Theoret. Chim. Acta (Berl.) 64, 171–180 (1983)

THEORETICA CHIMICA ACTA

Simple molecular wavefunctions with correlation corrections

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It is shown that the main deficiencies of wavefunctions of Hartree–Fock type (wrong dissociation behavior and absence of correlation between electrons of unlike spin) may be corrected by a simple method. Just sufficient CI is admitted to ensure qualitatively correct dissociation, while the short-range correlation energy is estimated with the Colle–Salvetti functional. Potential energy curves for H_2 and LiH are computed at various levels of approximation and the main features of the method are discussed.

Key words: Correlation energy—Potential-energy curves—Molecular wavefunctions.

1. Introduction

It is well-known that the closed-shell self-consistent field (SCF) method, even when carried to the Hartree–Fock (HF) limit, possesses two main defects when applied to molecules: (i) incorrect description of the short-range correlation between electrons of unlike spin as $r_{12} \to 0$, and (ii) incorrect behavior of the wavefunction at large internuclear distances. The origin of these deficiencies has been extensively discussed (see, for example, Refs. [1, 2]): the standard way of overcoming them is to admit configuration interaction (CI) in one form or another. Unfortunately, in order to reproduce the expected behavior of an "exact" wavefunction [3,4], and an "exact" pair distribution function [5], as two electrons approach, it is necessary to include an extremely large number of configurations in the CI expansion even for small molecules [6, 7]. Consequently, the present

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trend in *ab initio* quantum chemistry is towards vast CI calculations involving as many as 10^5 configurational functions.

In the present paper, by contrast, we explore an alternative way of dealing with the deficiencies exhibited by a simple reference function, the aim being to treat (i) and (ii) (above) *separately*, whilst retaining a wavefunction of very simple (*few*-configuration) form. The wrong dissociation behavior (ii) is corrected by using a multiconfiguration (MC) SCF wavefunction, containing only sufficient CI to obtain a qualitatively satisfactory description at large internuclear distances. The *short*-range correlation "cusp" (responsible for (i)) is introduced by the method of Colle and Salvetti [8], and leads to a correlation energy functional involving one- and two-electron density matrices derived (in the present case) from the MC SCF reference function. Although evaluation of the correlation functional requires the development of numerical integration techniques, the total computational effort involved is very small by presesnt-day standards and the wavefunction retains a conceptual simplicity.

In the next section we briefly review the Colle–Salvetti approach and then we present and discuss some results for the molecules LiH and H_2.

2. The Colle–Salvetti functional

In the approach used by Colle and Salvetti [8, 9], an already known reference function, of HF or limited MC SCF form, is improved by adding a short-range correlation factor. The wave-function is thus taken to be

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \Psi^{\mathrm{MC}}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \prod_{i>j} [1-\phi(\mathbf{r}_i, \mathbf{r}_j)] \tag{2.1}$$

where the MC SCF function Ψ^{MC} will usually be derived by optimizing a short CI expansion, while $\phi(\mathbf{r}_i, \mathbf{r}_j)$ is a short-range correlation function. It is convenient to choose

$$\phi(\mathbf{r}_i, \mathbf{r}_j) = \exp(-\beta^2 \mathbf{r}_{ij}^2)[1-\Phi(\mathbf{R}_{ij})(1+\tfrac{1}{2}r_{ij}/a_0)] \tag{2.2}$$

where $\mathbf{r}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)$, $\mathbf{R}_{ij} = \frac{1}{2}(\mathbf{r}_j + \mathbf{r}_i)$. This function behaves correctly for $r_{12} \to 0$, while $\beta(\mathbf{R}_{ij})$ and $\Phi(\mathbf{R}_{ij})$ allow the form of the "correlation hole" [5] to depend on the position of the pairs *ij*. Integral conditions impose a relationship between Φ and β which may be accurately fitted by taking

$$\Phi(\mathbf{R}) = \sqrt{\pi}\, a_0 \beta / (1 + \sqrt{\pi}\, a_0 \beta) \tag{2.3}$$

and only one function, $\beta(\mathbf{R})$, then remains; if this is assumed to depend, in first approximation, only on the electron density $P(\mathbf{R})$, then dimensional consistency requires

$$\beta(\mathbf{R}) = qP(\mathbf{R})^{1/3} \tag{2.4}$$

where q is a dimensionless constant.

The correlation correction to the reference-function energy is then found to be

$$E_c = -\frac{2\pi}{q^3}\int \frac{P_2^{\mathrm{MC}}(\boldsymbol{R},\boldsymbol{R})}{P^{\mathrm{MC}}(\boldsymbol{R})} G(\beta, W)\, d\boldsymbol{R} \tag{2.5}$$

where P^{MC} and P_2^{MC} are the one- and two-electron (spinless) density matrices, respectively, while[1]

$$G(\beta, W) = \frac{0.121 - 0.0167\mathrm{W} + 0.0458/\beta - 0.0102\mathrm{W}/\beta}{1 + 1.1284\beta + 0.3183/\beta^2} \tag{2.6}$$

and the quantity W is given by

$$W = \frac{\nabla_{\boldsymbol{r}}^2 P_2^{\mathrm{MC}}(\boldsymbol{R} - \tfrac{1}{2}\boldsymbol{r}, \boldsymbol{R} + \tfrac{1}{2}\boldsymbol{r})}{P_2^{\mathrm{MC}}(\boldsymbol{R},\boldsymbol{R})\beta^2}. \tag{2.7}$$

An alternative expression for the correlation energy, also used by Colle and Salvetti, is obtained on replacing $G(\beta, W)$ by a somewhat simpler function $H(\beta, W)$ which may be chosen to fit $G(\beta, W)$ quite closely. This procedure leads to the expression

$$E_c = -(0.09836)\int \frac{P_2^{\mathrm{MC}}(\boldsymbol{R},\boldsymbol{R})}{P(\boldsymbol{R})}\,\frac{1 + 0.173W\exp(-0.58/\beta)}{1 + 0.8/\beta}\, d\boldsymbol{R} \tag{2.8}$$

When the reference function is of Hartree–Fock form, there is a further simplification, affecting (2.7) as well as (2.5) and (2.8), since[2]

$$P_2^{\mathrm{HF}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = P(\boldsymbol{r}_1)P(\boldsymbol{r}_2) - 1/2P(\boldsymbol{r}_2; \boldsymbol{r}_1)P(\boldsymbol{r}_1; \boldsymbol{r}_2) \tag{2.9}$$

and expressions (2.5) and (2.8) then reduce to the original forms used by Colle and Salvetti [8].

The results of numerical calculations of the correlation energy for a number of closed-shell atoms and molecules, using the HF reference function, are extremely good. Salvetti and co-workers have also applied the method to the excited states of the BeF radical [10] and to the V–N transition of planar ethylene [11], again with encouraging results.

The same functional (2.2) was also discussed by McWeeny [12] who applied it to the uniform electron gas, obtaining good results not only at the high and low-density limits but over the whole density range.

In testing our numerical integration programmes we repeated some of the calculations of Colle and Salvetti and, using Eq. (2.8), were able to reproduce their results; for this reason we have adopted (2.8) instead of (2.7) as a simpler and more satisfactory (though perhaps more empirical) expression for the correlation energy.

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[1] The coefficient of W/β in (2.6) appears to be given incorrectly (as -0.005) in Ref. [8]. Henceforth, we use atomic units e, $\hbar$, a_0 (Bohr radius) and E_h (Hartree).

[2] $P(\boldsymbol{r}_1; \boldsymbol{r}_2)$ is the "off-diagonal" element of the one-electron density matrix, reducing to $P(\boldsymbol{r})$ when $\boldsymbol{r}_1 = \boldsymbol{r}_2 = \boldsymbol{r}$.

3. Results and discussion

For our test calculations we first chose the $^1\Sigma^+$ ground state of the molecule LiH, partly for simplicity of the system and partly in view of a number of careful theoretical and experimental investigations already published [7, 13–16].

3.1. Calculation I

The first calculation was performed with a non-optimized minimal (Slater) basis set [17]. The SCF and MC SCF results and the correlation corrections for both wavefunctions are listed in Tables 1 and 2, while Figs. 1 and 2 make comparisons with the Morse curve [14]. The MC SCF function used in this calculation includes only *two* configurations ($1\sigma^2 2\sigma^2$ and $1\sigma^2 3\sigma^2$), this being sufficient to correct the wrong dissociation behavior of the HF function [13].

The following points should be noted
(i) At small and intermediate distances ($R < 4.0a_0$) the correlation corrections are rather accurate. In particular, at equilibrium ($R = 3.015a_0$), the computed SCF correlation energy is $-0.08413E_h$, which can be compared with the figure of $-0.08259E_h$ derived from Cade and Huo's results [16]. For $R = 1.0a_0$ the correlation energy is $-0.092890E_h$, which is again in very good agreement with the united-atom (Be, in this case) correlation energy which is $-0.0940E_h$ [8].
(ii) At large internuclear distances the SCF results confirm our expectation that the computed correlation energy would not be reliable (owing to the incorrect dissociation behavior of this wavefunction). In this region, it would be reasonable to expect a correlation energy approximately equal to that of the Li atom, which is $-0.046E_h$ [18]; the computed value ($-0.077E_h$) is much too large.

Table 1. Energies (E) and correlation corrections (E_c) for LiH (a.u.) SCF calculation using Ransil's minimal basis set

R	E(SCF)	E_c(SCF)	$E + E_c$(SCF)
1.00	−7.183031	−0.092793	−7.275824
2.00	−7.880674	−0.090064	−7.979738
2.50	−7.948610	−0.086689	−8.035299
2.80	−7.962935	−0.085068	−8.048003
3.015	−7.966663	−0.084128	−8.050791
3.20	−7.966916	−0.083425	−8.050341
3.50	−7.963268	−0.082434	−8.046114
4.00	−7.950356	−0.081166	−8.031522
5.00	−7.914427	−0.079488	−7.993915
6.00	−7.877545	−0.078484	−7.956029
7.00	−7.845303	−0.077805	−7.923108
10.00	−7.785500	−0.077314	−7.855769
13.00	−7.762256	−0.077410	−7.839966

Table 2. Energies (E) and correlation corrections (E_c) for LiH (a.u.) MCSCF (2 config.) calculation using Ransil's minimal basis set

R	$E(MC)$	$E_c(MC)$	$E+E_c(MC)$
1.00	−7.196864	−0.088391	−7.285255
2.00	−7.893033	−7.978258	−7.978258
2.50	−7.961983	−0.081391	−8.043374
2.80	−7.977282	−0.079378	−8.056660
3.015	−7.981907	−0.078050	−8.059957
3.20	−7.983084	−0.076971	−8.060055
3.50	−7.981275	−0.075260	−8.056535
4.00	−7.972457	−0.072483	−8.044940
5.00	−7.949202	−0.066508	−8.015710
−6.00	−7.93185$	−0.060264	−7.992114
7.00	−7.923448	−0.055747	−7.979195
−10.00	−7.918564	−0.052037	−7.970601
13.00	−7.918342	−0.051712	−7.970053

(iii) The MC SCF correlation corrections are, as expected, consistently smaller than the corresponding SCF results; the difference increases with the internuclear distance. This is due to the overestimation of $P_2(\mathbf{r}_1, \mathbf{r}_2)$ in the SCF approximation, an error which increases with the internuclear distance.

(iv) Although not as accurate as the SCF at small and intermediate distances, the MC SCF correlation corrections are quite satisfactory. The errors in these corrections are of the order of 5%. More important, the MC SCF results have

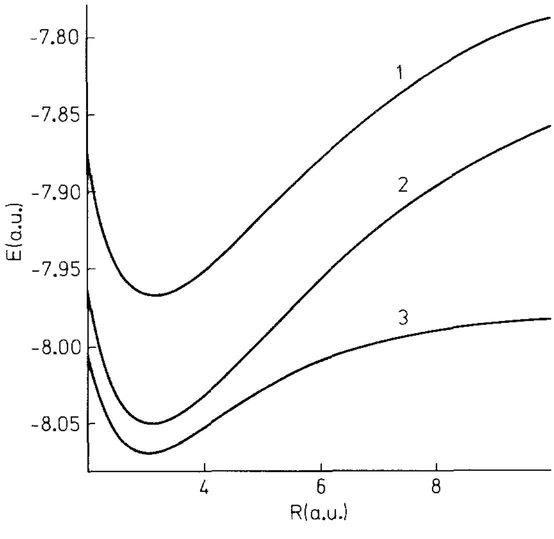

Fig. 1. Comparison of SCF potential curves with experiment for LiH (1) SCF; (2) SCF plus correlation correction; (3) Morse curve

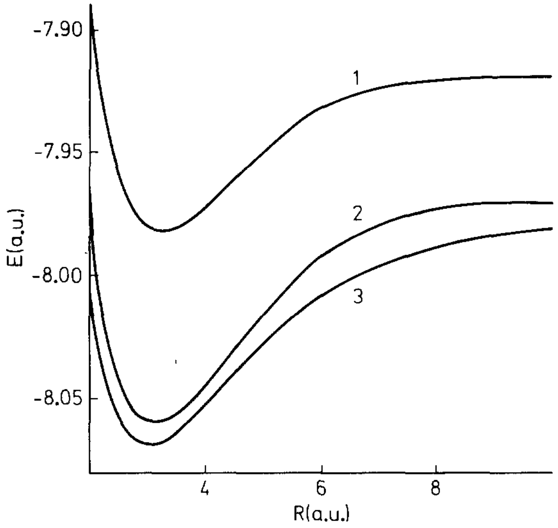

Fig. 2. Comparison of MCSCF (2 config.) potential curves with experiment for LiH (1) MCSCF; (2) MCSCF plus correlation correction; (3) Morse curve

the expected behavior at large internuclear separation; at $R = 13.0a_0$, for example, the correction is $-0.051E_h$ which is very close to the correlation energy of the Li atom.

To examine whether the computed value of E_c depends significantly on the number of configurations in the MC SCF wavefunction, we repeated the previous calculation using all possible excitations from the reference wavefunction (9 configurations). The computed correlation corrections (E_c) change by not more than about 5% from their values in Table 2. This supports the view that further (limited) CI is not effective in improving P_2 in the cusp region and that the same short-range correction (E_c) may be applied whenever reasonably well-behaved density functions are available, without the need for a full re-calculation whenever the wavefunction is improved.

3.2. Calculation II

To study the dependence on the basis set we repeated our calculations using an improved basis set proposed by Kahalas and Nesbet [19], except that the $2p$ functions on H were given the same exponent ($\zeta = 1.00$). The MC SCF wavefunction was constructed from two configurations, as in the first calculation. The SCF results are summarized in Fig. 3 and the MC SCF in Fig. 4.

The main features of these results are as follows:

(i) The correlation corrections (E_c) derived from both the SCF and MCSCF functions differ only slightly (by about 1–2%) from those in the minimal basis calculations.

(ii) The correlated SCF potential curve is very accurate at small and intermediate internuclear distances and again, as expected, incorrect at large distances.

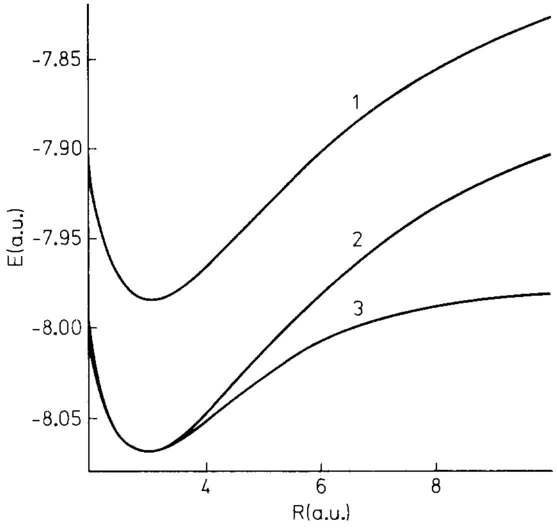

Fig. 3. Comparison of SCF potential curves with experiment for LiH (1) SCF, (2) SCF plus correlation correction; (3) Morse curve (Improved basis—see text)

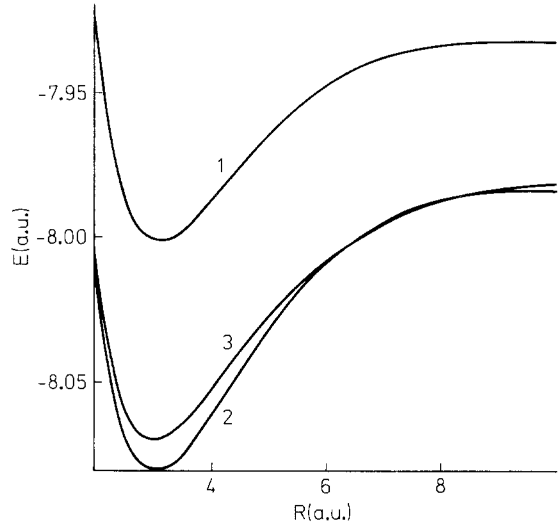

Fig. 4. Comparison of MCSCF (2 config.) potential curves and experiment for LiH (1) MCSCF; (2) MCSCF plus correlation correction; (3) Morse curve (Improved basis - see text)

(iii) The correlated MC SCF potential curve lies *below* the experimental curve for most internuclear distances. The largest discrepancy appears around the equilibrium geometry, where the correlation correction is overestimated by 16%.

The results of Calculations I and II lead to the following preliminary conclusions:
(a) The use of an improved basis set is not crucial to the evaluation of the correlation correction using the Colle-Salvetti functional. This means that even a calculation involving a minimal basis set can be used to obtain a good estimate of the correlation correction.
(b) When the computed correlation correction is added to the MC SCF potential energy curve a significant *over*-correction may result.

A reasonable explanation of (b) is not hard to find. The parameter q in the Colle–Salvetti functional was chosen ($q = 2.29$) so that E_c would give the whole of the correlation energy for the He atom, using an uncorrelated (SCF) reference function; in other words, the functional was adapted to give a good account of the intra-atomic correlation correction needed, without CI. The situation in our LiH calculation is somewhat different; two of the four electrons are valence electrons, in a bond region, and "left-right" correlation (accounting for about 17% of the total correlation energy) has been admitted already in the MC SCF function. It is therefore not surprising that addition of E_c, parameterized for an uncorrelated atomic SCF function, leads to over-correction of the molecular MC SCF result.

4. Conclusion

The results reported in Sect. 3 indicate that accurate potential energy curves can be obtained by applying a Colle–Salvetti correlation correction to the results obtained from MC SCF calculations with minimal CI. The choice of the q parameter, however, is crucial if high accuracy is required and the original method of fitting q, by reference to a HF calculation on the He atom, is clearly both provisional and somewhat unsatisfactory.

The need to allow for some variation of parameters has been recognized already by Colle and Salvetti [9], and has also been proposed by Moscardo and Delgado–Barrio [14]. The latter authors reached the unfortunate conclusion that the only way to get an accurate potential energy curve for LiH was to use an empirical relationship between q and the internuclear distance R – a procedure which would be so arbitrary as to make the whole approach worthless. We find their conclusion erroneous, possibly as a result of their use of expression (2.5) with the incorrect coefficient noted in Footnote 1.

Colle and Salvetti [9], on the other hand, proposed that q in (1.4) should become a function of R, so chosen as to reduce the size of the correlation hole to zero for an "exact" (e.g. extended CI) reference function. They obtain good potential curves in this way for H_2 and Li_2, but the complexity of the computation is greatly increased.

The argument in Sect. 3 suggests that the much simpler procedure of keeping q constant, but with a value dependent on the molecule considered and on the quality of the wavefunction, might be satisfactory. Clearly the value chosen should take account of the limited CI used and it should refer to the molecular situation (not to an atomic reference calculation). It would therefore seem natural to choose q by reference to one point on the potential energy curve, the obvious choice being that which corresponds to the equilibrium geometry.

To test the validity of such a procedure we have repeated the extended basis set MC SCF calculation on LiH, choosing the value of q so as to reproduce the empirical correction needed ($E_{\text{exp}} - E_{\text{MCSCF}}$) at the equilibrium distance; and we have used the same method for the molecule H_2, this being the unique case in which *all* the electrons are valence electrons and the use of $q = 2.29$ (for the helium atom) seems particularly inappropriate.

The results of these calculations are displayed in Figs. 5, 6. The q values used are $q = 1.966$ for LiH (2 core electrons, 2 valence electrons) and $q = 1.576$ for H_2 (no core electrons), figures which seem to support the argument at the end of Section 3. The almost perfect agreement of our H_2 potential with that given by Kolos and Wolniewicz [20] is particularly pleasing.

Our main conclusion, then, is that a simple MC SCF reference function, with a Colle–Salvetti correlation correction, is capable of yielding highy accurate potential energy curves for simple molecules. Only one parameter is needed (q) and

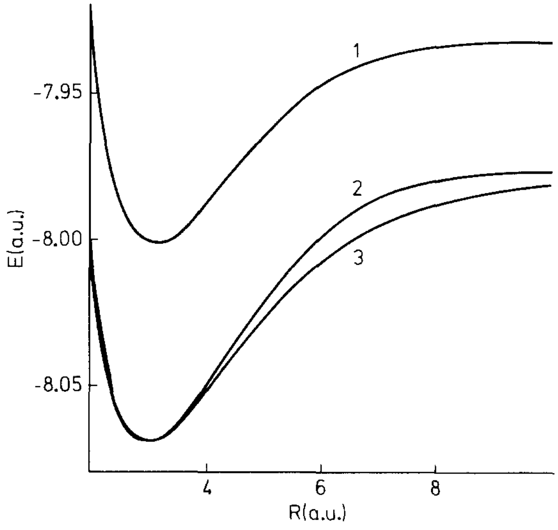

Fig. 5. Comparison of MCSCF (2 config.) potential curves and experiment for LiH (1) MCSCF; (2) MCSCF plus correlation correction; (3) Morse curve. (Parameter $q = 1.966$)

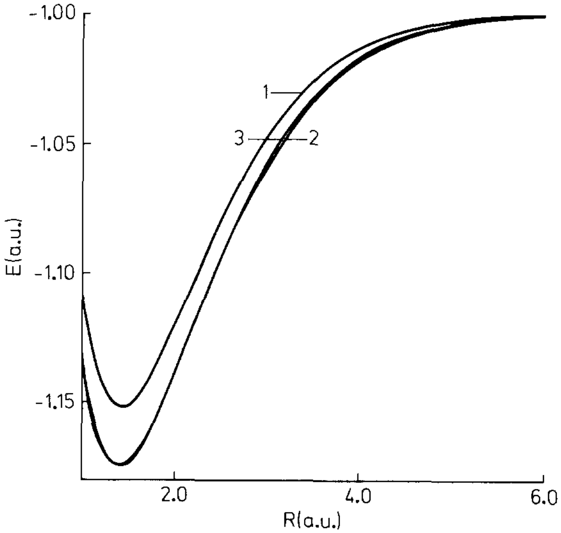

Fig. 6. Comparison of MCSCF (2 config.) potential curves with experiment for H_2 (1) MCSCF; (2) MCSCF plus correlation correction; (3) Kolos and Wolniewicz's results. (Parameter $q = 1.576$)

this is independent of molecular geometry. Further calculations, to be reported eslsewhere, confirm that the value $q=2.29$ remains appropriate for molecules containing atoms with uncorrelated inner-shell wavefunctions. Only when a substantial fraction of the total correlation energy is already accounted for in the valence-electron function (as in our H_2 and LiH calculations), is it necessary to reduce the q value somewhat to avoid overestimation of the correlation energy; in such cases q may be fixed by reference to one point on the potential energy curve.

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Received June 10, 1983