Improvement of Multiconfigurational Wave Functions and Energies by Correlation Energy Functionals

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Several aspects of hybrid methods resulting from combining multiconfigurational (MC) wave functions with correlation energy functionals are discussed, in particular for a family of functionals recently proposed.[1,2] It is found that adding the correlation at the end of a MC calculation instead of including it in the self-consistent procedure constitutes an excellent approximation. MC potential energy curves and spectroscopic constants show a significant improvement after being corrected with correlation energies from this family of functionals.

1. Introduction

Reliable potential energy surfaces are crucial for chemical simulations. Since high-quality descriptions such as full-CI wave functions are out of the question for most systems, it would be particularly interesting to develop a hybrid scheme combining qualitatively correct multiconfigurational (MC) wave functions with cheap but accurate approximations to the unaccounted correlation energy.

These qualitatively correct wave functions have to be sought beyond the monoconfigurational Hartree−Fock (HF) method, which gives a poor description[3] of bond dissociation. For example, for the H_2 molecule, the restricted HF model (RHF) severely overestimates the dissociation energy, while the unrestricted HF model (UHF) breaks the spin symmetry. A biconfigurational general valence bond[4] (GVB) treatment of the same molecule gives, on the other hand, a rather good description of the bond, including *proper dissociation*[5] into atomic fragments.

Correlation energy is the difference between the exact and HF energies. Density-functional theory[6,7] (DFT) provides accurate estimates of the correlation energy at a reasonable cost, through approximations to the *correlation energy functional* $E_c[\rho]$, where ρ is the electron density (for a review on common approximations, see, for example, ref 8). A particularly simple approach is the *Hartree−Fock−Kohn−Sham method*[7,9−13] (HFKS), where the exact energy is expressed as the HF functional $E_{HF}[\rho]$ plus the DFT correlation energy functional

$$E_{exact} = E_{HF}[\rho] + E_c[\rho] \quad (1)$$

An appealing feature of the $E_c[\rho]$ is the possibility of implementing it within a post-SCF step,[14] because correlation is a small perturbation that can be added afterward in a non-SCF fashion. Practical experience shows that the following approximation is very accurate[12,15−17]

$$E_{HF}[\rho] + E_c[\rho] \approx E_{HF} + E_c[\rho_{HF}] \quad (2)$$

so that it is possible to obtain good estimates of the exact energy by adding the correlation energy obtained from the HF density ρ_{HF} to the HF energy. The main advantage of such a post-SCF procedure is that the functional derivative $\delta E_c[\rho]/\delta\rho$ is *not* needed.

Although quite good for atoms,[18] the HFKS method does not seem to be much of an improvement over the HF method for molecular spectroscopic constants such as equilibrium distances or vibrational frequencies.[19] The reason is, as we have said, the poor behavior of the HF method for bond dissociation. One would expect that the use of MC wave functions instead of the HF determinant would yield better results

$$E_{exact} \equiv E_{MC} + E_{c,MC} \quad (3)$$

where $E_{c,MC}$ is, by definition, the difference between the exact and MC energies. Conventional DFT $E_c[\rho]$ functionals cannot be expected to provide a very good approximation to $E_{c,MC}$ because $E_{c,MC}$ is only a fraction of the total correlation energy.

Approximations[1,2,20−39] to $E_{c,MC}$ typically depend on quantities such as natural orbitals or reduced density matrices.[40] Often they are expressed as functionals of the *reduced density matrix of second order* Γ

$$E_{c,MC} \approx E_c[\Gamma] \quad (4)$$

These functionals can be applied indistinctly to mono- or multiconfigurational Γ's. For example, if Γ_{HF} and Γ_{MC} come, respectively, from HF and MC wave functions, then $E_c[\Gamma_{HF}]$ is a good approximation to $E_{c[\rho HF]}$ and $E_c[\Gamma_{MC}]$ is a good approximation to $E_{c,MC}$.

Recently, in our laboratory, a family of $E_c[\Gamma]$ functionals has been developed.[1,2,38] Results over atomic Γ_{HF}'s have been encouraging so far. The goal of the present study is twofold. First, we will check this family of functionals over molecular Γ_{MC}'s. Second, we will check if a post-SCF procedure analogous to eq 2 is also accurate for $E_c[\Gamma]$.

2. Self-Consistent Calculations for GVB Wave Functions

In order to check the accuracy of the post-SCF scheme, we need, as a reference, a self-consistent procedure for GVB wave functions. We briefly outline it next. For simplicity, we will restrict ourselves to the H_2 molecule and to this wave function,

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although we are working on other larger systems and more sophisticated wave functions.

For hydrogen, the GVB wave function[3,4] is composed of two determinants

$$\Psi_{\mathrm{GVB}} = C_1|\phi_1\bar{\phi}_1\rangle + C_2|\phi_2\bar{\phi}_2\rangle \tag{5}$$

where the symbol $|\phi_i\bar{\phi}_i\rangle$ denotes a Slater determinant, ϕ_1 and ϕ_2 are α orbitals, and are $\bar{\phi}_1$ and $\bar{\phi}_2$ their respective β counterparts.

A self-consistent calculation for the previous wave function is carried out in two steps. During the first step, the coefficients C_i are kept fixed while the orbitals are optimized. During the second step, the situation is reversed, and the orbitals are kept fixed while the coefficients are optimized. These two steps are repeated iteratively until self-consistency is achieved.

The first step is carried by means of a Fock-like operator (note, however, that unlike the HF operator, this GVB operator takes a different form for each orbital). The correlation functional $E_c[\Gamma]$ enters the calculations here, as a correlation potential that is added to the Fock-like operator. The correlation potential is the functional derivative of $E_c[\Gamma]$ with respect to ϕ_i, $\delta E_c[\Gamma]/\delta\phi_i$. The explicit form of this potential for our family of functionals[1,2] is given in ref 2.

The second step, the optimization of the coefficients, is simply the minimization of

$$\langle\Psi_{\mathrm{GVB}}|\hat{H}|\Psi_{\mathrm{GVB}}\rangle \tag{6}$$

while the orbitals are kept constant and where $\hat{H}$ is the Hamiltonian operator. It is carried out by diagonalization of the 2 × 2 matrix **H**, with elements

$$H_{ij} = \langle\phi_i\bar{\phi}_i|\hat{H}|\phi_j\bar{\phi}_j\rangle \tag{7}$$

We explain next how to include, in an approximate way, the contribution from the correlation functional to the optimization of the coefficients.

Our approximation[1,2] to $E_c[\Gamma]$ depends on Γ through the *on-top* density $\rho_2(\mathbf{r})$, which can be expressed as

$$\rho_2(\mathbf{r}) = \int \Gamma(\mathbf{r}\boldsymbol{\sigma}_1, \mathbf{r}\boldsymbol{\sigma}_2; \mathbf{r}\boldsymbol{\sigma}_1, \mathbf{r}\boldsymbol{\sigma}_2)\, \mathrm{d}\boldsymbol{\sigma}_1 \mathrm{d}\boldsymbol{\sigma}_2 \tag{8}$$

(Löwdin criterion[40] is assumed) or, alternatively, as

$$\rho_2(\mathbf{r}) = \langle\Psi_{\mathrm{GVB}}|\delta(\mathbf{r} - \mathbf{r}_1)\, \delta(\mathbf{r} - \mathbf{r}_2)|\Psi_{\mathrm{GVB}}\rangle \tag{9}$$

$E_c[\Gamma]$ is given[1,2] by

$$E_c[\Gamma] = 2\pi \int \rho_2(\mathbf{r})\, \mathbf{I}(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{10}$$

where $I(\mathbf{r})$ is a function with explicit dependence on ρ and ρ_2. Taking into account eq 9, we can rewrite $E_c[\Gamma]$ as

$$E_c[\Gamma] = 2\pi\, \langle\Psi_{\mathrm{GVB}}|\, I(\mathbf{r}_1)\, \delta(\mathbf{r}_1 - \mathbf{r}_2)|\Psi_{\mathrm{GVB}}\rangle \tag{11}$$

Comparison with eq 6 would suggest that diagonalization of the 2 × 2 matrix **H′** with elements

$$H'_{ij} = H_{ij} + 2\pi\, \langle\phi_i\bar{\phi}_i|I(\mathbf{r}_1)\, \delta(\mathbf{r}_1 - \mathbf{r}_2)|\phi_j\bar{\phi}_j\rangle \tag{12}$$

would yield the optimum coefficients. This is not strictly so, because $I(\mathbf{r})$ depends explicitly on the coefficients that are being optimized. We will assume, however, that this dependence is weak and can be neglected. As we will see in the next section, inclusion of correlation in a self-consistent fashion has very little effect on the results. We do not believe that consideration of the explicit dependence of $I(\mathbf{r})$ on the coefficients will change this conclusion.

TABLE 1: Spectroscopic Constants for the H_2 Molecule

	R_e (au)	ω_e (cm^{-1})	D_e (eV)
GVB	1.426	4226	4.142
GVB+CS	1.411	4340	4.725
GVB+MPJ1	1.409	4358	4.753
GVB+MPJ1 (SCF)	1.409	4354	4.751
GVB+MPJ5	1.400	4429	4.937
GVB+MPJ5 (SCF)	1.400	4422	4.938
exact	1.401	4405	4.748

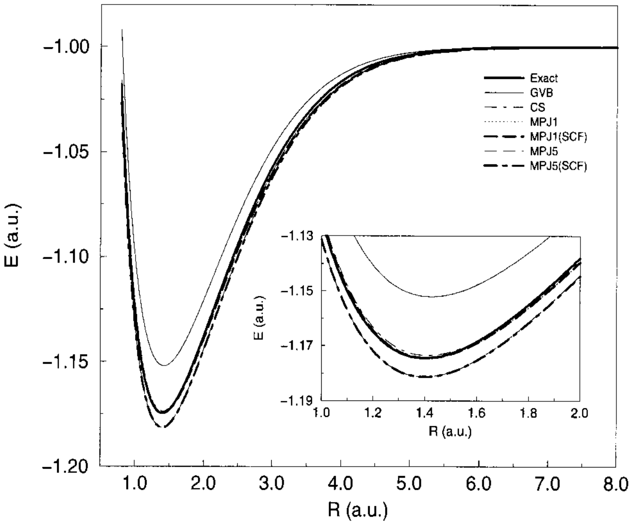

Figure 1. Potential energy curves for the H_2 molecule.

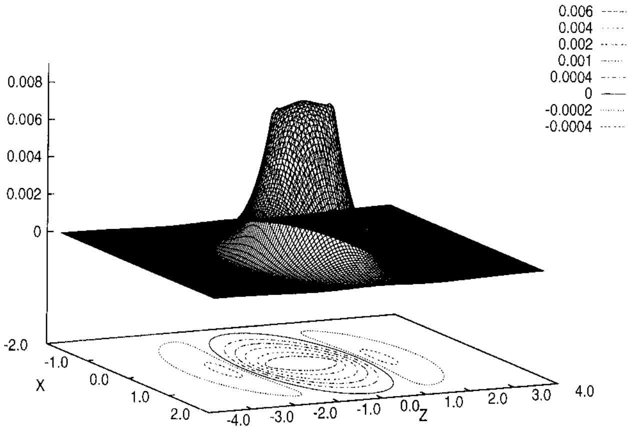

Figure 2. Difference, $\delta\rho$, between GVB+MPJ1 (SCF) and GVB+MPJ1 densities at $R = 1.40$ au (both axes in au).

3. Results and Conclusions

In this section we present some results for the H_2 molecule. All the calculations in Table 1 and Figures 1 and 2 have been carried out with the package GAMESS,[41] using the basis set aug-cc-pVQZ.[42] The correlation energy is evaluated by numerical integration.[43] “GVB” refers to a GVB calculation, “GVB+···” is a GVB calculation corrected by adding a given correlation energy model in a post-SCF non-self-consistent fashion, and “GVB+···(SCF)” denotes the analogous calculation but with the correlation included in the SCF procedure, in the way explained in the previous section. The ellipsis may stand for “CS” (Colle−Salvetti[23]), “MPJ1” (Moscardó and Pérez-Jiménez, level 1[1,2]), or “MPJ5” (Moscardó and Pérez-Jiménez, level 5[1,2]). Entries labeled “exact”, used here as a reference, come from the work of Kolos and Wolniewicz.[44]

The spectroscopic constants in Table 1 and the curves in Figure 1 have been obtained from sets of energy−distance points on the potential energy curve, ranging from 0.7 to 10.0 au at intervals of 0.1 au, giving a total of 94 points. The spectroscopic constants have been computed from a least-squares fit of the 94 points to a polynomial in the variable[45]

$$z = \frac{R - R_0}{R + R_0} \tag{13}$$

where R is the internuclear distance and R_0 is an adjustable parameter. The order of the fitting polynomial and the value of R_0 have been optimized so that they minimize the round-off error. An identical technique has been applied to the "exact" data points from Kolos and Wolniewicz's[44] paper. We have applied the same procedure to half the data points (even points) in order to check the accuracy of our values. We feel confident that all the constants shown in Table 1 are correct, except perhaps the last digit of ω_e. The hydrogen atom mass is required for the calculation of the vibrational frequency ω_e, and in all cases it has been taken from the periodic table.[46]

From the results in Table 1 and Figures 1 and 2, we can draw the following conclusions:

From Table 1 and Figure 1, we see that the non-SCF values are almost identical to the SCF ones. Therefore, the post-SCF procedure constitutes an excellent approximation.

With the aim of studying the effect of the correlation potential on the wave function, we have analyzed its influence in the electron density. Figure 2 shows the difference between the density obtained when the MPJ1 correlation potential is used in the SCF procedure (GVB+MPJ1(SCF)) and that obtained without this correlation potential (GVB or GVB+MPJ1). These difference, $\delta\rho$, is quite small, although greater than the difference in energy, which is of second order[15,17] in $\delta\rho$. There is an increase in charge in the nuclear and internuclear regions, where the correlation energy potential is stronger.

Regarding the quality of the different approximations to the correlation energy, we see that in all cases there is a significant improvement over the GVB values. We can order the functionals as follows (from best to worst): MPJ1, CS, and MPJ5. MPJ1 and CS show a similar quality, while MPJ5 overestimates the dissociation energy D_e for this system, although in ref 1 the MPJ5 functional gives a smaller average error than MPJ1 for the correlation energy of first-row atoms.

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