CORRELATION ENERGY CONTRIBUTIONS FROM LOW-LYING STATES TO DENSITY FUNCTIONALS IN THE KLI APPROXIMATION

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Abstract

In this paper we consider a criterion to allow a new coupling between density functional theory and configuration interaction methods. We study as a possible criterion the ordering of the orbital energies produced by the exchange-only KLI potential. This idea arises from the observation that the KLI potential behaves as \(- 1/r\) for large \(r\) in agreement with the known properties of the exact Kohn-Sham potential. The KLI bound states can thus be classified into valence and Rydberg orbitals, the latter not expected to make an important contribution to the correlation energy. We verify this assumption for the first terms of the He and Be series, as in the former only dynamical correlation is supposed to be present, whereas in the latter peculiar near-degeneracy effects intervene. In addition, exact results are given for the Be series in the limit of infinite nuclear charge. Although the contribution to the correlation energy from the low lying virtual states are significantly different for the two series (saturating as \(Z\) increases for the He series and being proportional to \(Z\) for large \(Z\) for the Be series) the remaining contributions to the correlation energy for both series saturate suggesting the application of DFT to the calculation of this latter contribution.
1 Motivation

While fitting to experimental data produces density functionals for the exchange-correlation energy with average errors approaching the 1 kcal/mol limit, some fundamental problems still remain. For example, the Kohn-Sham (KS) eigenstate is constructed from a single determinant, which may not even yield the correct density in the case of degeneracy ("non v-representability", see, e.g. [1]). Moreover, the nature of the KS determinant may rapidly change by the influence of a vanishingly small perturbation. While the standard resolution of this problem is the ensemble treatment (see, e.g., [2,3]) an alternative approach is to use the multi- (and not single-) determinant wave functions to describe the reference state. This approach has been initiated by Lie and Clementi 25 years ago [4,5] and is based on the observation that a few Slater determinants might describe an important, system specific part of the correlation energy, the remaining part showing an easy transferable behavior from system to system. A general definition of this separation of the correlation energy (often called "static" and "dynamic", respectively) is not unique, as can be seen by the treatment given in the Lie and Clementi paper quoted above [5] (for more recent discussions, see, e.g. [6,7]). In their first paper [4], Lie and Clementi treated diatomic molecules by considering the minimum number of Slater determinants to guarantee the proper dissociation of the molecule. The dynamic correlation energy was obtained by using an approximate density functional (DF). In the second one [5], it is shown that a few configurations remain important, and that they have to be added to the wave function calculation in order to achieve good results. Other methods to couple a multi-determinant treatment to density functionals have been proposed (see, e.g., Ref. [8–12]). Essentially, there are two ways of resolving the problem of the choice of the "important" determinants:

a) finding an appropriate separation into determinants yielding the "static" correlation energy,

b) using a criterion allowing an arbitrary number of Slater determinants.

The second approach is of course more flexible, as it allows the user to decide upon the most convenient separation. It also allows one to check the quality of the result by changing the separation, and to approach the exact value along with the reduction of the DF contribution and the increase of the wave function part. The former approach is, however, simpler for a systematic study and "black-box" applications; this is the approach we followed in the present paper. We will limit ourselves (for the present) to wave function calculations, but briefly mention some implications of adding approximate density functionals to correct for the remaining part of the correlation energy. The systems that we will study are deliberately simple: the He and Be series, as in the latter the origin of the near-degeneracy is well understood. Linderberg and Shull [13] have shown that in the Be series (in contrast to the He series) a two-configuration (1s\(^2\)2s\(^2\) and 1s\(^2\)2p\(^2\)) treatment is required, due to the degeneracy of the 2s and 2p levels when the nuclear charge, Z, goes to infinity. A confirmation of the regular behavior of the correlation energy in the series can be seen in, e.g., the numerical study of Clementi [14], and is
confirmed by more recent estimations of the exact correlation energy (cf. [15]). In fact, as \( Z \) becomes very large, the dominant term in the correlation energy becomes constant (\( Z \)-independent) in the He series, while in the Be series it is linear in \( Z \), the proportionality constant being \(-0.011727\) [13]. The difficulty of approximate DFs to describe this behavior was recognized long ago [16], and has not been solved to this day in approximate Kohn-Sham methods. We would like to recall that the careful treatment of quasi-degenerate states is also important in wave-function methods [17].

2 Method

The philosophy of our approach is based upon a simple observation: molecules normally possess an energy gap, while the uniform electron gas, used as a starting point in LDA and GGA’s, does not. Furthermore we expect the states contributing to the dynamic correlation to lie in the continuum, based on the observation of Davidson [18] that the most important natural orbitals of He are significantly different from the Rydberg orbitals: the correlating orbitals have to be localized in the same spatial region as the strongly occupied ones, in order to describe the formation of the correlation hole. We thus expect that among the states below the ionization limit only a few (the valence states) contribute significantly to the correlation energy. To be more specific, we will consider the one-particle states to be eigenstates of some one-particle hamiltonian:

\[
h_0 \phi_i = \varepsilon_i \phi_i
\]

and treat the correlation by standard quantum mechanics methods in the space of the orbitals with negative eigenvalues (\( \varepsilon_i < 0 \)). \(^1\) The choice of \( h_0 \) can play a major role. It is well known that obtaining the Hartree-Fock wave function does not have any implication on the non-occupied (virtual) states. The freedom of choosing the virtual states has been used, for example, in constructing improved virtual orbitals (see, e.g., [19]) or other types of orbitals (see, e.g., [20]). Conventional Hartree-Fock calculations very often show that the eigenvalues of the virtual orbitals are positive, and thus not suited for our purpose. We will consider in this paper a well-defined one-body hamiltonian, with a local potential: the Krieger-Li-Iafrate (KLI) [21] hamiltonian. This has been already done, e.g., by Engel et al. [22]. Using orbitals which do not originate from a Fock potential is, of course, not new (cf. the use of orbitals which originate from density functional calculations, e.g., in Ref. [23]). Fritsche [24] has argued that taking the Kohn-Sham (KS) determinant as the starting point of a wave function expansion guarantees that density is already

\(^1\)The potentials, and the orbital energies are, of course, determined only up to an arbitrary constant, which does not modify the eigenstates. As we are interested only in a selection of the eigenstates, the choice of the constant is immaterial. In our case, we choose all states which are below ionization for the non-interacting system, which corresponds to the negative eigenvalues for a potential which vanishes at infinity.
correct at zeroth order. Görling and Levy [25] have constructed a perturbation
theory which guarantees that the density is correct to each given order. Their
second-order energy expression does not contain the correlation potential, and
thus one may consider the KLI potential (as giving an excellent approximation
to the exact exchange potential, in the DF sense) as a "best" starting point, to
second order. Furthermore, the exact KS potential requires the knowledge of the
exact density, while the KLI potential can be obtained with an effort comparable
to that of an Hartree-Fock calculation. We thus write:

\[ h_0 = -\frac{1}{2} \nabla^2 + V_{KLI} \]  

(2)

Let us now analyse the behavior of \( V_{KLI} \) for \( Z \to \infty \). Following the treatment
of Linderberg and Shull [13], we will change to modified Hartree units \( (E \to \bar{E} = 
E/Z^2, r \to \bar{r} = Zr; \bar{E} \) is the energy, \( r \) the distance of the electron from the
nucleus in atomic units.) The exact hamiltonian in these units becomes for atomic
systems:

\[ \hat{\mathcal{H}} = \hat{T} - \sum_{i=1}^{N} \frac{1}{\bar{r}_i} + \frac{1}{Z} \sum_{i<j} \frac{1}{\bar{r}_{ij}} \]  

(3)

where \( T \) is the operator for the kinetic energy, \( N \) the number of electrons, \( r_i \)
the distance of the \( i^{th} \) electron from the nucleus and \( r_{ij} \) the distance between
electrons \( i \) and \( j \). For \( Z \to \infty \), the system is that of \( N \) non-interacting electrons in
the external potential of the hydrogen atom. As the electron-electron interaction
has been turned off as \( 1/Z \) in \( \hat{\mathcal{H}} \), it will also disappear in \( \hat{V}_{KLI} \) as \( 1/Z \) so that

\[ V_{KLI} (r) = Z^2 \bar{V}_{KLI} (\bar{r}) \to -\frac{Z}{\bar{r}} \text{ as } Z \to \infty \]  

(4)

In the modified Hartree units (cf. text preceding Eq. 3) we thus obtain,

\[ \bar{V}_{KLI} (\bar{r}) = -\frac{1}{\bar{r}} + \frac{1}{Z} \bar{V}_{KLI}^{(1)} (\bar{r}) + \mathcal{O} \left( \frac{1}{Z^2} \right) \]  

(5)

where \( \bar{V}_{KLI}^{(1)} \) is \( Z \)-independent. \( \bar{V}_{KLI}^{(1)} \) for the Be series is shown in Figure 1. Details
about how to compute to first order the Coulomb and exchange parts of \( V_{KLI} \),
namely \( V_h \) and \( V_z \) in the limit of very large \( Z \), are given in Appendix 1. The shape
of \( \bar{r} \) times \( \bar{V}_{KLI}^{(1)} \) (cf. Fig. 1) is consistent with the asymptotic expression:

\[ V_{KLI} (r) \to -\frac{Z - N + 1}{r} \text{ as } r \to \infty \]  

(6)
which implies that Rydberg states exist both in the He and the Be series.

Let us now analyse the behavior of the KLI orbital energies as \( Z \to \infty \). As for the potential expansion in \( Z \), we write for the \( i^{th} \) orbital energy, in modified Hartree units

\[
\tilde{\varepsilon}_i = \varepsilon_i^{(0)} + \frac{1}{Z} \varepsilon_i^{(1)} + \mathcal{O} \left( \frac{1}{Z^2} \right)
\]

(7)

Introducing Eq. 4 into Eq. 2 and applying perturbation theory, it turns out that the zeroth order is just the hydrogenic orbital energy

\[
\varepsilon_{i,H} = \int \phi_{i,H}^* (\vec{r}) \left( -\frac{1}{2} \nabla^2 - \frac{1}{\vec{r}} \right) \phi_{i,H} (\vec{r}) \, d^3\vec{r}
\]

(8)

(\( \phi_{i,H} \) being the \( i^{th} \) orbital of the H atom), whereas we get the first-order change in the \( \tilde{\varepsilon}_i \) to be

\[
\varepsilon_i^{(1)} = \frac{1}{Z} \int |\phi_{i,H} (\vec{r})|^2 \tilde{V}_{KLI} (\vec{r}) \, d^3\vec{r}
\]

(9)

in modified Hartree units (or \( \sim Z \) in Hartree units). The difference between the 2s and 2p orbital energies is thus proportional to \( Z \) at most, for \( Z \to \infty \). For \( i = 2s \) and \( 2p \), we obtain for the integral, 0.530147 and 0.591788, respectively. We expect the KLI orbitals to have first-order changes with respect to \( \phi_{i,H} \)

\[
\tilde{\phi}_i (\vec{r}) = \phi_{i,H} (\vec{r}) + \frac{1}{Z} \tilde{\phi}_i^{(1)} (\vec{r}) + \mathcal{O} \left( \frac{1}{Z^2} \right)
\]

(i=1s,2s,2p \cdots)

(10)
where $\tilde{\phi}_i$ is $Z$-independent. A similar expansion will arise for Slater determinants constructed from the $\tilde{\phi}_i$, $\tilde{\Phi}_I$ yielding

$$
\tilde{\Phi}_I = \Phi_{I,H} + \frac{1}{Z} \tilde{\phi}_I + O \left( \frac{1}{Z^2} \right)
$$

(11)

where $\Phi_{I,H}$ is constructed from $\phi_{i,H}$ (e.g., $i = 1s, 2s$ for the Be $\Phi_{0,H}$), and $\tilde{\phi}_I$ satisfies $\langle \Phi_{I,H} | \tilde{\phi}_I \rangle = 0$, since it differs from $\Phi_{I,H}$ by the orbital $\phi_i^{(1)}$ which is orthogonal to $\phi_{i,H}$. These results allow us to calculate the behavior of the energy for $Z \to \infty$.

Starting with KLI determinant in modified Hartree units $\tilde{\Phi}_0$ and according to perturbation theory, we express the energy up to second order in $1/Z$ as

$$
\tilde{E}^{(0)} + \tilde{E}^{(1)} + \tilde{E}^{(2)} = \langle \tilde{\Phi}_0 | \tilde{H} | \tilde{\Phi}_0 \rangle + \sum_{I \neq 0} \sum_{i \in \tilde{\Phi}_0} \frac{\langle \tilde{\Phi}_0 | \tilde{H} | \tilde{\phi}_i \rangle^2}{2\tilde{\varepsilon}_i} - \sum_{i \in \tilde{\Phi}_0} \frac{\langle \tilde{\Phi}_0 | \tilde{H} | \tilde{\phi}_i \rangle^2}{2\tilde{\varepsilon}_i}
$$

(12)

i.e. in Hartree units for Be

$$
E^{(0)} + E^{(1)} + E^{(2)} = -1.25 Z^2 + 1.550111 Z + O \left( \frac{1}{Z^0} \right)
$$

(13)

We have used the following formulas

$$
\langle \tilde{\Phi}_0 | \tilde{H} | \tilde{\Phi}_0 \rangle = \langle \Phi_{0,H} | \sum_i \frac{1}{2} \tilde{\varepsilon}_i^2 - \frac{1}{\tilde{r}_i^2} | \Phi_{0,H} \rangle + \frac{1}{Z} \langle \Phi_{0,H} | \sum_{i < j} \frac{1}{\tilde{r}_{ij}} | \Phi_{0,H} \rangle + O \left( \frac{1}{Z^2} \right)
$$

(14)

$$
\langle \tilde{\Phi}_0 | \tilde{H} | \tilde{\phi}_I \rangle = \frac{1}{Z} \langle \Phi_{0,H} | \sum_{i < j} \frac{1}{\tilde{r}_{ij}} \Phi_{i,H} \rangle + O \left( \frac{1}{Z^2} \right)
$$

(15)

$$
\sum_{i \in \Phi_0} 2\tilde{\varepsilon}_i - \sum_{i \in \tilde{\Phi}_0} 2\tilde{\varepsilon}_i = \frac{2}{Z} \int \tilde{\phi}_I^{(1)} (\tilde{r}) \left( | \phi_{2s,H} (\tilde{r}) |^2 - | \phi_{2p,H} (\tilde{r}) |^2 \right) d^3\tilde{r} + O \left( \frac{1}{Z^2} \right)
$$

(15)

$$
-\frac{1}{Z} \int \tilde{\phi}_I^{(1)} (\tilde{r}) \left( | \phi_{2s,H} (\tilde{r}) |^2 - | \phi_{2p,H} (\tilde{r}) |^2 \right) d^3\tilde{r} + O \left( \frac{1}{Z^2} \right)
$$

(16)

\(^2\)For the sake of simplicity we did not include single particle excitations into Eq. 12, as they contribute only to order $1/Z^2$ and higher. The reason is that the degenerate hydrogen orbitals, which might generate terms in $1/Z$, have different symmetry, and the matrix elements between orbitals of different symmetry are zero.
where the term proportional to $Z^2$ in Eq. 13 is provided by $\tilde{\Phi}_0$ alone, while part of the term linear in $Z$ comes from the second-order contribution.

The correlation energy to order linear in $Z$ is thus given by

$$E^{(2)} = -0.020887Z + O(Z^0) \quad \text{(Be series)}$$

(17)

The second order energy does not have a divergent term, in contrast to the one obtained using the hydrogen hamiltonian at zeroth order. As the source of this term linear in $Z$ is the $2s$-$2p$ degeneracy in the hydrogen atom, we can also diagonalize the hamiltonian matrix in this space [13]

$$
\begin{bmatrix}
\langle \tilde{\Phi}_s | H | \tilde{\Phi}_s \rangle & \langle \tilde{\Phi}_s | H | \tilde{\Phi}_p \rangle \\
\langle \tilde{\Phi}_p | H | \tilde{\Phi}_s \rangle & \langle \tilde{\Phi}_p | H | \tilde{\Phi}_p \rangle
\end{bmatrix}
= \begin{bmatrix}
-1.25 + \frac{1}{2}1.571000 + O \left( \frac{1}{Z^2} \right) & \frac{1}{2}0.050744 + O \left( \frac{1}{Z^2} \right) \\
\frac{1}{2}0.050744 + O \left( \frac{1}{Z^2} \right) & -1.25 + \frac{1}{2}1.778847 + O \left( \frac{1}{Z^2} \right)
\end{bmatrix}
$$

(18)

where $\tilde{\Phi}_s$ is the $1s^22s^2$ configuration, and $\tilde{\Phi}_p$ is the $1s^22p^2$ configuration. To order $Z^{(0)}$, the expression for $E$ is identical to that obtained when constructing the perturbation series with hydrogenic orbitals (instead of using KLI orbitals)[13]:

$$E = -1.25Z^2 + 1.559273Z + O(Z^0)$$

(19)

The resulting correlation energy is $-0.011727Z$ (using Eq. 14 for the KLI energy), which yields thus the exact leading term in the correlation energy. Notice that the KLI second-order energy overestimates the quasi-degeneracy effect: the coefficient of $Z$ in Eq. 17 was nearly twice the exact one. Of course, higher order terms compensate for this discrepancy. (We get for the third order energy a correction of $0.0035\overline{\phi} mH.$)

### 3 Numerical results

Usually, the correlation energy is defined with respect to the non-relativistic Hartree-Fock energy. In density functional theory, the expectation value of the KS determinant is used as a reference. As we start with a KLI determinant, we use still another definition of the correlation energy. In this paper, we will mean by ‘correlation energy’ the difference between the energy obtained at a given level and the expectation value of the hamiltonian obtained with the KLI determinant. In particular, we will compare the exact correlation energies, $E_{c}$, with those obtained within second-order perturbation theory, $E^{(2)}_{q}$ (cf. Tab. 1 and Tab. 2 for He and Be, respectively), $E^{(2)}_{q}$, the second-order contribution from the space of $1s,2s$ and $2p$ orbitals, $E_{c_{qp}}$, the configuration interaction correlation energy in the
Table 1: Energies in the He series.
$E^{(0)} + E^{(1)}$ is the expectation value of the hamiltonian with the KLI wave function; $E^{(2)}$ the correlation energy in second-order perturbation theory (Eq. 39); $E_{exact}$ is taken from Ref. [15].

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$E^{(0)} + E^{(1)}$</th>
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<th>$E_{exact}$</th>
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</table>

Table 2: Energies in the Be series.
$E^{(0)} + E^{(1)}$ is the expectation value of the hamiltonian with the KLI wave function; $E^{(2)}$ the correlation energy in second-order perturbation theory (Eq. 39); $E_{exact}$ is taken from Ref. [15].

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$E^{(0)} + E^{(1)}$</th>
<th>$E^{(0)} + E^{(1)} + E^{(2)}$</th>
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same space, and finally the contribution to the second-order energy coming from the orbitals with negative orbital energies, $E^{(2)} (\epsilon_i < 0)$. The values for $E^{(2)}_{eq}$, $E^{(2)}_{approx}$, $E^{(2)}_{approx2}$ (\epsilon_i < 0) can be inferred from the data given in Tables 1 and 3 for He, and Table 2 for Be. $E^{(2)}_{eq}$, $E^{(2)}_{approx}$, $E^{(2)}_{approx2}$ (\epsilon_i < 0) are compared to $E_{c}$ in Figs. 2 and 3 (for He and Be respectively). Technical details concerning our calculations are deferred to Appendix 2. We want to mention, however, that we estimate our second-order energies to be 1-2 mH too high, due to the basis sets limitations.

While for the He series, it turns out that the total energy is only slightly too low within second-order perturbation theory based upon KLI (cf. Tab. 1 and Fig. 2), a severe over-estimate of the correlation can be observed for the Be series (cf. Tab. 2 and Fig. 3). If we use only the orbitals with negative energies to obtain the correlation energy, $E^{(2)} (\epsilon_i < 0)$, we observe that in the He series, there

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3We considered the $1s^22s^22p^2$ configurations in the He series, and the $1s^22s^2$ and $1s^22p^2$ configurations in the Be series.
Table 3: Energies in the He series in restricted subspaces.

$E^{(2)}_c$ is the correlation energy in second-order perturbation theory taking into account only the configurations $1s^2, 2s^2$ and $2p^2$ built from KLI orbitals; $E_0$ is the total energy obtained from a configuration interaction calculation in the same space; $E^{(2)}(\varepsilon < 0)$ is the correlation energy in second-order perturbation theory obtained in the space of the KLI orbitals with negative orbital energies.

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$E^{(0)} + E^{(1)} + E^{(2)}_c$</th>
<th>$E_0$</th>
<th>$E^{(0)} + E^{(1)} + E^{(2)}(\varepsilon &lt; 0)$</th>
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Table 4: Energies in the Be series in restricted subspaces.

$E^{(2)}_c$ is the correlation energy in second-order perturbation theory taking into account only the configurations $1s^22s^2$ and $1s^22p^2$ built from KLI orbitals; $E_0$ is the total energy obtained from a configuration interaction calculation in the same space; $E^{(2)}(\varepsilon < 0)$ is the correlation energy in second-order perturbation theory obtained in the space of the KLI orbitals with negative orbital energies; $E_{MCHF}$ is the multiconfiguration Hartree-Fock energy taken from Ref. [15].

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$E^{(0)} + E^{(1)} + E^{(2)}_c$</th>
<th>$E_0$</th>
<th>$E^{(0)} + E^{(1)} + E^{(2)}(\varepsilon &lt; 0)$</th>
<th>$E_{MCHF}$</th>
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</table>

is only a negligible contribution coming from these orbitals, while in the Be series it decreases linearly with $Z$, in accordance with the asymptotic behavior given by Eq. 17. Notice that the slope is more pronounced for $E^{(2)}_c(Z)$ and $E^{(2)}(\varepsilon < 0)$ than for $E_c(Z)$ and $E_{c,q}(Z)$ (cf. Eqs. 17 and 19 and Fig. 3). Of course, higher order terms in the perturbation series will correct this effect. At infinite order in perturbation theory, using only the space of $1s^22s^2$ and $1s^22p^2$ configurations, we get the same result as that obtained by diagonalizing the Hamiltonian in this space.

As the overestimation of the second-order correlation energy could be traced back to the quasi-degeneracy effect, a simple correction is the one suggested by Eggarter and Eggarter in their analysis of Hartree-Fock based second-order per-
turbation theory [26], namely that the correlation energy can be approximated by

\[ E_c \approx E^{(2)} + \left( E_{c,q} - E_{g}^{(2)} \right) \tag{20} \]

This expression gives the correct linear term for \( Z \to \infty \) as the erroneous linear term appearing in \( E^{(2)} \) is compensated by that in \( E_{g}^{(2)} \) (cf. Eq. 17). Using Eq. 20 the errors are reduced from maximally 43 to 13 mH in the Be series (cf. Tab. 4 and Fig. 4). For the He series a calculation in the space of determinants having the doubly occupied orbitals 1s, 2s or 2p shows virtually no effect in comparison with a second-order energy calculation in the same space (cf. Tab. 3 and Fig. 4).

In the Be series, we notice some difference between the second-order contributions in the 1s, 2s, 2p (\( E_{g}^{(2)} \)) space vs. \( E_{g}^{(2)}(\varepsilon_i < 0) \) (cf. Fig. 3). (In the He series, both \( E_{g}^{(2)} \) and \( E_{g}^{(2)}(\varepsilon_i < 0) \) are very small, cf. Fig. 2.) Lower bounds for the energy obtainable in the space of the 1s, 2s, 2p orbitals are given by the multi-configuration Hartree-Fock (MCHF) calculations [15], which yield the lowest energies in the 1s, 2s, 2p space. We see from Tab. 4 that optimizing the orbitals in the MCHF calculation lowers the energy by roughly 10 mH in the Be series; this difference is similar to that obtained when comparing \( E^{(2)}(\varepsilon_i < 0) \) with \( E_{g}^{(2)} \). Thus, taking care of \( E^{(2)}(\varepsilon_i < 0) \) might be used to compensate for orbital optimization.

We believe that a density functional might be used to obtain the total energies once the effect of quasi-degenerate states on the correlation energy is taken into account. In fact, introducing a gap in the uniform electron gas is possible. Several variants might be investigated, e.g.

a) shifting all virtual states by a gap

b) excluding all states above the Fermi level within a range for the remaining part of the correlation energy.

For both cases electron gas calculations were done, and the latter variant was already used in molecular calculations in a scheme combining multi-configuration wave-functions with density functionals (see, e.g., Ref. [10]). The uniform electron gas with a gap shift was also used in molecular calculations assuming that one can define a local gap \( \frac{1}{n^2} (|\nabla n|/n)^2 \) (where \( n \) is the electron density of the system considered) which asymptotically is equal to the ionization potential [28]. It turns out that one has to take into account also the self-interaction correction and a gradient correction. In connection with recent exchange density functionals, quite good results could be obtained [30]. Such a treatment neglects, in principle, all contributions coming from states within the gap. It thus seems natural to add the correlation energy of such a functional to that missing in a full calculation within the space of orbitals with negative energies. As shown above, this quantity is quite safely estimated from a configuration interaction within the space of quasi-degenerate states. Thus, the density functional should describe only \( E_c = E_{c,q} \) which changes very little with \( Z \) (cf. Fig. 5; the fluctuations in the plot might be due to our numerical accuracy). To estimate the effect of the higher states with \( \varepsilon_i < 0 \) we use an equation similar to Eq. 20:
Figure 2: Correlation energies (i.e., differences to $\langle \Phi_0 | H | \Phi_0 \rangle$) in various approximations for the He series vs. the nuclear charge, $Z$: a) exact (taken from Ref. [15]); b) calculated up to second order in full space; c) calculated up to second order in the space of orbitals with negative energies; d) calculated with a configuration interaction in $1s^22s^22p$ subspace; e) calculated up to second order in $1s^22s^22p$ subspace.
Figure 3: Correlation energies (i.e., differences to $\langle \Phi_0 | H | \Phi_0 \rangle$) in various approximations for the Be series vs. the nuclear charge, $Z$:

a) full line: exact taken from Ref.1 [5] ($E_c$);
b) long dashed line: calculated up to second order in full space ($E^{(2)}$);
c) short dashed line: calculated up to second order in the space of orbitals with negative energies ($E^{(2)} (\varepsilon < 0)$);
d) dotted line: calculated with a configuration interaction in $1s2s2p$ subspace ($E_{c12}$);
e) dashed dotted line: calculated up to second order in $1s2s2p$ subspace ($E^{(2)}_{c12}$).
Figure 4: Errors of second-order energies and of Eq. 20 with respect to nuclear charge, $Z$.

a) He series, $E_c - E^{(2)}$;
b) He series, $[E_c - (E^{(2)} + E_{c,q}) - E^{(2)}_q)]$, cf. Eq. 20;
c) Be series, full line: $E_c - E^{(2)}$; broken line: $[E_c - (E^{(2)} + E_{c,q}) - E^{(2)}_q)]$, cf. Eq. 20.

He series:

- $E_c - E^{(2)}$
- $E_c - (E^{(2)} + E_{c,q} - E^{(2)}_q)$

Be series:

- $E_c - E^{(2)}$
- $E_c - (E^{(2)} + E_{c,q} - E^{(2)}_q)$
Figure 5: Correlation energy not described by states in the gap, with respect to nuclear charge, $Z$:

a) He series, $E_c - E_c^{(2)} (\varepsilon < 0)$;  
b) He series, $E_c - E_{c,q}$;  
c) He series, $E_c - (E_{c,q} + E_c^{(2)} (\varepsilon < 0) - E_q^{(2)})$, cf. Eq. 21;  
d) Be series, full line: $E_c - E_c^{(2)} (\varepsilon < 0)$, long dashed line $E_c - E_{c,q}$, short dashed line: $(E_c - (E_{c,q} + E_c^{(2)} (\varepsilon < 0) - E_q^{(2)}))$, cf. Eq. 21.

**He series:**

\begin{align*}
\text{a) } E_c - E_c^{(2)} (\varepsilon < 0)
\end{align*}

\begin{align*}
\text{b) } E_c - E_{c,q}
\end{align*}

\begin{align*}
\text{c) } E_c - (E_{c,q} + E_c^{(2)} (\varepsilon < 0) - E_q^{(2)})
\end{align*}

**Be series:**

\begin{align*}
\text{d) } E_c - E_c^{(2)} (\varepsilon < 0); \ E_c - E_{c,q}; \ E_c - (E_{c,q} + E_c^{(2)} (\varepsilon < 0) - E_q^{(2)}).
\end{align*}
\[ E_c(\varepsilon_i < 0) \approx E_{c,q} + \left( E^{(2)}(\varepsilon_i < 0) - E^{(2)}_q \right) \] (21)

We plot in Fig. 5 the part of the correlation energy which has to be described by the density functional, viz., \( E_c - E_c(\varepsilon_i < 0) \) which we approximate by \( E_c \) minus the r.h.s. of Eq. 20. We also show in Fig. 5 \( E_c - E_{c,q} \) which differs only little from the preceding quantity. In both cases we notice that there is a very small change of this quantity with respect to \( Z \), and this is in part due to our numerical inaccuracies. It would not be difficult to generate a functional having a behavior like that shown for \( E_c - E_{c,q} \), or \( E_c - E_c(\varepsilon_i < 0) \). It turns out, however, that using the functional of Ref. [30] for Be already yields a quite reasonable correlation energy, and using \( E_{c,q} \) (cf. Fig. 6) plus this density functional for \( E_c - E_{c,q} \) would yield a too large correlation energy. We also show the difference between \( E_c \) and \( E^{(2)}(\varepsilon < 0) \) to show that the latter is not so easy to describe with the same type of \( Z \)-dependence, due to the error in the \( Z \)-dependent term, mentioned before.

4 Conclusion

Our results demonstrate that even when the nearly exact KLI exchange potential (cf. [21, 22]) is employed as the zeroth order KS potential, it is not possible to even qualitatively account for the correlation energy by employing second order

![Figure 6: Difference between the energies in the space of Slater determinants constructed by doubly occupying the 1s, 2s, 2p orbitals, and the expectation values with the KLI determinants, \( \langle \Phi_0 | H | \Phi_0 \rangle \), vs. the nuclear charge, \( Z \). a) triangles connected by a full line: in the He series \( E_{c,q} \); b) squares connected by a full line: in the Be series \( E_{c,q} \).]
perturbation theory in a system such as the Be isoelectronic series in which virtual states exist which are quasi-degenerate with occupied orbitals. This follows from the fact that the coefficient of the term linear in $Z$, which dominates the correlation energy, is in error by nearly a factor of two when second order perturbation is employed. However, we find that diagonalizing the Hamiltonian in the space of quasi-degenerate orbitals by employing a linear combination of determinants leads to the correct linear dependence on $Z$ of the correlation energy. Moreover, the remaining correlation energy due to contributions from all the other virtual orbitals in the system including those in the continuum (which actually make the largest contribution) rapidly saturate as $Z$ increases as in the case of the He isoelectronic series in which there is no quasi-degeneracy of virtual with occupied orbitals. This encourages us to believe that it will be possible to construct density functionals for this component of the correlation energy since the latter tend to saturate in the high density limit when properly constructed to satisfy certain scaling conditions (25,28). The inclusion of quasi-degeneracy effects, although generally ignored in DF calculations, can have important effects on calculated ionization potentials, electron affinities and molecular atomization energies because the addition or subtraction of an electron or the creation of a chemical bond can easily change a system from one having a quasi-degeneracy to one that does not and vice-versa, leading to significant changes in the correlation energy. We therefore anticipate that the inclusion of the considerations discussed above will make significant contributions to the accurate calculation of the ground state properties of atoms and molecules.

5 Appendix

5.1 1/Z term of $\hat{V}_{KLI}$

In order to see what happens in order $1/Z$ in KLI, let us recall a few expressions. We take for the Coulomb term:

$$\hat{V}_h (\vec{r}) = \frac{1}{Z} \int \frac{n_H (\vec{r}')}{|\vec{r} - \vec{r}'|} e^{2i} + O \left( \frac{1}{Z^2} \right)$$ (22)

where

$$n_H (\vec{r}) = \sum_{i=1, \eta, \zeta} |\phi_i H (\vec{r})|^2$$ (23)

and get the following expressions from mathematica[29]:

a) in the He series:

$$\hat{V}_h (\vec{r}) = \frac{1}{Z} \left( -\frac{2(1 + \vec{r})}{\vec{r}} e^{-2\vec{r}} + \frac{2}{\vec{r}} \right) + O \left( \frac{1}{Z^2} \right)$$ (24)
b) in the Be series:

\[
\tilde{V}_h (\vec{r}) = \frac{1}{Z} \left( -\frac{2(1+\vec{r})}{\vec{r}} e^{-2\vec{r}} - \frac{8 + 6\vec{r} + 2\vec{r}^2 + \vec{r}^3}{4\vec{r}} e^{-\vec{r}} + \frac{4}{\vec{r}} \right) + \mathcal{O} \left( \frac{1}{Z^2} \right)
\]  

(25)

Using notations similar to those of [21], but dropping the spin index, as we restrict ourselves to closed-shells, we have for the exchange energy:

\[
\tilde{E}_x = -\frac{1}{2} \sum_{ij} \left( \tilde{\phi}_i \tilde{\phi}_j \tilde{\phi}_j \tilde{\phi}_i \right) \frac{1}{Z}
\]  

(26)

and its functional derivative, employing real wavefunctions, is

\[
\frac{\delta \tilde{E}_x}{\delta \tilde{\phi}_i (\vec{r})} = \frac{1}{Z} \sum_j \tilde{\phi}_j (\vec{r}) \int \frac{\tilde{\phi}_i (\vec{r}') \tilde{\phi}_j (\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 \vec{r}'
\]  

(27)

From Eq. 12 of Ref. [21]

\[
\tilde{v}_i (\vec{r}) = -\frac{1}{Z} \sum_j \tilde{\phi}_j (\vec{r}) \int \frac{\tilde{\phi}_i (\vec{r}') \tilde{\phi}_j (\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 \vec{r}'
\]  

(28)

From Eq. 48 of Ref. [21] and developing the \( \tilde{\phi}_i \) according to Eq. 10, we get for the local exchange part of KLI potential:

a) in the He series:

\[
\tilde{V}_z (\vec{r}) = -\frac{1}{Z} \int \frac{\phi_{i,n,\text{H}} (\vec{r}') \phi_{i,n,\text{H}} (\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 \vec{r}' + \mathcal{O} \left( \frac{1}{Z^2} \right)
\]  

(29)

b) in the Be series:

\[
\tilde{V}_z (\vec{r}) = \left\{ \sum_{i=1,2,3} |\phi_{i,n,\text{H}} (\vec{r})|^2 \tilde{v}_i (\vec{r}) + |\phi_{i,n,\text{H}} (\vec{r})|^2 \tilde{C} \right\} \frac{1}{n_{\text{H}} (\vec{r})} + \mathcal{O} \left( \frac{1}{Z^2} \right)
\]  

(30)

and the constant \( \tilde{C} \) is determined by the requirement (Eq. 18 of Ref. [21]):

\[
\int [\tilde{V}_z (\vec{r}) - \tilde{v}_1,2 (\vec{r})] |\tilde{\phi}_{1,2} (\vec{r})|^2 d^3 \vec{r} = \tilde{C}
\]  

(31)

Substituting into the above equation the expression of \( \tilde{V}_z (\vec{r}) \) and integrating over \( \vec{r} \), we get for the Be series:
\[ C \left( 1 - \int \frac{\phi_{1s,H} (\vec{r})^2}{n_H (\vec{r})} d^3r + \mathcal{O} \left( \frac{1}{Z} \right) \right) = \]

\[ - \frac{1}{Z} \sum_{i,j=1s,2s} \int \frac{\phi_{1s,H} (\vec{r})^2}{n_H (\vec{r})} \phi_{i,H} (\vec{r}) \phi_{j,H} (\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \phi_{j,H} (\vec{r}') d^3r d^3r' + \frac{1}{Z} \sum_{i=1s,2s} \phi_{i,H} \phi_{i,H} \phi_{1s,H} \phi_{1s,H} \]

(32)

From the following values for the integrals involving hydrogenic orbitals:

\[
\begin{align*}
\langle \phi_{1s,H} \phi_{1s,H} | \phi_{1s,H} \phi_{1s,H} \rangle &= 0.624999 \\
\langle \phi_{2s,H} \phi_{2s,H} | \phi_{2s,H} \phi_{2s,H} \rangle &= 0.150390 \\
\langle \phi_{1s,H} \phi_{1s,H} | \phi_{2s,H} \phi_{2s,H} \rangle &= 0.209876 \\
\langle \phi_{1s,H} \phi_{2s,H} | \phi_{1s,H} \phi_{2s,H} \rangle &= 0.021948
\end{align*}
\]

(33)

we obtain with Mathematica[29]

\[ C = -0.0360971 \frac{1}{Z} + \mathcal{O} \left( \frac{1}{Z^2} \right) \]

(34)

and

\[ \tilde{v}_{1s} (\vec{r}) = \frac{1}{Z} \left( \frac{1}{\vec{r}} + \frac{3\vec{r}^2 - 4\vec{r} - 1}{54} + \frac{1 + \vec{r}}{\vec{r}} e^{-2\vec{r}} \right) + \mathcal{O} \left( \frac{1}{Z^2} \right) \]

(35)

\[ \tilde{v}_{2s} (\vec{r}) = \frac{1}{Z} \left( -\frac{1}{\vec{r}} + \frac{8 + 6\vec{r} + 2\vec{r}^2 + \vec{r}^3}{8\vec{r} e^{\vec{r}}} + \frac{16(2 + 3\vec{r})}{27(\vec{r} - 2)} e^{-2\vec{r}} \right) + \mathcal{O} \left( \frac{1}{Z^2} \right) \]

(36)

### 5.2 Technical details

The KLI potentials were obtained with the numerical program [31].

The zeroth, first and second-order energies were calculated according to the formulas:
\[ E_{KLI}^{(0)} = \sum_a \langle \phi_a | \hat{T} + \hat{V}_{ne} + \hat{V}_{KLI} | \phi_a \rangle \] (37)

\[ E_{KLI}^{(1)} = \sum_a \left( -2 \langle \phi_a | \hat{V}_{KLI} | \phi_a \rangle + \langle \phi_a \phi_a | \phi_a \phi_a \rangle \right) \]
\[ + \sum_{a < b} \left( 4 \langle \phi_a \phi_b | \phi_a \phi_b \rangle - 2 \langle \phi_a \phi_b | \phi_b \phi_a \rangle \right) \] (38)

\[ E_{KLI}^{(2)} = 2 \sum_a \sum_r \frac{1}{\varepsilon_a - \varepsilon_r} \left[ \langle \phi_a | \hat{T} | \phi_r \rangle + \langle \phi_a \phi_a | \phi_r \phi_r \rangle \right] \]
\[ + \sum_a \sum_{r < s} \frac{1}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \left[ \langle \phi_a \phi_b | \phi_r \phi_s \rangle \right]^2 \] (39)

where \( \phi_a, \phi_b \) (respectively \( \phi_r, \phi_s \)) are occupied (respectively virtual) KLI orbitals with energies \( \varepsilon_a, \varepsilon_b \) (respectively \( \varepsilon_r, \varepsilon_s \)).

The correlation energies in the space of the configurations generated by doubly occupying the 1s, 2s and 2p KLI orbitals were obtained with Mathematica [29].

The KLI orbitals were obtained in a Slater type even-tempered basis set (available on request).

The second-order energies, using all orbitals, can be compared for the He series to the more accurate ones obtained by Engel et al [22], which quote 48.2 and 46.8 for He and Ne\(^{3+}\), respectively for their correlated OPM results (cf. Tab.5 of [22]) from which we estimate our errors to be \( \lesssim 2mH \), which may well be attributed to the missing \( f, g, \ldots \) functions in our basis set. As the \( 4f, 5g, \ldots \) states are not expected to yield a significant contribution to the correlation energy, we believe that our results for \( \varepsilon_i < 0 \) should be accurate to the same order of magnitude.

References


[31] Y. Li, unpublished