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Correlated One-Center Wavefunctions for Two-Electron Molecules

IV. Integrals for a Cutoff Correlation Factor. Application to H_3^+

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Integrals are evaluated in closed form for one-center two-electron CI wavefunctions which are multiplied by a cutoff correlation factor. Computational results are reported for the ground state of equilateral triangular H_3^+.

Integrale werden in geschlossener Form ausgeführt, welche für Ein-Zentrum Konfigurationswechselwirkung-Wellenfunktionen für Moleküle mit zwei Elektronen benötigt werden. Ergebnisse für den Grundzustand von H_3^+, mit der Struktur des gleichseitigen Dreieckes, werden mitgeteilt.

Evaluation sous forme analytique d'intégrales pour des fonctions d'onde d'I.C. à deux électrons monocentriques multipliées par un facteur de corrélation avec coupure. Des résultats numériques sont donnée pour l'état fondamental de H_3^+ en triangle équilatéral.

Introduction

In the previous papers of this series (hereafter referred to as I [1], II [2] and III [3]) configuration-interaction (CI) and SCF-type one-center wavefunctions for two-electron systems were multiplied by the correlation factor $1+\alpha r_{12}$. Integrals were evaluated and computations performed with various wavefunctions on equilateral triangular H_3^+ and HeH^+, in order to demonstrate the improvement in energy due to the correlation factor, ΔE, as a function of the number of terms, m, in the CI or SCF expansion. The results obtained so far indicate that ΔE increases with m for SCF functions [3] but decreases rapidly for CI functions [2]. For a SCF expansion (H_3^+) $\Delta E/E^0$ increased from 0.3 to 1.8% and α from 0.049 to 0.189 for m from 1 to 9, whereas for a CI expansion (HeH^+) $\Delta E/E^0$ decreased from 3 to 0.12% and α from 0.40 to 0.17 with m going from 1 to 20. E^0 is the energy resulting from the uncorrelated wavefunction. In the case of HeH^+ ΔE increased with the internuclear distance R.

In this paper we derive the integrals needed if one-center two-electron wavefunctions consisting of s-type STO's are multiplied by a cutoff correlation factor $1+\alpha h(r_{12})$, with

$$h(r_{12})=\begin{cases} r_{12} & \text{if} \quad 0\leqq r_{12}\leqq D \\ D & \text{if} \quad D\leqq r_{12}\leqq \infty\,. \end{cases}$$

This correlation factor has been introduced by Gimarc, Cooney, and Parr [4], and applied to two-electron atoms. The parameter D allows to describe the effective range of correlation in a well-defined way.

The computations by Gimarc *et al.* gave the minimum energy at $D=\infty$, but for some of their CI functions the energy passed through a relative minimum at finite D. The range of correlation, defined as the value of D for which 90 to 95% of the energy improvement due to the correlation $1+\alpha r_{12}$ is obtained, was about 2 Bohr radii for He, and decreased approximately as $1/Z$, Z being the atomic number of the two-electron atom [5].

In this work computations will be performed on equilateral triangular H_3^+, based on Joshi's [6] one-center SCF calculations.

Evaluation of Integrals

The trial wavefunction for two-electrons will be written as

$$\begin{aligned}\Psi^{\alpha}(\vec{r}_1,\vec{r}_2)&=\{1+\alpha h(r_{12})\}\,\Psi^0(r_1,r_2)\\&=\{1+\alpha h(r_{12})\}\sum_{k=1}^{M}C_k\Phi_k^0(r_1,r_2)\\&=\sum_{k=1}^{M}C_k\Phi_k(r_1,r_2)\,.\end{aligned}\tag{1}$$

Ψ^0 and Φ^0 are uncorrelated one-center wavefunctions, built from s-type STO's. As in Eq. (2) of II, the spin-free Hamiltonian operator is written as

$$\boldsymbol{H}=\boldsymbol{T}+\boldsymbol{V}_1+\boldsymbol{V}_2+\boldsymbol{V}_3+\boldsymbol{V}_4\,,$$

where $\boldsymbol{T}$ stands for the kinetic energy operator of the two electrons, $\boldsymbol{V}_1$ for the Coulomb attraction between central nucleus and electrons, $\boldsymbol{V}_3$ between off-center nuclei and electrons, $\boldsymbol{V}_2$ for the Coulomb repulsion between the electrons, and $\boldsymbol{V}_4$ between the nuclei.

We define for an arbitrary operator $\boldsymbol{B}$

$$\begin{aligned}B_{ij}&=\langle\Phi_i|\boldsymbol{B}|\Phi_j\rangle\,,\\B_{ij}^k&=\langle\Phi_i^0|\{h(r)\}^k\boldsymbol{B}|\Phi_j^0\rangle\,,\\S_{ij}&=\langle\Phi_i|\Phi_j\rangle\,,\\S_{ij}^k&=\langle\Phi_i^0|\{h(r)\}^k|\Phi_j^0\rangle\,,\end{aligned}\tag{2}$$

where $r\equiv r_{12}$.

Then one obtains for $\boldsymbol{V}=\boldsymbol{V}_1,\,\boldsymbol{V}_2,\,\boldsymbol{V}_3$

$$V_{ij}=V_{ij}^0+2\alpha V_{ij}^1+\alpha^2V_{ij}^2\,,$$

and

$$S_{ij}=S_{ij}^0+2\alpha S_{ij}^1+\alpha^2S_{ij}^2\,.\tag{3}$$

We expand

$$\Phi_i^0(r_1,r_2)=A_i\sum_{p_i,q_i,\eta_i,\zeta_i}c_i(p_i,q_i,\eta_i,\zeta_i)\,r_1^{p_i}r_2^{q_i}e^{-\eta_ir_1}e^{-\zeta_ir_2}\,,\tag{4}$$

where A_i is a symmetrization operator in the case of singlet states. Defining

$$(p,\eta/q,\zeta)^{m,n}=\iint r_1^pr_2^qe^{-\eta r_1}e^{-\zeta r_2}\{h(r)\}^mr^n\,dv_1\,dv_2\,,\tag{5}$$

and similarly $[p, \eta/q, \zeta]^{m,n}_X$ with the additional factor R^{-1}_{1X} in the integrand, we obtain (for s-orbitals only)

$$\begin{aligned} V^m_{1ij} &= -2Z_0 A_i A_j \sum c_i c_j (p-1, \eta/q, \zeta)^{m,0} , \\ V^m_{2ij} &= A_i A_j \sum c_i c_j (p, \eta/q, \zeta)^{m,-1} , \\ V^m_{3ij} &= -2A_i A_j \sum c_i c_j \Big\{ \sum_X Z_X [p, \eta/q, \zeta]^{m,0}_X \Big\} , \\ S^m_{ij} &= A_i A_j \sum c_i c_j (p, \eta/q, \zeta)^{m,0} , \end{aligned} \tag{6}$$

where $p = p_i + p_j$, $q = q_i + q_j$, $\eta = \eta_i + \eta_j$, $\zeta = \zeta_i + \zeta_j$.

Now we evaluate the matrix elements for the kinetic energy operator $\boldsymbol{T}$.

$$\begin{aligned} T_{ij} &= \iint (\vec{\nabla}_1 \Phi_i) \cdot (\vec{\nabla}_1 \Phi_j)\, dv_1\, dv_2 \\ &= \mathscr{T}^0_{ij} + 2\alpha \mathscr{T}^1_{ij} + \alpha^2 \mathscr{T}^2_{ij} , \end{aligned}$$

with

$$\mathscr{T}^0_{ij} = \mathscr{t}^0_{ij}, \quad \mathscr{T}^1_{ij} = \mathscr{t}^1_{ij} + 0.5\, t^1_{ij},$$

$$\mathscr{T}^2_{ij} = \mathscr{t}^2_{ij} + t^2_{ij} + s_{ij} .$$

$\mathscr{t}^k_{ij}$, t^k_{ij} and s_{ij} are defined by

$$\begin{aligned} \mathscr{t}^k_{ij} &= \iint [h(r)]^k (\vec{\nabla}_1 \Phi^0_i) \cdot (\vec{\nabla}_1 \Phi^0_j)\, dv_1\, dv_2 , \\ t^k_{ij} &= \iint \gamma(r)\, r^{k-1} \frac{r_1^2 - r_2^2 + r^2}{2 r_1 r} \left\{ \Phi^0_i \frac{\partial \Phi^0_j}{\partial r_1} + \Phi^0_j \frac{\partial \Phi^0_i}{\partial r_1} \right\} dv_1\, dv_2 , \end{aligned} \tag{7}$$

with

$$\gamma(r) = \begin{cases} 1 & \text{if} \quad r \leqq D \\ 0 & \text{if} \quad r > D , \end{cases}$$

and

$$s_{ij} = \iint \gamma(r)\, \Phi^0_i \Phi^0_j\, dv_1\, dv_2 .$$

The following definition will be needed in the further evaluation of $\mathscr{t}^k_{ij}$, t^k_{ij} and s_{ij}.

$$(p, \eta/q, \zeta)^{*,n} = \int r_1^p r_2^q e^{-\eta r_1} e^{-\zeta r_2} (r)\, r^n\, dv_1\, dv_2 .$$

Then

$$\begin{aligned} \mathscr{t}^k_{ij} = A_i A_j \sum c_i c_j \{ & p_i p_j (p-2, \eta/q, \zeta)^{k,0} - (p_i \eta_j + p_j \eta_i) \\ & \times (p-1, \eta/q, \zeta)^{k,0} + \eta_i \eta_j (p, \eta/q, \zeta)^{k,0} \} , \end{aligned} \tag{8}$$

$$\begin{aligned} t^k_{ij} = 0.5 A_i A_j \sum c_i c_j \{ & (p_i + p_j) [(p, \eta/q, \zeta)^{*,k-2} \\ & - (p-2, \eta/q+2, \zeta)^{*,k-2} + (p-2, \eta/q, \zeta)^{*,k}] \\ & - \eta [(p+1, \eta/q, \zeta)^{*,k-2} - (p-1, \eta/q+2, \zeta)^{*,k-2} \\ & + (p-1, \eta/q, \zeta)^{*,k}] \} , \end{aligned} \tag{9}$$

$$s_{ij} = A_i A_j \sum c_i c_j (p, \eta/q, \zeta)^{*,0} , \tag{10}$$

where $p = p_i + p_j$, $q = q_i + q_j$, $\eta = \eta_i + \eta_j$; $\zeta = \zeta_i + \zeta_j$.

Now we have expressed all occurring matrix elements in terms of the integrals $(p, \eta/q, \zeta)^{m,n}$, $[p, \eta/q, \zeta]_X^{m,n}$ and $(p, \eta/q, \zeta)^{*,n}$. In order to work them out, we refer to the general integrals (ac/bd) and $[ac/bd]$, evaluated by Calais and Löwdin [7] and Grein and Hawton [1], respectively. Both were expanded in a series containing the integrals $Q(f, g, h, \lambda)$ and $Q(f^n, g, h, \lambda)$. Defining

$$G\left(p, q, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n, \lambda\right) = \int_0^\infty r_1^p e^{-\eta r_1} \mathrm{d}r_1 \times \int_0^\infty r_2^q e^{-\zeta r_2} \mathrm{d}r_2 \times \int_0^\pi \begin{Bmatrix} h(r)^m \\ \gamma(r) \end{Bmatrix} r^n P_\lambda^0(\cos\vartheta_{12}) \sin\vartheta_{12} \mathrm{d}\vartheta_{12} \tag{11}$$

and similarly $G^0\left(p, q, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n, \lambda\right)$, with an additional factor $R_>^{-1}$ in the integrand, we have the correspondence

$$Q(f, g, h, 0) \to G\left(p+2, q+2, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n, 0\right),$$

$$Q(f^0, g, h, 0) \to G^0\left(p+2, q+2, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n, 0\right).$$

The notation $\begin{Bmatrix} m \\ * \end{Bmatrix}$ and $\begin{Bmatrix} h(r)^m \\ \gamma(r) \end{Bmatrix}$ means that either the upper or the lower part is to be taken. For *s*-orbitals λ equals zero. In papers I and II we expressed the G-integrals by further introducing F-integrals (see Eq. (23) of I and Eq. (13) of II). Correspondingly we define here

$$F\left(p, q, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n\right) = \int_0^\infty r_1^p e^{-\eta r_1} \mathrm{d}r_1 \times \int_0^\infty r_2^q e^{-\zeta r_2} \mathrm{d}r_2 \times \int_{|r_1-r_2|}^{r_1+r_2} \begin{Bmatrix} h(r)^m \\ \gamma(r) \end{Bmatrix} r^n \mathrm{d}r, \tag{12}$$

and similarly F^0 with a factor $R_>^{-1}$ in the integrand of the first integral.

Then

$$G^0\left(p+2, q+2, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n, 0\right) = F^0\left(p+1, q+1, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n+1\right),$$

and

$$G\left(p+2, q+2, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n, 0\right) = F\left(p+1, q+1, \eta, \zeta, \begin{Bmatrix} m \\ * \end{Bmatrix}, n+1\right). \tag{13}$$

The F-integrals lead to expressions

$$\int_D^\infty r^s \mathrm{d}r \times \int_0^\infty r_1^p e^{-\eta r_1} R_>^a \, \mathrm{d}r_1 \times \int_{|r_1-r|}^{r_1+r} r_2^q e^{-\zeta r_2} \mathrm{d}r_2,$$

with a being 0 or -1, which can be solved by standard integration methods.

Equilateral Triangular $\mathbf{H_3^+}$

For $\Psi^0(r_1, r_2)$ we used Joshi's [6] one-center SCF wavefunctions up to four terms (1*s* to 4*s*). In the first series of computations we leave the linear

Table 1. *Results with cutoff correlation factor for* H_3^+

m	1	2	3	4
terms	1s	+2s	+3s	+4s
R [a.u.]	0.923	0.897	0.897	0.895
D [R]	1.8	2	2.6	2.6
α	0.359	0.300	0.233	0.230
$-E^{\alpha,D}$ [a.u.]	1.0522	1.1347	1.1908	1.1916
$-E^0$ [a.u.]	1.0260	1.1099	1.1663	1.1672
$-E^{\alpha,\infty}$ [a.u.]	1.0290	1.1196	1.1873	1.1883
$(E^0-E^{\alpha,D})/E^0$	2.5%	2.1%	2.1%	2.1%
$(E^{\alpha,\infty}-E^{\alpha,D})/E^{\alpha,\infty}$	2.2%	1.3%	0.3%	0.3%

coefficients, orbital exponents and internuclear distances unchanged. We have

$$\Psi^0(r_1,r_2)=\varphi(r_1)\varphi(r_2)\,,$$

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

Optimization was performed with respect to α and D only. As in the computations reported in paper III, the geometric center of the molecule was chosen to be the origin of the coordinate system. The results are given in Table 1. D is expressed in units of R, R being the distance from the center of the molecule to one of the protons, or $R=R_{\mathrm{HH}}/\sqrt{3}$.

$E^{\alpha,D}$ is the energy obtained by using the cutoff correlation factor. For comparison E^0, the energy of the uncorrelated wavefunction, and $E^{\alpha,\infty}$, the energy of the correlated wavefunction using the correlation factor $1+\alpha r_{12}$, are also given.

The smallest increment of D was 0.2 R, the smallest increment of α was 0.001. It is of interest to observe that there is an absolute minimum for finite D. This minimum with respect to D was broad, becoming broader with increasing m. α decreases but D increases with m, so the "range of correlation" increases with the larger expansion. If this trend continues the cutoff correlation factor $1+\alpha h(r_{12})$ goes over into the correlation factor over all space, $1+\alpha r_{12}$. The product αD is approximately constant in the $m=2$ to $m=4$ computations, namely about 0.60 R.

In Table 2 we give some percentage lowerings of two-electron probability densities, due to the inclusion of the cutoff correlation factor. We define

$$\Delta\Psi^2=\{\Psi^0(r_1,r_2)\}^2-\{\Psi^\alpha(\vec{r}_1,\vec{r}_2)\}^2\,,$$

with normalized wavefunctions. In parentheses the corresponding values for the correlation factor $1+\alpha r_{12}$ are given.

Notice that initial lowerings are high, and that they decrease with increasing m. This tendency was opposite in the case of the correlation factor $1+\alpha r_{12}$. At $m=4$ the percentage lowerings are similar. This again demonstrates that the

Table 2. *Lowering of two-electron probability densities*

m	$\Delta\Psi^2/\Psi^{02}$ % $r_1=r_2=R,\quad r_{12}=0$	$\Delta\Psi^2/\Psi^{02}$ % $r_1=r_{12}=R/2,\quad r_2=R$
1	58 (18)	42 (15)
2	53 (31)	40 (25)
3	49 (43)	37 (34)
4	48 (44)	37 (35)

Table 3. *Complete optimization of various wavefunctions*

Wavefunction	η	R [a.u.]	$D\,[R]$	α	$-E$ [a.u.]
$\Psi^0(m=1)$	1.0136	0.923	0	0	1.02605
$\Psi^{\alpha,\infty}(m=1)$	1.1146	0.929	∞	0.245	1.0369
$\Psi^{\alpha,D}(m=1)$	1.0805	0.926	2.07	0.434	1.0595

cutoff correlation factor allows for strong electron correlation in the case of short expansions, but it loses its efficiency as m increases.

Complete optimization of all parameters, namely η (the orbital exponent), α, and R was performed for $m=1$. The results are shown in Table 3, and compared with corresponding calculations for the uncorrelated wavefunction (Ψ^0) and for $\Psi^{\alpha,\infty}$, referring to the correlation factor $1+\alpha r_{12}(D=\infty)$.

All increments are 0.001 or less. The energy obtained from $\Psi^{\alpha,D}$ is again lower than the energy resulting from $\Psi^{\alpha,\infty}$.

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