orbital energies are expected to be somewhat different.

It remains to examine the effect of correlation contributions. Therefore, we have implemented the CS functional (73) for E_c in our fully numerical basis-set-free code for diatomic molecules, which is based on the Xα program developed by Laaksonen, Sundholm and Pyykkö [50]. The solution of the Kohn–Sham equation and the exchange energy integrals are calculated by means of relaxation techniques

Table III. 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 [32] 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 IV. X-only results for N_2 with bond length of 2.07 a.u. HF values from [50]. Q_2^{tot} and Q_4^{tot} denote the total quadrupole and hexadecapole moments, respectively, calculated from the center of mass. All numbers in atomic units. Taken from [39] and modified.

	HF	KLI	xPW91	xLDA
E_{TOT}	−108.9936	−108.9856	−109.0581	−107.7560
$\varepsilon_{1\sigma g}$	−15.6822	−14.3722	−14.0717	−13.8950
$\varepsilon_{1\sigma u}$	−15.6787	−14.3709	−14.0703	−13.8936
$\varepsilon_{2\sigma g}$	−1.4726	−1.3076	−1.0014	−0.9875
$\varepsilon_{2\sigma u}$	−0.7784	−0.7453	−0.4611	−0.4434
$\varepsilon_{3\sigma g}$	−0.6347	−0.6305	−0.3927	−0.3335
$\varepsilon_{1\pi g}$	−0.6152	−0.6818	−0.3478	−0.3887
Q_2^{tot}	−0.9372	−0.9488	−1.1962	−1.1643
Q_4^{tot}	−7.3978	−6.7476	−6.1809	−6.2553
$\langle 1/r \rangle_N$	21.6543	21.6439	21.6921	21.5820

on a two-dimensional grid. For comparison, we have also performed calculations employing the conventional density dependent xcLDA and PW91 functionals for E_{xc}.

Table V. Results for the Neon atom using various DFT approaches. 1D denotes the exact values obtained with our one-dimensional code, 2D the results from our 2D code with a bond distance of 1 a.u. and one nuclear charge set to zero. 1D calculations performed with a grid size of 800 points, 2D calculations with a grid size of 145×241 points. All numbers in atomic units.

| | KLICS | | PW91 | | xcLDA | |
	1D	2D	1D	2D	1D	2D
E_{TOT}	−128.920235	−128.920234	−128.946580	−128.946580	−128.229914	−128.229915
ε_{1s}	−30.841442	−30.841447	−30.507920	−30.507920	−30.305770	−30.305770
ε_{2s}	−1.741044	−1.741044	−1.334970	−1.334970	−1.322601	−1.322601
$\varepsilon_{2p\sigma}$	−0.884057	−0.884057	−0.494228	−0.494228	−0.497847	−0.497847
$\varepsilon_{2p\pi}$	−0.884057	−0.884057	−0.494228	−0.494228	−0.497847	−0.497847
$\langle 1/r \rangle$	3.111736	3.111751	3.110075	3.110091	3.099824	3.099840
$\langle r \rangle$	0.787235	0.787235	0.799878	0.799878	0.801547	0.801547
$\langle r^2 \rangle$	0.931987	0.931987	0.982608	0.982608	0.985199	0.985200

Table VI. Calculated bond lengths of the closed-shell-first-row dimers and hydrides. HF values taken from [51]. Experimental values from [52] except where noted. All values in atomic units.

	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	–	4.588	4.522	–	4.63[b]
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 [53].
[b]From [54].

Table VII. Absolute total ground-state energies of the closed-shell-first-row dimers and hydrides calculated at the bond lengths given in Table VI. Estimates for exact values calculated using dissociation energies from Table VIII and non-relativistic, infinite nuclear mass atomic ground-state energies from [55]. All numbers in Hartrees.

	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 [53].
[b]Calculated at the experimental bond length of 4.63 a.u.

To demonstrate the accuracy of our implementation, we show results for the neon atom obtained with our molecular code and compare them with the ones from our one-dimensional atomic structure program in Table V. It is obvious from the table that the accuracy of our molecular code is very good, the deviation from the exact results obtained with the atomic code is a few μHartrees at the most.

We have calculated the ground-state properties of the closed-shell-first-row dimers and hydrides in the approximations mentioned above in a fully self-consistent fashion. As our program uses no basis functions, the results are free

Table VIII. Dissociation energies of the closed-shell-first-row dimers and hydrides calculated at the bond lengths given in Table VI. HF values taken from [51]. All numbers in mHartrees.

	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 [53].
[c]From [54].
[d]From [52].
[e]From [56].

Table IX. 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 VI. Experimental values are the ionization potentials taken from [52]. All numbers in Hartrees.

	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].

of basis-set truncation errors. Where available, we have also included HF results which, however, were obtained with conventional codes using basis-set expansions.

In Table VI we display results for the bond lengths. It is apparent that the KLICS scheme results in distances which are generally too short, an effect present in the HF approximation as well. The LDA and PW91 functionals give values which are clearly superior, the latter further reducing the error of the former.

Total absolute ground-state energies calculated at the bond lengths given in Table VI are shown in Table VII. The exact values for the dimers are from [54], for the hydrides they are calculated by the same method using the exact non-relativistic ground state energies for atoms in [55] and the experimental dissociation energies in [52]. 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 form H_2 and LiH, the dissociation energies as obtained within the KLICS approach are disappointing, as may be read in Table VIII. In most cases, the magnitude is considerably underestimated and for Be_2 and F_2 even the wrong sign is obtained. Since the corresponding *atomic* ground-state energies given in the previous subsection are of excellent quality, the error must be due to correlation effects present in molecules only. In particular, the left-right correlation error well-known in HF theory also occurs in DFT when the exact Fock expression (27) for E_x is employed. Apparently, the error is not sufficiently corrected for by the Colle-Salvetti functional. The LDA and PW91 results are clearly much better, the latter reducing the over-binding tendencies of the former.

Despite all of these shortcomings, the asymptotic form of the KLICS xc potential is of much better quality than that of all the conventional xc-functional approximations. In Table IX we list the absolute values of the highest occupied molecular orbital energies. In an *exact* implementation their values should be equal to 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 30 to 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 behaviour of the KLICS xc potential for large r.

4. Conclusions

Due to the wealth of exact properties satisfied by the OEP, we argue that this third generation of density functional theory provides a promising basis for further advances. While the results for atoms are very encouraging, the construction of correlation functionals better adapted to correct the left-right deficiency of the exact exchange energy functional is necessary if reliable results for molecular systems are to be obtained.

Acknowledgments

References

1. E. K. U. Gross and R. M. Dreizler (eds.): *Density Functional Theory*, Vol. 337 of NATO ASI Series B, Plenum Press, New York (1995).
2. R.M. Dreizler and E. K. U. Gross: *Density Functional Theory*, Springer, Berlin (1990).
3. R. G. Parr and W. Yang: *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York (1989).
4. P. Hohenberg and W. Kohn: *Phys. Rev.* **136**, B864 (1964).
5. Q. Zhao and R.G. Parr: *Phys. Rev. A* **46**, 2337 (1992).
6. C. J. Umrigar and X. Gonze: in *High Performance Computing and its Application to the Physical Sciences*, D. A. Browne *et al.* (eds.), World Scientific, Singapore (1993).
7. C. J. Umrigar and X. Gonze: *Phys. Rev. A* **50**, 3827 (1994).
8. R. van Leeuven and E.J. Baerends: *Phys. Rev. A* **49**, 2421 (1994).
9. A. Görling and M. Ernzerhof: *Phys. Rev. A* **51**, 4501 (1995).
10. V. E. Ingamells and N. C. Handy: *Chem. Phys. Lett.* **248**, 373 (1996).
11. W. Kohn and L. J. Sham: *Phys. Rev.* **140**, A1133 (1965).
12. J. P. Perdew, J. A. Cheavry, S. H. Vosko, K. A. Jackson, M. A. Pederson, D. J. Singh, and C. Fiolhais: *Phys. Rev. B* **46**, 6671 (1992).
13. J. B. Krieger, Y. Li, and G. J. Iafrate: *Phys. Lett. A* **146**, 256 (1990).
14. J. B. Krieger, Y. Li, M. R. Norman, and G. J. Iafrate: *Phys. Rev. B* **44**, 10437 (1991).
15. J. B. Krieger, Y. Li, G. J. Iafrate: *Phys. Rev. A* **45**, 101 (1992).
16. J. B. Krieger, Y. Li, and G. J. Iafrate: *Phys. Rev. A* **46**, 5453 (1992).
17. J. B. Krieger, Y. Li, and G. J. Iafrate: *Int. J. Quantum Chem.* **41**, 489 (1992).
18. Y. Li, J. B. Krieger, and G. J. Iafrate: *Chem. Phys. Lett.* **191**, 38 (1992).
19. Y. Li, J. B. Krieger, and G. J. Iafrate: *Phys. Rev. A* **47**, 165 (1993).
20. J. B. Krieger, Y. Li, and G. J. Iafrate: in *Density Functional Theory*, R.M. Dreizler and E.K.U. Gross (eds.), Plenum Press, New York (1995).
21. J. B. Krieger, J. Chen, Y. Li, and G. J. Iafrate: *Int. J. Quantum Chem. Symp.* **29**, 79 (1995).
22. C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross: *Phys. Rev. Lett.* **74**, 872 (1995).
23. C. A. Ullirich, S. Erhard, and E. K. U. Gross: in *Superintense Laser Atom Physics IV*, NATO ASI series 3/13, edited by H. G. Muller and M. V. Fedorov, Kluwer, Dordrecht (1996).
24. M. Petersilka, U. J. Gossmann, and E. K. U Gross: *Phys. Rev. Lett.* **76**, 1212 (1996).
25. E. K. U. Gross, J. F. Dobson, and M. Petersilka: in *Topics in Current Chemistry*, R.F. Nalewajski (ed.), Springer, Berlin (1996).
26. U. von Barth and L. Hedin: *J. Phys. C* **5**, 1629 (1972).
27. M. M. Pant and A. K. Rajagopal: *Sol. State Commun.* **10**, 1157 (1972).
28. A. Görling and M. Levy: *Phys. Rev. A* **50**, 196 (1994).
29. A. Görling and M. Levy: *Int. J. Quantum Chem. Symp.* **29**, 93 (1995).
30. R. T. Sharp and G. K. Horton: *Phys. Rev.* **90**, 317 (1953).
31. J. D. Talman and W. F. Shadwick: *Phys. Rev. A* **14**, 36 (1976).
32. T. Grabo and E. K. U. Gross: *Chem. Phys. Lett.* **240**, 141 (1995).
33. V. Sahni, J. Gruenebaum, and J. P. Perdew: *Phys. Rev. B* **26**, 4371 (1982).
34. J. P. Perdew and M. R. Norman: *Phys. Rev. B* **26**, 5445 (1982).
35. E. Engel and S. H. Vosko: *Phys. Rev. A* **47**, 2800 (1993).

36. T. Kotani: *Phys. Rev. B* **50**, 14816 (1994); ibid., **51,** 13903 (1995)(E).
37. T. Kotani: *Phys. Rev. Lett.* **74,** 2989 (1995).
38. T. Kotani and H. Akai: *Phys. Rev. B* **52,** 17153 (1995).
39. T. Grabo and E. K. U. Gross: *Int. J. Quantum Chem.* **64**, 95 (1997).
40. A. D. Becke: *Phys. Rev. A* **38**, 3098 (1988).
41. J. P. Perdew, K. Burke, and Y. Wang: *Phys. Rev. B* **54**, 16533 (1996).
42. E. K. U. Gross, M. Petersilka, and T. Grabo: in *Chemical Applications of Density Functional Theory*, ACS Symposium Series 629, B. B. Laird, R. B. Ross, and T. Ziegler (eds.), American Chemical Society, Washington, DC (1996).
43. R. Colle and D. Salvetti: *Theoret. Chim. Acta* **37,** 329 (1975).
44. R. Colle and D. Salvetti: *Theoret. Chim. Acta* **53,** 55 (1979).
45. J. A. Montgomery, J. W. Ochterski, and G. A. Petersson: *J. Chem. Phys.* **101**, 5900 (1994).
46. E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. Froese Fischer: *Phys. Rev. A* **44**, 7071 (1991).
47. J. P. Perdew and Y. Wang: *Phys. Rev. B* **45,** 13244 (1992).
48. C. Lee, W. Yang, and R. G. Parr: *Phys. Rev. B* **37**, 785 (1988).
49. A. A. Radzig and B. M. Smirnov: *Reference Data on Atoms and Molecules*, Springer, Berlin (1985).
50. L. Laaksonen, P. Pyykkö, and D. Sundholm: *Comp. Phys. Reports* **4,** 313 (1986).
51. B. G. Johnson, P. M. W. Gill, and J. A. Pople: *J. Chem. Phys.* **98**, 5612 (1993).
52. K. P. Huber and G. Herzberg: *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules,* Van Nostrand Reinhold, New York (1979).
53. W. Kolos and L. Wolniewicz: *J. Chem. Phys.* **49**, 404 (1968).
54. C. Filippi and C. J. Umrigar: *J. Chem. Phys.* **105,** 213 (1996).
55. S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. Froese Fischer: *Phys. Rev. A* **47**, 3649 (1993).
56. K. A. Peterson, R. A. Kendall, and T. H. Dunning: *J. Chem. Phys.* **99,** 1930 (1993).
57. O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends: *J. Chem. Phys.* **104,** 8535 (1996).