

Molecular calculations for HeH^+ with two-center correlated orbitals

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A two-center correlated orbital approach was used to calculate the electronic ground state energy for the HeH^+ molecular ion. The wavefunctions were constructed from the exact solution of the Schrödinger equation for the HeH^{++} problem in prolate-spheroidal coordinates taken together with a Hylleraas type correlation factor. With a simple single term wavefunction, we obtained ground state energy of -2.95308691 hartree without any variational parameters in the calculation. When a two-configuration-state wavefunction was used and effective charges were allowed to be adjusted, we found an energy of -2.97384868 hartree, which is to be compared with -2.97869074 hartree obtained by an 83 term configuration interaction wavefunction or -2.97364338 hartree by an *ab initio* calculation (at the MP4(SDQ)/6-311++G(3df, 3dp) level) using the well-known “canned” code.

HeH^+ , two-center orbitals, prolate-spheroidal coordinates, correlation function

1 Introduction

The exact two-center orbitals obtained by solving the Schrödinger equation for the H_2^+ ion are the most useful building blocks for constructing the electronic wavefunctions of the homonuclear H_2 molecule^[1]. The electronic wavefunction for the ground state constructed with two-center orbitals takes the form:

$$\Psi_{\text{H}_2}(1,2) = \Psi_{\text{H}_2^+,1\sigma}(1)\Psi_{\text{H}_2^+,1\sigma}(2)\chi_{00}\left(1+\frac{1}{2}r_{12}\right) \quad (1)$$

where $\Psi_{\text{H}_2^+,1\sigma}$ is the solution of the Schrödinger equation for the H_2^+ in prolate-spheroidal (ellipsoidal) coordinates, $\chi_{00} = \left[\left|\uparrow_1\downarrow_2\right\rangle - \left|\downarrow_1\uparrow_2\right\rangle\right]/\sqrt{2}$ is singlet spin function, and $(1+\frac{1}{2}r_{12})$ is the Hylleraas correlation factor. This wavefunction yields a binding energy of 4.5 eV for H_2 molecule without any variational parameters. Variation with respect to a couple of parameters in the function (1) shifts the binding energy to 4.7 eV, being in remarkable agreement with the experimental value. To achieve the

same result, more than 80 single-center atomic orbitals or more than 200 Hylleraas type wavefunctions that explicitly include the interelectronic distance are usually used, as demonstrated by the earlier work of Kolos et al.^[2,3] and James et al.^[4], respectively.

The two-center wavefunction appropriately describes the motion of electrons in the field of two nuclei, thus resulting in a very accurate ground state energy. The excited state is similarly suggested. Unlike the Hylleraas type wavefunction or single-center atomic orbitals, the two-center wavefunction leads physical meaning to the chemical bond between two atoms by solving the Schrödinger equation exactly. By incorporating the correlation factor, which expresses the repulsive tendency of two electrons because of their Coulomb charges, the wavefunction (1) considers the electron correlation effects in a physically appealing approach. In addition, the

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construction of the accurate wavefunctions of the excited state based on the two-center orbitals is straightforward, as discussed in ref. [1].

In the present calculation, we apply the same ideas to a heteronuclear case, HeH^+ molecular ion. Like H_2^+ , the exact solutions of the Schrödinger equation for HeH^{++} problem in prolate-spheroidal coordinates can also be calculated. The accurate calculation for the ground state energy of this molecular ion has been performed several years ago^[5-7] and the electronic transition to the excited state has been investigated recently^[8]. Similar calculations for the ground state energy of H_2^+ and HeH^{++} have also been reported^[9]. Very recently, Nakashima and Nakatsuji used an ICI method to solve the Schrödinger equation for helium atom and its isoelectronic ions exactly^[10].

First, we apply a simple wavefunction for the ground state of HeH^+ molecular ion:

$$\Psi_{\text{HeH}^+}^{\text{I}}(1,2) = \Psi_{\text{HeH}^{++},1s\sigma}(1)\Psi_{\text{HeH}^{++},1s\sigma}(2) \chi_{00}\left(1 + \frac{1}{2}r_{12}\right) \quad (2)$$

where $\Psi_{\text{HeH}^{++},1s\sigma}$ is the ground state wavefunction of the HeH^{++} molecular ion, obtained by solving the Schrödinger equation for heteronuclear problem in prolate-spheroidal coordinates, and the rest items have the same meaning as in eq. (1). The electronic energy of the ground state is found to be -2.95308691 hartree without any variational parameters. However, by adjusting effective charges, we obtain the ground state electronic energy of -2.95964085 hartree from a variational calculation. We then repeat the above calculations using a two-configuration-state wavefunction of eq. (3):

$$\Psi_{\text{HeH}^+}^{\text{II}}(1,2) = \left[c_1 \Psi_{(\text{HeH}^{++},1s\sigma)^2} + c_2 \Psi_{(\text{HeH}^{++},2p\sigma)^2} \right] \chi_{00}\left(1 + \frac{1}{2}r_{12}\right) \quad (3)$$

where

$$\Psi_{(\text{HeH}^{++},1s\sigma)^2} = \Psi_{\text{HeH}^{++},1s\sigma}(1)\Psi_{\text{HeH}^{++},1s\sigma}(2) \quad (4)$$

$$\Psi_{(\text{HeH}^{++},2p\sigma)^2} = \Psi_{\text{HeH}^{++},2p\sigma}(1)\Psi_{\text{HeH}^{++},2p\sigma}(2) \quad (5)$$

In eq. (5), $\Psi_{\text{HeH}^{++},2p\sigma}$ is the first electronically excited state wavefunction for HeH^{++} . The electronic energy of the ground state is then -2.96640131 hartree obtained

from the calculation without variational parameters and -2.97384868 hartree from the variational calculation with respect to the effective charges. These results are summarized in Table 1.

Table 1 The ground state energy for HeH^+ molecular ions obtained for different types of wavefunctions with different approximations

Wavefunction	Energy (hartree)	
	no variational parameters	2 adjustable parameters
$\Psi_{\text{HeH}^+}^{\text{I}}$	-2.95308691	-2.96640131
$\Psi_{\text{HeH}^+}^{\text{II}}$	-2.95964085	-2.97384868

The electronic energy calculated with the exact two-center wavefunction is to be compared with -2.97869074 hartree obtained by 83 terms of Hylleraas type of wavefunction^[6] or -2.97364338 hartree by an *ab initio* calculation at MP4/6-311++G(3df, 3dp) level^[11].

2 Methodology

In this section, we present the details of the calculation. Using the exact solution of the Schrödinger equation for HeH^{++} problem in ellipsoidal coordinates, we are able to construct the simple wavefunction (2) and two-configuration-state wavefunction (3) for HeH^+ molecular ion. The electronic integrals are calculated by numerical algorithm using a code recently developed by our group.

The wavefunction for the heteronuclear ion HeH^{++} in ellipsoidal coordinates is given by^[12]

$$\Psi(\lambda, \mu, \phi) = A(\lambda)M(\mu)e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots \quad (6)$$

where

$$A(\lambda) = e^{-\alpha\lambda} L(\lambda) \quad (7)$$

$$L(\lambda) = (\lambda^2 - 1)^{|m|/2} (\lambda + 1)^\sigma \sum_n a_n \left(\frac{\lambda - 1}{\lambda + 1} \right)^n \quad (8)$$

$$M(\mu) = e^{-\alpha\mu} \sum_{s=0}^{\infty} b_{2s} P_{m+2s}^m(\mu) \quad (9)$$

$P_{m+2s}^m(\mu)$ is the associated Legendre function of the first kind, α is a function of R , and σ is related to effective charge Z_a^* and Z_b^* by

$$\sigma = \frac{R(Z_a^* + Z_b^*)}{2\alpha} - m - 1 \quad (10)$$

and λ , μ and ϕ are the ellipsoidal coordinates of an electron, as defined in Figure 1. In the above definition of the wavefunction, $Z_a^* = 2$ and $Z_b^* = 1$ in the exact wavefunction

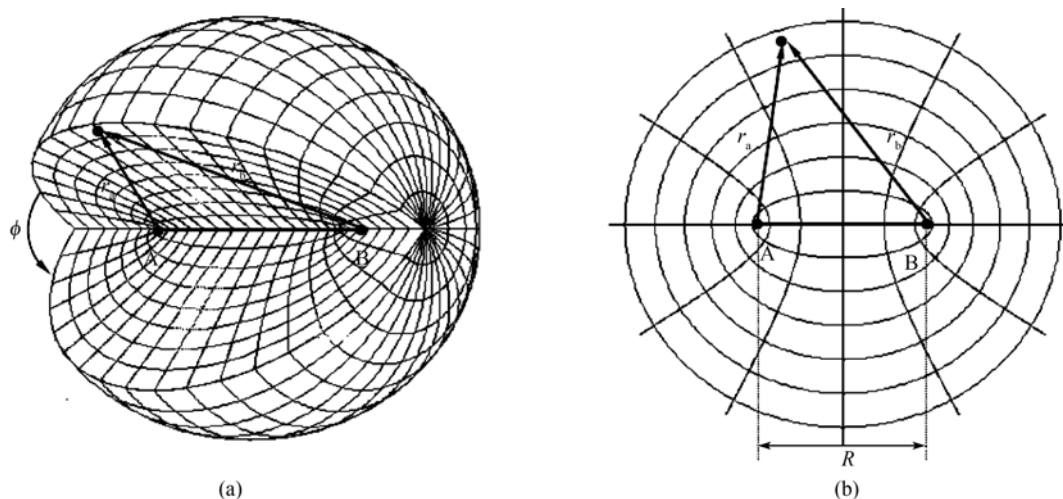


Figure 1 (a) Prolate spheroidal coordinates (λ, μ, ϕ) with $\lambda = (r_a + r_b)/R$ and $\mu = (r_a - r_b)/R$. The range of coordinates is $1 \leq \lambda < \infty$, $-1 \leq \mu \leq 1$ and $0 \leq \phi < 2\pi$; (b) elliptical coordinates (λ, μ) .

for HeH^{++} problem, whereas they could be variational parameters in the trial wavefunction for HeH^+ . For the case $m=0$, we have the ground state solutions:

$$\Psi_{\text{HeH}^{++}, 1s\sigma}(\lambda, \mu) = N e^{-\alpha\lambda} e^{-\alpha\mu} (\lambda + 1)^\sigma \times \left[1 + a_1 \left(\frac{\lambda - 1}{\lambda + 1} \right) + a_2 \left(\frac{\lambda - 1}{\lambda + 1} \right)^2 + \dots \right] \times [1 + b_2 P_2(\mu) + b_4 P_4(\mu) + \dots] \quad (11)$$

where $P_i(\mu)$ is a Legendre polynomial. The coefficients $a_1, a_2, b_2, b_4, \dots$ are determined by recursion relations^[13].

The solution for the first electronically excited state, $\Psi_{\text{HeH}^{++}, 2p\sigma}$, has the same form as that for the ground state but the different sets of coefficients since the two kinds of state have the same symmetric character.

HeH^+ molecular ion, a two nuclei and two valence electron system, has the Hamiltonian in atomic units

$$H = H_0(1) + H_0(2) + \frac{1}{r_{12}} + \frac{Z_a Z_b}{R} \quad (12)$$

in the Born-Oppenheimer approximation, where

$$H_0(i) = -\frac{1}{2} \nabla_i^2 - \frac{Z_a}{r_{ai}} - \frac{Z_b}{r_{bi}}, \quad i = 1, 2 \quad (13)$$

is the one-electron Hamiltonian. The notation is illustrated in Figure 2.

For wavefunction (2), the ground state energy is given by

$$E_I = \frac{\langle \Psi^I | H | \Psi^I \rangle}{\langle \Psi^I | \Psi^I \rangle} = \frac{H}{S} \quad (14)$$

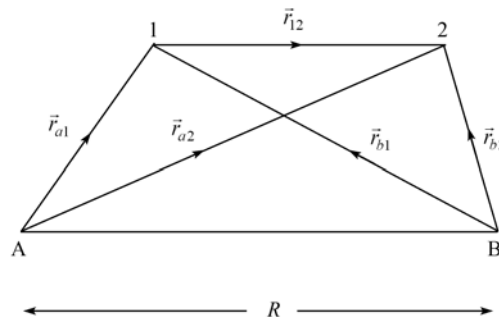


Figure 2 Electronic distances in diatomic molecules. A and B are the positions of the nuclei with nuclear charges Z_a and Z_b , respectively. The nuclei are fixed and the distance between them is taken as the equilibrium bond length for the given molecule, $R = R_0$. The positions of the electrons are denoted by 1 and 2.

where $H = \langle \Psi^I | \mathbf{H} | \Psi^I \rangle$ is Hamiltonian matrix element and $S = \langle \Psi^I | \Psi^I \rangle$ is overlap matrix element. Wavefunction (3) can be simplified as

$$\Psi^{\text{II}}(1, 2) = c_1 \Psi_a^{\text{II}} + c_2 \Psi_b^{\text{II}} \quad (15)$$

where

$$\Psi_a^{\text{II}} = \Psi_{(\text{HeH}^{++}, 1s\sigma)^2} \chi_{00} \left(1 + \frac{1}{2} r_{12} \right) \quad (16)$$

and

$$\Psi_b^{\text{II}} = \Psi_{(\text{HeH}^{++}, 2p\sigma)^2} \chi_{00} \left(1 + \frac{1}{2} r_{12} \right) \quad (17)$$

Then, following the variational principle, the ground state electronic energy is the smaller one of two solutions of the parabolic equation for E_{II} :

$$D_2 E_{\text{II}}^2 - D_1 E_{\text{II}} + D_0 = 0 \quad (18)$$

where

$$D_0 = H_{aa}H_{bb} - H_{ab}H_{ba} \quad (19)$$

$$D_1 = H_{aa}S_{bb} + H_{bb}S_{aa} - H_{ab}S_{ba} - H_{ba}S_{ab} \quad (20)$$

and

$$D_2 = S_{aa}S_{bb} - S_{ab}S_{ba} \quad (21)$$

The Hamiltonian matrix element H_{ab} is given by:

$$\begin{aligned} H_{ab} &= \langle \Psi_a^{\Pi} | \mathbf{H} | \Psi_b^{\Pi} \rangle \\ &= \left\langle \Psi_a^{\Pi} \left| \mathbf{H}_0(1) + \mathbf{H}_0(2) + \frac{1}{r_{12}} + \frac{Z_a Z_b}{R} \right| \Psi_b^{\Pi} \right\rangle \\ &= 2 \langle \Psi_a^{\Pi} | \mathbf{H}_0(i) | \Psi_b^{\Pi} \rangle + \left\langle \Psi_a^{\Pi} \left| \frac{1}{r_{12}} \right| \Psi_b^{\Pi} \right\rangle \\ &\quad + \frac{Z_a Z_b}{R} \langle \Psi_a^{\Pi} | \Psi_b^{\Pi} \rangle \\ &= - \langle \Psi_a^{\Pi} | \nabla_i^2 | \Psi_b^{\Pi} \rangle + 2 \langle \Psi_a^{\Pi} | \mathbf{d}(r_i) | \Psi_b^{\Pi} \rangle \\ &\quad + \left\langle \Psi_a^{\Pi} \left| \frac{1}{r_{12}} \right| \Psi_b^{\Pi} \right\rangle + \frac{Z_a Z_b}{R} S_{ab} \end{aligned} \quad (22)$$

where

$$\mathbf{d}(r_i) = -\frac{Z_a}{r_{ai}} - \frac{Z_b}{r_{bi}} \quad (23)$$

Inserting eqs. (4) and (5), the H_{ab} has the form:

$$\begin{aligned} H_{ab} &= - \sum_{l=0}^1 \sum_{l'=0}^1 A_{ll'} \langle \Psi_a | r_{12}^l \nabla_i^2 r_{12}^{l'} | \Psi_b \rangle \\ &\quad + 2 \sum_{l=0}^2 B_l \langle \Psi_a | r_{12}^l \mathbf{d}(r_i) | \Psi_b \rangle \\ &\quad + \sum_{l=1}^1 C_l \langle \Psi_a | r_{12}^l | \Psi_b \rangle + \frac{Z_a Z_b}{R} S_{ab} \end{aligned} \quad (24)$$

In eq. (22), $\Psi_a = \Psi_{(\text{HeH}^{++}, 1s\sigma)^2}$, $\Psi_b = \Psi_{(\text{HeH}^{++}, 2p\sigma)^2}$, $i = 1$ or 2 , and coefficients $A_{ll'}$, B_l , and C_l have the following values:

$$A_{00} = 1, A_{01} = A_{10} = \frac{1}{2}, A_{11} = \frac{1}{4} \quad (25)$$

$$B_0 = 1, B_1 = 1, B_2 = \frac{1}{4} \quad (26)$$

and

$$C_{-1} = 1, C_0 = 1, C_1 = \frac{1}{4} \quad (27)$$

The first term in the right hand side of eq. (24) then can

be written as

$$\begin{aligned} \langle \Psi_a | r_{12}^l \nabla_i^2 r_{12}^{l'} | \Psi_b \rangle &= -\frac{1}{2} \frac{l'}{l+l'} \langle \nabla_i^2 \Psi_a | r_{12}^{l+l'} | \Psi_b \rangle \\ &\quad + \frac{1}{2} l l' \langle \Psi_a | r_{12}^{l+l'-2} | \Psi_b \rangle \\ &\quad - \frac{1}{2} \frac{l}{l+l'} \langle \Psi_a | r_{12}^{l+l'} | \nabla_i^2 \Psi_b \rangle \end{aligned} \quad (28)$$

by applying the partial integration method and first Green theorem^[14]. The derivation for eq. (28) is given in Appendix A. The overlap matrix element S_{ab} has a form:

$$S_{ab} = \sum_{l=0}^2 F_l \langle \Psi_a | r_{12}^l | \Psi_b \rangle \quad (29)$$

with

$$F_0 = 1, F_1 = 1, F_2 = \frac{1}{4} \quad (30)$$

The function r_{12}^{-1} is calculated using the Neumann expansion, r_{12}^{-1} is obtained by multiplying r_{12}^{-1} by the expression for r_{12}^2 which in prolate spheroidal coordinates can be expressed as:

$$\begin{aligned} r_{12}^2 &= \left(\frac{R}{2} \right)^2 \left\{ \lambda_1^2 + \lambda_2^2 + \mu_1^2 + \mu_2^2 - 2 - 2\lambda_1 \lambda_2 \mu_1 \mu_2 \right. \\ &\quad \left. - \left[(\lambda_1^2 - 1)(\lambda_2^2 - 1)(1 - \mu_1^2)(1 - \mu_2^2) \right]^{\frac{1}{2}} \right. \\ &\quad \left. \times \left(e^{i(\varphi_1 - \varphi_2)} + e^{-i(\varphi_1 - \varphi_2)} \right) \right\} \end{aligned} \quad (31)$$

The final form of each integral is a linear combination of the products of one-dimensional integrals for μ and two-dimensional integrals for λ . These integrals are evaluated numerically using the TD01AHF routine of the NAG library for one-dimensional integral and the D01DAF routine of the same library for two-dimensional integrals. The numerical results are confirmed to be accurate to at least 8 significant digits when compared with the analytical calculation for some function that the analytical solution is available.

The wavefunction is truncated after a_4 for λ part and b_7 for μ part, as defined in (11). The inclusion of the more terms does not affect the accuracy of the electronic energy in the first 8 significant digits. $R = 1.4632a_0$ for all calculations presented in this paper.

3 Results and discussion

Tables 2 and 3 list the electronic energy for the ground

Table 2 The ground state energy for HeH^+ molecular ion calculated with two different types of wavefunctions. The wavefunction is constructed out of the exact solution for the HeH^{++} problem. Note that there are no variational parameters in the calculations

Parameters ^{a)}	$\Psi_{\text{HeH}^+}^I(1,2)$	$\Psi_{\text{HeH}^+}^{II}(1,2)$	
		$\Psi_{\text{HeH}^{++},1s\sigma}$	$\Psi_{\text{HeH}^{++},2p\sigma}$
N	2.02611147	1.00000000	1.00000000
Z_a^*	2.00000000	2.00000000	2.00000000
Z_b^*	1.00000000	1.00000000	1.00000000
α	1.70440901	1.70440901	1.21922754
a_0	1.00000000	1.00000000	1.00000000
a_1	0.01015796	0.01015796	0.11891186
a_2	0.00026121	0.00026121	0.00033503
a_3	0.00002220	0.00002220	0.00001851
a_4	0.00000311	0.00000311	0.00000219
b_1	0.78734871	0.78734871	2.20691957
b_2	0.41592151	0.41592151	1.14183549
b_3	0.16903326	0.16903326	0.38509497
b_4	0.05582834	0.05582834	0.09898837
b_5	0.01551570	0.01551570	0.02074046
b_6	0.00371927	0.00371927	0.00368141
b_7	0.00078337	0.00078337	0.00056787
$2\langle H(1) \rangle$	-5.32698004	-5.32015599	
$\langle 1/r_{12} \rangle$	1.00702602	0.99364800	
E	-2.95308688	-2.95964085	

a) Matrix elements and energy in hartree unit.

Table 3 The ground state energy for HeH^+ molecular ion calculated with two different types of wavefunctions. The wavefunction is constructed out of the exact solution for the HeH^{++} problem. The only variational parameters here are the nuclear charges Z_a^* and Z_b^* , and all other parameters are calculated by solving the HeH^{++} eigenvalue problem for the variationally best effective charges

Parameters ^{a)}	$\Psi_{\text{HeH}^+}^I(1,2)$	$\Psi_{\text{HeH}^+}^{II}(1,2)$	
		$\Psi_{\text{HeH}^{++},1s\sigma}$	$\Psi_{\text{HeH}^{++},2p\sigma}$
N	2.03523068	1.00000000	1.00000000
Z_a^*	1.89079000	1.89202000	1.89202000
Z_b^*	1.08161800	1.10519000	1.10519000
α	1.65907615	1.66593703	1.23659210
a_0	1.00000000	1.00000000	1.00000000
a_1	0.01217866	0.01258354	0.10881554
a_2	0.00030006	0.00030449	0.00038873
a_3	0.00002533	0.00002549	0.00002217
a_4	0.00000357	0.00000357	0.00000266
b_0	1.00000000	1.00000000	1.00000000
b_1	0.90223336	0.92510029	2.31292298
b_2	0.49592865	0.51480773	1.29526193
b_3	0.20433645	0.21405043	0.46272619
b_4	0.06760165	0.07135789	0.12463027
b_5	0.01869091	0.01986454	0.02718471
b_6	0.00443795	0.00474649	0.00500167
b_7	0.00092315	0.00099324	0.00079727
$2\langle H(1) \rangle$	-5.27332706	-5.26320548	
$\langle 1/r_{12} \rangle$	0.94005861	0.92248966	
E	-2.96640131	-2.97384868	

a) Matrix elements and energy in hartree unit.

state for HeH^+ molecular ion obtained with different approximations respectively. In Table 2, there are no any variational parameters in the calculations, whereas in Table 3 only the effective nuclear charges Z_a^* and Z_b^* are allowed to be adjusted. Using the simple single term wavefunction $\Psi_{\text{HeH}^+}^I$ excluding any variational parameters, the ground state electronic energy -2.95308688 hartree yields. The result can be further improved by some physically meaningful approaches, for example, by adjusting effective nuclear charges and performing the configuration interaction (CI) calculation.

The CI can be effectively dealt with since each configuration is constructed with exact two-center orbital. In this work, a double excited state mixed with the ground state, as shown in eq. (3), is applied. The CI calculation raises the kinetic energy but lowers the electronic repulsive energy. As shown in Table 3, the kinetic energy increases by 0.006824 hartree whereas the electronic repulsive energy increases by 0.01337802 hartree. The total energy for the electronic ground state shifts 0.00655397 hartree after CI calculation. Similarly, the consideration of CI effect in the calculations of Table 3 drops the energy down by 0.00744737 hartree. To achieve a better accuracy, more excited state is required to be included in the computation.

The Hylleraas correlation factor has a general form of $(1 + kr_{12})$. The choice of $k = 1/2$ is based on the analysis of asymptotic behavior of the exact two-particle wavefunction at small distance and was discussed in detail in ref. [1]. Here we would like to point out that this choice generates a accurate ground state energy for HeH^+ molecular ion. This can be justified by a comparison of energy variations with Z_a^* between $k = 1/2$ and that obtained by minimizing Hamiltonian matrix element, as shown in Figure 3, where the energy variation for $k = 0$ is also presented. Excluding the correlation function, the minimum energy for the electronic ground state is found to be $E = -2.91905091$ hartree at $Z_a^* = 1.7250$. The introduction of correlation factor $(1 + 0.5r_{12})$ shifts this energy to -2.96478925 hartree at $Z_a^* = 1.89079$. More interestingly, this modification of the two-center orbitals makes the effective nuclear charge at atom He for the minimum ground state energy very close to its formal value, 2. The optimization of k results in a minimum energy of -2.96744570 hartree at $Z_a^* = 1.8580$. Therefore, both the

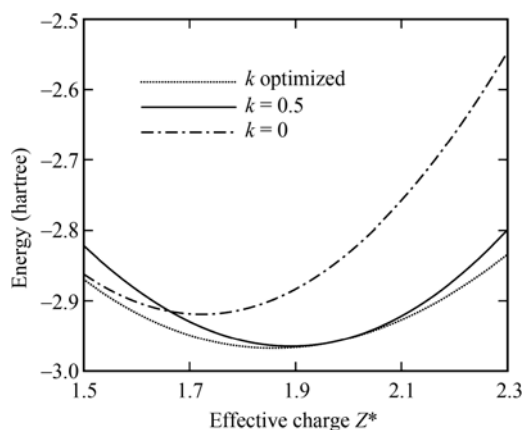


Figure 3 Energy minimization with respect to Z_a^* for three different values of k for the electronic ground state of HeH^+ molecular ion.

minimum energy and the effective nuclear charge are slightly different from those obtained by fixed k (at $1/2$) and optimized k . Although when the Z_a^* is away from the value at the energy well, regardless of being greater or less, the optimized k produces the slightly lower ground state energy, which breaks the interelectronic cusp condition. The same arguments are applicable to the energy minimization calculations with respect to Z_b^* for different k .

One of the other approaches to minimize the electronic energy for the ground state is to allow some of the coefficients a_i or b_i to be adjusted. However, the more variational parameters are involved in the calculation, and the less physical meaning of wavefunction maintains. This is in fact similar to James-Coolidge's approach in which the coefficient for each term of function is variational parameter. It has been demonstrated^[1] that the various terms in the James-Coolidge function are closely related to the two-center orbitals when the $A(\lambda)$ part of the solution for the Schrödinger equation is expressed in terms of Laguerre functions.

The two-center correlated orbital model is also a promising approach for obtaining reliable electronic energy of the excited state for HeH^+ molecular ion. The difficulties in the calculation of the excited state energy, including proper treatment of the correlation interaction and electronic polarization^[15], are well handled in the present model. The correlation effect is described by a simple function of r_{12} without any variational parameter involved and the solution for the electronic polarization is included in two-center orbital as the Schrödinger equation for HeH^{++} describes the effect of two nuclei on the electron exactly. The effectiveness of treating the CI

helps to obtain more accurate energy. In addition, as shown for H_2 molecule^[1], constructing the electronic excited state wavefunction is straightforward in terms of two-center correlated orbitals. In addition, the characters of the two-center correlated orbitals described above make the present approximation suitable for studying the potentials of both the electronic ground and the excited state for HeH^+ molecular ion at long range and intermediate internuclear distances. This will be reported in a future publication.

Finally, we would like to state that the two-center orbitals obtained by solving the Schrödinger equation for two-center problem in prolate-spheroidal coordinates can be used to describe systems numerically with more than two electrons if electron correlations can be included directly, for example, in Monte Carlo simulations^[13]. In this case, excellent results can be obtained with very compact wave function, as in the two-electron cases. It is a challenge to use the two-center orbitals for molecules with more than two nuclei. Recent progress in numerical calculations of the overlap and the kinetic integrals for the numerical atomic orbitals in the prolate spheroidal coordinates^[16] might shed light on the application of the two-center orbitals to multiple-nuclei systems. Moreover, one-electron, and many-center orbitals, which in concept are similar to the two-center orbitals, have been obtained analytically by Shibuya and Wulfman in terms of integral equations on the unit hypersphere of the 4-dimensional momentum space^[17]. There seems to be abundant room for the exploitation of these orbitals in molecular physics computation in future.

4 Conclusions

The two-center correlated orbital approach is successfully applied to the calculation of the ground state electronic energy for the heteronuclear molecular ion, HeH^+ . A simple single wavefunction yields a good accurate electronic energy for the ground state. The result can be further improved by including CI and adjusting effective nuclear charges. The CI can be effectively treated with a simple two-configuration-state wavefunction. The effectiveness for CI calculation, the simple form for the correlation function, and the exact description of the electronic polarization of two nuclear charges to the electron make the two-center correlated orbital model into a promising approach to study the potential energy curves of both the electronic ground and excited state for HeH^+ .

molecular ion at long range and intermediate internuclear distances.

Appendix A: The derivation of kinetic energy integral

The general form for the kinetic energy integral is

$$\langle \Psi_a | r_{12}^l \nabla_j^2 r_{12}^{l'} | \Psi_b \rangle = \langle \Psi_{\sigma_1} \Psi_{\sigma_2} | r_{12}^l \nabla_j^2 r_{12}^{l'} | \Psi_{\sigma_1} \Psi_{\sigma_2} \rangle, \quad j=1,2 \quad (32)$$

where $\Psi_{\sigma_i} = \Psi_{\text{HeH}^{++}, \sigma}(i)$ is the exact solution of the Schrödinger equation for HeH^{++} problem. Using the identities

$$\nabla_1 r_{12}^{l'} = \frac{d}{dr_{12}} r_{12}^{l'} \hat{\mathbf{r}}_{12} = l' r_{12}^{l'-1} \hat{\mathbf{r}}_{12} = l' r_{12}^{l'-2} \hat{\mathbf{r}}_{12} \quad (33)$$

$$\nabla_j^2 r_{12}^{l'} = \frac{1}{r_{12}^2} \frac{d}{dr_{12}} r_{12}^2 \frac{d}{dr_{12}} r_{12}^{l'} = l'(l'+1) r_{12}^{l'-2} \quad (34)$$

we can rewrite the integral as

$$\begin{aligned} \langle \Psi_a | r_{12}^l \nabla_j^2 r_{12}^{l'} | \Psi_b \rangle &= l'(l'+1) \langle \Psi_a | r_{12}^{l+l'-2} | \Psi_b \rangle \\ &+ l' \langle \Psi_a | r_{12}^{l+l'-2} \mathbf{r}_{12} \cdot \nabla_j | \Psi_b \rangle + \langle \Psi_a | r_{12}^{l+l'} \cdot \nabla_j^2 | \Psi_b \rangle \end{aligned} \quad (35)$$

Following the similar arguments and also using the Green theorem, we can have

$$\begin{aligned} \langle \Psi_a | \nabla_j^2 r_{12}^{l+l'} | \Psi_b \rangle &= \langle \nabla_j^2 \Psi_a | r_{12}^{l+l'} | \Psi_b \rangle \\ &= (l+l')(l+l'+1) \langle \Psi_a | r_{12}^{l+l'-2} | \Psi_b \rangle \\ &+ (l+l') \langle \Psi_a | r_{12}^{l+l'-2} \mathbf{r}_{12} \cdot \nabla_j | \Psi_b \rangle \\ &+ \langle \Psi_a | r_{12}^{l+l'} \nabla_j^2 | \Psi_b \rangle \end{aligned} \quad (36)$$

Inserting eq. (36) into eq. (35), we obtain eq. (28).

Appendix B: Calculations of two-center and two-electron integrals

In Prolate-Spheroidal coordinates, the volume element is given by

$$dV = \left(\frac{R}{2}\right)^3 (\lambda^2 - \mu^2) d\lambda d\mu d\phi \quad (37)$$

$$\begin{aligned} \left(\frac{R}{2}\right) \nabla_j^2 dV &= \left\{ \frac{\partial}{\partial \lambda_j} \left[(\lambda_j^2 - 1) \frac{\partial}{\partial \lambda_j} \right] \right. \\ &\left. + \frac{\partial}{\partial \mu_j} \left[(1 - \mu_j^2) \frac{\partial}{\partial \mu_j} \right] \right\} d\lambda d\mu d\phi \end{aligned}$$

$$= [\hat{P}(\lambda_j) - \hat{P}(\mu_j)] d\lambda d\mu d\phi \quad (38)$$

where

$$\hat{P}(x) = \frac{\partial}{\partial x} \left[(x^2 - 1) \frac{\partial}{\partial x} \right] \quad (39)$$

The integrand can be written as

$$\begin{aligned} \left(\frac{R}{2}\right) \nabla_j^2 \Psi_{\sigma_j} dV &= [\hat{P}(\lambda_j) - \hat{P}(\mu_j)] \Psi_{\sigma_j} d\lambda d\mu d\phi \\ &= [\Lambda'(\lambda) M(\mu) e^{im\phi} + \Lambda(\lambda) M'(\mu) e^{im\phi}] d\lambda d\mu d\phi \\ &= [\Psi'_{\sigma_j} + \Psi''_{\sigma_j}] d\lambda d\mu d\phi \end{aligned} \quad (40)$$

where

$$\begin{aligned} \Lambda'(\lambda) &= \hat{P}(\lambda_j) \Lambda(\lambda), \quad M'(\mu) = \hat{P}(\mu_j) M(\mu), \\ \Psi'_{\sigma_j} &= \Lambda'(\lambda) M(\mu) e^{im\phi}, \quad \Psi''_{\sigma_j} = \Lambda(\lambda) M'(\mu) e^{im\phi} \end{aligned} \quad (41)$$

The general form of two-center and two-electron integrals is,

$$\langle \Psi_{\sigma_1} \Psi_{\sigma_2} | r_{12}^k | \Psi'_{\sigma_1} \Psi'_{\sigma_2} \rangle, \quad k = -1, 0, 1, 2 \quad (42)$$

or

$$\langle \Psi_{\sigma_1} \Psi_{\sigma_2} | r_{12}^k | \Psi''_{\sigma_1} \Psi''_{\sigma_2} \rangle \quad (43)$$

or a similar form. In these integrals, Ψ'_{σ_i} and Ψ''_{σ_i} are no longer the exact solution of Schrödinger equation for HeH^{++} problem, but they have the similar form to Ψ_{σ_i} , as shown by eq. (41). In the following discussion, we drop off the ' and ' for convenience.

r_{12}^{-1} is expressed by the Neumann expansion:

$$\begin{aligned} r_{12}^{-1} &= \frac{2}{R} \sum_{n=0}^{\infty} \sum_{m=-n}^n h_{nm} P_l^{(m)}(\lambda_{<}) Q_l^{(m)}(\lambda_{>}) P_l^{(m)}(\mu_1) \\ &\cdot P_l^{(m)}(\mu_2) e^{im(\phi_1 - \phi_2)} \end{aligned} \quad (44)$$

where

$$h_{nm} = (-1)^m (2n+1) \left(\frac{(n-|m|)!}{(n+|m|)!} \right)^2 \quad (45)$$

and $Q_l^{(m)}(\lambda)$ is the associated Legendre function of the second kind, and $\lambda_{<}$ and $\lambda_{>}$ are smaller λ and greater λ respectively.

Let's consider the integral $\langle \Psi_{\sigma_1} \Psi_{\sigma_2} | r_{12}^{-1} | \Psi_{\sigma_1} \Psi_{\sigma_2} \rangle$,

$$\begin{aligned}
& \left\langle \Psi_{\sigma_1 \sigma_2} \left| r_{12}^{-1} \right| \Psi_{\sigma_1 \sigma_2} \right\rangle \\
&= \left\langle \Psi_{\sigma_1 \sigma_2} \left| \frac{2}{R} \sum_{n=0}^{\infty} \sum_{m=-n}^n h_{nm} P_n^{(m)}(\lambda_{<}) Q_n^{(m)}(\lambda_{>}) P_n^{(m)}(\mu_1) \right. \right. \\
&\quad \left. \left. P_n^{(m)}(\mu_2) e^{im(\phi_1 - \phi_2)} \right| \Psi_{\sigma_1 \sigma_2} \right\rangle \\
&= \frac{2}{R} \sum_{n=0}^{\infty} \sum_{m=-n}^n h_{nm} \left\langle \Psi_{\sigma_1 \sigma_2} \left| P_n^{(m)}(\lambda_{<}) Q_n^{(m)}(\lambda_{>}) P_n^{(m)}(\mu_1) \right. \right. \\
&\quad \left. \left. P_n^{(m)}(\mu_2) e^{im(\phi_1 - \phi_2)} \right| \Psi_{\sigma_1 \sigma_2} \right\rangle \quad (46)
\end{aligned}$$

The summation over m can be very much restricted by considering the forms of the wavefunctions. For the ground state, for example, no ϕ function is involved and we can rewrite eq. (46) as:

$$\begin{aligned}
& \left\langle \Psi_{\sigma_1 \sigma_2} \left| r_{12}^{-1} \right| \Psi_{\sigma_1 \sigma_2} \right\rangle \\
&= \frac{2}{R} \sum_{n=0}^{\infty} \sum_{m=-n}^n h_{nm} \left\langle \Psi_{\sigma_1 \sigma_2} \left| P_n^{(m)}(\lambda_{<}) Q_n^{(m)}(\lambda_{>}) \right. \right. \\
&\quad \left. \left. P_n^{(m)}(\mu_1) P_n^{(m)}(\mu_2) \right| \Psi_{\sigma_1 \sigma_2} \right\rangle \left\langle e^{im(\phi_1 - \phi_2)} \right\rangle \\
&= \frac{2}{R} \sum_{n=0}^{\infty} h_{nm} \left\langle \Psi_{\sigma_1 \sigma_2} \left| P_n^{(m)}(\lambda_{<}) Q_n^{(m)}(\lambda_{>}) P_n^{(m)}(\mu_1) \right. \right. \\
&\quad \left. \left. P_n^{(m)}(\mu_2) \right| \Psi_{\sigma_1 \sigma_2} \right\rangle; m=0 \quad (47)
\end{aligned}$$

In obtaining eq. (47), the following integral is used.

$$\int_0^{2\pi} e^{im\phi} d\phi = 2\pi \delta(m, 0) \quad (48)$$

After inserting the function forms of eq. (6) or (40),

the integral on the right hand side of eq. (47) can then be evaluated by

$$\begin{aligned}
& \left\langle \Psi_{\sigma_1 \sigma_2} \left| P_n^{(m)}(\lambda_{<}) Q_n^{(m)}(\lambda_{>}) P_n^{(m)}(\mu_1) P_n^{(m)}(\mu_2) \right| \Psi_{\sigma_1 \sigma_2} \right\rangle \quad (49) \\
&= \int_0^\infty \int_0^\infty \int_{-1}^1 \int_{-1}^1 d\mu_1 d\mu_2 d\lambda_1 d\lambda_2 \{ \Lambda(\lambda_1) M(\mu_1) \Lambda(\lambda_2) M(\mu_2) \\
&\quad \times P_n^{(m)}(\lambda_{<}) Q_n^{(m)}(\lambda_{>}) P_n^{(m)}(\mu_1) \\
&\quad \times P_n^{(m)}(\mu_2) \Lambda(\lambda_1) M(\mu_1) \Lambda(\lambda_2) M(\mu_2) \} \\
&= \left[\int_{-1}^1 d\mu_1 M^2(\mu_1) P_n^{(m)}(\mu_1) \right] \times \left[\int_{-1}^1 d\mu_2 M^2(\mu_2) P_n^{(m)}(\mu_2) \right] \\
&\quad \times \left[\int_0^{\lambda_1} \int_0^\infty d\lambda_1 d\lambda_2 \Lambda^2(\lambda_1) \Lambda^2(\lambda_2) P_n^{(m)}(\lambda_2) Q_n^{(m)}(\lambda_1) \right. \\
&\quad \left. + \int_{\lambda_1}^\infty \int_0^\infty \lambda_1 d\lambda_2 \Lambda^2(\lambda_1) \Lambda^2(\lambda_2) P_n^{(m)}(\lambda_1) Q_n^{(m)}(\lambda_2) \right] \\
&= \left[\int_{-1}^1 d\mu_1 M^2(\mu_1) P_n^{(m)}(\mu_1) \right] \times \left[\int_{-1}^1 d\mu_2 M^2(\mu_2) P_n^{(m)}(\mu_2) \right] \\
&\quad \times \left[\int_0^{\lambda_1} \int_0^\infty d\lambda_1 d\lambda_2 \Lambda^2(\lambda_1) \Lambda^2(\lambda_2) P_n^{(m)}(\lambda_2) Q_n^{(m)}(\lambda_1) \right. \\
&\quad \left. + \int_0^{\lambda_1} \int_0^\infty d\lambda_1 d\lambda_2 \Lambda^2(\lambda_1) \Lambda^2(\lambda_2) P_n^{(m)}(\lambda_2) Q_n^{(m)}(\lambda_1) \right]. \quad (50)
\end{aligned}$$

Here, we use the relation:

$$\begin{aligned}
& \int_{\lambda_1}^\infty \int_0^\infty \lambda_1 d\lambda_2 \Lambda^2(\lambda_1) \Lambda^2(\lambda_2) P_n^{(m)}(\lambda_1) Q_n^{(m)}(\lambda_2) \\
&= \int_0^{\lambda_1} \int_0^\infty \lambda_1 d\lambda_2 \Lambda^2(\lambda_1) \Lambda^2(\lambda_2) P_n^{(m)}(\lambda_2) Q_n^{(m)}(\lambda_1). \quad (51)
\end{aligned}$$

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