Accuracy of the Krieger-Li-Iafrate approximation for molecules

E. Engel, A. Höck, and R. M. Dreizler

Institut für Theoretische Physik, Universität Frankfurt, D-60054 Frankfurt/Main, Germany

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Accurate electronic structure calculations for diatomic molecules have been performed, using the Krieger-Li-Iafrate (KLI) approximation to the optimized potential method (OPM) for the evaluation of the exact exchange potential of density-functional theory. It is found that the KLI scheme provides an excellent approximation to the full OPM for these systems. The deviations between both variants of the OPM are smaller than the differences resulting from the use of different basis sets. Furthermore, it is shown that the spectroscopic constants obtained with the exchange-only KLI approach are very close to Hartree-Fock values.

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I. INTRODUCTION AND SUMMARY OF CONCLUSIONS

The concept of implicit exchange-correlation (XC) energy functionals, in which not only the single-particle density but also the Kohn-Sham (KS) orbitals are used to represent the effective single-particle potential of density-functional theory (DFT) [1], is attracting more and more interest [2–17]. This approach has the advantage that it allows to treat the exchange part $E_x$ of the XC functional in an exact fashion, which guarantees the complete cancellation of self-interaction. As a consequence, it permits a discussion of negative ions (see, e.g., Refs. [4,9]), in contrast to the standard density functionals, i.e., the local-density (LDA) or generalized-gradient approximations (GGA). Moreover, it has recently been demonstrated that the combination of the exact $E_x$ with an orbital-dependent correlation functional allows the description of van der Waals bond systems [17], in contrast to the LDA and GGA. This fosters the hope that appropriate implicit functionals will be able to overcome other limitations of the LDA and GGA, as the prediction of electronic results for diatomic molecules including a full optimization of the bond lengths.

For implicit XC functionals the corresponding multiplicative XC potential $\nu_{XC}$ has to be calculated via the optimized potential method (OPM) [18,19]. In the OPM an integral equation has to be solved to obtain $\nu_{XC}$, requiring the knowledge of the complete KS single-particle spectrum, irrespective of the nature of the XC functional. Consequently, the full solution of the OPM integral equation is a rather time-consuming procedure (especially for nonspherical systems). A very efficient approximation to the OPM equation has been introduced by Krieger, Li, and Iafrate (KLI) [2]. It has been shown that the KLI approximation gives very accurate results both for light [5] and heavy [20] atoms. The KLI approximation has also been applied to molecules [11,14,17] and, within the pseudopotential approximation, to solids [8,10] (see also Ref. [3] where a combination of the KLI approximation inside the muffin tin with the LDA in the interstitial regime was used). Recently, first results for molecules beyond $\text{H}_2$ (for $\text{H}_2$ see Ref. [12]) have been presented in which the full OPM integral equation has been solved using basis set schemes [15,16]. Relying on these results, we assess in this contribution the accuracy of the KLI approximation in the molecular context. In addition, we provide all-electron results for diatomic molecules including a full optimization of the bond lengths.

For this conceptual study we restrict ourselves as in Refs. [15,16] to the exchange-only ($X$ only) limit (the addition of LDA or GGA correlation does not lead to a systematic improvement; compare Refs. [12,14]). We find that the differences between full OPM and KLI results are smaller than the deviations originating from different basis sets and that the spectroscopic constants obtained with the KLI approximation are in very good agreement with Hartree-Fock (HF) data. Given these observations, the KLI approximation appears to be fully justified in the case of molecules. In fact, compared with the full OPM the KLI approximation either allows to employ larger basis sets within the same computational budget, in this way providing access to larger systems, or to reduce the computational demands for given basis-set size.

II. TECHNICAL DETAILS

The general concept of the OPM and of the KLI approximation has been extensively discussed in the literature (see, e.g., Ref. [12]). Here we thus restrict ourselves to providing the technical details of our approach to diatomic molecules. For the solution of the two-center Kohn-Sham equations we use prolate spheroidal coordinates $\xi, \eta, \varphi$,

$$\xi = \frac{r_1 + r_2}{R}, \quad 1 \leq \xi < \infty,$$ (1)

$$\eta = \frac{r_1 - r_2}{R}, \quad -1 \leq \eta \leq 1,$$ (2)

$$\varphi = \tan^{-1} \left( \frac{y}{x} \right), \quad 0 \leq \varphi \leq 2 \pi,$$ (3)

where $r_1, r_2$ are the distances between the electronic coordinate $\mathbf{R}$ and the two nuclei at the positions $(0,0,\pm R/2)$, $r_{1,2} = \sqrt{x^2 + y^2 + (z \pm R/2)^2}$. Assuming rotational symmetry of the total KS potential $\nu_{s,\sigma}$ with respect to the internuclear axis

$$\nu_{s,\sigma}(r) = \nu_{s,\sigma}(\xi, \eta),$$
where the projection quantum number \( E \). ENGEL, A. HÖCK, AND R. M. DREIZLER PHYSICAL REVIEW A

eigenstates as
\[
\psi_{\kappa\sigma}(\xi, \eta) = \sum_{n=0}^{n_{max}} \sum_{l_{max}+|m|} c_{\kappa\sigma}^{l_{max}+|m|} P_{l_{max}+|m|}^{m}(\eta)(\xi^2 - 1)^{|m|/2} \exp\left(-\frac{\xi-1}{2\alpha}\right) L_n^m\left(\frac{\xi-1}{\alpha}\right),
\]

where the \( L_n^m \) and \( P_{l_{max}+|m|}^{m} \) are generalized Laguerre polynomials and associated Legendre functions, respectively, and \( \alpha \) is an (the only) adjustable parameter. With this expansion the KS equations
\[
\{\hat{t}(\xi+\alpha) + v_{s,\sigma}(\xi, \eta)\} \psi_{\kappa\sigma}(\xi, \eta) = \epsilon_{\kappa\sigma} \psi_{\kappa\sigma}(\xi, \eta),
\]
\[
\hat{t}(\xi+\alpha) = -\frac{2}{R^2(\xi^2 - \eta^2)} \left[ \partial_\xi (\xi^2 - 1) \partial_\xi + \partial_\eta (1 - \eta^2) \partial_\eta - \frac{(\xi^2 - \eta^2)^2}{(\xi^2 - 1)(1 - \eta^2)} \right],
\]
can be recast as an algebraic eigenvalue problem
\[
\sum_{n'=0}^{n_{max}} \sum_{l'=m}^{l_{max}} \left[ \langle nlm|\hat{t}(\xi+\alpha) + v_{s,\sigma}|n'l'm\rangle - \epsilon_{\kappa\sigma}(nlm)|n'l'm\rangle \right] c_{\kappa\sigma}^{n'l'm} = 0,
\]

where \( m = 0, 1, \ldots, m_{\text{max}} \) and
\[
\langle \xi, \eta|nlm\rangle = P_{l_{max}+|m|}^{m}(\eta)(\xi^2 - 1)^{|m|/2}\exp\left(-\frac{\xi-1}{2\alpha}\right) L_n^m\left(\frac{\xi-1}{\alpha}\right).
\]

The overlap and kinetic matrix elements \( \langle nlm|n'l'm \rangle \) and \( \langle nlm|t_{\xi,\alpha}|n'l'm \rangle \) can be evaluated analytically [22]. The potential matrix elements \( (nlm|v_{s,\sigma}|n'l'm) \) have to be integrated numerically. Eq. (8) has to be solved self-consistently, with \( v_{s,\sigma} \) corresponding to the spin densities
\[
n_{\sigma}(\xi, \eta) = \sum_{\epsilon_{\kappa\sigma}<\epsilon_F} |\psi_{\kappa\sigma}(\xi, \eta)|^2,
\]

where \( \epsilon_F \) is the Fermi energy.

In the X only limit considered here \( v_{s,\sigma} \) consists of the nuclear potential \( v_{\text{ext}} \), the Hartree potential \( v_H \) and the OPM exchange potential \( v_{s,\sigma} \).
\[
v_{s,\sigma} = v_{\text{ext}} + v_H + v_{s,\sigma},
\]

For the evaluation of \( v_H \) a multipole expansion has been used,
\[
v_H(\xi, \eta) = \frac{1}{2} \sum_{L=0}^{\infty} (2L+1) \xi_L(\xi) P_L(\eta).
\]

The expansion coefficients \( \xi_L \) have been calculated by solution of the corresponding differential equations
\[
\{\partial_\xi (\xi^2 - 1) \partial_\xi - L(L+1)\} \xi_L(\xi) = -4 \pi \int_{-1}^{1} d\eta (\xi^2 - \eta^2) P_L(\eta) n(\xi, \eta),
\]

\((n=n_1+n_2)\) via a shooting procedure. Compared with a direct integration [on the basis of Eq. (17)] this leads to much more accurate Hartree potentials and energies [for the boundary conditions for Eq. (12) see Ref. [23]].

The evaluation of \( v_{s,\sigma} \) requires the solution of the OPM integral equation, which for the present, two-dimensional situation reads
\[
2 \pi \left(\frac{R}{2}\right)^3 \int_{-1}^{1} d\eta_2 \int_{-1}^{1} d\eta_2 (\xi_2^2 - \eta_2^2) K_{\sigma}(\xi_1, \eta_1; \xi_2, \eta_2) v_{s,\sigma}(\xi_2, \eta_2)
\]
\[
= \sum_{\epsilon_{\kappa\sigma}} \int_{-1}^{1} d\eta_2 \psi_{\kappa\sigma}(\xi_1, \eta_1) G_{\kappa\sigma}(\xi_1, \eta_1; \xi_2, \eta_2) \frac{\delta E_{\sigma}}{\delta \psi_{\kappa\sigma}(\xi_2, \eta_2)}.
\]

with
\[
G_{\kappa\sigma}(\xi_1, \eta_1; \xi_2, \eta_2) = \sum_{k' \neq k} \frac{\psi_{k'\sigma}(\xi_1, \eta_1) \psi_{k\sigma}(\xi_2, \eta_2)}{\epsilon_{k'\sigma} - \epsilon_{k\sigma}}.
\]

\[
K_{\sigma}(\xi_1, \eta_1; \xi_2, \eta_2) = 2 \sum_{\epsilon_{\kappa\sigma}<\epsilon_F} \psi_{\kappa\sigma}(\xi_1, \eta_1) G_{\kappa\sigma}(\xi_1, \eta_1; \xi_2, \eta_2) \psi_{\kappa\sigma}(\xi_2, \eta_2).
\]
For the calculation of the central ingredient of the exact exchange $E_x$, the Slater integral $(ab \parallel cd)$, a multipole expansion of the Coulomb interaction [24] can be utilized,

$$(ab \parallel cd) = (2\pi)^5 \frac{R}{2} \delta_{a \cdot a'} \delta_{b \cdot b'} \delta_{d \cdot d'} \delta_{m_a + m_b, m_c + m_d} \left( -1 \right)^M 
\times \sum_{L=M}^{\infty} \left( \frac{L-M}{L+M} \right)^2 \int_1^\infty d\xi_1 \int_1^\infty d\xi_2 
\times \left\{ \xi_1^2 J_{L}^{2}(\xi_1) - B_{L}^{0}(\xi_1) \right\} \left\{ \xi_2^2 J_{L}^{2}(\xi_2) - B_{L}^{0}(\xi_2) \right\} 
\times \left\{ \Theta(\xi_1 - \xi_2) Q_{L}^{M}(\xi_1) P_{L}^{M}(\xi_2) 
+ \Theta(\xi_2 - \xi_1) Q_{L}^{M}(\xi_2) P_{L}^{M}(\xi_1) \right\} 
\right.$$

(16)

with $M = |m_a - m_c| = |m_b - m_d|$, $f_{ab}^L(\xi) = \int_{-1}^{1} d\eta \, P_{L}^{m_a - m_b}(\eta) \frac{\psi_{k_{m_a} a'}(\xi, \eta)}{\psi_{k_{m_b} b}(\xi, \eta)}$, $g_{ab}^L(\eta) = \int_{-1}^{1} d\eta \, \eta^2 P_{L}^{m_a - m_b}(\eta) \frac{\psi_{k_{m_a} a'}(\xi, \eta)}{\psi_{k_{m_b} b}(\xi, \eta)}$, and $Q_{L}^{M}$ denoting the associated Legendre functions of second kind (for arguments $\xi \geq 1$). Insertion of Eq. (5) and an equivalent expansion of $v_{x,\sigma}$ into Eq. (13) allows us to rewrite the OPM integral equation as an algebraic problem.

However, the full solution of the OPM integral equation is a rather time-consuming procedure, requiring the evaluation (and storage) of all excited KS states for the determination of the Greens function (14). In prolate elliptic coordinates the much more efficient KLI approximation [2] to Eq. (13), which results from a closure approximation for $G_{k_{m}\sigma}$, is given by

$$v_{x,\sigma}(\xi, \eta) = \frac{1}{\eta(\xi, \eta)} \sum_{k_{m}\sigma < \epsilon_{F,\sigma}} \left\{ \frac{\psi_{k_{m}\sigma}(\xi, \eta)}{4\pi f^2(\xi^2 - \eta^2)} \frac{\delta E_x}{\delta \psi_{k_{m}\sigma}(\xi, \eta)} 
+ \psi_{k_{m}\sigma}(\xi, \eta)^2 (\bar{v}_{k_{m}\sigma} - \tilde{E}_{k_{m}\sigma}) \right\} 
\right.$$

(18)

$\delta E_x / \delta \psi_{k_{m}\sigma}$ is easily evaluated from Eqs. (16),(17). At this point Eq. (18) still represents an integral equation for $v_{x,\sigma}$. However, this character may be dealt with either by evaluation of $\bar{v}_{k_{m}\sigma}$ [5] or by self-consistent iteration of Eq. (18) [20] (which has been applied in this work).

As in the general situation, the integral equations (13) and (18) determine $v_{x,\sigma}$ only up to some global constant. This constant is fixed by requiring $\lim_{\xi \to \infty} v_{x,\sigma}(\xi, \eta) = 0$. For the implementation of this requirement one needs the asymptotic behavior of $v_{x,\sigma}$ far from the molecule. Neglecting all corrections which are exponentially suppressed, only the highest occupied orbital $\Psi$ is relevant on both sides of Eq. (13) and one ends up with

$$v_{x,\sigma}(\xi, \eta) \sim -e^{2} \frac{\pi}{2} \frac{R^2}{\xi} \sum_{L=0}^{\infty} \left( 2L + 1 \right) P_{L}^{0}(\eta) Q_{L}^{M}(\xi) 
\times \int_{-1}^{1} d\xi' \int_{-1}^{1} d\eta' \left( \xi'^2 - \eta'^2 \right) 
\times P_{L}^{0}(\eta') P_{L}^{0}(\xi') \Psi(\xi', \eta')^2. 
\right.$$

(21)

The asymptotically dominant monopole contribution reads

$$v_{x,\sigma}(\xi, \eta) \sim -e^{2} \frac{R}{\xi} \ln \left( \frac{\xi + 1}{\xi - 1} \right). 
\right.$$

(22)

Finally, for $r_1, r_2 \gg R$ Eq. (22) reduces to the standard relation $v_{x,\sigma} \sim -e^2 / r$. However, in view of the finite grid used for the present calculations (see below) Eq. (21) has been used to normalize $v_{x,\sigma}$.

In our calculations the basis parameter $a$ has been chosen so that the position $r_1 + r_2$ of the outermost node of the highest Laguerre polynomial $L_{n-1}^{m-1}((\xi - 1)/a)$ in the basis remains invariant when $R$ varies. This essentially leads to a proportionality of $a$ with $1/R$. For both the Hartree and the exchange term the multipole expansion has been truncated at the highest angular momentum available in the basis $l_{\text{max}}$. This is consistent with the fact that the multipole expansion of the density is completely determined via Eq. (9) only up to $l = l_{\text{max}}$. The actual values for $l_{\text{max}}$ (between 19 and 29) have been chosen so that the atomic ground-state energies obtained with the two-center basis did not vary on the 0.01 mhartree level for the complete range of $R$ values required. $n_{\text{max}}$ was set between 14 and 19. All numerical integrations were performed via Gauss-Legendre quadrature. The $\xi$ grid always covered the range $r_1 + r_2 \approx R + 40$ bohr. A transformation made sure that the mesh point distribution was close to the standard logarithmic grid used in atomic calculations for the core region. $\xi$-grid sizes of 128 to 512 points and an $\eta$-grid size of 64 points have been used for the evaluation of Eq. (17).
TABLE I. Atomic ground-state energies from X-only OPM calculations within the KLI approximation: Basis set (BS) versus finite differences (FD) approach and impact of nonspherical density.

<table>
<thead>
<tr>
<th>atom</th>
<th>method</th>
<th>state</th>
<th>(-E_{\text{tot}}) [hartree]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>OPM FD</td>
<td>2s</td>
<td>7.43250</td>
</tr>
<tr>
<td></td>
<td>KLI FD</td>
<td>2s</td>
<td>7.43249</td>
</tr>
<tr>
<td></td>
<td>KLI BS</td>
<td>2\sigma</td>
<td>7.43238</td>
</tr>
<tr>
<td>N</td>
<td>OPM Fd</td>
<td>2s2p³</td>
<td>54.40340</td>
</tr>
<tr>
<td></td>
<td>KLI Fd</td>
<td>2s2p³</td>
<td>54.40304</td>
</tr>
<tr>
<td></td>
<td>KLI BS</td>
<td>2\sigma\pi²3\sigma</td>
<td>54.40312</td>
</tr>
<tr>
<td>O</td>
<td>OPM Fd</td>
<td>2s2p³</td>
<td>74.81208</td>
</tr>
<tr>
<td></td>
<td>KLI Fd</td>
<td>2s2p³</td>
<td>74.81167</td>
</tr>
<tr>
<td></td>
<td>KLI BS</td>
<td>2\sigma\pi²3\sigma</td>
<td>74.81715</td>
</tr>
<tr>
<td>Ne</td>
<td>OPM Fd</td>
<td>2s2p³</td>
<td>128.54542</td>
</tr>
<tr>
<td></td>
<td>KLI Fd</td>
<td>2s2p³</td>
<td>128.54483</td>
</tr>
<tr>
<td></td>
<td>KLI BS</td>
<td>2\sigma\pi²3\sigma</td>
<td>128.54500</td>
</tr>
</tbody>
</table>

For the determination of the energy surface

\[ E_b(R) = E_{\text{tot}}[XY](R) - E_{\text{tot}}[X](R) - E_{\text{tot}}[Y](R) \]

the atomic reference energies \( E_{\text{tot}}[X](R) \) have been evaluated with the same code, grid, and basis used for the molecular calculations at the complete set of \( R \) values, in order to cancel errors due to the finite grid and basis-set sizes as much as possible. As in our OPM approach the dominating source of numerical errors is the \( \xi \) integration required for the Slater integrals (17) (compare the discussion in Ref. [17]) inaccurate energies mainly originate from integrations involving the core orbitals. When subtracting constant values for \( E_{\text{tot}}[X](R) \), the accuracy of \( E_b(R) \) is thus enhanced by at least one order of magnitude.

III. RESULTS

A. Atoms

The absolute accuracy achieved by the procedure of Sec. II can be gleaned from Table I where the ground-state energies of some prototype first row atoms are listed. The energies obtained with the present two-center basis set (BS) approach are compared with those resulting from a highly accurate one-center code relying on finite differences (FD) methods \([6,12]\). For all closed-(spin)shell elements studied the differences between the BS and FD energies are smaller than 0.2 mhartree. The error becomes somewhat larger with increasing \( Z \), in accordance with the limited capability of the Hylleraas basis (5) to represent deep-lying core levels.

The fact that for nitrogen our basis-set energy is 0.08 mhartree below the exact \( E_{\text{tot}} \) is due to the neglect of all multipoles in the repulsive Hartree potential (11) beyond \( l_{\text{max}} = 19 \) as well as the numerical integration over \( \xi \). It should be emphasized that the description of closed-shell atoms represents a particularly critical test for the two-center basis employed here: There are no basis functions centered on the nucleus and no finite combination of basis functions can restore the spherical symmetry exactly. A further measure of the accuracy of our BS approach thus is the eigenvalue splitting observed for \( p \) levels of closed-shell atoms: The single-particle energies of the \( 3\sigma \) and \( 1\pi \) states of Nitrogen (forming the \( 2p \) level) agree within 1 \( \mu \)hartree, those of Neon within 3 \( \mu \)hartree. The level of degeneracy is thus even higher than the accuracy of the total energies, corroborating the fact that for the latter the representation of the \( 1s \) orbitals is the dominating source of error.

For comparison the corresponding full OPM ground-state energies \([12]\) are also given in Table I. As is obvious from the table the deviations introduced by our basis sets are of the same order of magnitude as the differences between the FD OPM and KLI energies. As an example for an open-shell atom we list the ground-state energy of oxygen. In this case the basis set approach allows for a nonspherical (i.e., cylindrical) density which leads to an energy gain of about 5 mhartree, clearly beyond both our accuracy limit and the difference between OPM and KLI energy. All molecular dissociation energies given below have been calculated with respect to nonspherical densities in the case of open-shell atoms.

B. Molecules

In order to demonstrate the fact that the KLI potential is an excellent approximation to the full OPM potential also for molecules we first list the ground-state energies \( E_{\text{tot}} \) of a number of diatomic molecules in Table II. The full OPM results in Table II are taken from Ref. [15] in which Gaussian-type basis sets have been used. As is obvious from this table the size of the basis (and, if relevant, grid) has more impact on the value of the ground-state energy than the choice between the full and the KLI version of the OPM potential. For a given basis set the full OPM ground-state energy must be lower than that obtained within the KLI approximation, as, by construction, the full OPM potential is the one that minimizes the total energy functional. The only exception is \( H_2 \) as a spin-saturated two-electron system: For \( H_2 \) the KLI potential in principle coincides with the full
OPM potential and the OPM-KLI ground-state energy is identical with the HF value [25]. In fact, the KLI energy of $-1.133 \pm 0.629$ hartree obtained with the present Hylleraas basis (for \( R = 1.4 \) bohr) is very close to the extremely accurate finite-element HF-value of $-1.133 \pm 0.643 \pm 0.97$ hartree of Ref. [26]. On the other hand, the KLI energy is 0.6 hartree lower than the OPM energy obtained with the Gaussian basis. The differences become even larger for the heavier molecules. For instance, for \( N_2 \) the KLI energy is 6 hartree below the full OPM value of Ref. [15], although for atomic nitrogen the OPM energy is 0.36 hartree lower than the KLI energy. We have carefully checked that our molecular results are stable against variation of the basis and grid size on the 0.2 hartree level even for the heaviest systems, which is the same accuracy as achieved for atoms. Moreover, our result for \( N_2 \) is in excellent agreement with the energy presented in Ref. [11]. In view of this accuracy, it only remains to attribute the differences between full OPM and KLI energies to the more complete basis sets used in the present KLI calculations.

In a second step we demonstrate the very good agreement between X-only KLI, OPM, [16] and HF results for the spectroscopic constants of first row diatomic molecules. The corresponding data are given in Table III (in the case of HF we have combined the results from various references in order to provide the most accurate values for the individual quantities). Note that all KLI and most HF energies have been evaluated at the self-consistent minimum of the Born-Oppenheimer surface, while the OPM values of Ref. [16] have been calculated at the experimental bond lengths. Consistent with this fact one finds that the OPM dissociation energies are somewhat smaller than the KLI values for some molecules and agree within the rounding errors for the others. It remains an open question to what extent basis-set limitations affect this comparison. (We have taken great pains to make sure that the KLI dissociation energies are converged with respect to basis and grid size beyond the 0.01 eV level; bond lengths are converged within 0.01 bohr, vibrational frequencies should be reliable within 10–20 cm$^{-1}$.)

The differences between KLI and HF results are even smaller [25]. For bond lengths a maximum deviation of 0.04 bohr is found for \( Li_2 \), while the average deviation is 0.02 bohr (which is less than 1%). For the dissociation energy the differences are of the order of 0.02 eV (thus being below the standard quantum chemical accuracy criterion of 1 kcal/mol), for force constants they are not larger than 30 cm$^{-1}$. No systematic trend of the deviations can be extracted, consistent with the fact that the error introduced by the basis-set expansions dominates over the error introduced by use of the KLI approximation. One can thus conclude that, as far as spectroscopic properties are concerned, the

\[
\begin{array}{cccc}
\text{mode} & R_e \text{ (bohr)} & D_e \text{ (eV)} & \omega \text{ (cm}^{-1}) \\
H_2 & OPM & 1.386 & 3.638 & 4603 \\
 & KLI & 1.386 & 3.631 & 4583 \\
 & HF [27,28] & 1.386 & 3.631 & 4583 \\
 & OPM & 0.17 & & \\
Li_2 & KLI & 5.265 & 0.167 & 336 \\
 & HF [27,28] & 5.224 & 0.160 & 316 \\
B_2 & KLI & 3.068 & 0.608 & 973 \\
 & HF [29] & 3.096 & 0.75 & 939 \\
C_2 & KLI & 2.332 & 0.281 & 1934 \\
 & OPM & 4.86 & & \\
N_2 & KLI & 2.011 & 4.972 & 2737 \\
 & HF [30,28] & 2.04 & 4.952 & 2738 \\
 & OPM & 1.30 & & \\
O_2 & KLI & 2.183 & 1.440 & 1975 \\
 & HF [30,28] & 2.21 & 1.455 & 2002 \\
 & OPM & -1.82 & & \\
F_2 & KLI & 2.496 & -1.607 & 1285 \\
 & HF [31,28] & 2.508 & -1.627 & 1257 \\
 & OPM & 1.47 & & \\
LiH & KLI & 3.035 & 1.482 & 1425 \\
 & HF [29,28] & 3.038 & 1.462 & 1406 \\
 & OPM & 4.25 & & \\
FH & KLI & 1.692 & 4.202 & 4488 \\
 & HF [31,28] & 1.695 & 4.197 & 4472 \\
 & OPM & 7.46 & & \\
CO & KLI & 2.077 & 7.525 & 2446 \\
 & HF [30,28] & 2.105 & 7.534 & 2439 \\
\end{array}
\]

X-only OPM is physically equivalent to the standard HF approach. An analogous observation has been made for the noble gas dimers He$_2$ and Ne$_2$ [17].

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[25] As a matter of principle, the X-only OPM ground-state energy must be higher than the corresponding HF energy: While in both cases the same energy expression is minimized, the variational freedom of the OPM is somewhat reduced by the fact that the self-consistent OPM exchange potential is restricted to be multiplicative. Thus, in general, one has $E_{\text{OPM}} > E_{\text{HF}}$. However, for the ground state of spin-saturated two-electron systems the HF equation with its nonlocal exchange potential can be rewritten as an equation with a multiplicative $\nu_x$ which agrees with both the OPM and KLI exchange potentials.


