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 $\alpha$ 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 $\alpha$ 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 $-1.28028$ u. a. (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 due au facteur de corrélation ainsi que la valeur optimale de $\alpha$ augmentent 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$_3$ by Kolos and Roothaan [5], and for H$_4^+$ 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 $\Psi^0$ with the SCF-MO $\phi$ is available for the two-electron molecule under consideration. The correlated wavefunction $\Psi^a$ will then be written as

$$\Psi^a(r_1, r_2) = (1 + \alpha r_{12}) \psi^0(r_1, r_2) = (1 + \alpha r_{12}) \phi(r_1) \phi(r_2),$$

with

$$\phi(r) = \sum_{i=1}^{m} a_i \chi_i(r),$$

and real $\alpha$. The spin part has been separated out, and will not be mentioned further. $\chi_i$ is generally of the form

$$\chi_i(r) = c_i(p_i, q_i) d_i(l_i, m_i) r^{p_i} e^{-\eta r} Y_{l_i, m_i}(\theta, \phi).$$

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

By substitution one obtains

$$\Psi^a(1, 2) = (1 + \alpha r_{12}) \sum_{s,t} a_s a_t \chi_s(1) \chi_t(2)$$

$$= (1 + \alpha r_{12}) \sum_{s \geq t} a_s a_t A_{st} \chi_s(1) \chi_t(2)$$

$$= (1 + \alpha r_{12}) \sum_{s \geq t} a_s a_t \Phi^0_{st}(1, 2) = \sum_{s \geq t} a_s a_t \Phi^0_{st}(1, 2),$$

with

$$\Phi^0_{st}(1, 2) = A_{st} \chi_s(1) \chi_t(2),$$

$$\Phi^0_{st}(1, 2) = (1 + \alpha r_{12}) \Phi^0_{st}(1, 2),$$

and

$$\Phi^0_{st}(1, 2) = A_{st} \sum c_c c_d d_p d_q e^{-\eta r_1} e^{-\eta r_2} Y_{l_i, m_i}(1) Y_{l_i, m_i}(2).$$

$A_{st}$ is a symmetrization operator. $\Phi^0_{st}$ is equivalent to $\Phi^0$ of papers I and II. The double notation is necessary for the identification of this function. The coordinates $(r_i)$, and also $(\theta_i, \phi_i)$ 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 $E^a$, obtained by the variation method, is

$$E^a = \int \Psi^a H \Psi^a dv_1 dv_2/\int \Psi^a \Psi^a dv_1 dv_2.$$

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

3. Application to Equilateral Triangular $\text{H}_3^+$

Joshi's [4] one-center SCF-calculations of equilateral triangular $\text{H}_3^+$ 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