Correlation Energy Contributions from Low-Lying States to Density Functionals Based on an Electron Gas with a Gap

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ABSTRACT: Orbitals having negative orbital energies in density functional theory define a space for generating correlated wave functions and contributions to the correlation energies. The most important contribution from such states comes from the valence orbitals, while the Rydberg orbitals make a much smaller contribution. This provides a significant correction to the correlation energy obtained from a functional based on the uniform electron gas with a gap when there is a near degeneracy between the ground state and a two-particle excited state. Int J Quant Chem 75: 885–888, 1999

Key words: correlation energy; energy gap; density functional; second-order perturbation energy

Introduction

Recently, a correlation energy density functional has been proposed [1]. It relies on the following ideas:

1. Atoms and molecules have energy gaps, the uniform electron gas, used as the reference in the construction of density functionals, does not. This can be corrected by considering for the local approximation the uniform electron gas with an enforced gap [2]. Locally, the gap was defined as $G = \frac{1}{8}|\nabla n|^2/n^2$. This choice of the gap is based upon (a) the exact asymptotic behavior of the electron density (in the asymptotic region G becomes equal to the ionization energy) and (b) the observed piecewise exponential behavior of the density [3–5].
2. The self-interaction correction, as given by Becke [6].
3. The incorporation of the requirements of Perdew, Burke, and Ernzerhof [7] for the

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construction of correlation functionals (correct slowly and rapidly varying density limits, uniform scaling to high-density limit).

For atoms the functional gives quite good results when combined with the practically exact exchange treatment via the Krieger–Li–Iafrate (KLI) approach [8]. Kurth and Perdew have recently reported quite encouraging results obtained with this functional for molecular atomization energies when combined with their new exchange functional [9]. One of the central approximations made was the neglect of any contribution to the correlation energy from states lying below the ionization energy limit. In Ref. [1] it was suggested that these contributions would generally be a small fraction of the correlation energy except for those atoms with a near degeneracy, in which case further wave function calculations would be required to include this contribution. The aim of this article is to explore the validity of this approximation by explicitly calculating the contribution to the correlation energy from the states below the ionization limit. For our test we chose He, Li^+, Be, and B^+, as in the first two only dynamical correlation is supposed to be present while in the last two cases the degeneracy present at infinite nuclear charge is believed to be felt [10].*

Technical Details

In order to obtain the correlation energy, we considered two approaches. In the first, we diagonalized the Hamiltonian in a small subspace. In the second, we used perturbation theory. We define a zeroth-order one-electron Hamiltonian having a local potential defined as in the KLI approach [8]. Thus, up to first order, the energy is the expectation value of the physical Hamiltonian obtained with the KLI Slater determinant. As the KLI wave function is slightly different from the Hartree–Fock one, there will be a small difference between this expectation value and the Hartree–Fock energy. Furthermore, there is a small contribution of single excited zeroth-order Slater determinants to the second-order perturbation energy term. (Our perturbation energy series is very close to that of Görling and Levy [13].) As we are interested in the contributions to the second-order energy of the states below the ionization limit, we will consider the contributions coming from orbitals having negative orbital energies. (In the Kohn–Sham theory, the energy of the last occupied orbital is equal to minus the exact ionization energy [14].)

We performed our calculations in even-tempered Slater-type basis sets (of $1s$, $2p$, and $3d$ type). Their exponents are $\zeta_i = \zeta_1 f^{i-1}$, where $1 \leq i \leq 9$, $\zeta_1 = 0.2$, and $f = 1.5$.

Results

In order to understand the results obtained, we would like to recall that the virtual KLI (and Kohn–Sham, KS) eigenvalues behave differently from the canonical Hartree–Fock equivalents. While in Hartree–Fock most of the virtual eigenvalues are positive, in KLI or KS, an infinity of negative eigenvalues appear, which can be understood from the asymptotic $-1/r$ behavior of the potentials. In fact, it turns out that the difference between the highest occupied KS eigenvalue and of the unoccupied ones is quite close to experimental excitation energies [15]. Davidson noticed that the correlating (natural) orbitals are in the same spatial region as the (strongly) occupied ones [16]. In order to achieve this, they usually will be linear combinations of the KLI or KS orbitals, with positive eigenvalues. For valence states, however, the unoccupied states may well be in the same spatial region as the occupied ones and contribute to the correlation energy.

Another observation comes from the study of the adiabatic coupling of the electron–electron interaction which shows that the dependence on the interaction strength parameter λ is roughly given by $a\lambda^2/(1 + b\lambda)$, where a and b are system-dependent constants (see, e.g., Ref. [17] and references therein): a corresponds to the second-order correlation energy, while b turned out to be positive (small in the He series, becoming more and more important as the nuclear charge increases in the Be series and is related to the near-degeneracy effect in the Be series). As the physical correlation energy is given at $\lambda = 1$, we expect the magnitude of the second-order energy to be larger than that of the correlation energy.

*Using many-determinant wave functions is not new [11]. Using Kohn–Sham calculations for configuration interaction calculations was suggested by Fritsche [12], with the argument that the zeroth order already gives the correct density.

Our present calculations confirm these observations. For He and Li^+ second-order perturbation theory yields a correlation energy of 1 and 2 mhartrees, respectively, when only orbitals with negative energies are considered. When the contributions of all the states are taken into account, we obtain at second order 46 and 45 mhartrees for He and Li^+, respectively. (These values are in good agreement with the fitted values of the constants a for He and Ne^{8+} given in Ref. [17]: 47.5 and 46, respectively.) The second-order energies in the Be series are quite large, 118 and 134 mhartrees, for Be and B^+, respectively. (This also is in agreement with the fitted values of a given in Ref. [17] for Be and Ne^{6+}: 123 and 285 mhartrees, respectively.) The second-order energies in the space of the orbitals with negative energies are 57 and 78 mhartrees for Be and B^+, in contrast to the results obtained for He and Li^+. A configuration interaction calculation considering just the two near-degenerate configurations $1s^2 2s^2$ and $1s^2 2p^2$ yields 34 and 54 mhartrees for Be and B^+. These values are smaller than those obtained when the orbitals are optimized (Davidson et al. [18] report 44 and 59 mhartrees from a complete active space calculation). This shows that the KLI orbitals are good but not perfect for describing the near-degeneracy effect. We noticed nonnegligible contributions in second-order perturbation theory coming from $1s^2 pp'$ configurations which are indicative of orbital relaxation effects. We finally mention that density functional second-order perturbation theory limited to the $2s^2 \rightarrow 2p^2$ excitation yields too much correlation energy (46 and 72 mhartrees for Be and B^+) while the Hartree–Fock equivalent seems not to yield enough [19].

We have also performed exploratory calculations with accurate Kohn–Sham orbitals (from Ref. [17]) for He and Be and obtained similar trends. The results for He were practically unchanged, while there were differences of a few millihartrees for Be, e.g., 39 mhartrees in the 2×2 configuration interaction calculation (instead of 34 mhartrees).

Conclusion

Our calculations show that KLI Rydberg orbitals seem to contribute little to the second-order correlation energy and may be quite safely neglected. On the other hand, the valence unoccupied orbitals may have a significant contribution. Taking these few states into consideration, correct for the deficiency of electron gas correlation energy density functionals previously remarked, namely that there may be systems which are more strongly correlated than the uniform electron gas, and thus cannot be fully described by gap, gradient, or self-interaction corrected electron gas [2]. While such a treatment makes computer programs more complex than they are for usual Kohn–Sham calculations, they should not be much more time-consuming, as only valence basis sets are needed. Finally, in its present form, this combined many-determinant and density functional method does not allow for systematic improvement, in contrast to previously proposed methods (see, e.g., [20, 21]) We note, however, that, if needed, the method presented here can be easily extended to such a method, by introducing the gap in the uniform electron gas not at the Fermi level but at an arbitrary level above. By changing this level, one has a continuous transition toward the full wave function calculation.

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