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Correlated One-Center Wavefunctions for Two-Electron Molecules

III. Correlated SCF Functions and Application to H_3^+

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A one-center self-consistent field (SCF) wavefunction for two electrons, built from a m-term molecular orbital, is multiplied by the correlation factor $1+\alpha r_{12}$. All integrals required for a variational treatment are obtained from previous papers in this series. Application to the ground state of equilateral triangular H_3^+ shows that the energy improvement due to the correlation factor and the optimized value of α increase as m increases. Joshi's [4] SCF-functions were used. For $m=9$ our best energy is -1.3037 a.u. for $\alpha=0.189$, compared with Joshi's energy of -1.28028 a.u., at $R_{HH}=1.607$ a.u.

Eine Ein-Zentrum-Wellenfunktion für zwei Elektronen vom SCF-Typ wird mit dem Korrelationsfaktor $1+\alpha r_{12}$ multipliziert. Alle Integrale, die für eine Variationsrechnung benötigt werden, können aus früheren Ergebnissen hergeleitet werden. Eine Anwendung auf den Grundzustand von H_3^+ mit der Struktur des gleichseitigen Dreieckes zeigt, daß sowohl die Energieverbesserung als auch die optimalen Werte von α mit m zunehmen, wobei m die Zahl der Terme in dem MO darstellt. Joshis [4] SCF-Funktionen bilden die Grundlage. Für $m=9$ erhielten wir die Energie $-1{,}3037$ a.E. und $\alpha=0{,}189$. Joshis Energie war $-1{,}28028$ a.E. ($R_{HH}=1{,}607$ a.E.).

Une fonction d'onde SCF monocentrique pour deux électrons, construite à partir d'une orbitale moléculaire à m termes, est multipliée par le facteur de corrélation $1+\alpha r_{12}$. Toutes les intégrales nécessaires pour un traitement variationnel sont obtenues à partir des articles précédents de cette série. L'application à l'état fondamental de H_3^+ (triangle équilatéral) montre que l'amélioration de l'énergie dûe au facteur de corrélation ainsi que la valeur optimale de α augmente lorsque m augmente. On a utilisé les fonctions SCF de Joshi [4]. Pour $m=9$, notre meilleure énergie est $-1{,}3037$ u. a., pour $\alpha=0{,}189$, alors que Joshi obtient $-1{,}28028$ u. a. à $R_{HH}=0{,}928$ u. a.

1. Introduction

In papers I and II of this series [2, 3] (hereafter referred to as I and II, respectively) we presented all the integrals in closed form which are required for a configuration-interaction (CI) wavefunction, built from general exponential-type orbitals, associated with the correlation factor $1+\alpha r_{12}$. Since a CI-wavefunction can lead, in principle, to the exact energy, the efficiency of the correlation factor is decreasing with an increasing number of terms.

Self-consistent field molecular orbitals (SCF-MO) are usually expanded in terms of m atomic orbitals. As m increases, the SCF-wavefunctions improve. Since such wavefunctions do not account for the correlation between electrons, the lowering of the energy obtained by multiplying SCF-functions by a correlation factor is not expected to decrease as m increases.

Similar calculations were performed for two-electron atoms by Roothaan and Weiss [8], for H_2 by Kolos and Roothaan [5], and for H_3^+ by Lester and Krauss [7].

In Part 2 the theory developed in papers I and II will be reviewed for the special case of a SCF-wavefunction. In Part 3, the method will be applied to one-center SCF-functions of equilateral triangular H_3^+, obtained by Joshi [4].

2. Wavefunction and Integrals

We assume that a one-center SCF-wavefunction Ψ^0 with the SCF-MO φ is available for the two-electron molecule under consideration. The correlated wavefunction Ψ^α will then be written as

$$\Psi^\alpha(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1 + \alpha r_{12})\, \Psi^0(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1 + \alpha r_{12})\, \varphi(\boldsymbol{r}_1)\, \varphi(\boldsymbol{r}_2)\,, \tag{1}$$

with

$$\varphi(\boldsymbol{r}) = \sum_{i=1}^{m} a_i \chi_i(\boldsymbol{r})\,, \tag{2}$$

and real α. The spin part has been separated out, and will not be mentioned further. χ_i is generally of the form

$$\chi_i(\boldsymbol{r}) = \sum_{p_i, \eta_i, l_i, m_i} c_i(p_i, \eta_i)\, d_i(l_i, m_i)\, r^{p_i} e^{-\eta_i r}\, Y_{l_i m_i}(\vartheta, \varphi)\,. \tag{3}$$

In the following the summation indices and arguments of c_i and d_i will be omitted.

By substitution one obtains

$$\begin{aligned} \Psi^\alpha(1,2) &= (1 + \alpha r_{12}) \sum_{s,t} a_s a_t \chi_s(1)\, \chi_t(2) \\ &= (1 + \alpha r_{12}) \sum_{s \geqq t} a_s a_t A_{st} \chi_s(1)\, \chi_t(2) \\ &= (1 + \alpha r_{12}) \sum_{s \geqq t} a_s a_t \Phi^0_{st}(1,2) = \sum_{s \geqq t} a_s a_t \Phi_{st}(1,2) \end{aligned} \tag{4}$$

with

$$\begin{aligned} \Phi^0_{st}(1,2) &= A_{st} \chi_s(1)\, \chi_t(2)\,, \\ \Phi_{st}(1,2) &= (1 + \alpha r_{12})\, \Phi^0_{st}(1,2)\,, \end{aligned} \tag{5}$$

and

$$\Phi^0_{st}(1,2) = A_{st} \sum c_s c_t d_s d_t r_1^{p_s} r_2^{p_t} e^{-\eta_s r_1 - \eta_t r_2}\, Y_{l_s m_s}(1)\, Y_{l_t m_t}(2)\,. \tag{6}$$

A_{st} is a symmetrization operator. Φ^0_{st} is equivalent to Φ^0_i of papers I and II. The double notation is necessary for the identification of this function. The coordinates $(\boldsymbol{r}_i)$, and also (ϑ_i, φ_i) were written as (i).

The correlated SCF-functions will be treated in the same way as the correlated CI-functions of papers I and II, with the only difference that the coefficients $a_s a_t$ will remain fixed and not be subjected to optimization.

The energy E^α, obtained by the variation method, is

$$E^\alpha = \iint \Psi^{\alpha *} H\, \Psi^\alpha\, dv_1\, dv_2 \Big/ \iint \Psi^{\alpha *}\, \Psi^\alpha\, dv_1\, dv_2\,.$$

All integrals which may occur in this expression have been discussed in papers I and II. E^0 is the energy resulting from Ψ^0.

3. Application to Equilateral Triangular H_3^+

Joshi's [4] one-center SCF-calculations of equilateral triangular H_3^+ formed the basis of our correlation work. This molecule was also the subject of paper I.

The geometric center of the molecule was chosen to be the origin of the coordinate system. V_1 and all integrals $V_{1,ij}$ are then zero. The coordinate system was rotated so that the polar axis pointed towards one of the protons. Joshi studied molecular orbitals which consisted of 1 to 18 basis functions. We were interested in the improvement of the energy and in the optimized value of α as a function of m, the number of terms in an SCF-MO. We used Joshi's 1 to 9-term functions, omitting $m=6$ and 8. The results are given in Table 1. E^0 is Joshi's energy, E^α the energy obtained by using the correlated wavefunction Ψ^α. E^α has been minimized with respect to α, but not with respect to the orbital exponents η_i and the linear coefficients a_i. They are Joshi's values, and therefore not reproduced in Table 1. ΔE is defined as $E^0 - E^\alpha$.

Table 1. *Ground state energies (in a.u.) of equilateral triangular* H_3^+

m	R_{HH} (a.u.)	α	$-E^0$	$-E^\alpha$	ΔE	$\Delta E/E^0$ [%]
1	1.599	0.049	1.02604	1.02900	0.003	0.3
2	1.554	0.102	1.10994	1.11959	0.0096	0.9
3	1.554	0.175	1.16629	1.18730	0.0211	1.8
4	1.550	0.180	1.16722	1.18834	0.0211	1.8
5	1.568	0.185	1.22391	1.2465	0.0226	1.8
7	1.602	0.188	1.27389	1.2973	0.0234	1.8
9	1.607	0.189	1.28028	1.3037	0.0234	1.8

Contrary to a CI-wavefunction, ΔE and α increase with increasing number of terms. This is understandable, since, as Joshi points out, the maximum in the orbital density curves becomes sharper as m increases, and no correlation is introduced by the SCF-wavefunction. Since ΔE seems to approach a saturation value, we expect E^α for Joshi's 18-term MO to be about -1.310 a.u.

Schwartz and Schaad [9] estimate the correlation energy of H_3^+ to be -0.043 to -0.048 a.u., whereas Kutzelnigg *et al.* [6] calculate a correlation energy of -0.039 a.u. Accordingly, our improvement $\Delta E = 0.0234$ a.u. for $m=9$ represents 50–60% of the correlation energy. We did not intend to optimize Ψ^α with respect to the linear coefficients a_i and the orbital exponents η_i, in order to preserve the SCF-character of the uncorrelated wavefunctions. However, it is to be expected that such optimization would have further improved our results.

Some percentage lowerings of two-electron probability densities for $m=1$ to 4 are given in Table 2. $\Delta\Psi^2$ is defined by

$$\Delta\Psi^2 = \Psi^{02}(\mathbf{r}_1, \mathbf{r}_2) - \Psi^{\alpha 2}(\mathbf{r}_1, \mathbf{r}_2).$$

R_{OH} is the distance between the geometric center of the molecule and one of the protons.

Table 2. *Percentage lowerings of two-electron probability densities*

m	$\Delta\Psi^2/\Psi^{02}$ [%] $r_1 = r_2 = R_{OH}$, $r_{12}=0$	$\Delta\Psi^2/\Psi^{02}$ [%] $r_1 = r_{12} = R_{OH}/2$, $r_2 = R_{OH}$
1	18	15
2	31	25
3	43	34
4	44	35

The Hatree-Fock energy of equilateral triangular H_3^+ is about -1.30 a.u. [9]. Joshi's lowest energy was -1.28626 a.u. Probably he would have needed orbitals of higher angular momentum quantum numbers to obtain a lower energy.

Minimization of E^α with respect to η and R_{HH} for $m = 1$ gave $E^\alpha = -1.0369$ a.u. at $R_{HH} = 1.609$ a.u., with $\eta = 1.1146$ and $\alpha = 0.245$.

Calculations with a cutoff correlation factor for this molecule using Joshi's orbitals with $m = 1$ to 4 have been performed, and will be published soon.

For all details on the theory and computations we refer to Ref. [1].

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