Theoret. Chim. Acta (Berl.) 53, 55–63 (1979)

THEORETICA CHIMICA ACTA

Approximate Calculation of the Correlation Energy for the Closed and Open Shells

Renato Colle and Oriano Salvetti

Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R., Via Risorgimento, 35, I-56100 Pisa, Italy

A formula is derived for the approximate calculation of the correlation energy of both open and closed shell systems. The formula integrates a functional of the one- and two-electron density matrices, obtained from a wavefunction built up by one or several Slater determinants.

Some test calculations on the ground state of diatomic molecules at several internuclear distances and on many excited states of atoms and molecules show the goodness of this method.

Key words: Correlation energy – Open shells

In a preceding paper [1] we have derived a formula for the approximate calculation of the correlation energy for the closed shells, starting from the knowledge of the HF wavefunction and its one-electron and two-electron density matrices. By means of this formula the calculation of the correlation energy is reduced to the evaluation of the integral of an electronic density functional. Its application to a great number of closed-shell systems gives good results: the mean error is about 3–4% of the correlation energy value. Taking into account the goodness of these results, we decided to work out an analogous formula which can be applied to a more complex type and larger number of systems. We are especially interested in the calculation of the correlation energy for two different types of problem: the excited electronic states of atoms and molecules and the potential energy curves of diatomic molecules. In the first case we are concerned with open shell systems, usually described by a suitable combination of two determinants. The second problem requires us to build a two- or three-determinants wavefunction, according to whether the molecule is homonuclear or heteronuclear. By these statements we mean obviously that the wavefunction must be a linear combination of the lowest number of

0040–5744/79/0053/0055/$01.80

determinants, which assures both a right spatial symmetry and spectral multiplicity and, for the diatomic molecules, the right behaviour at the dissociation limit.

Adapting our formula for the calculation of the correlation energy to the needs of the new form of the wavefunction, we have taken into account, on one hand, the obvious modification of the density matrix structure, and on the other hand, the fact that our starting wavefunction is already partially correlated in a different way for the different parts of the space.

According to the formalism of our preceding paper [1], we write the wavefunction of the system in the form:

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \Psi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \prod_{i>j} (1 - \varphi(\boldsymbol{r}_i, \boldsymbol{r}_j)) \tag{1}$$

where $\boldsymbol{x}_i$ indicates the spatial and the spin coordinates of the electron i, while $\boldsymbol{r}_i$ only its spatial coordinates. The function $\varphi(\boldsymbol{r}_i, \boldsymbol{r}_j)$ is thus defined:

$$\varphi(\boldsymbol{r}_i, \boldsymbol{r}_j) = \exp(-\beta^2 r^2) \cdot \left(1 - \Phi(\boldsymbol{R})\left(1 + \frac{r}{2}\right)\right) \tag{2}$$

where $r = |\boldsymbol{r}_i - \boldsymbol{r}_j|$; $\boldsymbol{R} = (\boldsymbol{r}_i + \boldsymbol{r}_j)/2$ in a.u. β is a function of $\boldsymbol{R}$ and $\varphi(\boldsymbol{r}_i, \boldsymbol{r}_j)$ fulfils the cusp condition for $\boldsymbol{r}_i \to \boldsymbol{r}_j$ [2]. Making the same approximations as in [1], we obtain that

$$P_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') = P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')(1 - \varphi(\boldsymbol{r}_1, \boldsymbol{r}_2) - \varphi(\boldsymbol{r}_1', \boldsymbol{r}_2') + \varphi(\boldsymbol{r}_1, \boldsymbol{r}_2)\varphi(\boldsymbol{r}_1', \boldsymbol{r}_2')),$$

where $P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')$ is the two-electron density matrix without spin [3], calculated starting from $\Psi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ function. We maintain also the approximation, according to which the correlation factor in (1) does not modify the one-electron density matrix, that is, we impose the condition:

$$P_1(\boldsymbol{r}_1, \boldsymbol{r}_1') = P_1^0(\boldsymbol{r}_1, \boldsymbol{r}_1').$$

This last assumption has as the necessary and sufficient condition that the following relationship (and its symmetrical one) be satisfied:

$$\int P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2)(\varphi(\boldsymbol{r}_1, \boldsymbol{r}_2)\varphi(\boldsymbol{r}_1', \boldsymbol{r}_2) - \varphi(\boldsymbol{r}_1, \boldsymbol{r}_2) - \varphi(\boldsymbol{r}_1', \boldsymbol{r}_2))\, d\boldsymbol{r}_2 = 0, \quad (\forall \boldsymbol{r}_1, \boldsymbol{r}_1'). \tag{3}$$

If $\varphi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is such that (3) is satisfied, the total energy can be written as a sum of two terms:

$$E = E_0 + \frac{1}{2}\int P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2) \cdot (\varphi(\boldsymbol{r}_1, \boldsymbol{r}_2)^2 - 2\varphi(\boldsymbol{r}_1, \boldsymbol{r}_2)) \frac{1}{r}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \tag{4}$$

where $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$ and the other summand is defined, by us, as the correlation energy, in analogy to what is established in the closed-shell case. In order to calculate the correlation energy, it is therefore sufficient to determine the $\varphi(\boldsymbol{r}_1, \boldsymbol{r}_2)$

function only in the diagonal points ($\mathbf{r}_1' = \mathbf{r}_1$). Putting (2) in (3) with $\mathbf{r}_1' = \mathbf{r}_1$, we obtain:

$$\begin{aligned} &\int \Phi^2(\mathbf{R})\cdot P_2^0(\mathbf{r}_1, \mathbf{r}_2) \exp(-2\beta^2 r^2)\cdot\left(1 + \frac{r}{2}\right)^2 d\mathbf{r}_2 \\ &\quad + 2\int \Phi(\mathbf{R})\cdot P_2^0(\mathbf{r}_1, \mathbf{r}_2) \exp(-\beta^2 r^2)(1 - \exp(-\beta^2 r^2))\cdot\left(1 + \frac{r}{2}\right) d\mathbf{r}_2 \\ &\quad - \int P_2^0(\mathbf{r}_1, \mathbf{r}_2) \exp(-\beta^2 r^2)(2 - \exp(-\beta^2 r^2))\, d\mathbf{r}_2 = 0. \end{aligned} \tag{5}$$

Since the function $\exp(-\beta^2 r^2)$ decreases rapidly as $r \to \infty$, we determine the value of $\Phi(\mathbf{R})$, which satisfies (5) when the functions P_2^0, Φ, β are kept fixed in $\mathbf{r} = 0$. Proceeding as in [1], we obtain for Φ this approximate expression:

$$\Phi \simeq \frac{\sqrt{\pi}\cdot\beta}{1 + \sqrt{\pi}\cdot\beta}.$$

Now we observe that, in the range of our approximation, this solution for Φ is correct even for points off the diagonal ($\mathrm{r}_1 \neq \mathbf{r}_1'$). Here indeed, according to our approximation, (3) is reduced to:

$$\begin{aligned} &-P_2^0(\mathbf{r}_1, \mathbf{r}_1; \mathbf{r}_1', \mathbf{r}_1) \int \exp(-\beta^2 r^2)\left(1 - \Phi\left(1 + \frac{r}{2}\right)\right) d\mathbf{r} \\ &\quad - P_2^0(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_1', \mathbf{r}_1') \int \exp(-\beta^2 r^2)\left(1 - \Phi\left(1 + \frac{r}{2}\right)\right) d\mathbf{r} = 0. \end{aligned}$$

Equating to zero either or both of the two integrals in this equation, we obtain again $\Phi = (\sqrt{\pi}\cdot\beta)/(1 + \sqrt{\pi}\cdot\beta)$. This approximate expression of Φ is probably quite sufficient, since we use it only for the calculation of the correlation energy, as defined in (4). That integral indeed does not contain any terms which can have a critical behaviour.

Therefore we obtain for the correlation energy the following relation:

$$\begin{aligned} E_c = -\frac{1}{2}\int P_2^0(\mathbf{R}, \mathbf{R})\Bigg(\int \frac{P_2^0(\mathbf{r}_1, \mathbf{r}_2)}{P_2^0(\mathbf{R}, \mathbf{R})}\Bigg(&2\exp(-\beta^2 r^2)\left(1 - \Phi(\mathbf{R})\left(1 + \frac{r}{2}\right)\right) \\ &- \exp(-2\beta^2 r^2)\left(1 - \Phi(\mathbf{R})\left(1 + \frac{r}{2}\right)\right)^2\Bigg) \frac{d\mathbf{r}}{r}\Bigg)\, d\mathbf{R}. \end{aligned} \tag{6}$$

Since again $\exp(-\beta^2 r^2)$ goes rapidly to zero for $r \to \infty$, we approximate the integral in $d\mathbf{r}$, developing $P_2^0(\mathbf{r}_1, \mathbf{r}_2)$ until the 2nd order in $\mathbf{r}$. So (6) becomes:

$$\begin{aligned} E_c = -2\pi\int \frac{P_2^0(\mathbf{R}, \mathbf{R})}{\beta^3}\Bigg[&2\beta\int \exp(-t^2)\left(1 - \Phi(\mathbf{R})\left(1 + \frac{t}{2\beta}\right)\right) t\, dt \\ &- \frac{\beta}{2}\int \exp(-t^2)\left(1 - \Phi(\mathbf{R})\left(1 + \frac{t}{\beta\sqrt{8}}\right)\right)^2 t\, dt \\ &+ \frac{K}{3\beta}\int \exp(-t^2)\left(1 - \Phi(\mathbf{R})\left(1 + \frac{t}{2\beta}\right)\right) t^3\, dt \\ &- \frac{K}{24\beta}\int \exp(-t^2)\left(1 - \Phi(\mathbf{R})\left(1 + \frac{t}{\beta\sqrt{8}}\right)\right)^2 t^3\, dt\Bigg] d\mathbf{R} \end{aligned}$$

where

$$K = \left(\frac{\nabla_r^2 P_2^0\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}; \boldsymbol{R} + \frac{\boldsymbol{r}}{2}\right)}{P_2^0\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}; \boldsymbol{R} + \frac{\boldsymbol{r}}{2}\right)} \right)_{\boldsymbol{r}=0}.$$

The integral in square brackets is well represented by an expression of the type:

$$H(\beta, W) = 0.18794 \frac{1 + 0.173 W \exp(-0.58/\beta)}{1 + 0.8/\beta}$$

where $W = K/\beta^2$, as it is shown in [1]. Therefore we obtain the final formula:

$$E_c = -2\pi \int \frac{P_2^0(\boldsymbol{R}, \boldsymbol{R})}{\beta^3} H(\beta, W)\, d\boldsymbol{R}. \tag{7}$$

This formula has already been used by us to calculate the correlation energy of excited states [4, 5], taking for β the same expression, previously described in [1] for closed-shell systems. In the case of excited levels, formula (7) has to be regarded as substantially correct, since it allows one to ignore, in the calculation, the contributions relative to singly occupied orbitals. These incorrect contributions remain unavoidable when one uses formulae which integrate functions of the electronic density only.

Since (7) must be valid, whatever the starting wavefunction Ψ_0 be, the problem now is how to find an expression for the β function which takes into account the goodness of the Ψ_0 itself. The correlation factor, added to the Ψ_0, must introduce in the wavefunction such terms which should modify it only to account for the electron collisions. Its zone of influence must therefore be restricted to a narrow volume, around each electron, inside which it changes the probability of finding another electron. Making this volume proportional to the volume of the exclusion in Wigner's formula, we have obtained for β in [1] the expression $\beta = q \cdot \rho^{1/3}$ with $\rho = P_{1\mathrm{HF}}(\boldsymbol{R}, \boldsymbol{R})$ and found $q = 2.29$ as the best value for a very large number of cases. If now we suppose to improve, step by step, the goodness of the wavefunction, it is reasonable to assume that the volume in which the correlation function (2) works must decrease monotonically and be zero when Ψ_0 is the exact wavefunction. In order to meet this requirement, we propose the following expression for β:

$$\beta = q\left[1 + a\left(\frac{(-h(1) - h(2))P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')}{P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')} - \frac{(-h(1) - h(2))P_{2\mathrm{HF}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')}{P_{2\mathrm{HF}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')}\right)^2_{\substack{\boldsymbol{r}_1' = \boldsymbol{r}_1 \\ \boldsymbol{r}_2' = \boldsymbol{r}_2 \\ \boldsymbol{r}=0}}\right] \rho(\boldsymbol{R})^{1/3}, \tag{8}$$

where $h(i) = -\frac{1}{2}\nabla_i^2 - \sum_\alpha Z_\alpha/(|\boldsymbol{R}_\alpha - \boldsymbol{r}_i|)$ and $\rho(\boldsymbol{R}) = P_1^0(\boldsymbol{R}, \boldsymbol{R})$. $P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')$, $P_{2\mathrm{HF}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')$ are the two-electron density matrices, without spin, derived respectively from Ψ_0 and Ψ_{HF}. By Ψ_{HF} we mean the wavefunction of the system expressed in terms of the lowest possible number of determinants, which shall assure the right spatial symmetry and spectral multiplicity. The use of (8) is clear for the case of closed shell systems, when one starts with the HF wavefunction and improves it, adding other determinants to obtain a partially correlated wavefunction Ψ_0. This procedure is essential if one wishes to calculate, for instance, the energy of a molecule, increasing successively the length of one bond and obtain the right behaviour of the wavefunction at the dissociation limit.

Although (8) must be considered fundamentally as an empirical formula, it can be justified as follows. The factor $q \cdot \rho^{1/3}$ represents a quantity analogous to the volume of exclusion in Wigner's formula, as in [1]. The factor in the square brackets is equal to 1 if Ψ_0 coincides with Ψ_{HF}, as defined above, while it becomes infinity in case Ψ_0 is the exact wavefunction. This last statement is justified as follows. If Ψ_0 satisfies exactly to the time independent Schrödinger equation

$$H\Psi_0 = E\Psi_0 \tag{9}$$

where H is the usual electrostatic Hamiltonian $H = \sum_i^N h(i) + \frac{1}{2}\sum_{i,j} 1/r_{ij}$, then premultiplying both the members in (9) by $\Psi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)^*$ and integrating in $d\sigma_1\, d\sigma_2 \cdots d\sigma_N\, d\boldsymbol{r}_3 \cdots d\boldsymbol{r}_N \equiv d\sigma\, d\boldsymbol{r}_{3\ldots N}$, we obtain:

$$\begin{aligned}
&\frac{1}{N(N-1)}\left(h(1) + h(2) + \frac{1}{r_{12}}\right)P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') \\
&\quad + \sum_{j=3}^{N}\int \Psi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)^*\left(\frac{1}{r_{1j}} + \frac{1}{r_{2j}}\right)\Psi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\, d\sigma\, d\boldsymbol{r}_{3\ldots N} \\
&\quad + \int \Psi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)^* H(3, \ldots, N)\Psi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\, d\sigma\, d\boldsymbol{r}_{3\ldots N} \\
&\quad = \frac{E}{N(N-1)} \cdot P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')
\end{aligned}$$

from which

$$\left(h(1) + h(2) + \frac{1}{r_{12}}\right)P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') = EP_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') + F(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2'). \tag{10}$$

After we have acted on $P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')$ with $(h(1) + h(2))$, removed the apices and sought the limit for $\boldsymbol{r}_1 \to \boldsymbol{r}_2$, we see that the second member in (10) reaches a finite value. As in general $\lim_{\boldsymbol{r}_1 \to \boldsymbol{r}_2} P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2) \neq 0$, it must be true that:

$$\lim_{\boldsymbol{r}_1 \to \boldsymbol{r}_2}\left[\frac{(h(1) + h(2))P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')}{P_2^0(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2')}\right]_{\substack{\boldsymbol{r}_1' = \boldsymbol{r}_1 \\ \boldsymbol{r}_2' = \boldsymbol{r}_2}} = -\infty.$$

It follows from (8) that, if Ψ_0 is an exact solution of the time-independent Schrödinger equation, β must be equal to infinity and therefore $\varphi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 0$. To check the goodness of an expression like (8) for β, we have made a set of calculations drawing empirically the best value for a in (8).

With $a = 7$ we have calculated the energy of the ground state of the He, by means of

$$\Psi_0 = c_1|1s(1)\overline{1s}(2)| + c_2|2s(1)\overline{2s}(2)|$$

obtaining $E_{HF} = -2.8617$ a.u., $E_0 = -2.8775$ a.u., $E_c = -0.0248$ a.u., $E_0 + E_c = -2.9023$ a.u., $E_{exp} = -2.9037$ a.u. and the potential energy curves for $H_2(X^1\Sigma_g^+)$ and $Li_2(X^1\Sigma_g^+)$ respectively by means of

$$\Psi_0 = c_1|1\bar{\nu}_g(1)\overline{1\bar{\nu}_g}(2)| + c_2|1\bar{\nu}_u(1)\overline{1\bar{\nu}_u}(2)|$$

$$\Psi_0 = c_1|\text{core } 2\sigma_g(5)\overline{2\sigma_g}(6)| + c_2|\text{core } 2\sigma_u(5)\overline{2\sigma_u}(6)|.$$

The results are reported in Table 1 and Figs. 1 and 2 for H_2 and in Table 2 and Figs. 3 and 4 for Li_2.

Finally we have calculated the energies of some electronic excited states of Be and other more complex systems, like C_2H_4 and CH_2O, already previously studied [4, 5]. In these cases we have $\Psi_0 \equiv \Psi_{HF}$. The results are shown in Table 3.

Table 1. HF, E_0, correlation, total and exact non-relativistic energies for $H_2(X^1\Sigma_g^+)$ at various bond lengths. All units are given in atomic units

R	E_{HF}	E_0	E_c	$E_0 + E_c$	E_{exp}[11]
1.0	−1.0849	−1.0984	−0.0243	−1.1227	−1.1245
1.4	−1.1334	−1.1519	−0.0229	−1.1748	−1.1745
2.0	−1.0914	−1.1208	−0.0194	−1.1402	−1.1381
3.0	−0.9892	−1.0482	−0.0119	−1.0601	−1.0573
8.0	−0.7860	−0.99991	−0.00131	−1.0012	−1.0001

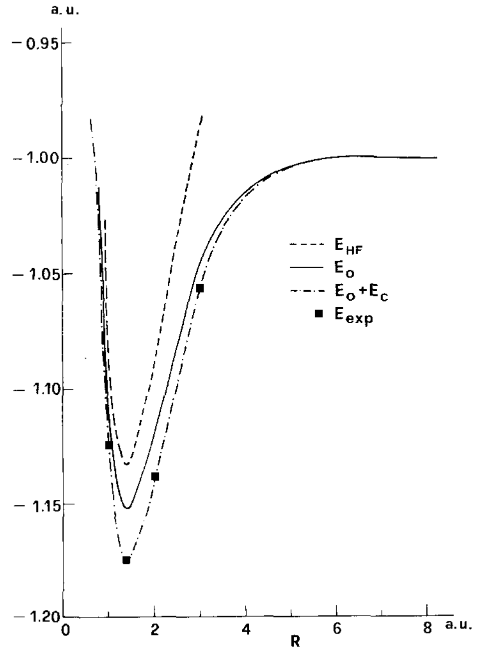

Fig. 1. Behaviours of $E_{HF}, E_0, E_0 + E_c$ as functions of R (interatomic distance) for H_2

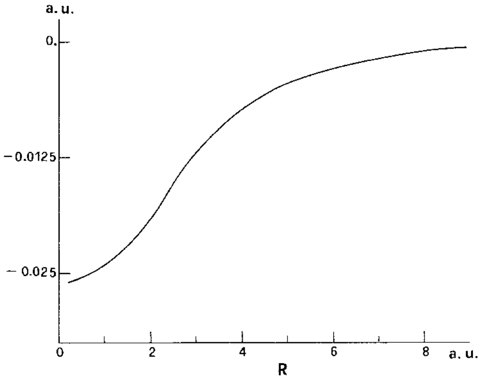

Fig. 2. Behaviour of E_c as a function of R for H_2

Table 2. HF, E_0, correlation, total and exact non-relativistic energies for $Li_2(X^1\Sigma_g^+)$ at various bond lengths. All units are given in atomic units

R	E_{HF}	E_0	E_c	$E_0 + E_c$	E_{exp}[10]
4.0	−14.8523	−14.8598	−0.1208	−14.9806	−14.9830
5.4	−14.8708	−14.8812	−0.1139	−14.9951	−14.9958
6.0	−14.8674	−14.8805	−0.1106	−14.9911	−14.9915
8.5	−14.8395	−14.8698	−0.1016	−14.9714	−14.9689

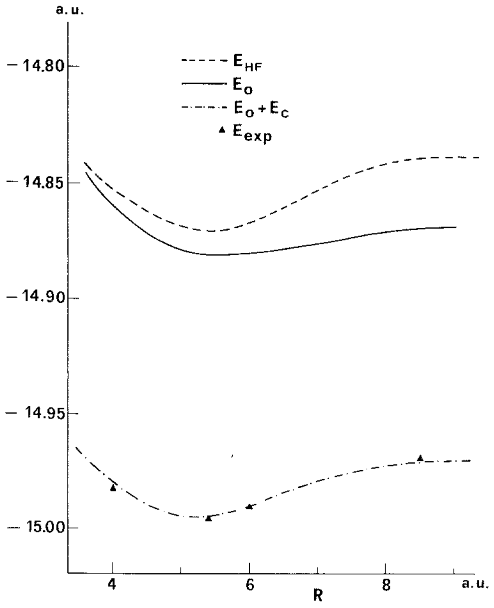

Fig. 3. Behaviours of E_{HF}, E_0, $E_0 + E_c$ as functions of R for Li_2

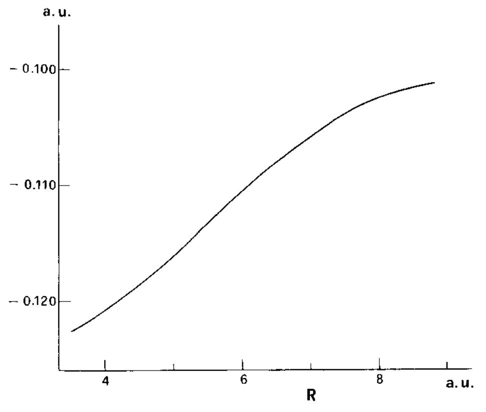

Fig. 4. Behaviour of E_c as a function of R for Li_2

A set of modified Gaussian functions [6, 7] centred on the various atoms, has been employed; we got the orbital exponents from Refs. [8–10].

The accuracy of the calculations reported above seems to prove that formula (7), with β given by (8), works in a very satisfactory way. It restricts the calculation of the correlation energy only to those parts of the space in which the electronic collisions really take place. The formula (8) allows us to improve progressively the wavefunction Ψ_0 and eventually to centre this improvement in those parts of the space more interesting for particular purposes (for instance, a special bond during its dissociation). Such an improvement is indeed already taken into account by means of the structure of β, so that the total effect is balanced.

Table 3. HF, correlation, total and vertical transition energies of some states of Be, C_2H_4 and CH_2O

System	Excitation	$E_{HF} \equiv E_0$ (a.u.)	E_c (a.u.)	$E_c + E_0$ (a.u.)	ΔE_{tot} (eV)	ΔE_{exp} (eV)
Be ^1S	Ground state	−14.5726	−0.0949	−14.6675	—	—
^1S	$2s \rightarrow 3s$	−14.3541	−0.0664	−14.4205	6.7	6.8[a]
^1S	$2s \rightarrow 4s$	−14.3101	−0.0612	−14.3713	8.1	8.1[a]
C_2H_4 ^1A_g	Ground state	−78.0382	−0.492	−78.5302	—	—
$^1B_{1u}$	$1b_{3u} \rightarrow 1b_{2g}$	−77.762	−0.481	−78.243	7.8	7.66[b]
CH_2O $^1A_1$	Ground state	−113.9086	−0.5407	−114.4493	—	—
$^1B_2$	$2b_2 \rightarrow 6a_1$	−113.6722	−0.5146	−114.1868	7.14	7.10[c]
$^2B_3$	Ion	−113.5530	−0.5050	−114.0580	10.65	10.88[c]

[a] Atomic energy levels . . . Ref. [12].
[b] Colle, R. *et al.* Ref. [4].
[c] Colle, R. *et al.* Ref. [5].

References

1. Colle, R., Salvetti, O.: Theoret. Chim. Acta (Berl.) **37**, 329 (1975)
2. Bingel, W. A.: Theoret. Chim. Acta (Berl.) **8**, 54 (1967)
3. McWeeny, R.: Rev. Mod. Phys. **32**, 335 (1960)
4. Colle, R., Moscardo, F., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **44**, 1 (1977)
5. Colle, R., Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **49**, 37 (1978)
6. Golebiewski, A., Mrozek, J.: Intern. J. Quantum Chem. **7**, 623 (1973)
7. Golebiewski, A., Mrozek, J.: Intern. J. Quantum Chem. **7**, 1021 (1973)
8. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
9. Huzinaga, S., Sakai, Y.: J. Chem. Phys. **50**, 1371 (1969)
10. Clementi, E.: From quantum mechanics to statistical thermodynamics. (V Coloquio Internacional de Químicos Teóricos de Expresión Latina 1974), IBM Research Laboratory, San Jose, California, U.S.A.
11. Kolos, W., Wolniewicz, L.: J. Chem. Phys. **43**, 2429 (1965)
12. Atomic Energy Levels, Circular 467, U.S. Department of Commerce, National Bureau of Standards (1949)

Received January 14, 1979