Theoret. chim. Acta (Berl.) 12, 57—65 (1968)

Correlated One-Center Wavefunctions for Two-Electron Molecules

II. Configuration-Interaction Functions and Application to HeH^+

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Received July 26, 1968

A one-center configuration-interaction wavefunction for two-electron systems, built from nonorthogonal exponential-type orbitals may be multiplied by the correlation factor $1 + \alpha r_{12}$ and subjected to a variational treatment. All integrals can be evaluated, and are given in closed form. Applications are made to the ground state and an excited $^1\Sigma^+$ state of HeH^+. The uncorrelated wavefunctions are based on the work by Stuart and Matsen. Due to the correlation factor the ground state energy at R = 1.4 a.u. improves by 2.3 % for a one-term and by 0.49 % for a twenty-term wavefunction. The optimized value of α decreases as the number of terms increases. The best energy obtained for the ground state is -2.97458 a.u. at $R = 1.4$ a.u. with $\alpha = 0.27$. Energy improvements for different R and changes in the orbital exponents were also studied. For the excited state the energy lowering due to the correlation factor becomes insignificant as the number of terms increases.

Eine Konfigurationenwechselwirkungs-Einzentrums-Wellenfunktion für zwei Elektronen kann mit dem Korrelationsfaktor $1 + \alpha r_{12}$ multipliziert und die Energie mit Hilfe der Variationsmethode berechnet werden. Die Orbitale sind nichtorthogonale Funktionen vom Exponentialtyp. Alle Integrale werden in geschlossener Form gegeben. Die Methode wird auf den Grundzustand und einen angeregten Zustand vom HeH^+ angewandt. Die nichtkorrelierten Wellenfunktionen von Stuart und Matsen dienen als Ausgangspunkt. Infolge des Korrelationsfaktors verbessert sich die Grundzusstandsenergie um 2,3 % für eine 1-Term, und um 0,49 % für eine 20-Term-Wellenfunktion. In jedem Fall ist $R = 1{,}4$ a.u. Der Optimalwert von α nimmt mit zunehmender Termzahl ab. Die beste berechnete Energie für den Grundzustand ist -2,97458 a.u. für $R = 1{,}4$ a.u. und $\alpha = 0{,}27$. Energieverbesserungen für verschiedene R und Änderungen im Exponentialfaktor wurden ebenfalls untersucht. Die durch den Korrelationsfaktor bedingte Energieerniedrigung für den angeregten Zustand wird mit zunehmender Termzahl unbedeutend.

Une fonction d'onde d'interaction de configurations monocentrique pour un système à deux électrons, construite à partir d'orbitales exponentielles non orthogonales, peut être multipliée par le facteur de corrélation $1 + \alpha r_{12}$ et soumise à un traitement variationnel. Toutes les intégrales sont calculables et sont données sous forme implicite. Ceci est appliqué à l'état fondamental et à un état excité $^1\Sigma^+$ de HeH^+. Les fonctions d'onde non corrélées sont extraites du travail de Stuart et Matsen. Le facteur de corrélation permet d'améliorer l'énergie de l'état fondamental à $R = 1{,}4$ u. a. de 2,3 % pour une fonction d'onde à un terme et de 0,49 % pour une fonction d'onde à 20 termes. La valeur optimale de α diminue lorsque le nombre de termes augmente. La meilleure énergie obtenue pour l'état fondamental est —2,97458 u. a. à $R = 1{,}4$ u. a. avec $\alpha = 0{,}27$. Les améliorations de l'énergie pour différentes valeurs de R et des exposants orbitaux ont aussi été étudiées. Pour l'état excité l'abaissement de l'énergie dû au facteur de corrélation devient insignifiant lorsque le nombre de termes augmente.

1. Introduction

In the first paper of this series [4] (hereafter referred to as I) we derived the integrals required for a one-center variational treatment of two-electron molecules involving the correlation factor $1 + \alpha r_{12}$. Detailed expressions were given for a configuration-interaction (CI) wavefunction built from orthogonal Shull-Löwdin orbitals, multiplied by this correlation factor. Application to the two lowest ${}^1A_1'$ states of equilateral triangular H_3^+ showed promising results.

In this paper we extend the method to include nonorthogonal orbitals. Detailed expressions for a CI wavefunction using general non-Gaussian orbitals will be derived in Part 2. In Part 3 we apply the method to the ground state and a low-lying excited ${}^1\Sigma^+$ state of HeH^+.

2. Theory

The spatial part Ψ of the two-electron trial wavefunction takes the form

$$\Psi^{\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1+\alpha r_{12})\,\Psi^0(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{k=1}^{m} C_k \Phi_k(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1+\alpha r_{12}) \sum_{k=1}^{m} C_k \Phi_k^0(\boldsymbol{r}_1, \boldsymbol{r}_2) \quad (1)$$

with real α. The spin-free Hamiltonian operator (in atomic units, which will be used throughout this paper) is

$$H = T + V_1 + V_2 + V_3 + V_4,$$

with

$$\begin{aligned} T &= -1/2(\nabla_1^2 + \nabla_2^2), \\ V_1 &= -Z_0/r_1 - Z_0/r_2, \\ V_2 &= 1/r_{12}, \\ V_3 &= -\left(\sum_X Z_X/R_{1X} + \sum_X Z_X/R_{2X}\right), \\ V_4 &= Z_0 \sum_X Z_X/R_{0X} + \sum_{X<Y} Z_X Z_Y/R_{XY}. \end{aligned} \quad (2)$$

The nucleus at the origin of the coordinate system is designated by the subscript 0, the other nuclei by subscripts X and Y. The Z's are nuclear charges. r and R have the usual meaning.

To express the matrix elements in a convenient form we introduce the following notation for an arbitrary operator B.

$$\begin{aligned} B_{ij} &= \iint \Phi_i^* B \Phi_j \, dv_1\, dv_2, \\ B_{ij}^h &= \iint r_{12}^h \Phi_i^{0*} B \Phi_j^0 \, dv_1\, dv_2, \end{aligned} \quad (3)$$

$$\begin{aligned} S_{ij} &= \iint \Phi_i^* \Phi_j \, dv_1\, dv_2, \\ S_{ij}^h &= \iint r_{12}^h \Phi_i^{0*} \Phi_j^0 \, dv_1\, dv_2. \end{aligned} \quad (4)$$

The matrix elements of the kinetic energy operator T differ slightly from Eq. (14) of paper I due to the non-orthogonality of the orbitals. They are

$$T_{ij} = T_{ij}^0 + \alpha(T_{ij}^1 + T_{ji}^{1*}) + \alpha^2[0.5(T_{ij}^2 + T_{ji}^{2*}) + S_{ij}^0]. \quad (5)$$

The matrix elements of the potential energy terms in (2) are

$$V_{ij} = V_{ij}^0 + 2\alpha V_{ij}^1 + \alpha^2 V_{ij}^2 \quad \text{for} \quad V = V_1, V_2, V_3, \quad \text{and} \quad V_{4ij} = S_{ij} V_4,$$

with

$$S_{ij} = S_{ij}^0 + 2\alpha S_{ij}^1 + \alpha^2 S_{ij}^2. \quad (6)$$

We write the symmetry-adapted functions Φ_i^0 in the most general form for exponential-type orbitals.

$$\Phi_i^0(\boldsymbol{r}_1, \boldsymbol{r}_2) = A_i \sum_{\substack{(p_i, q_i, \eta_i, \zeta_i, \\ l_i, \lambda_i, m_i, \mu_i)}} c_i(p_i, q_i, \eta_i, \zeta_i) \cdot d_i(l_i, \lambda_i, m_i, \mu_i) \cdot r_1^{p_i} \cdot r_2^{q_i} \cdot e^{-\eta_i r_1 - \zeta_i r_2} \times Y_{l_i m_i}(\vartheta_1, \varphi_1) \cdot Y_{\lambda_i \mu_i}(\vartheta_2, \varphi_2) \,. \tag{7}$$

In the following the summation indices and the arguments of c_i and d_i will be omitted. Eq. (7) differs from Eq. (18) of paper I through the introduction of the orbital exponents η_i and ζ_i. A_i is an operator that makes Φ_i^0 symmetric with respect to interchange of electrons in the case of singlet states, and antisymmetric in the case of triplet states.

Instead of the integrals $(p/q)_{ij}^k$ and $[p/q]_{X,ij}^k$ of paper I we define here

$$(p, \eta/q, \zeta)_{ij}^k \equiv \int\int r_1^p r_2^q e^{-\eta r_1 - \zeta r_2} r_{12}^k \, Y_{l_i m_i}{}^*(\vartheta_1, \varphi_1) \times Y_{\lambda_i \mu_i}{}^*(\vartheta_2, \varphi_2) \, Y_{l_j m_j}(\vartheta_1, \varphi_1) \, Y_{\lambda_j \mu_j}(\vartheta_2, \varphi_2) \, dv_1 \, dv_2 \,, \tag{8}$$

and similarly $[p, \eta/q, \zeta]_{X,ij}^k$, with the additional factor $1/R_{1X}$ in the integrand.

Now the matrix elements B_{ij}^h will be given in terms of the newly defined integrals.

$$T_{ij}^h = -A_i A_j \sum_i \sum_j c_i c_j d_i d_j [\{p_j(p_j+1) - l_j(l_j+1)\} \times (p-2, \eta/q, \zeta)_{ij}^h - 2\eta_j(p_j+1)(p-1, \eta/q, \zeta)_{ij}^h + \eta_j^2 (p, \eta/q, \zeta)_{ij}^h] \,. \tag{9}$$

$T_{ji}^{h\,*}$ is obtained from T_{ij}^h by interchanging the indices i and j.

$$\begin{aligned} V_{1ij}^h &= -2Z_0 A_i A_j \sum_i \sum_j c_i c_j d_i d_j (p-1, \eta/q, \zeta)_{ij}^h \\ V_{2ij}^h &= A_i A_j \sum_i \sum_j c_i c_j d_i d_j (p, \eta/q, \zeta)_{ij}^{h-1} \\ V_{3ij}^h &= -2A_i A_j \sum_i \sum_j c_i c_j d_i d_j \sum_X Z_X [p, \eta/q, \zeta]_{X,ij}^h \\ S_{ij}^h &= A_i A_j \sum_i \sum_j c_i c_j d_i d_j (p, \eta/q, \zeta)_{ij}^h \,, \end{aligned} \tag{10}$$

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

The final step is the evaluation of the integrals $(p, \eta/q, \zeta)_{ij}^h$ and $[p, \eta/q, \zeta]_{X,ij}^h$. They are special cases of the integrals (ac/bd) and $[ac/bd]$. The former was worked out by Calais and Löwdin [1], the latter in paper I. Both can be expanded in a series containing the integrals $Q(f, g, h, \lambda)$ and $Q(f'', g, h, \lambda)$, respectively. For non-orthogonal orbitals

$$Q(f, g, h, \lambda) \rightarrow G(p+2, q+2, \eta, \zeta, k, \lambda) \equiv \int_0^\infty r_1^{p+2} e^{-\eta r_1} dr_1 \int_0^\infty r_2^{q+2} e^{-\zeta r_2} dr_2 \int_0^\pi r_{12}^k P_\lambda^0(\cos\vartheta_{12}) \sin\vartheta_{12} d\vartheta_{12} \,. \tag{11}$$

Similarly

$$Q(f^n, g, h, \lambda) \rightarrow G^n(p+2, q+2, \eta, \zeta, k, \lambda)$$

$$\equiv \int_0^\infty r_1^{p+2} e^{-\eta r_1} [R_<^n / R_>^{n+1}] \, r_1^2 \, dr_1 \int_0^\infty r_2^{q+2} e^{-\zeta r_2} \, dr_2 \times \int_0^\pi r_{12}^k P_\lambda^0(\cos\vartheta_{12}) \sin\vartheta_{12} \, d\vartheta_{12} . \tag{12}$$

$R_<$ and $R_>$ are the smaller and greater, respectively, of r_1 and R_{0X}. The P_λ^0 are Legendre polynomials.

For the further evaluation of the G-integrals we introduce the F-integrals which are similarly defined as in paper I.

$$F^n(p', q', \eta, \zeta, k') \equiv \int_0^\infty r_1^{p'} e^{-\eta r_1} [R_<^n / R_>^{n+1}] \, dr_1 \times \int_0^\infty r_2^{q'} e^{-\zeta r_2} \, dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12}^{k'} \, dr_{12} . \tag{13}$$

$F(p', q', \eta, \zeta, k')$ is similar, but without $R_<^n / R_>^{n+1}$. The integrals $f^n(p'', a)$, $f(p'', a)$, and $f_1^n(p'', a)$ are defined and solved as in paper I. Eq. (23) of paper I, expressing the G-integrals by F-integrals, can be retained if the parameters η and ζ are included with the arguments. Instead of Eq. (24) of paper I we have

$$\begin{aligned} F^n(p', q', \eta, \zeta, k') = {} & k'! \sum_{t=0}^{k'+1} \{(q'+t)!/[t!(k'+1-t)!]\} \\ & \times \{1/[\zeta^{q'+t+1}]\} \{[1-(-1)^t] \, f^n(p'+k'+1-t, \eta) + (-1)^t [1+(-1)^{k'}] \\ & \times \sum_{j=0}^{q'+t} [\zeta^j / j!] \, f^n(p'+k'+1-t+j, \eta+\zeta)\} . \end{aligned} \tag{14}$$

$F(p', q', \eta, \zeta, k')$ is solved by the same expression with the superscripts n omitted.

If p'' of $f(p'', a)$ becomes -1, then F has to be evaluated differently. In this case the lowest value of p' is also -1 for Slater orbitals, and

$$\begin{aligned} F(-1, q', \eta, \zeta, k') = {} & k'! \sum_{t=0}^{k'} \quad \{\text{same as Eq. (14) with } f\} \\ & + [1+(-1)^{k'}] \{(q'+k'+1)!/(k'+1)\} \{1/\zeta^{q'+k'+2}\} \{\ln(1+\zeta/\eta) \\ & - \sum_{j=1}^{q'+k'+1} [\zeta^j / j!] \, f(j-1, \eta+\zeta)\} . \end{aligned} \tag{15}$$

3. Application to $^1\Sigma^+$ States of HeH$^+$

Despite the fact that our method is not restricted to the treatment of diatomic molecules we chose HeH$^+$ as an example for two reasons. First, the one-center wavefunction, with the center at the position of the helium nucleus, has the right asymptotic behavior for the ground state of this molecule. Second, extensive and successful one-center CI calculations have been performed on this molecule by Stuart and Matsen [10]. Their functions and optimized orbital exponents served us as a convenient basis from which we started the more time-consuming correlation calculations.

The functions and designations of Table 1 were chosen. All orbitals are Slater orbitals. m indicates the number of terms in the CI wavefunction.

Two sets of calculations were performed for the ground state of HeH$^+$ at the internuclear separation $R = 1.4$ a.u. The difference lies in the choice of orbital exponents. In set I (indicated by the subscript I) the orbital exponents for all functions $\Psi^0(m)$ and $\Psi^\alpha(m)$ were those of Stuart's and Matsen's 30-term wavefunction, at $R = 1.4$ a.u. The energy was minimized with respect to α and the linear coefficients C_i only. The results are presented in Table 2. E_I^0 and E_I^α refer

Table 1. *Wavefunctions*

m	$\Psi^0(m)$
1	$(1s1s)$
3	$(1)+(1s2s')+(2s'2s')$
6	$(3)+(1s3s')+(2s'3s')+(3s'3s')$
7	$(6)+(1s2p_0)$
8	$(7)+(1s3p_0)$
9	$(8)+(1s4p_0)$
10	$(9)+(1s3d_0)$
11	$(10)+(1s4d_0)$
12	$(11)+(1s4f_0)$
13	$(12)+(1s5f_0)$
14	$(13)+(2p'_0 2p'_0)$
15	$(14)+(2p''_{\pm 1} 2p''_{\pm 1})$
17	$(15)+(2p''_{\pm 1} 3p''_{\pm 1})+(3p''_{\pm 1} 3p''_{\pm 1})$
18	$(17)+(1s5g_0)$
19	$(18)+(1s6h_0)$
20	$(19)+(3d'_{\pm 1} 3d'_{\pm 1})$

Table 2. *Ground state energies (in a.u.) of* HeH$^+$, *obtained for fixed orbital exponents at* $R = 1.4$ *a.u.*

m	α_I	$-E_\mathrm{I}^0$	$-E_\mathrm{I}^\alpha$	ΔE_I	$\Delta E_\mathrm{I}/E_\mathrm{I}^0$ %
1	0.40	2.76506	2.84792	0.08286	2.30
3	0.37	2.80045	2.85000	0.04955	1.77
6	0.30	2.82832	2.85336	0.02504	0.89
7	0.30	2.85734	2.88513	0.02779	0.97
8	0.28	2.89073	2.91673	0.02600	0.90
9	0.28	2.89810	2.92146	0.02341	0.88
10	0.28	2.91562	2.94195	0.02633	0.90
11	0.25	2.92514	2.95107	0.02593	0.89
12	0.28	2.93313	2.96081	0.02768	0.94
13	0.25	2.93786	2.96544	0.02758	0.94
14	0.28	2.94083	2.96546	0.02463	0.84
15	0.25	2.95068	2.96549	0.01481	0.50
17	0.25	2.95266	2.96561	0.01295	0.44
18	0.28	2.95650	2.97055	0.01405	0.48
19	0.28	2.95930	2.97440	0.01510	0.51
20	0.27	2.96013	2.97458	0.01445	0.49

Orbital exponents:

s: 1.93 s': 2.35 p: 2.92 p': 4.06 p'': 3.17
d: 2.91 d': 3.46 f: 3.61 g: 4.38 h: 3.87

to the energies obtained by using the uncorrelated wavefunctions $\Psi_{\rm I}^0$ and the correlated $\Psi_{\rm I}^\alpha$, respectively. $\Delta E_{\rm I} = E_{\rm I}^0 - E_{\rm I}^\alpha$. In the process of minimization, the smallest variation of α was chosen to be 0.03 for $m = 1$ to 19, and 0.01 for $m = 20$.

In set II (indicated by the subscript II) the orbital exponents were optimized both for Ψ^0 and Ψ^α. The results are shown in Table 3. For the purpose of comparison, E^α was also minimized using the orbital exponents of $\Psi_{\rm II}^0$. Such results are indicated by an asterisk. The smallest variation of α was 0.01. The smallest variation of η^α was 0.01 for $m = 1$ to 6 and 0.02 for $m = 7$ and 8. The energies $E_{\rm II}^0$ and orbital exponents agree with Stuart's and Matsen's "intermediate" results. The orbital exponents have not been published [11]. $\Delta E_{\rm II} = E_{\rm II}^0 - E_{\rm II}^\alpha$, and $\Delta E_{\rm II}{}^* = E_{\rm II}^\alpha{}^* - E_{\rm II}^\alpha$.

Table 3. *Ground state energies (in a.u.) of* HeH$^+$, *obtained for optimized orbital exponents at* $R = 1.4$ *a.u.*

m	$-E_{\rm II}^0$	$-E_{\rm II}^{\alpha}{}^*$	$-E_{\rm II}^\alpha$	$\Delta E_{\rm II}$	$\dfrac{\Delta E_{\rm II}}{E_{\rm II}^0}$ %	$E_{\rm II}^{\alpha}{}^* - E_{\rm II}^\alpha$	$\dfrac{E_{\rm II}^{\alpha}{}^* - E_{\rm II}^\alpha}{E_{\rm II}^{\alpha}{}^*}$ %
1	2.80736	2.83065	2.84852	0.04116	1.47	0.01787	0.63
3	2.82657	2.84693	2.85293	0.02636	0.93	0.00600	0.21
6	2.82851	2.85234	2.85358	0.02507	0.89	0.00124	0.04
7	2.89469	2.91800	2.91947	0.02478	0.86	0.00147	0.05
8	2.89769	2.92101	2.92151	0.02382	0.82	0.00050	0.02

Optimized orbital exponents and α-values

m	$\eta_{\rm II}^0(s)$	$\eta_{\rm II}^0(s')$	$\eta_{\rm II}^0(p)$	$\eta_{\rm II}^\alpha(s)$	$\eta_{\rm II}^\alpha(s')$	$\eta_{\rm II}^\alpha(p)$	$\alpha_{\rm II}{}^*$	$\alpha_{\rm II}$
1	1.73			1.91			0.18	0.38
3	2.64	1.95		2.75	2.16		0.23	0.30
6	1.77	2.44		1.93	2.57		0.28	0.29
7	1.90	2.32	1.61	1.90	2.48	1.77	0.25	0.27
8	1.92	2.32	2.29	1.90	2.59	2.41	0.26	0.27

In Table 4 we give the results for the 9-term wavefunction $\Psi(9)$ at different internuclear separations R. The orbital exponents were not optimized. They are taken from Stuart's and Matsen's 30-term wavefunction at the corresponding R. For $R = 1.7$ and 1.8 a.u. we obtained them by interpolation. The smallest variation of α was 0.01. $\Delta E = E^0 - E^\alpha$.

Tables 2 and 3 show that the correlated energy E^α converges rapidly as the number of terms in the wavefunction increases. $\Psi_{\rm I}^\alpha(18)$ leads to an energy better than Stuart's and Matsen's 30-term energy. $\Psi_{\rm I}^\alpha(20)$ gives an energy of -2.97458 a.u. which is better than the energy obtained in most of the previous computations. (A bibliography of calculations for the ground state of HeH$^+$ until 1965 is given by Michels [8]. For more recent calculations see references [3], [5], [6], [7], [9] and [14].) Only Conroy [2] and Wolniewicz [13] report a better result at $R = 1.4$ a.u. We have not optimized the orbital exponents. The improvement, $E_{\rm I}^0(20) - E_{\rm I}^\alpha(20)$,is 0.49 % of $E_{\rm I}^0(20)$, and about 30 % of the total correlation energy. Assuming that $\Psi^\alpha(30)$ would give the energy -2.97797 a.u., reported by Wolniewicz, the improvement due to the correlation factor would still be 0.3 % of $E_{\rm I}^0$. Although small on an absolute scale, such improvements are not easily obtained by adding more terms to a CI-type wavefunction.

Table 4. *Ground state energies (in a.u.) of* HeH^+, *obtained for fixed orbital exponents at different R (in a.u.)*

R	$\eta(s)$	$\eta(s')$	$\eta(p)$	α	$-E^0$	$-E^\alpha$	ΔE	$\Delta E/E^0$ %
0.1	2.44	3.84	5.80	0.57	−12.89633	−12.77526	0.12107	0.94
0.5	2.14	3.11	4.04	0.38	1.85391	1.91893	0.06502	3.51
1.0	1.96	2.82	3.49	0.27	2.80930	2.83888	0.02958	1.05
1.2	1.94	2.55	3.19	0.26	2.87355	2.89928	0.02573	0.90
1.3	1.93	2.44	3.05	0.26	2.88898	2.91337	0.02439	0.84
1.4	1.93	2.35	2.92	0.26	2.89810	2.92151	0.02341	0.81
1.5	1.94	2.27	2.79	0.27	2.90308	2.92576	0.02268	0.78
1.6	1.94	2.20	2.68	0.27	2.90535	2.92755	0.02220	0.76
1.7	1.95	2.13	2.58	0.27	2.90583	2.92771	0.02188	0.75
1.8	1.95	2.08	2.48	0.27	2.90520	2.92695	0.02175	0.75
2.0	1.96	2.00	2.32	0.27	2.90222	2.92399	0.02177	0.75
3.0	1.98	1.85	1.79	0.28	2.88680	2.90985	0.02305	0.80
4.0	1.97	1.89	1.51	0.29	2.88125	2.90486	0.02361	0.82
5.0	1.97	1.92	1.38	0.29	2.87950	2.90329	0.02379	0.83

The optimized values of α are seen to decrease slightly as m increases. This tendency is expected whenever the correlation factor is associated with a CI wavefunction. As such a wavefunction leads to energies that approach the exact energy closer and closer, the role of the correlation factor diminishes, which is indicated by a decrease of α. The question how rapidly such a lessening would take place led to this work.

The computations with $\Psi_{\rm II}$ (Table 3) were undertaken in order to find out how beneficial to the energy an optimization of all orbital exponents in $\Psi_{\rm II}^\alpha$ would be. Orbital exponents generally increase by the introduction of the correlation factor due to the reduced shielding effect. Changes become smaller with increasing m. The energy improvements $E_{\rm II}^0 - E_{\rm II}^\alpha$ are all smaller than the corresponding $E_{\rm I}^0 - E_{\rm I}^\alpha$. The differences $E_{\rm II}^{\alpha}{}^* - E_{\rm II}^\alpha$ decrease much faster than the differences $E_{\rm II}^0 - E_{\rm II}^\alpha$ as m increases, indicating that a minimization of $E_{\rm II}^\alpha$ with respect to all orbital exponents may become less worthwhile for larger m.

In Fig. 1 the results of $\Psi^0(9)$ and $\Psi^\alpha(9)$, Table 4, are compared with those of Stuart's and Matsen's 30-term wavefunction. Also shown are several energies computed by Wolniewicz, and our result $E_{\rm I}^\alpha(20)$ at $R = 1.4$ a.u. The improvement of the energy due to the correlation factor is approximately constant over that region of R which is of interest. Therefore our correlated 9-term wavefunction, although inferior to Stuart's and Matsen's 30-term function around R_e, leads to lower energies for $R \geqq 4$ a.u. Interesting is the behaviour of α. Beginning with $R = 0.1$ a.u. it decreases, goes through a minimum around $R = 1.4$ a.u., and increases slightly for larger R.

A few exploratory computations on low-lying excited states of $^1\Sigma^+$ symmetry were performed. The results for the second lowest root of the secular equations at $R = 8.5$ a.u. are given in Table 5. This root corresponds to the energy of the second excited $^1\Sigma^+$ state of HeH^+, since the first excited state of this symmetry does not dissociate according to $HeH^+ \rightarrow He + H^+$. All wavefunctions were optimized with respect to the orbital exponents and α, with the smallest variation of η being

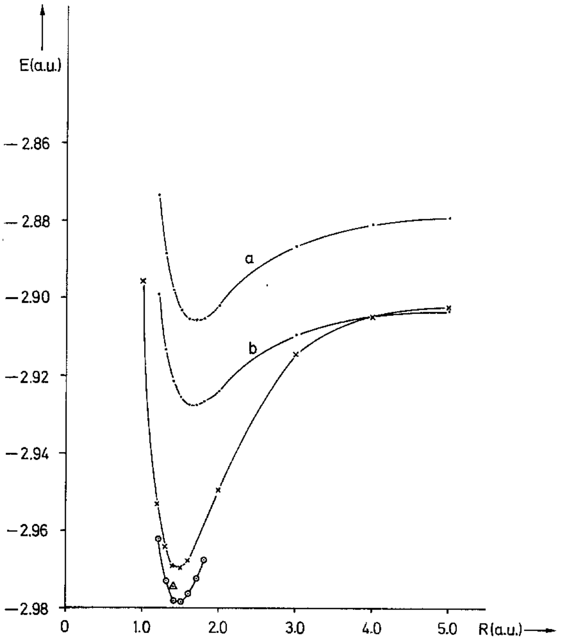

Fig. 1. Comparison of computed energies of HeH$^+$. *a* $E^{\circ}(9)$ of this work, *b* $E^{\alpha}(9)$ of this work, × Stuart and Matson, ⊙ Wolniewicz, △ lowest energy of this work

0.01 for $\Psi^0(m)$ with $m=3, 6, 7$; 0.02 for $\Psi^0(8)$; 0.01 for $\Psi^{\alpha}(3)$ and $\Psi^{\alpha}(6)$, and 0.05 for $\Psi^{\alpha}(7)$ and $\Psi^{\alpha}(8)$. The smallest variation of α was 0.01. $\Delta E = E^0 - E^{\alpha}$.

The energy of the dissociated ions, corresponding to this state, is −2.14597 a.u. Michels [8] computed a lowest energy of −2.18177 for the second excited $^1\Sigma^+$ state of HeH$^+$, also at $R=8.5$ a.u., slightly lower than our best energy of −2.18174 a.u. Interesting from our standpoint is the fact that the improvement of the energy due to the correlation factor is much smaller than in the case of the ground state, and decreases rapidly to insignificant values as m increases. Also α is smaller and decreases fast.

Details on theory and computations, including tables of the linear coefficients, can be found in reference [12].

Table 5. *Energies (in a.u.) of second excited* $^1\Sigma^+$ *state of* HeH$^+$ *at* $R=8.5$ *a.u.*

m	$\eta^0(s)$	$\eta^0(s')$	$\eta^0(p)$	$\eta^{\alpha}(s')$	$\eta^{\alpha}(s')$	$\eta^{\alpha}(p)$	α	$-E^0$	$-E^{\alpha}$	ΔE	$\Delta E/E^0$ %
3	1.95	0.43		1.99	0.57		0.31	2.12947	2.13635	0.00688	0.32
6	1.99	0.72		2.00	0.78		0.06	2.14238	2.14357	0.00119	0.06
7	1.99	0.66	0.43	1.99	0.71	0.47	0.05	2.18052	2.18095	0.00043	0.02
8	2.00	0.66	0.33	2.00	0.70	0.36	0.04	2.18135	2.18174	0.00039	0.02

Acknowledgments. We are grateful to the National Research Council of Canada and the University of New Brunswick for financial support. We thank the members of the computing centers at the University of New Brunswick and at McGill University for their assistance and the grant of computer time.

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