The Optimized Effective Potential Method of Density Functional Theory: Applications to Atomic and Molecular Systems

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Abstract
Using the optimized effective potential method in conjunction with the semi-analytical approximation due to Krieger, Li and Iafrate, we have performed fully self-consistent exact exchange-only density-functional calculations for diatomic molecules with a fully numerical basis-set-free molecular code. The results are very similar to the ones obtained with the Hartree Fock approach. Furthermore we present results for ground states of positive atomic ions including correlation contributions in the approximation of Colle and Salvetti. It is found that the scheme performs significantly better than conventional Kohn-Sham calculations.

1 Introduction

Since its development by Talman and Shadwick [1], following the original idea of Sharp and Horton [2], the optimized effective potential (OEP) method has been recognized [3, 4] as the exact implementation of exchange-only density functional theory (DFT) [5, 6, 7, 8]. Due to the rather large computational effort involved, this scheme has not been used extensively. In the last years, however, the situation has changed. Using an accurate analytical approximation due to Krieger, Li and Iafrate (KLI) [9, 10, 11] the effort involved in numerical calculations based on the OEP has become comparable to conventional Kohn-Sham calculations, while the gain in accuracy is considerable.

In the following, we will briefly review the theoretical foundations of the OEP method and the KLI approximation and present, in section 3, applications of the method to molecular systems. Finally, in section 4, calculations for atomic systems
including correlation effects are discussed and compared with conventional Kohn-Sham results.

2 Basic formalism

We start from ordinary spin DFT [12, 13], where the basic variables are the spin-up and spin-down densities \( \rho_\uparrow(r) \) and \( \rho_\downarrow(r) \), respectively. They are obtained by self-consistently solving the single-particle Schrödinger equations (atomic units are used throughout)

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

where

\[
\rho_\sigma(r) = \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(r)|^2, \quad (2)
\]

The Kohn-Sham potentials \( V_\sigma(r) \) may be written in the usual way as

\[
V_\sigma(r) = v_{\text{ext}}(r) + \int d^3r' \frac{\rho(r')}{|r - r'|} + V_{\text{xc}}(r), \quad (3)
\]

\[
\rho(r) = \sum_{\sigma=\uparrow, \downarrow} \rho_\sigma(r) \quad (4)
\]

where \( v_{\text{ext}}(r) \) represents the Coulomb potential of the nuclei and \( V_{\text{xc}}(r) \) is a local exchange-correlation (xc) potential formally defined as functional derivative of the xc energy

\[
V_{\text{xc}}(r) := \frac{\delta E_{\text{xc}}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma(r)}. \quad (5)
\]

In order to understand the nature of the OEP method we recall that the Hohenberg-Kohn theorem [3], applied to non-interacting systems, ensures that the ground-state determinant and hence all occupied orbitals are unique functionals of the spin densities:

\[
\varphi_{j\sigma}(r) = \varphi_{j\sigma}[\rho_\uparrow, \rho_\downarrow](r). \quad (6)
\]

As a consequence of (3), any orbital functional \( E_{\text{xc}}[\{\varphi_{j\sigma}\}] \) is an implicit functional of \( \rho_\uparrow \) and \( \rho_\downarrow \), provided that the orbitals come from a local potential.

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

\[
E_{\text{tot}}^{\text{OEP}} [\rho_\uparrow, \rho_\downarrow] = \frac{1}{2} \sum_{\sigma=\uparrow, \downarrow} \sum_{i=1}^{N_\sigma} \int d^3r \varphi_{i\sigma}^*(r) \left( -\frac{\nabla^2}{2} \right) \varphi_{i\sigma}(r) + \int d^3r v_{\text{ext}}(r) \rho(r) + \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r - r'|} + E_{\text{xc}}^{\text{OEP}} [\{\varphi_{j\sigma}\}] \quad (7)
\]
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 $\rho_\downarrow$. As a consequence of this fact, the calculation of the xc potentials from Eq. (5) is somewhat more complicated: We use the chain rule for functional derivatives to obtain

$$V_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}[\{\varphi_{ij}\}]}{\delta \rho_\alpha(r)} = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int d^3r' \frac{\delta E_{\text{xc}}[\{\varphi_{ij}\}]}{\delta \varphi_{i\alpha}(r')} \frac{\delta \varphi_{i\alpha}(r')}{\delta \rho_\alpha(r)} + \text{c.c.} \quad (8)$$

and, by applying the functional chain rule once more,

$$V_{\text{xc}}(r) = \sum_{\alpha=\uparrow,\downarrow} \sum_{\beta=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int d^3r' \int d^3r'' \left( \frac{\delta E_{\text{xc}}[\{\varphi_{ij}\}]}{\delta \varphi_{i\alpha}(r')} \frac{\delta \varphi_{i\alpha}(r')}{\delta V_\beta(r'')} + \text{c.c.} \right) \frac{\delta V_\beta(r'')}{\delta \rho_\alpha(r)}. \quad (9)$$

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

$$\chi_{s\alpha,\beta}(r,r') := \frac{\delta \rho_\alpha(r)}{\delta V_\beta(r')} \quad (10)$$

This quantity is diagonal with respect to the spin variables so that Eq. (6) reduces to

$$V_{\text{xc}}(r) = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int d^3r' \int d^3r'' \left( \frac{\delta E_{\text{xc}}[\{\varphi_{ij}\}]}{\delta \varphi_{i\alpha}(r')} \frac{\delta \varphi_{i\alpha}(r')}{\delta V_\alpha(r'')} + \text{c.c.} \right) \chi_{s\alpha}(r'',r). \quad (11)$$

Acting with the response operator (10) on both sides of Eq. (11) one obtains

$$\int d^3r' V_{\text{xc}}(r') \chi_{s\alpha}(r',r) = \sum_{\alpha=\uparrow,\downarrow} \sum_{i=1}^{N_\alpha} \int d^3r' \frac{\delta E_{\text{xc}}[\{\varphi_{ij}\}]}{\delta \varphi_{i\alpha}(r')} \frac{\delta \varphi_{i\alpha}(r')}{\delta V_\alpha(r)} + \text{c.c..} \quad (12)$$

Finally, the second functional derivative on the right-hand side of Eq. (12) is calculated using first-order perturbation theory. This yields

$$\frac{\delta \varphi_{i\alpha}(r')}{\delta V_\alpha(r)} = \delta_{\alpha,\sigma} \sum_{k=1}^\infty \frac{\varphi_{ka}(r') \varphi_{ka}^*(r)}{\varepsilon_{i\sigma} - \varepsilon_{k\alpha}} \varphi_{i\alpha}(r). \quad (13)$$

Using the fact that the Kohn-Sham response function can be written as

$$\chi_{s\alpha}(r,r') = \sum_{i=1}^{N_\sigma} \sum_{k=1}^\infty \frac{\varphi_{i\alpha}^*(r) \varphi_{ka}^*(r) \varphi_{ka}(r') \varphi_{i\alpha}(r')}{\varepsilon_{i\sigma} - \varepsilon_{k\alpha}} + \text{c.c.} \quad (14)$$

the integral equation (12) takes the form

$$\sum_{i=1}^{N_\sigma} \int d^3r' \left( V_{\text{xc}}(r') - u_{\text{xc}\alpha}(r') \right) G_{s\sigma}(r',r) \varphi_{i\sigma}(r) \varphi_{i\sigma}(r') + \text{c.c.} = 0 \quad (15)$$
where

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

(16)

and

\[ G_{i\sigma}(r, r') := \sum_{k=1}^{\infty} \frac{\varphi_{k\sigma}(r) \varphi_{k\sigma}^*(r')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}}. \]  

(17)

The derivation of the OEP integral equation (15) described here was first given by Görling and Levy [14]. It is important to note that the same expression results [1, 9, 15] if one demands that the local one-particle potential appearing in Eq. (1) be the optimized one yielding orbitals minimizing the total energy functional (7), i.e. that

\[ \frac{\delta E_{\text{tot}}^{\text{OEP}}}{\delta V_{\sigma}(r)} \bigg|_{V = V_{\text{OEP}}} = 0. \]  

(18)

The main advantage of the OEP method is that it allows for the exact treatment of the exchange energy. Splitting up the total xc-functional into an exchange and a correlation part

\[ E_{\text{xc}}^{\text{OEP}}[\{\varphi_{j\tau}\}] = E_{\text{x}}[\{\varphi_{j\tau}\}] + E_{\text{c}}[\{\varphi_{j\tau}\}] \]  

(19)

we can use the exact Fock expression

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

(20)

Performing the functional derivative with respect to the orbitals one obtains for the x-part \( u_{\text{xc}i\sigma}(r) \) of the function

\[ u_{\text{xc}i\sigma}(r) = -\frac{1}{\varphi_{i\sigma}^*(r)} \sum_{k=1}^{N_\sigma} \varphi_{k\sigma}^*(r) \int d^3r' \frac{\varphi_{i\sigma}^*(r') \varphi_{k\sigma}(r')}{|r - r'|}. \]  

(21)

The use of the exact exchange energy has several advantages over the conventional explicitly density dependent xc functionals. Most importantly it ensures the correct \(-1/r\) decay of the xc-potential for large \( r \), reflecting the fact that it is self-interaction free. One has to emphasize that the OEP has the correct \(-1/r\) tail for all orbitals, i.e. for both the occupied and the unoccupied ones. By contrast, the conventional Hartree-Fock (HF) approach, which uses the same expression (20) for the exchange energy but a nonlocal potential defined via the equation [21]

\[ \left(V_{\text{xc}i\sigma}\varphi_{i\sigma}\right)(r) = -\sum_{j=1}^{N_\sigma} \int d^3r' \frac{\varphi_{i\sigma}^*(r') \varphi_{j\sigma}(r')}{|r - r'|} \varphi_{j\sigma}(r) \]  

(22)

is self-interaction free only for the occupied orbitals. However, x-only OEP calculations [1, 16, 17, 18, 19, 9], i.e. with the approximation \( E_{\text{c}}[\{\varphi_{j\tau}\}] = 0 \), performed on atomic systems have shown that the results for various physical quantities of interest such as total ground-state energies are very similar to HF results despite the different nature of the corresponding x-potentials. As - by construction - the
HF scheme gives the variationally best, i.e. lowest, total energy, the x-only OEP solutions are always slightly higher in energy.

The solution of the full integral equation (15) is numerically very demanding and has been achieved so far only for systems with spherical symmetry [1, 16, 17, 18, 9]. Therefore, one has to resort to further approximations for practical reasons. Krieger, Li and Iafrate [9] have suggested the analytical approximation

\[
G_{\sigma i\sigma}(\mathbf{r}, \mathbf{r}') \approx \frac{1}{\Delta \epsilon} \left( \delta(\mathbf{r} - \mathbf{r}') - \varphi_{i\sigma}(\mathbf{r})\varphi^*_{i\sigma}(\mathbf{r}') \right)
\]

(23)

for the Green’s-function-type quantity (17). Substituting this into the integral equation (15) and performing some algebra one arrives at the approximate equation

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

(24)

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

\[
\bar{u}_{xc i\sigma} = \int d^3r \, |\varphi_{i\sigma}(\mathbf{r})|^2 u_{xc i\sigma}(\mathbf{r})
\]

(25)

and similarly for \(\bar{V}_{xc i\sigma}^{KLI}\). In contrast to the exact integral equation (15) the KLI equation (24) can be solved explicitly for \(V_{xc i\sigma}^{\sigma}(\mathbf{r})\) by multiplication with \(\rho_\sigma(\mathbf{r})\) and subsequent integration. This leads to linear \((N_\sigma - 1) \times (N_\sigma - 1)\) equations for the unknown constants \(\left( \bar{V}_{xc i\sigma}^{KLI} - \bar{u}_{xc i\sigma} \right)\):

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

(26)

with \(j = 1, \ldots, N_\sigma - 1\),

\[
M_{ji\sigma} := \int d^3r \, \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})}
\]

(27)

and

\[
\bar{V}_{xc j\sigma}^{S}(\mathbf{r}) := \int d^3r \, \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \frac{1}{2} \left( u_{xc i\sigma}(\mathbf{r}) + u_{xc i\sigma}^*(\mathbf{r}) \right).
\]

(28)

The orbitals corresponding to the highest single-particle energy eigenvalues \(\varepsilon_{N_\sigma}\) have to be excluded from the linear equations (26) in order to ensure the correct long-range behaviour of \(V_{xc i\sigma}^{OEP}(\mathbf{r})\) [9]. It is an important property of the KLI approximation that it is exact for two-particle systems, where one has only one electron per spin projection. In this case, the OEP integral equation (15) may be solved exactly to yield (24). Furthermore, for these systems the OEP is also identical with the HF potential (22).

At first sight, the KLI approximation (23) might appear rather crude. The final result (24) for the KLI potential, however, can also be understood [20] as a well-defined mean-field approximation. Explicit calculations on atoms performed in the x-only limit [9, 10, 11] show that the KLI-approximation yields excellent results which differ only by a few ppm from the much more time-consuming exact solutions of the full integral equation (15).
3 Exchange-only results for molecular systems

In order to demonstrate the validity of the KLI-approach for more complex systems, we have performed x-only OEP calculations for diatomic molecules in KLI approximation employing the exact exchange energy functional as defined by equation (20) and neglecting correlation effects. This approach will, in the following, be referred to as x-only KLI. Our calculations have been performed with a fully numerical basis-set-free code, developed from the Xα program written by Laaksonen, Sundholm and Pyykkö [21, 22, 23]. The code solves the one-particle Schrödinger equation for diatomic molecules

\[
\left( -\frac{\nabla^2}{2} - \frac{Z_1}{|R_1 - r|} - \frac{Z_2}{|R_2 - r|} + V_H(r) + V_{KLI}^x(r) \right) \varphi_{j\sigma}(r) = \varepsilon_{j\sigma} \varphi_{j\sigma}(r), \quad (29)
\]

where \( R_i \) denotes the location and \( Z_i \) the nuclear charge of the \( i \)-th nucleus in the molecule. The partial differential equation is solved in prolate spheroidal coordinates on a two-dimensional mesh by a relaxation method, while the third variable, the azimuthal angle, is treated analytically. The Hartree potential

\[
V_H(r) = \int d^3r' \frac{\rho(r')}{|r - r'|} \quad (30)
\]

and the functions \( u_{x\sigma}(r) \) (cf. Eq. (21)) needed for the calculation of the exchange potential \( V_{x\sigma}^{KLI}(r) \) (cf. Eq. (24)) are computed as solutions of a Poisson and Poisson-like equation, respectively. In this step, the same relaxation technique as for the solution of the Schrödinger equation (29) is employed. Starting with an initial guess for the wave functions \( \varphi_{i\sigma}(r) \), equations (29), (30), (21) together with (24) are iterated until self-consistent. A very detailed description of the code is given in [24].

In order to test the accuracy of the program, we have performed calculations on the Beryllium and Neon atom which are compared in Table 1 to exact results obtained with a one-dimensional atomic code. The results agree to all decimals given. Furthermore, from Table 2 it is evident that our program gives results for the two-electron molecules He\(_2\) and HeH\(^+\) which are identical to the HF ones obtained by Laaksonen et al [23] as they should be, as the HF and x-only KLI schemes are identical for these systems.

For comparison, we have performed additional x-only calculations with two other approximations of \( V_{x\sigma}(r) \) and \( E_x \), respectively. The first one of these, denoted by Slater in the following, uses - like the HF and x-only KLI method - the exact orbital representation of \( E_x \) given in equation (20) but the averaged exchange potential due to Slater [23] given by

\[
V_{x\sigma}^S(r) = -\frac{1}{\rho_0(r)} \sum_{i,j=1}^{N_r} \varphi_{j\sigma}^*(r) \varphi_{i\sigma}(r) \int d^3r' \frac{\varphi_{i\sigma}^*(r') \varphi_{j\sigma}(r')}{|r - r'|}, \quad (31)
\]

which may be obtained from (24) by setting the constants \( \bar{V}_{x\sigma} - \bar{u}_{x\sigma} \) equal to zero for all \( i \). The other is the well known x-only local density approximation (LDA) of conventional DFT. As for the KLI calculations, we have successfully tested our implementations on atomic systems.
Table 1: X-only KLI results for the Beryllium and Neon atom. 1D denotes exact values obtained with our one-dimensional code, 2D the results from our two-dimensional code with one nuclear charge set equal to zero. All numbers in atomic units.

|          | Beryllium | Neon |
|----------|-----------|------|
|          | 1D        | 2D   | 1D   | 2D   |
| Grid     | 400       | 153 \times 249 | 400 | 153 \times 249 |
| $E_{TOT}$ | -14.5723  | -14.5723 | -128.5448 | -128.5448 |
| $\varepsilon_{HOMO}$ | -0.3089 | -0.3089 | -0.8494 | -0.8494 |
| $<1/r>$  | 2.1039    | 2.1039 | 3.1100 | 3.1100 |
| $<r^2>$  | 4.3255    | 4.3255 | 0.9367 | 0.9367 |

Table 2: Comparison of results for two electron molecules with assumed bond length R. HF values from [22]. $Q_1^f$, $Q_2^f$, $Q_3^f$, $Q_4^f$, denote the electronic contributions to the dipole, quadrupole, octopole and hexadecapole moments, respectively, determined from the molecular midpoint. All numbers in atomic units.

|          | H$_2$       | HeH$^+$    |
|----------|-------------|------------|
|          | R | 1.4 | 1.455 |
|          | HF | x-only KLI | HF | x-only KLI |
| $E_{TOT}$ | -1.133630 | -1.133630 | -2.933103 | -2.933103 |
| $\varepsilon_{1\sigma}$ | -0.594659 | -0.594659 | -1.637451 | -1.637451 |
| $Q_1^f$  | 0  | 0  | -0.494460 | -0.494460 |
| $Q_2^f$  | 0.243289 | 0.243289 | 0.373727 | 0.373727 |
| $Q_3^f$  | 0  | 0  | -0.231525 | -0.231525 |
| $Q_4^f$  | 0.090721 | 0.090721 | 0.173962 | 0.173962 |
| $<r^2>$  | 2.573930 | 2.573930 | 1.340832 | 1.340832 |

Table 3: X-only results for LiH. HF values for bond length of 3.015 a.u. from [24]. Present calculations performed on a 153 \times 193 grid with bond length of 3.015 a.u. All numbers in atomic units.
### Table 4: X-only results for BH. HF values for bond length of 2.336 a.u. from [24]. Present calculations performed on a 193 × 265 grid with bond length of 2.336 a.u. All numbers in atomic units.

|       | HF       | x-only KLI | Slater | x-only LDA |
|-------|----------|------------|--------|------------|
| $E_{\text{TOT}}$ | -25.1316 | -25.1290 | -25.1072 | -24.6299 |
| $\varepsilon_{1\sigma}$ | -7.6863 | -6.8624 | -7.4837 | -6.4715 |
| $\varepsilon_{2\sigma}$ | -0.6482 | -0.5856 | -0.6358 | -0.3956 |
| $\varepsilon_{3\sigma}$ | -0.3484 | -0.3462 | -0.3721 | -0.1626 |
| $Q_1^e$ | 5.3525  | 5.3498    | 5.2991  | 5.3154    |
| $Q_2^e$ | 12.1862 | 12.1416   | 11.4720 | 11.9542   |
| $Q_3^e$ | 15.6411 | 15.5618   | 14.3328 | 14.0904   |
| $Q_4^e$ | 25.8492 | 25.4188   | 25.2152 | 21.9134   |

### Table 5: X-only results for FH. HF values for bond length of 1.7328 a.u. from [24]. Present calculations performed on a 161 × 321 grid with bond length of 1.7328 a.u. All numbers in atomic units.

|       | HF       | x-only KLI | Slater | x-only LDA |
|-------|----------|------------|--------|------------|
| $E_{\text{TOT}}$ | -5.72333 | -5.72332  | -5.72332 | -5.44740 |
| $\varepsilon_{1\sigma}^g$ | -0.92017 | -0.91929  | -0.91977 | -0.51970 |
| $\varepsilon_{1\sigma}^u$ | -0.91570 | -0.91566  | -0.91614 | -0.51452 |
| $Q_1^e$ | 31.36165 | 31.35931  | 31.35907 | 31.35507  |
| $Q_2^e$ | 245.8779 | 245.8643  | 245.8615 | 245.8255  |

### Table 6: X-only results for He$_2$. HF values for bond length of 5.6 a.u. from [24]. Present calculations performed on a 209 × 225 grid with bond length of 5.6 a.u. All numbers in atomic units.

|       | HF       | x-only KLI | Slater | x-only LDA |
|-------|----------|------------|--------|------------|
| $E_{\text{TOT}}$ | -5.72333 | -5.72332  | -5.72332 | -5.44740 |
| $\varepsilon_{1\sigma}^g$ | -0.92017 | -0.91929  | -0.91977 | -0.51970 |
| $\varepsilon_{1\sigma}^u$ | -0.91570 | -0.91566  | -0.91614 | -0.51452 |
| $Q_1^e$ | 31.36165 | 31.35931  | 31.35907 | 31.35507  |
| $Q_2^e$ | 245.8779 | 245.8643  | 245.8615 | 245.8255  |
|    | HF         | x-only KLI  | Slater    | x-only LDA  |
|----|------------|-------------|-----------|-------------|
| $E_{\text{TOT}}$ | -14.8716   | -14.8706    | -14.8544  | -14.3970    |
| $\varepsilon_{1\sigma g}$ | -2.4531    | -2.0276     | -2.3875   | -1.7869     |
| $\varepsilon_{1\sigma u}$ | -2.4528    | -2.0272     | -2.3873   | -1.7864     |
| $\varepsilon_{2\sigma g}$ | -0.1820    | -0.1813     | -0.1989   | -0.0922     |
| $Q_2^c$  | 27.6362    | 27.4993     | 29.0014   | 29.4401     |
| $Q_4^c$  | 159.9924   | 159.6809    | 169.1300  | 172.8505    |

Table 7: X-only results for Li$_2$. HF values for bond length of 5.051 a.u. from [24]. Present calculations performed on a 209 \times 225 grid with bond length of 5.051 a.u. All numbers in atomic units.

|    | HF         | x-only KLI  | Slater    | x-only LDA  |
|----|------------|-------------|-----------|-------------|
| $E_{\text{TOT}}$ | -29.1337   | -29.1274    | -29.0939  | -28.4612    |
| $\varepsilon_{1\sigma g}$ | -4.73150   | -4.09876    | -4.60353  | -3.78576    |
| $\varepsilon_{1\sigma u}$ | -4.73147   | -4.09872    | -4.60351  | -3.87571    |
| $\varepsilon_{2\sigma g}$ | -0.39727   | -0.33452    | -0.37659  | -0.23067    |
| $\varepsilon_{2\sigma u}$ | -0.24209   | -0.23489    | -0.26524  | -0.13163    |
| $Q_2^c$  | 46.0878    | 46.2475     | 43.4833   | 46.2501     |
| $Q_4^c$  | 261.774    | 277.365     | 249.135   | 281.950     |

Table 8: X-only results for Be$_2$. HF values for bond length of 4.6 a.u. from [24]. Present calculations performed on a 209 \times 225 grid with bond length of 4.6 a.u. All numbers in atomic units.

|    | HF         | x-only KLI  | Slater    | x-only LDA  |
|----|------------|-------------|-----------|-------------|
| $E_{\text{TOT}}$ | -108.9936  | -108.9856   | -108.9110 | -107.7560   |
| $\varepsilon_{1\sigma g}$ | -15.6822   | -14.3722    | -15.2692  | -13.8950    |
| $\varepsilon_{1\sigma u}$ | -15.6787   | -14.3709    | -15.2682  | -13.8936    |
| $\varepsilon_{2\sigma g}$ | -1.4726    | -1.3076     | -1.3316   | -0.9875     |
| $\varepsilon_{2\sigma u}$ | -0.7784    | -0.7453     | -0.7473   | -0.4434     |
| $\varepsilon_{3\sigma g}$ | -0.6347    | -0.6305     | -0.6521   | -0.3335     |
| $\varepsilon_{1\pi g}$  | -0.6152    | -0.6818     | -0.6960   | -0.3887     |
| $Q_2^\text{tot}$ | -0.9372    | -0.9488     | -1.1756   | -1.1643     |
| $Q_4^\text{tot}$  | -7.3978    | -6.7476     | -7.1266   | -6.2553     |
| $< 1/r >_N$  | 21.6543    | 21.6439     | 21.9749   | 21.5820     |

Table 9: X-only results for N$_2$. HF values for bond length of 2.07 a.u. from [24]. Present calculations performed on a 209 \times 225 grid with bond length of 2.07 a.u. All numbers in atomic units.
Results are given in Tables 3 through 9 for LiH, BH, FH, He₂, Li₂, Be₂ and N₂. For each system we show the total ground state energy \( E_{\text{TOT}} \), the various orbital energy eigenvalues \( \varepsilon \) and the nonzero electronic contributions to the dipole, quadrupole, octopole and hexadecapole moments denoted by \( Q_{e1} \), \( Q_{e2} \), \( Q_{e3} \) and \( Q_{e4} \) calculated from the geometrical center of the molecule, respectively, except for FH and N₂, where the total moments (including nuclear contributions) calculated from the center of mass are given, denoted by \( Q_{\text{tot}}^{L} \). For these two molecules we also present the expectation values of \( 1/r \), denoted by \( \langle 1/r \rangle \), calculated at the nuclei.

For all physical quantities of interest, i.e. for \( E_{\text{TOT}} \), the energies \( \varepsilon_{\text{HOMO}} \) of the highest occupied orbitals and the multipole moments, the x-only KLI and HF results differ only slightly, usually by a few hundredths of a percent for total energies, a few tenths of a percent for \( \varepsilon_{\text{HOMO}} \) and a few percent for the multipole moments. The largest difference between the \( \varepsilon_{\text{HOMO}} \) values occurs for Be₂, where they differ by 3\%. For N₂, the energetic order of the \( 1\pi_u \) and \( 3\sigma_g \) orbital is reversed in all DFT approaches as compared to the HF result, which corresponds to the experimentally observed order of the outer valence ionization potentials [26]. As far as the multipole moments are concerned, the largest discrepancy between the x-only KLI and HF approaches occurs for the total hexadecapole moment of N₂, where the results differ by 8.8\%. In this case, the Slater approximation gives a value differing only by 3.7\% from the HF one. The \( 1/r \) expectation values obtained with the HF and x-only KLI method are almost identical, differing by only a few hundredths of a percent with the exception of the one for the Hydrogen nucleus in FH, where the difference is an order of magnitude larger. In this case, both the Slater as well as the x-only LDA approximations give values closer to the HF results.

The Slater method gives - with a few exceptions mentioned above - values for \( E_{\text{TOT}} \), \( \varepsilon_{\text{HOMO}} \), the multipole moments and \( 1/r \) expectation values which differ to a larger extent from both the KLI and HF results than the latter from each other. From the energy eigenvalues of the inner orbitals, on the other hand, it is obvious that the Slater exchange potential \( V_{\sigma \sigma}^{S}(r) \) is deeper than the one obtained in the KLI method, giving results closer to the HF ones.

Finally, the x-only LDA results differ more strongly from the other methods, yielding much higher total energies. The difference is most pronounced for the values of \( \varepsilon_{\text{HOMO}} \), which are roughly twice as large as the ones from any of the other methods. This is due to the wrong exponential decay of \( V_{x\sigma}^{\text{LDA}}(r) \) for large \( r \).

We point out that the bulk part of the difference between the x-only KLI and the HF results are not due to the KLI approximation, but to the different nature of the HF and the DFT approaches. This is an established fact for atomic systems [4, 10, 11] and we see no reason why it should not hold for molecular systems as well. We mention that the difference between the HF and the exact x-only DFT results also implies that the exact quantum chemical correlation energy and the exact DFT correlation energy are not identical [27].
4 Correlation contributions to the OEP

The inclusion of correlation effects into the OEP scheme is straightforward, as anticipated by the indices $x_c$ in section 2, once an explicit functional for $E_c[\{\phi_{j\tau}\}]$ has been specified. It has been shown \[15, 27\] that the orbital-dependent Colle-Salvetti functional \[28, 29\] is well suited for this purpose. It yields excellent results for atoms, surpassing the accuracy of conventional Kohn-Sham calculations. In this approximation, $E_c$ is given by \[15\]

$$E_c[\{\phi_{j\tau}\}] = -ab \int d^3r \, \gamma(r) \xi(r) \left[ \sum_{\sigma} \rho_{\sigma}(r) \sum_i |\nabla \phi_{i\sigma}(r)|^2 - \frac{1}{4} |\nabla \rho(r)|^2 ight.$$ 

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

$$- a \int d^3r \, \gamma(r) \frac{\rho(r)}{\eta(r)}, \tag{32}$$

where

$$\gamma(r) = 4 \frac{\rho_{\uparrow}(r) \rho_{\downarrow}(r)}{\rho(r)^2}, \tag{33}$$

$$\eta(r) = 1 + d \rho(r)^{- \frac{1}{2}}, \tag{34}$$

$$\xi(r) = \frac{\rho(r)^{- \frac{5}{2}} e^{-c \rho(r)^{- \frac{1}{2}}}}{\eta(r)}, \tag{35}$$

and

$$a = 0.04918, \quad b = 0.132,$$
$$c = 0.2533, \quad d = 0.349.$$

4.1 Two-Electron Systems

In order to study the correlation contributions more thoroughly, we first concentrate on two-electron atoms for two reasons. First of all, as pointed out above, the solution of the full OEP integral equation for these systems is identical to the one obtained from the KLI-scheme. As the exchange energy functional is also known exactly, c.f. equation (20), the only error made is due to the approximation for $E_c$. Secondly there exist practically exact solutions \[31\] of the two-particle Schrödinger equation so that various DFT-related quantities of interest can be compared with exact results.

In Table 10 we show the total absolute ground-state energies of the atoms isoelectronic with helium. The first column, denoted by KLICS, displays the results obtained with the above described method, including the Colle-Salvetti functional for $E_c$ into the OEP scheme. The next two columns show results obtained with the conventional Kohn-Sham method for comparison. BLYP denotes the use of the exchange-energy functional by Becke \[32\] combined with the correlation energy functional by Lee, Yang and Parr \[33\], whereas the third column headed PW91 refers to the generalized gradient approximation by Perdew and Wang \[34\]. The exact nonrelativistic results in the last column are taken from \[30\]. Note that there
Table 10: Total absolute ground-state energies for the Helium iso-electronic series from various self-consistent calculations. $\triangle$ denotes the mean absolute deviation from the exact values from [30]. All numbers in atomic units.

|        | KLICS     | BLYP      | PW91      | exact     |
|--------|-----------|-----------|-----------|-----------|
| H$^-$  | 0.5189    | 2.9033    | 2.9000    | 0.5278    |
| He     | 7.2803    | 7.2794    | 7.2676    | 7.2799    |
| Li$^+$ | 13.6556   | 13.6500   | 13.6340   | 13.6556   |
| Be$^{2+}$ | 22.0301 | 22.0200   | 21.9996   | 22.0310   |
| B$^{3+}$ | 32.4045   | 32.3896   | 32.3649   | 32.4062   |
| C$^{4+}$ | 44.7888   | 44.7592   | 44.7299   | 44.7814   |
| N$^{5+}$ | 59.1531   | 59.1286   | 59.0948   | 59.1566   |
| O$^{6+}$ | 75.5274   | 75.4981   | 75.4595   | 75.5317   |
| Ne$^{8+}$ | 93.9017   | 93.8675   | 93.8241   | 93.9068   |
| Na$^{9+}$ | 114.2761  | 114.2369  | 114.1886  | 114.2819  |
| Mg$^{10+}$ | 136.6505  | 136.6064  | 136.5531  | 136.6569  |
| Al$^{11+}$ | 161.0250  | 160.9758  | 160.9175  | 161.0320  |
| Si$^{12+}$ | 187.3995  | 187.3453  | 187.2819  | 187.4070  |
| P$^{13+}$ | 215.7740  | 215.7147  | 215.6462  | 215.7821  |
| S$^{14+}$ | 246.1485  | 246.0842  | 246.0105  | 246.1571  |
| Cl$^{15+}$ | 278.5231  | 278.4536  | 278.3748  | 278.5322  |
| Ar$^{16+}$ | 312.8977  | 312.8231  | 312.7390  | 312.9072  |
| K$^{17+}$ | 349.2723  | 349.1926  | 349.1032  | 349.2822  |
| Ca$^{18+}$ | 387.6470  | 387.5620  | 387.4674  | 387.6572  |
| $\triangle$ | 0.0053    | 0.0450    | 0.0943    |           |

is no convergence for negative ions in the conventional Kohn Sham method. All of our calculations have been performed with a basis-set-free, fully numerical atomic code which solves the radial Schrödinger equation (1) by the Numerov-method as described in [35]. The angular parts are treated analytically.

In Figure 1, we have plotted the errors $E_{tot}^{DFT} - E_{tot}^{exact}$ of the numbers shown in Table 10. It is obvious that the KLICS scheme gives superior results. The mean absolute error, denoted by $\triangle$, is smaller by an order of magnitude for the KLICS results as compared to the two conventional Kohn Sham approaches. This comes as no surprise, as the exchange part is treated exactly in the OEP method, whereas only approximative functionals can be used in the Kohn-Sham scheme. As may be read off Table 11, where we show the exchange and correlation contributions to the total energy separately for systems where exact values are available, an error cancellation occurs in the BLYP and PW91 approaches - the exchange energies being too large and the correlation energies being too small in magnitude. The KLICS results for these two quantities are clearly much better. However, for the highly charged two-electron ions the quality of the results decreases substantially in all approaches. For these systems the LYP-functional appears to perform best.

In order to assess the quality of the xc potentials resulting from various approx-
Figure 1: Energy differences corresponding to Table 10

| element  | KLICS | BLYP | PW91 | exact     |
|----------|-------|------|------|-----------|
| H⁻       | 0.4053|      |      | 0.3809    |
| He       | 1.0275| 1.0183| 1.0095| 1.0246    |
| Be²⁺     | 2.2768| 2.2573| 2.2367| 2.2766    |
| Ne⁸⁺     | 6.0272| 5.9749| 5.9189| 6.0275    |
| Hg⁷⁸⁺    | 49.7779| 49.3412| 48.8806| 49.7779   |

| element  | −Eₓ   |      |      |           |
|----------|-------|------|------|-----------|
| H⁻       | 0.0312|      |      | 0.0420    |
| He       | 0.0416| 0.0437| 0.0450| 0.0421    |
| Be²⁺     | 0.0442| 0.0493| 0.0530| 0.0443    |
| Ne⁸⁺     | 0.0406| 0.0504| 0.0615| 0.0457    |
| Hg⁷⁸⁺    | 0.0276| 0.0506| 0.0805| 0.0465    |

Table 11: Exchange and correlation energies from various approximations. Exact values from [31]. All values in atomic units.
imate functionals, it is informative to look at the highest occupied orbital energy of the system. In an exact implementation of DFT this value should be equal to the ionization potential of the system. Therefore, the resulting values from approximate schemes are an indication of the quality of the corresponding xc potential. From Table 12, where we have listed these numbers for various self-consistent approximations together with the exact ones, it is obvious that the KLICS scheme performs much better than the conventional Kohn-Sham schemes. The difference is less pronounced for the highly charged ions as the nuclear potential becomes the dominant term in the Kohn-Sham potential (3). A glance at the second column, in which we give the corresponding values from an x-only KLI calculation, shows, however, that the reason for the superior quality is due to the inclusion of the exact exchange in the KLI scheme, which results in the correct $-1/r$ asymptotic behaviour of the xc potential. In fact, adding the Colle-Salvetti formula for the correlation energy slightly worsens the results, as may be seen by comparing the second and third columns: The correlation contribution lowers the already too small values from the x-only calculations for the highest occupied orbital energy even more.

|      | KLI x-only | KLI xc | BLYP xc | PW91 xc | exact        |
|------|------------|--------|---------|---------|--------------|
| He   | 0.9180     | 0.9446 | 0.5849  | 0.5833  | 0.9037       |
| Li$^+$ | 2.7924     | 2.8227 | 2.2312  | 2.2269  | 2.7799       |
| Be$^{2+}$ | 5.6671     | 5.6992 | 4.8760  | 4.8701  | 5.6566       |
| B$^{3+}$ | 9.5420     | 9.5751 | 8.5201  | 8.5129  | 9.5310       |
| C$^{4+}$ | 14.4169    | 14.4507 | 13.1638 | 13.1554 | 14.4062      |
| N$^{5+}$ | 20.2918    | 20.3261 | 18.8072 | 18.7978 | 20.2814      |
| O$^{6+}$ | 27.1686    | 27.2014 | 25.4504 | 25.4401 | 27.1566      |
| F$^{7+}$ | 35.0418    | 35.0766 | 33.0935 | 33.0823 | 35.0317      |
| Ne$^{8+}$ | 43.9167    | 43.9517 | 41.7366 | 41.7245 | 43.9068      |
| Na$^{9+}$ | 53.7917    | 53.8269 | 51.3796 | 51.3666 | 53.7819      |
| Mg$^{10+}$ | 64.6667   | 64.7020 | 62.0225 | 62.0086 | 64.6569      |
| Al$^{11+}$ | 76.5417   | 76.5770 | 73.6654 | 73.6506 | 76.5320      |
| Si$^{12+}$ | 89.4167    | 89.4521 | 86.3083 | 86.2926 | 89.4071      |
| P$^{13+}$ | 103.2917   | 103.3272 | 99.9511 | 99.9345 | 103.2821     |
| S$^{14+}$ | 118.1666   | 118.2022 | 114.5939 | 114.5764 | 118.1571     |
| Cl$^{15+}$ | 134.0416  | 134.0773 | 130.2367 | 130.2183 | 134.0322     |
| Ar$^{16+}$ | 150.9166   | 150.9523 | 146.8795 | 146.8602 | 150.9072     |
| K$^{17+}$ | 168.7916   | 168.8273 | 164.5223 | 164.5021 | 168.7822     |
| Ca$^{18+}$ | 187.6666   | 187.7024 | 183.1650 | 183.1439 | 187.6572     |

Table 12: Absolute highest occupied orbital energies from various self-consistent calculations. Exact values calculated from [30]. All values in atomic units.

The error in the correlation potential responsible for this behaviour is clearly visible from Figure 2 where we plot the exact [31] and various self-consistent corre-
Figure 2: Comparison of the exact and self-consistently calculated correlation potentials of helium

ation potentials. The potential obtained with the Colle-Salvetti functional within the KLICS scheme shows the same deficiencies as the conventional density functionals: Instead of a maximum with positive values of the potential, the approximations possess one or even two minima and spurious divergences occur at the origin, which may be traced back to gradients of the density and of the one-particle orbitals occurring in the various correlation energy functionals. The need for further improvement of the correlation energy functional in this respect is obvious.

4.2 Beryllium and Neon Isoelectronic Series

For further analysis we have calculated the total ground state energies of positive ions isoelectronic with Beryllium (shown in Table 13) and Neon (shown in Table 14). Again, we compare the various DFT methods with exact data from Ref. [36]. The errors are plotted in Figures 3 and 4, respectively. The data for both series show the same trends: The overall best results are obtained with the KLICS scheme, where the absolute mean deviation $\triangle$ from the exact values is smallest. The BLYP scheme is only slightly worse, but the PW91 functional gives errors which are roughly twice as large as compared to the other DFT approaches. From the plots in Figures 3 and 4 it is obvious that these statements hold for most ions individually.

There are two other trends to be noted in these results. First we point out that although the absolute errors rise within the isoelectronic series as the atomic number increases, the percentage errors remain almost constant. And secondly, the mean absolute error is smaller by almost an order of magnitude for the ten-electron
The ionization potentials from the various approaches as calculated from the highest occupied Kohn-Sham orbitals are shown in Tables 15 and 16 for the four- and ten-electron series, respectively. The exact nonrelativistic values have been calculated from the data given in [36]. Due to the correct asymptotic behaviour of the xc-potential for large $r$ within the OEP scheme it comes as no surprise that the KLICS data are superior to the conventional Kohn-Sham approach. The effect of the correlation potential within the OEP scheme is – like in the two-electron case – a lowering of the energy eigenvalue of the highest occupied orbital, as may be seen from a comparison of the second and third columns showing the OEP results in $\chi$-only approximation and with inclusion of correlation in the form of Colle-Salvetti in the KLI-scheme, respectively. As opposed to the Helium and Neon isoelectronic series, this effect improves the quality of the results in the Beryllium isoelectronic series compared to the four-electron series.

Table 13: Total absolute ground-state energies for the Beryllium isoelectronic series from various self-consistent calculations. $\Delta$ denotes the mean absolute deviation from the exact values from [36]. All numbers in atomic units.

| Element | KLICS | BLYP | PW91 | exact |
|---------|-------|------|------|-------|
| Be      | 14.6651 | 14.6615 | 14.6479 | 14.6674 |
| B$^+$   | 24.3427 | 24.3366 | 24.3160 | 24.3489 |
| C$^{2+}$| 36.5224 | 36.5143 | 36.4881 | 36.5349 |
| N$^{3+}$| 51.2025 | 51.1927 | 51.1618 | 51.2228 |
| O$^{4+}$| 68.3825 | 68.3713 | 68.3362 | 68.4117 |
| F$^{5+}$| 88.0624 | 88.0499 | 88.0110 | 88.1011 |
| Ne$^{6+}$| 110.2420 | 110.2285 | 110.1859 | 110.2909 |
| Na$^{7+}$| 134.9216 | 134.9071 | 134.8610 | 134.9809 |
| Mg$^{8+}$| 162.1010 | 162.0857 | 162.0361 | 162.1710 |
| Al$^{9+}$| 191.7803 | 191.7642 | 191.7113 | 191.8613 |
| Si$^{10+}$| 223.9595 | 223.9427 | 223.8864 | 224.0516 |
| P$^{11+}$| 258.6387 | 258.6212 | 258.5616 | 258.7420 |
| S$^{12+}$| 295.8178 | 295.7996 | 295.7367 | 295.9324 |
| Cl$^{13+}$| 335.4968 | 335.4781 | 335.4119 | 335.6229 |
| Ar$^{14+}$| 377.6758 | 377.6566 | 377.5870 | 377.8134 |
| K$^{15+}$| 422.3548 | 422.3350 | 422.2621 | 422.5040 |
| Ca$^{16+}$| 469.5338 | 469.5134 | 469.4372 | 469.6946 |
| Sc$^{17+}$| 519.2127 | 519.1919 | 519.1122 | 519.3851 |
| Ti$^{18+}$| 571.3917 | 571.3703 | 571.2873 | 571.5757 |
| V$^{19+}$| 626.0706 | 626.0487 | 625.9623 | 626.2663 |
| Cr$^{20+}$| 683.2495 | 683.2271 | 683.1373 | 683.4570 |
| Mn$^{21+}$| 742.9284 | 742.9056 | 742.8123 | 743.1476 |
| Fe$^{22+}$| 805.1072 | 805.0840 | 804.9873 | 805.3382 |
| Co$^{23+}$| 869.7861 | 869.7624 | 869.6623 | 870.0289 |
| Ni$^{24+}$| 936.9650 | 936.9408 | 936.8373 | 937.2195 |

$\Delta = 0.1180 \quad 0.1352 \quad 0.1973$
| Element | KLICS  | BLYP   | PW91   | exact   |
|---------|--------|--------|--------|---------|
| Ne      | 128.9202 | 128.9730 | 128.9466 | 128.9376 |
| Na⁺     | 162.0645 | 162.0956 | 162.0668 | 162.0659 |
| Mg²⁺    | 199.2291 | 199.2448 | 199.2136 | 199.2204 |
| Al³⁺    | 240.4071 | 240.4102 | 240.3768 | 240.3914 |
| Si⁴⁺    | 285.5945 | 285.5867 | 285.5509 | 285.5738 |
| P⁵⁺     | 334.7888 | 334.7712 | 334.7331 | 334.7642 |
| S⁶⁺     | 387.9885 | 387.9616 | 387.9212 | 387.9608 |
| Cl⁷⁺    | 445.1922 | 445.1567 | 445.1138 | 445.1622 |
| Ar⁸⁺    | 506.3993 | 506.3554 | 506.3101 | 506.3673 |
| K⁹⁺     | 571.6091 | 571.5570 | 571.5092 | 571.5754 |
| Ca¹⁰⁺   | 640.8211 | 640.7610 | 640.7107 | 640.7861 |
| Sc¹¹⁺   | 714.0350 | 713.9671 | 713.9141 | 713.9988 |
| Ti¹²⁺   | 791.2504 | 791.1748 | 791.1191 | 791.2132 |
| V¹³⁺    | 872.4671 | 872.3839 | 872.3255 | 872.4291 |
| Cr¹⁴⁺   | 957.6850 | 957.5942 | 957.5331 | 957.6463 |
| Mn¹⁵⁺   | 1046.9039 | 1046.8056 | 1046.7417 | 1046.8646 |
| Fe¹⁶⁺   | 1140.1237 | 1140.0179 | 1139.9511 | 1140.0838 |
| Co¹⁷⁺   | 1237.3442 | 1237.2309 | 1237.1613 | 1237.3039 |
| Ni¹⁸⁺   | 1338.5654 | 1338.4447 | 1338.3722 | 1338.5247 |

| Δ       | 0.0293  | 0.0334  | 0.0694  |

Table 14: Total absolute ground-state energies for the Neon isoelectronic series from various self-consistent calculations. Δ denotes the mean absolute deviation from the exact values from [36]. All numbers in atomic units. We mention that the ionization potentials are in much better agreement with the exact results if they are calculated as ground-state energy differences [15].
Figure 3: Energy differences corresponding to Table 13.

Figure 4: Energy differences corresponding to Table 14.
|      | KLI x-only | KLICS xc | BLYP xc | PW91 xc | exact     |
|------|------------|----------|---------|---------|-----------|
| Be   | 0.3089     | 0.3294   | 0.2009  | 0.2072  | 0.3426    |
| B⁺   | 0.8732     | 0.8992   | 0.7129  | 0.7185  | 0.9243    |
| C²⁺  | 1.6933     | 1.7226   | 1.4804  | 1.4856  | 1.7594    |
| N³⁺  | 2.7659     | 2.7975   | 2.5000  | 2.5049  | 2.8459    |
| O⁴⁺  | 4.0898     | 4.1231   | 3.7706  | 3.7754  | 4.1832    |
| F⁵⁺  | 5.6644     | 5.6991   | 5.2918  | 5.2964  | 5.7708    |
| Ne⁶⁺ | 7.4896     | 7.5253   | 7.0633  | 7.0678  | 7.6087    |
| Na⁷⁺ | 9.5652     | 9.6017   | 9.0850  | 9.0894  | 9.6967    |
| Mg⁸⁺ | 11.8910    | 11.9281  | 11.3569 | 11.3611 | 12.0348   |
| Al⁹⁺ | 14.4669    | 14.5047  | 13.8788 | 13.8829 | 14.6230   |
| Si¹⁰⁺| 17.2930    | 17.3312  | 16.6508 | 16.6548 | 17.4613   |
| P¹¹⁺| 20.3692    | 20.4078  | 19.6729 | 19.6768 | 20.5496   |
| S¹²⁺| 23.6955    | 23.7345  | 22.9450 | 22.9487 | 23.8880   |
| Cl¹³⁺| 27.2718    | 27.3111  | 26.4671 | 26.4707 | 27.4763   |
| Ar¹⁴⁺| 31.0982    | 31.1378  | 30.2393 | 30.2427 | 31.3147   |
| K¹⁵⁺| 35.1747    | 35.2145  | 34.2615 | 34.2647 | 35.4031   |
| Ca¹⁶⁺| 39.5012    | 39.5412  | 38.5336 | 38.5367 | 39.7416   |
| Sc¹⁷⁺| 44.0777    | 44.1179  | 43.0558 | 43.0587 | 44.3300   |
| Ti¹⁸⁺| 48.9043    | 48.9447  | 47.8280 | 47.8307 | 49.1684   |
| V¹⁹⁺| 53.9808    | 54.0214  | 52.8502 | 52.8527 | 54.2569   |
| Cr²⁰⁺| 59.3074    | 59.3481  | 58.1224 | 58.1247 | 59.5954   |
| Mn²¹⁺| 64.8840    | 64.9249  | 63.6447 | 63.6467 | 65.1838   |
| Fe²²⁺| 70.7107    | 70.7516  | 69.4169 | 69.4187 | 71.0223   |
| Co²³⁺| 76.7873    | 76.8284  | 75.4391 | 75.4408 | 77.1108   |
| Ni²⁴⁺| 83.1140    | 83.1551  | 81.7113 | 81.7128 | 83.4493   |

Table 15: Ionization potentials from highest occupied Kohn-Sham orbital energies for the Beryllium isoelectronic series from various self-consistent calculations. Exact nonrelativistic values calculated from [36]. All numbers in atomic units.
Table 16: Ionization potentials from highest occupied Kohn-Sham orbital energies for the Neon isoelectronic series from various self-consistent calculations. 
Exact nonrelativistic values calculated from [36]. All numbers in atomic units.

|       | KLI x-only | KLICS xc | BLYP xc | PW91 xc | exact    |
|-------|------------|----------|---------|---------|----------|
| Ne    | 0.8494     | 0.8841   | 0.4914  | 0.4942  | 0.7945   |
| Na⁺   | 1.7959     | 1.8340   | 1.3377  | 1.3416  | 1.7410   |
| Mg²⁺  | 3.0047     | 3.0450   | 2.4531  | 2.4579  | 2.9499   |
| Al³⁺  | 4.4706     | 4.5125   | 3.8285  | 3.8339  | 4.4161   |
| Si⁴⁺  | 6.1912     | 6.2343   | 5.4601  | 5.4661  | 6.1371   |
| P⁵⁺   | 8.1651     | 8.2091   | 7.3458  | 7.3524  | 8.1112   |
| S⁶⁺   | 10.3914    | 10.4362  | 9.4846  | 9.4917  | 10.3378  |
| Cl⁷⁺  | 12.8696    | 12.9150  | 11.8757 | 11.8832 | 12.8162  |
| Ar⁸⁺  | 15.5992    | 15.6451  | 14.5185 | 14.5264 | 15.5460  |
| K⁹⁺   | 18.5800    | 18.6263  | 17.4126 | 17.4209 | 18.5270  |
| Ca¹⁰⁺ | 21.8118    | 21.8585  | 20.5579 | 20.5665 | 21.7589  |
| Sc¹¹⁺ | 25.2943    | 25.3413  | 23.9541 | 23.9630 | 25.2416  |
| Ti¹²⁺ | 29.0274    | 29.0747  | 27.6010 | 27.6102 | 28.9748  |
| V¹³⁺  | 33.0112    | 33.0587  | 31.4986 | 31.5080 | 32.9586  |
| Cr¹⁴⁺ | 37.2453    | 37.2931  | 35.6467 | 35.6563 | 37.1929  |
| Mn¹⁵⁺ | 41.7299    | 41.7779  | 40.0453 | 40.0551 | 41.6776  |
| Fe¹⁶⁺ | 46.4649    | 46.5130  | 44.6943 | 44.7042 | 46.4126  |
| Co¹⁷⁺ | 51.4501    | 51.4984  | 49.5936 | 49.6037 | 51.3979  |
| Ni¹⁸⁺ | 56.6856    | 56.7341  | 54.7432 | 54.7535 | 56.6335  |
5 Conclusions

Our calculations for molecular systems reveal that the KLI approach is also feasible for more complex systems and gives results of similar quality as for atoms. We expect that an inclusion of correlation effects will result in a highly accurate DFT scheme. The studies of correlation contributions to atomic systems show that further improvement of the presently available correlation-energy functionals is necessary.

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