Density functional theory using an optimized exchange-correlation potential

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Abstract

We have performed self-consistent calculations for first and second row atoms using a variant of density-functional theory, the optimized effective potential method, with an approximation due to Krieger, Li and Iafrate and a correlation-energy functional developed by Colle and Salvetti. The mean absolute deviation of first-row atomic ground-state energies from the exact non-relativistic values is 4.7 mH in our scheme, as compared to 4.5 mH in a recent configuration-interaction calculation. The proposed scheme is significantly more accurate than the conventional Kohn-Sham method while the numerical effort involved is about the same as for an ordinary Hartree-Fock calculation.

1   Introduction

Since the development of modern density-functional theory (DFT) by Hohenberg, Kohn and Sham [1, 2] the accurate treatment of exchange and correlation (xc) poses a major challenge. Although there exist quite a number of approximations for the xc-energy functional [3, 4, 5, 6, 7, 8, 9], which give rather good results [10, 11], the need for further improvement is undisputable.

In conventional DFT the xc energy E_{xc} is approximated by *explicit* functionals of the density ρ. The local density approximation (LDA) [6] and the generalized gradient approximations (GGA) [7, 8, 9] fall in this category. However, there exists another approach within the framework of DFT, the so-called optimized effective potential (OEP) method first suggested by Sharp and Horton [12] and refined by Talman and Shadwick [13]. In this approach, the total energy (atomic units are used throughout)

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

is a functional of $N = N_\uparrow + N_\downarrow$ spin orbitals $\varphi_{j\sigma}$ resulting from a single-particle Schrödinger equation with a local effective potential:

$$
\left(-\frac{\nabla^2}{2} + V_\sigma(\mathbf{r})\right) \varphi_{j\sigma}(\mathbf{r}) = \varepsilon_{j\sigma}\varphi_{j\sigma}(\mathbf{r}) \qquad j = 1,\ldots,N_\sigma \qquad \sigma = \uparrow,\downarrow \,.
\tag{2}
$$

The *optimized* effective potential, $V_\sigma^{OEP}(\mathbf{r})$, is determined by the condition that its orbitals be the ones that minimize the energy functional (1). The stationarity condition

$$
\left. \frac{\delta E_{tot}^{OEP}}{\delta V_\sigma(\mathbf{r})} \right|_{V=V^{OEP}} = 0
\tag{3}
$$

may be written by virtue of the chain rule for functional derivatives as

$$
\sum_i \int d\mathbf{r}' \frac{\delta E_{tot}^{OEP}\left[\{\varphi_{j\sigma}\}\right]}{\delta\varphi_{i\sigma}(\mathbf{r}')} \left. \frac{\delta\varphi_{i\sigma}(\mathbf{r}')}{\delta V_\sigma(\mathbf{r})} \right|_{V=V^{OEP}} + c.c. = 0.
\tag{4}
$$

Given an approximation of $E_{xc}\left[\{\varphi_{j\sigma}\}\right]$, the first derivative in the integrand of equation (4) is easily computed from equation (1). To obtain a more accessible form of the second derivative in equation (4), one may use perturbation theory

for an infinitesimal perturbing potential $\delta V_\sigma(\mathbf{r})$ to get

$$\frac{\delta \varphi_{i\sigma}(\mathbf{r}')}{\delta V_\sigma(\mathbf{r})} = -\sum_{\substack{k=1 \\ k\neq i}}^{\infty} \frac{\varphi_{k\sigma}^*(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_{k\sigma} - \varepsilon_{i\sigma}} \varphi_{i\sigma}(\mathbf{r}). \tag{5}$$

Insertion of the functional derivative of (1) and equation (5) into equation (4), leads, via the one-particle equation (2), to the following integral equation:

$$\sum_{i=1}^{N_\sigma} \int d\mathbf{r}' \left(V_{xc\sigma}^{OEP}(\mathbf{r}') - u_{xci\sigma}(\mathbf{r}') \right) \left(\sum_{\substack{k=1 \\ k\neq i}}^{\infty} \frac{\varphi_{k\sigma}^*(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_{k\sigma} - \varepsilon_{i\sigma}} \right) \varphi_{i\sigma}(\mathbf{r})\varphi_{i\sigma}^*(\mathbf{r}') + c.c. = 0 \tag{6}$$

with

$$u_{xci\sigma}(\mathbf{r}) := \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_{xc}[\{\varphi_{j\sigma}\}]}{\delta\varphi_{i\sigma}(\mathbf{r})} \tag{7}$$

and

$$V_{xc\sigma}^{OEP}(\mathbf{r}) := V_\sigma^{OEP}(\mathbf{r}) + \frac{Z}{|\mathbf{r}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{8}$$

We emphasize that from a fundamental point of view the total-energy functional (1) is identical with the Hohenberg-Kohn energy functional

$$E_{tot}^{HK}[\rho_\uparrow, \rho_\downarrow] = T_S[\rho_\uparrow, \rho_\downarrow] - Z\int \frac{\rho(\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' + E_{xc}[\rho_\uparrow, \rho_\downarrow] \tag{9}$$

of conventional spin-DFT: By virtue of the Hohenberg-Kohn theorem for noninteracting systems, the spin orbitals $\varphi_{j\sigma}$ are functionals of the spin densities ρ_σ so that

$$E_{tot}^{HK}[\rho_\uparrow, \rho_\downarrow] = E_{tot}^{OEP}[\{\varphi_{j\sigma}[\rho_\uparrow, \rho_\downarrow]\}]. \tag{10}$$

In other words, the orbital functional (1) is an *implicit* density functional. If the (unknown) exact xc functional were used in equation (1) then the optimized effective potential determined by equation (6) would be the exact Kohn-Sham potential. Any approximation of E_{xc} in equation (1), on the other hand, leads to an approximate Kohn-Sham potential.

There are three non-trivial density functionals contributing to the Hohenberg-Kohn-total-energy functional (9): the non-interacting kinetic energy functional $T_S[\rho_\uparrow, \rho_\downarrow]$, the exchange part $E_x[\rho_\uparrow, \rho_\downarrow]$ and the correlation part $E_c[\rho_\uparrow, \rho_\downarrow]$ of $E_{xc}[\rho_\uparrow, \rho_\downarrow]$. If $T_S[\rho_\uparrow, \rho_\downarrow]$ is approximated by an LDA, one obtains the Thomas-Fermi model. The transition from Thomas-Fermi to modern Kohn-Sham theory is equivalent to replacing the *approximate* LDA functional by the *exact orbital representation*

$$T_S^{exakt}[\rho_\uparrow, \rho_\downarrow] = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \int \varphi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \varphi_{i\sigma}(\mathbf{r}) d\mathbf{r}. \tag{11}$$

The transition from standard Kohn-Sham theory to the OEP method can be viewed in much the same way: While in ordinary Kohn-Sham theory the exchange-energy functional is *approximated* by LDA or GGA-type functionals such as the one due to Becke [8], the OEP method allows one to employ the *exact orbital representation*

$$E_x^{exact}\left[\rho_\uparrow, \rho_\downarrow\right] = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k} \int d\mathbf{r} \int d\mathbf{r}' \frac{\varphi_{j\sigma}^*(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \qquad (12)$$

of the Kohn-Sham-exchange-energy functional[1], which leads, by virtue of equation (3), to the variationally *best local* exchange potential $V_{x\sigma}^{OEP}(\mathbf{r})$. Of particular importance is the fact that $V_{x\sigma}^{OEP}(\mathbf{r})$ is manifestly self-interaction free. Of course, the correlation part $E_c\left[\rho_\uparrow, \rho_\downarrow\right]$ still has to be approximated, but even for $E_c\left[\rho_\uparrow, \rho_\downarrow\right]$ the representation in terms of orbitals allows more flexibility in the construction of approximate functionals. In particular, $V_{xc\sigma}^{OEP}(\mathbf{r})$ is currently the only approximate xc potential featuring the required discontinuities as a function of the particle number N_σ [18].

The full OEP method, however, has a serious drawback: The solution of the integral equation (6) is numerically very involved. Recently, Krieger, Li and Iafrate [18, 19] have proposed an approximation (which we will refer to as KLI) to the OEP integral equation (6), in which $V_\sigma^{OEP}(\mathbf{r})$ is essentially obtained from the solution of two linear $(N_\sigma \times N_\sigma)$ equations. They also showed that in the x-only case, the results of the KLI approximation [18, 19, 20] are nearly identical with those of the exact x-only OEP-method [21, 22, 23]. In addition, the KLI approximation preserves all of the important advantages of the exact OEP method, such as the correct asymptotic $-\frac{1}{r}$ decay of $V^{OEP}(\mathbf{r})$ and the discontinuities of $V_{xc\sigma}^{OEP}(\mathbf{r})$ as a function of the particle number.

So far, the KLI approximation has been used exclusively in the x-only limit. In this letter, we present the first KLI calculations which include correlation effects. From the various available correlation-energy functionals we choose the one developed by Colle and Salvetti [24, 25]. This orbital-dependent functional gives correlation energies within a few percent of exact values if Hartree-Fock orbitals are inserted. The transformed version of it, the density functional of

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[1]The so-called Kohn-Sham-exchange-energy functional [23] is distinguished from the Hartree-Fock exchange energy expression by the fact that the orbitals in (12) come from a *local* single particle potential. It is this restriction to *local* potentials that allows one to establish the Hohenberg-Kohn 1-1 correspondence between densities and potentials which implies that the orbitals in equation (12) and thus E_x and E_c are implicit functionals of the *densities*. If the restriction to local potentials is dropped, then only a 1-1 mapping between (non-local) potentials $w(\mathbf{r},\mathbf{r}')$ and one-particle-density matrices $\rho(\mathbf{r},\mathbf{r}')$ can be established [14]. In this formalism *Hartree-Fock* exchange is treated *exactly* but the correlation energy becomes a functional of the *density matrix* rather than the density, which can lead to a N-representability problem [15]. For the density, on the other hand, N-representability is always satisfied [16, 17]. Therefore the restriction to local potentials and densities (rather than non-local potentials and density matrices) is essential.

Lee, Yang and Parr [9], has been shown to perform very well in self-consistent calculations [26], especially in connection with an exchange energy functional proposed by Becke [8].

2 Theory

In order to find an approximate solution to the OEP integral equation (6), Krieger, Li and Iafrate started from the Slater exchange potential [27], given by

$$V_{x\sigma}^S(\mathbf{r}) = \frac{1}{\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} \rho_{i\sigma}(\mathbf{r}) u_{xi\sigma}(\mathbf{r}), \tag{13}$$

with

$$\rho_{i\sigma}(\mathbf{r}) := |\varphi_{i\sigma}(\mathbf{r})|^2 \tag{14}$$

and

$$u_{xi\sigma}(\mathbf{r}) := \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_{x\sigma}[\{\varphi_{j\sigma}(\mathbf{r})\}]}{\delta \varphi_{i\sigma}(\mathbf{r})}, \tag{15}$$

where $E_{x\sigma}$ for $\sigma =\uparrow, \downarrow$ represents the spin-up and spin-down contribution, respectively, to the right-hand side of equation (12). KLI [18] argue that a generalized form of this potential, which differs from equation (13) only through orbital dependent constants $C_{i\sigma}$ added to $u_{xi\sigma}(\mathbf{r})$, should yield a better approximation than Slater's formula. Moreover, they were able to show through a series of manipulations [19], that the exact $V_{xc\sigma}^{OEP}(\mathbf{r})$ may be - up to within a small term they neglected - cast into a form similar to (13), namely

$$V_{xc\sigma}^{OEP}(\mathbf{r}) \approx V_{xc\sigma}^{KLI}(\mathbf{r}) = \frac{1}{\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} \rho_{i\sigma}(\mathbf{r}) \left[u_{xci\sigma}(\mathbf{r}) + \left(\bar{V}_{xci\sigma}^{OEP} - \bar{u}_{xci\sigma} \right) \right] \tag{16}$$

where the constants $\left(\bar{V}_{xci\sigma}^{OEP} - \bar{u}_{xci\sigma} \right)$ are the solution of the linear equation

$$\sum_{i=1}^{N_\sigma-1} (\delta_{ji} - M_{ji\sigma}) \left(\bar{V}_{xci\sigma}^{OEP} - \bar{u}_{xci\sigma} \right) = \bar{V}_{xcj\sigma}^S - \bar{u}_{xcj\sigma} \qquad j = 1, \ldots, N_\sigma - 1 \tag{17}$$

with

$$M_{ji\sigma} := \int d\mathbf{r} \, \frac{\rho_{j\sigma}(\mathbf{r})\rho_{i\sigma}(\mathbf{r})}{\rho_\sigma(\mathbf{r})}, \tag{18}$$

$$V_{xc\sigma}^S(\mathbf{r}) := \sum_{i=1}^N \frac{\rho_{i\sigma}(\mathbf{r})}{\rho_\sigma(\mathbf{r})} u_{xci\sigma}(\mathbf{r}). \tag{19}$$

$\bar{u}_{xcj\sigma}$ denotes the average value of $u_{xcj\sigma}(\mathbf{r})$ taken over the density of the $j\sigma$ orbital, i.e.

$$\bar{u}_{xcj\sigma} = \int \rho_{j\sigma}(\mathbf{r}) u_{xcj\sigma}(\mathbf{r}) d\mathbf{r} \tag{20}$$

5

and similarly for $\bar{V}^S_{xc\sigma}$. The indices in equation (17) run over all occupied orbitals except the one corresponding to the highest single-particle energy eigenvalue $\varepsilon_{N\sigma}$. If the highest occupied orbital is degenerate all orbitals with the energy $\varepsilon_{N\sigma}$ are excluded from the linear equation (17).

Splitting the exchange-correlation energy E_{xc}, as above, into an exchange and a correlation part, the exchange part (12) leads via equation (7) to the following expression for $u_{xj\sigma}$:

$$u_{xj\sigma}(\mathbf{r}) = -\frac{1}{\varphi^*_{j\sigma}(\mathbf{r})}\sum_k \int d\mathbf{r}'\,\frac{\varphi^*_{j\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r}')\varphi^*_{k\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}. \tag{21}$$

The correlation part, E_c, within the approximation by Colle and Salvetti [24, 25], is given by [9]

$$
\begin{aligned}
E_c =\ & -ab\int\gamma(\mathbf{r})\xi(\mathbf{r})\left[\sum_\sigma\rho_\sigma(\mathbf{r})\sum_i|\nabla\varphi_{i\sigma}(\mathbf{r})|^2\ -\ \frac{1}{4}|\nabla\rho(\mathbf{r})|^2\right.\\
& \left.-\frac{1}{4}\sum_\sigma\rho_\sigma(\mathbf{r})\triangle\rho_\sigma(\mathbf{r})\ +\ \frac{1}{4}\rho(\mathbf{r})\triangle\rho(\mathbf{r})\right]d\mathbf{r}\\
& -a\int\gamma(\mathbf{r})\frac{\rho(\mathbf{r})}{\eta(\mathbf{r})}\,d\mathbf{r},
\end{aligned}\tag{22}
$$

where

$$\gamma(\mathbf{r}) = 4\,\frac{\rho_\uparrow(\mathbf{r})\rho_\downarrow(\mathbf{r})}{\rho(\mathbf{r})^2}, \tag{23}$$

$$\eta(\mathbf{r}) = 1 + d\rho(\mathbf{r})^{-\frac{1}{3}}, \tag{24}$$

$$\xi(\mathbf{r}) = \frac{\rho(\mathbf{r})^{-\frac{5}{3}}e^{-c\rho(\mathbf{r})^{-\frac{1}{3}}}}{\eta(\mathbf{r})}. \tag{25}$$

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

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

Performing the functional derivative with respect to the one-particle orbitals, one obtains for $u_{cj\sigma}(\mathbf{r})$

$$
\begin{aligned}
u_{cj\sigma}(\mathbf{r}) =\ & -\frac{a}{\eta(\mathbf{r})}\left(\gamma(\mathbf{r}) + \rho(\mathbf{r})\frac{1}{\varphi^*_{j\sigma}(\mathbf{r})}\frac{\partial\gamma(\mathbf{r})}{\partial\varphi_{j\sigma}(\mathbf{r})}\right) - \frac{ad}{3}\gamma(\mathbf{r})\frac{\rho(\mathbf{r})^{-\frac{1}{3}}}{\eta(\mathbf{r})^2}\\
& -\frac{ab}{4}\frac{1}{\varphi^*_{j\sigma}(\mathbf{r})}\left[\frac{\partial}{\partial\varphi_{j\sigma}(\mathbf{r})}\big(\gamma(\mathbf{r})\xi(\mathbf{r})\big)\right]\left[4\sum_{\sigma'}\rho_{\sigma'}(\mathbf{r})\sum_i|\nabla\varphi_{i\sigma'}(\mathbf{r})|^2\right.\\
& \left.-\big(\nabla\rho(\mathbf{r})\big)^2 + \big(\rho_\uparrow(\mathbf{r})\triangle\rho_\downarrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})\triangle\rho_\uparrow(\mathbf{r})\big)\right]
\end{aligned}
$$

$$-\frac{ab}{2}\,\nabla\Big(\gamma(\mathbf{r})\xi(\mathbf{r})\Big)\Big(\nabla\rho(\mathbf{r})+\nabla\rho_{\tilde{\sigma}}(\mathbf{r})\Big)$$

$$-\frac{ab}{4}\,\triangle\Big(\gamma(\mathbf{r})\xi(\mathbf{r})\Big)\rho_{\tilde{\sigma}}(\mathbf{r})$$

$$-\,ab\;\gamma(\mathbf{r})\xi(\mathbf{r})\left[\sum_i\mid\nabla\varphi_{i\sigma}(\mathbf{r})\mid^2+\frac{1}{2}\Big(\triangle\rho(\mathbf{r})+\triangle\rho_{\tilde{\sigma}}(\mathbf{r})\Big)\right]$$

$$+\,ab\;\frac{\nabla\varphi_{j\sigma}^*(\mathbf{r})}{\varphi_{j\sigma}^*(\mathbf{r})}\nabla\Big(\gamma(\mathbf{r})\xi(\mathbf{r})\rho_\sigma(\mathbf{r})\Big)$$

$$+\,ab\;\frac{\triangle\varphi_{j\sigma}^*(\mathbf{r})}{\varphi_{j\sigma}^*(\mathbf{r})}\rho_\sigma(\mathbf{r})\gamma(\mathbf{r})\xi(\mathbf{r})\tag{26}$$

where $\tilde{\sigma}$ denotes the spin projection opposite to σ, i.e. $\tilde{\sigma}=\uparrow$ if $\sigma=\downarrow$ and vice versa.

In the numerical calculations, equation (16) is solved self-consistently together with the local one-particle equation

$$\left(-\frac{1}{2}\nabla^2+V_\sigma^{OEP}(\mathbf{r})\right)\varphi_{j\sigma}(\mathbf{r})=\varepsilon_{j\sigma}\varphi_{j\sigma}(\mathbf{r})\tag{27}$$

where

$$V_\sigma^{OEP}(\mathbf{r}):=V_{xc\sigma}^{KLI}(\mathbf{r})-\frac{Z}{\mathbf{r}}+\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'.\tag{28}$$

3 Results

Equation (27) is solved by expanding the single-particle orbitals in spherical harmonics. The resulting equation for the radial part of the wave functions is then solved numerically. The main features of the code are as described in Ref. 28.

For comparison, we have also performed calculations using the conventional Kohn-Sham method with two of the best standard exchange-correlation energy functionals. The first one of these is the exchange-energy functional by Becke [8] combined with the correlation-energy functional by Lee, Yang and Parr [9], referred to as BLYP. The other is the generalized gradient approximation by Perdew and Wang [7], referred to as PW91.

Table 1 shows the total absolute ground-state energies of the first-row atoms. For these atoms, there exist accurate estimates of the exact non-relativistic values obtained from experimental ionisation energies and improved *ab initio* calculations by Davidson et al. [30]. It is evident from the Table, that the density functional methods perform quite well. The mean absolute errors, $\bar{\triangle}$, given in the last row of Table 1, clearly show that the present approach is significantly more accurate than the conventional Kohn-Sham method and nearly as accurate as recent CI results by Montgomery et al. [29]. The situation is similar for second-row atoms, as can be seen from Table 2. As the relativistic effects

Table 1: *Total absolute ground-state energies for first-row atoms from various self-consistent calculations. CI values from Ref. 29. $\bar{\triangle}$ denotes the mean absolute deviation from the exact nonrelativistic values [30]. All numbers in Hartree units.*

	present	BLYP	PW91	CI	EXACT
He	2.9033	2.9071	2.9000	2.9049	2.9037
Li	7.4829	7.4827	7.4742	7.4743	7.4781
Be	14.6651	14.6615	14.6479	14.6657	14.6674
B	24.6564	24.6458	24.6299	24.6515	24.6539
C	37.8490	37.8430	37.8265	37.8421	37.8450
N	54.5905	54.5932	54.5787	54.5854	54.5893
O	75.0717	75.0786	75.0543	75.0613	75.067
F	99.7302	99.7581	99.7316	99.7268	99.734
Ne	128.9202	128.9730	128.9466	128.9277	128.939
$\bar{\triangle}$	0.0047	0.0108	0.0114	0.0045	

Table 2: *Total absolute ground-state energies for second-row atoms from various self-consistent calculations. $\bar{\triangle}$ denotes the mean absolute deviation from Lamb-shift corrected experimental values, taken from Ref. 3. All numbers in Hartree units.*

	present	BLYP	PW91	EXPT
Na	162.256	162.293	162.265	162.257
Mg	200.062	200.093	200.060	200.059
Al	242.362	242.380	242.350	242.356
Si	289.375	289.388	289.363	289.374
P	341.272	341.278	341.261	341.272
S	398.128	398.128	398.107	398.139
Cl	460.164	460.165	460.147	460.196
Ar	527.553	527.551	527.539	527.604
$\bar{\triangle}$	0.013	0.026	0.023	

Table 3: *Exchange and correlation energies from various approximations. All values in Hartree units.*

	$-E_x^{present}$	$-E_x^{BLYP}$	$-E_x^{PW91}$	$-E_c^{present}$	$-E_c^{BLYP}$	$-E_c^{PW91}$
He	1.028	1.018	1.009	0.0416	0.0437	0.0450
Li	1.784	1.771	1.758	0.0509	0.0541	0.0571
Be	2.674	2.658	2.644	0.0934	0.0954	0.0942
B	3.760	3.727	3.711	0.1289	0.1287	0.1270
C	5.064	5.028	5.010	0.1608	0.1614	0.1614
N	6.610	6.578	6.558	0.1879	0.1925	0.1968
O	8.200	8.154	8.136	0.2605	0.2640	0.2587
F	10.025	9.989	9.972	0.3218	0.3256	0.3193
Ne	12.110	12.099	12.082	0.3757	0.3831	0.3784
Na	14.017	14.006	13.985	0.4005	0.4097	0.4040
Mg	15.997	15.986	15.967	0.4523	0.4611	0.4486
Al	18.081	18.053	18.033	0.4905	0.4979	0.4891
Si	20.295	20.260	20.238	0.5265	0.5334	0.5322
P	22.649	22.609	22.587	0.5594	0.5676	0.5762
S	25.021	24.967	24.944	0.6287	0.6358	0.6413
Cl	27.530	27.476	27.453	0.6890	0.6955	0.7055
Ar	30.192	30.139	30.116	0.7435	0.7515	0.7687

for these atoms are more important and experiments increasingly difficult, the comparison of the calculated values with the Lamb-shift corrected experimental ones (from Ref. 3) has to be done cautiously and is by no means as rigorous as for first-row atoms. Nevertheless, our calculated values seem to mirror these experimental values more closely than the other approximations.

For further analysis, we list, in Table 3, the values of E_x and E_c separately. The data show two main features: First, the results for E_x are lowest for our method and highest for PW91, while the BLYP-values lie somewhere in between. And second, for E_c, this trend is reversed, as now our results are highest and the ones from BLYP and PW91 are lower in nearly all cases. In Table 4 we show results of various *x-only* calculations performed with only the exchange-energy parts of the respective functionals. For the spherical atoms listed, there exist exact x-only OEP values [22, 23]. It is evident, that the KLI-approximation gives values much closer to the exact ones than the generalized gradient approximations. ¿From this and from Table 3 one may conclude that in the BLYP and PW91 schemes an error cancellation between exchange and correlation energies occurs which leads to rather good total energies. Exchange and correlation energies *separately*, however, are poorly reproduced in the BLYP and PW91 approaches. By contrast, in our scheme, both exchange and correlation energies are

Table 4: *Total absolute exchange energies of spherical first and second row atoms for various self consistent x-only calculations. The exact OEP data are from Refs. 22 and 23. All values in Hartree units.*

	KLI	B88	PW91	OEP
He	1.026	1.016	1.005	1.026
Li	1.781	1.768	1.754	1.781
Be	2.667	2.652	2.638	2.666
N	6.603	6.569	6.547	6.604
Ne	12.099	12.086	12.061	12.105
Na	14.006	13.993	13.968	14.013
Mg	15.983	15.972	15.950	15.988
P	22.633	22.593	22.565	22.634
Ar	30.174	30.122	30.089	30.175

of high quality.

Limitations of the three DFT approaches studied here become evident for ionisation potentials and electron affinities. In Table 5 we show ionisation potentials calculated from ground-state-energy differences and CI values from Ref. 29 as well as experimental ones from Ref. 31. The performance of the three DFT methods is about the same, while the CI approach leads to clearly better results. Somewhat surprisingly, the DFT methods work better for the second-row than for the first-row atoms.

In *exact* DFT, the highest occupied orbital energy of the neutral atom is identical with the ionisation potential, while for negative ions the highest occupied energy level coincides with the electron affinity of the neutral atom [32]. How well ionisation potentials and electron affinities are reproduced by the highest occupied energy eigenvalues resulting from an *approximate* xc functional is therefore a measure of the quality of the functional. Table 6 shows the ionisation potentials obtained from the highest occupied single-particle-energy eigenvalue of the neutral atoms. The resulting values are worse than the ones in Table 5. While the deviation from experiment resulting from the BLYP and PW91 functionals is around 100 percent for all atoms, it is at most 10 percent in our approach. This is due to the fact that in our approach the xc potential has the correct $-\frac{1}{r}$ asymptotic behaviour for large r which is not properly reproduced with the BLYP and PW91 functionals.

For electron affinities, the situation is much worse, as may be seen from Table 7. First of all, because of the wrong asymptotic behaviour of the xc potential for large r, there is no convergence for negative ions within the self-consistent BLYP and PW91 schemes. This is not the case for our approach. However, the resulting electron affinities obtained either from ground-state-energy differences

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Table 5: *Ionisation potentials calculated from ground-state-energy differences of neutral atoms. CI values are from Ref. 29. $\bar{\triangle}$ denotes the mean absolute deviation from the experimental values, taken from Ref. 31. All values in Hartree units.*

	present	BLYP	PW91	CI	EXPT
He	0.903	0.912		0.905	0.903
Li	0.203	0.203	0.207	0.198	0.198
Be	0.330	0.330	0.333	0.344	0.343
B	0.314	0.309	0.314	0.304	0.305
C	0.414	0.425	0.432	0.413	0.414
N	0.527	0.542	0.551	0.534	0.534
O	0.495	0.508	0.505	0.499	0.500
F	0.621	0.656	0.660	0.639	0.640
Ne	0.767	0.808	0.812	0.792	0.792
$\bar{\triangle}$	0.009	0.010	0.014	0.001	
Na	0.191	0.197	0.198		0.189
Mg	0.275	0.280	0.281		0.281
Al	0.218	0.212	0.221		0.220
Si	0.294	0.294	0.305		0.300
P	0.379	0.376	0.389		0.385
S	0.380	0.379	0.379		0.381
Cl	0.471	0.476	0.482		0.477
Ar	0.575	0.576	0.583		0.579
$\bar{\triangle}$	0.004	0.005	0.004		

or from the highest orbital energies of negative ions are not very reliable, in fact, for the Boron atom, the wrong sign is obtained from the ground-state-energy differences. Here, quantum-chemical approaches, such as CI, are clearly superior.

4   Conclusions

We have studied a novel density-functional scheme combining the KLI approximation for the optimized effective potential with the correlation-energy functional of Colle and Salvetti. The total ground-state energies obtained with this method for first and second-row atoms are significantly more accurate than the ones from the standard BLYP and PW91 schemes and only slightly less accurate than recent CI calculations. Error cancellations between exchange and correlation energies, well known to be present in the standard LDA, BLYP and PW91 functionals are not found for the new scheme. Therefore, both exchange and correlation energies

Table 6: *Ionisation potentials from the highest occupied orbital energy of neutral atoms. Experimental values from Ref. 31. All values in Hartree units.*

	present	BLYP	PW91	EXPT
He	0.945	0.585	0.583	0.903
Li	0.200	0.111	0.119	0.198
Be	0.329	0.201	0.207	0.343
B	0.328	0.143	0.149	0.305
C	0.448	0.218	0.226	0.414
N	0.579	0.297	0.308	0.534
O	0.559	0.266	0.267	0.500
F	0.714	0.376	0.379	0.640
Ne	0.884	0.491	0.494	0.792
Na	0.189	0.106	0.113	0.189
Mg	0.273	0.168	0.174	0.281
Al	0.222	0.102	0.112	0.220
Si	0.306	0.160	0.171	0.300
P	0.399	0.219	0.233	0.385
S	0.404	0.219	0.222	0.381
Cl	0.506	0.295	0.301	0.477
Ar	0.619	0.373	0.380	0.579

Table 7: *Self-consistent electron affinities, (a) from ground-state-energy differences, and (b) from the highest occupied orbital energies of the negative ions. CI values are from Ref. 29, experimental ones from Ref. 31. All values in Hartree units.*

	present[a]	present[b]	CI	EXPT
Li	0.016	0.024	0.023	0.023
B	-0.002	0.033	0.008	0.010
C	0.028	0.083	0.045	0.046
O	0.017	0.110	0.052	0.054
F	0.082	0.208	0.125	0.125
Na	0.015	0.022		0.020
Al	0.007	0.024		0.016
Si	0.040	0.065		0.051
P	0.022	0.048		0.027
S	0.065	0.106		0.076
Cl	0.122	0.174		0.133

are separately of high accuracy.

The calculated atomic ionisation potentials are in satisfactory agreement with experiment but clearly inferior to CI results. If the ionisation potentials are calculated by taking ground-state-energy differences, the performance of the three DFT schemes is about the same. If, on the other hand, the ionisation potentials are calculated from the highest occupied orbital energy the new scheme is clearly superior to the BLYP and PW91 schemes. Percentage deviations are better by roughly an order of magnitude. This can be explained by the fact that the KLI approximation preserves the correct asymptotic $-\frac{1}{r}$ behaviour of the exact Kohn-Sham exchange potential while the BLYP and PW91 functionals are deficient in this respect. For the same reason, negative ions are not bound in the BLYP and PW91 self-consistent schemes so that electron affinities cannot be obtained, whereas the new scheme allows the calculation of these quantities. The calculated values, however, are not very reliable in comparison with experimental data and CI results. This clearly shows the need of further improving the correlation-energy functional. Work along these lines is in progress.

We finally emphasize that the numerical effort involved in the proposed scheme is only marginally higher than that of an ordinary Hartree-Fock calculation, whereas all the principles of standard DFT are preserved. We therefore expect that our approach can be used with great success in chemical studies of more complex and larger systems, improving the results [10, 11] obtained with the ordinary Kohn-Sham method.

5   Acknowledgements

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