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Simple molecular wavefunctions with correlation corrections II

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The potential curves for the ground state of Li_2 ($^1\Sigma_g^+$) and FH ($^1\Sigma_g^+$) are computed. The correlation energy is calculated using a functional of the one- and two-electron density matrices derived from an MC SCF reference wavefunction and is added to the reference energy to obtain a correlated potential curve.

Key words: Correlation energy—potential energy curves—molecular wavefunctions

1. Introduction

In this paper we report the computation of potential curves for the ground state of the molecules of FH ($^1\Sigma_g^+$) and Li_2 ($^1\Sigma_g^+$). The method of computation has already been explained in detail previously and successfully applied to H_2 and LiH [1]. The idea is to correct the two main deficiencies of wavefunctions of Hartree-Fock type (wrong dissociation behavior and absence of correlation between electrons of unlike spins) separately. A short CI expansion is admitted to ensure qualitatively correct dissociation, while the short-range correlation energy is estimated from the Colle-Salvetti functional [2, 3]. This functional prescribes the following expression for the correlation energy

$$E_c = -(0.09836)\int \frac{P_2^{\mathrm{MC}}(\boldsymbol{R},\boldsymbol{R})}{P^{\mathrm{MC}}(\boldsymbol{R})}\,\frac{1+0.173\,W\exp(-0.58/\beta)}{1+0.8/\beta}\,\mathrm{d}\boldsymbol{R}. \tag{1.1}$$

Here P^{MC} and P_2^{MC} are the one- and two-electron (spinless) density matrices derived from an MC SCF wavefunction, while

$$W = \frac{[\nabla_{\boldsymbol{r}}^2 P_2^{\mathrm{MC}}(\boldsymbol{R}-1/2\boldsymbol{r},\boldsymbol{R}+1/2\boldsymbol{r})]}{P_2^{\mathrm{MC}}(\boldsymbol{R},\boldsymbol{R})}\,(\boldsymbol{r}\to 0) \tag{1.2}$$

with

$$\beta = q[P^{\mathrm{MC}}(\boldsymbol{R})]^{1/3} \tag{1.3}$$

and

$$\boldsymbol{r} = \boldsymbol{r}_{ij} = (\boldsymbol{r}_j - \boldsymbol{r}_i), \qquad \boldsymbol{R} = \tfrac{1}{2}(\boldsymbol{r}_i + \boldsymbol{r}_j).$$

Using equation (1.1) and a wavefunction of MC SCF-type we were able to derive accurate potential curves for H_2 and LiH [1]. However, in this calculation we had to treat the parameter q in (1.3) as an empirical parameter in order to avoid an overestimation of energy when adding the computed correlation correction to the MC SCF energy. We recall that the value of q proposed by Colle and Salvetti ($q = 2.29$) was found by fitting the results using the functional to the results of the He atom, a system in which the two electrons are tightly bound to the nucleus. It was therefore not surprising to find that for H_2 and LiH we had to change the value of q, owing to the fact that for H_2 the electrons are valence electrons and for LiH two of the four electrons are valence electrons (for which substantial correlation is already admitted in the reference function).

In this paper we intend to show that the original value of q (=2.29) remains appropriate for molecules in which most of the electrons are described by uncorrelated inner-shell wavefunctions. We have chosen the molecules of Li_2 and FH for this test.

2. Results and Discussion

$Li_2(^1\Sigma_g^+)$

For this molecule we used a modest basis set proposed by Ransil [4] composed of 5 AO's on each atom. The MC SCF wavefunction included only the two configurations ($1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 + 1\sigma_g^2 1\sigma_u^2 2\sigma_u^2$) needed to ensure proper dissociation behavior. The results are set out in Table 1. As expected, the correlation energy

Table 1. Energies (E) and correlation energy (E_c) for Li_2 (a.u.)

R	E(SCF)	E(MC)	E_c(MC)	$E+E_c$(MC)
3.00	−14.752207	−14.759776	−0.124956	−14.884732
4.00	−14.820883	−14.826616	−0.124404	−14.951020
4.50	−14.835105	−14.841511	−0.122676	−14.964187
5.05	−14.841482	−14.849304	−0.120466	−14.969770
5.20	−14.842028	−14.850339	−0.119822	−14.970161
5.50	−14.842018	−14.851470	−0.118567	−14.970037
6.00	−14.839575	−14.851273	−0.116469	−14.967742
7.00	−14.829699	−14.847462	−0.112450	−14.959912
8.00	−14.817457	−14.843192	−0.109149	−14.952341
9.00	—	−14.840202	−0.106657	−14.946859
10.00	—	−14.838478	−0.104906	−14.943384
12.00	—	−14.837627	−0.103519	−14.941146

increases in magnitude as the atoms come closer, while as the atoms are pulled apart it tends to the limit of -0.1030 a.u. This value is reasonably close to twice the correlation energy of the Li atom (i.e. -0.092 a.u. [5]).

Our results for the correlation correction of this molecule are very close to those obtained by Colle and Salvetti [6] who used an improved basis set and an empirical procedure to adjust the parameter q in (1.3). This seems to confirm the conclusions of our previous paper [1] that, firstly, the correlation corrections from the Colle-Salvetti functional are practically insensitive to basis set changes and secondly that the original value of q $(=2.29)$ remains appropriate for a molecule containing atoms with uncorrelated inner-shell wavefunctions.

FH ($^1\Sigma_g^+$)

We used three different basis sets in the calculation for this molecule; the first was the optimized basis set of Ransil and Fraga [7] consisting of 6 AO's (calculation 1), the second was built from a double-zeta basis set proposed by Clementi [8] for the fluorine atom and two 1s functions (exponents 1.2 and 1.5) for the hydrogen atom (calculation 2) and in the third and final calculation we used the improved basis set proposed by Huzinaga [9] composed of 13 AO's on the fluorine atom and 6 AO's on hydrogen with following exponents $\alpha_{1s}=1.2$, $\alpha'_{1s}=1.5$, $\alpha_{2s}=1.5$ and $\alpha_{2p}=1.5$ (calculation 3).

The CI expansion was built from the Hartree-Fock wavefunction $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi^2 2\pi^2)$ and the configurations resulting from the following pair excitations: $2\sigma_g \to 2\sigma_u$ in the calculations 1 and 2 and $2\sigma_g \to 2\sigma_u$, $3\sigma_g$; $1\pi \to 2\sigma_u$, $3\sigma_g$; $2\pi \to 2\sigma_u$, $3\sigma_g$ in calculation 3.

The MC SCF energies are -99.5264 a.u., -100.0488 a.u. and -100.0790 a.u. at the equilibrium geometry ($R = 1.733$ a.u.) for calculations 1, 2 and 3 respectively. The results for the correlation energy from (1.3) are again practically independent of basis set. At $R = 1.733$, for instance, we have obtained -0.3536 a.u., -0.3529 a.u. and -0.3523 a.u. in the calculations 1, 2 and 3 respectively.

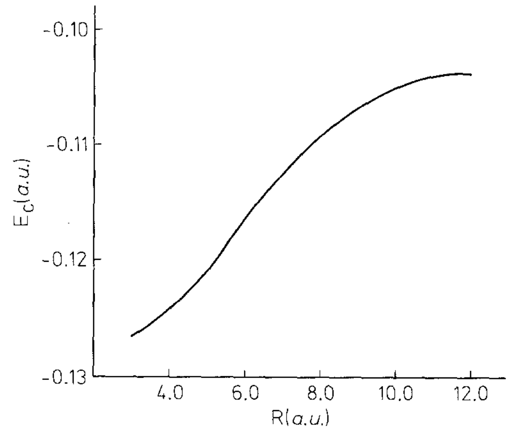

Fig. 1. Variation of the correlation energy with internuclear distance for Li_2

Table 2. Energies (E) and correlation energy (E_c) for FH (a.u.)

R	E(SCF)	E(MC)	E_c(MC)	$E+E_c$(MC)
1.40	−100.001175	−100.020779	−0.356046	−100.376825
1.50	−100.032146	−100.052837	−0.354881	−100.407718
1.60	−100.047894	−100.070662	−0.353749	−100.424411
1.733	−100.053140	−100.078955	−0.352324	−100.431279
1.90	−100.044156	−100.074064	−0.350417	−100.424481
2.00	−100.033845	−100.066545	−0.349239	−100.415784
2.50	−99.962415	−100.013331	−0.342696	−100.356027
3.00	−99.890468	−99.966540	−0.335560	−100.302100
3.50	−99.830319	−99.937386	−0.329133	−100.266520
4.00	−99.782366	−99.922312	−0.324511	−100.246823
5.00	−99.715179	−99.911542	−0.320054	−100.231600
6.00	−99.683555	−99.917851	−0.319546	−100.237397

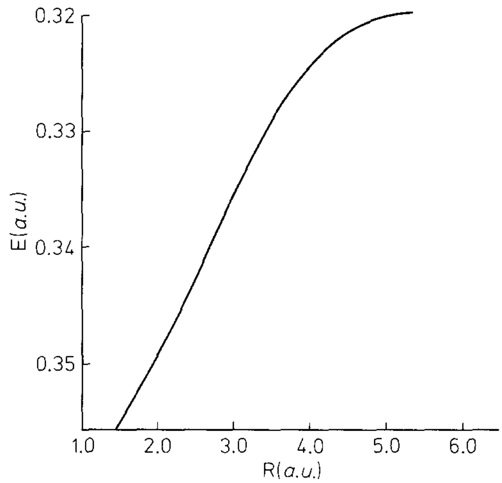

Fig. 2. Variation of the correlation energy with internuclear distance for FH

Table 2 contains all results for the calculation 3. As can be seen in Fig. 2 the variation of the correlation energy with internuclear distance is completely satisfactory: for small R it increases (negatively) approaching the united-atom (Neon) correlation energy of −0.372 a.u. [2], while for large R it tends to approximately −0.32 a.u. which is very close to the correlation energy of the fluorine atom, −0.315 a.u. [5].

The correlated MC SCF potential curve is shown in Fig. 3. The agreement with the "experimental" values derived from the Hulbert-Hirschfelder curve [10] is quite satisfactory.

In conclusion these calculations seem to confirm that the correlation corrections from (1.1) are very accurate and practically independent of the basis set. Also the value of the parameter q in (1.3) proposed by Colle and Salvetti ($q=2.29$)

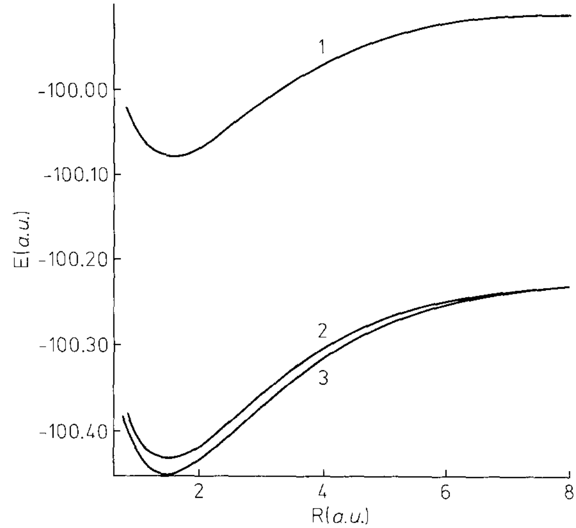

Fig. 3. Comparison of MCSCF potential curves with experiment for FH (1) MCSCF: (2) MCSCF plus correlation corrections (3) Hulbert-Hirschfelder curve

is appropriate for molecules containing atoms with uncorrelated inner-shell wavefunctions.

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