

Ground-state energy of HeH⁺

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The nonrelativistic ground-state energy of ⁴HeH⁺ is calculated using a variational method in Hylleraas coordinates. Convergence to a few parts in 10¹⁰ is achieved, which improves the best previous result of Pavanello *et al.* [J. Chem. Phys. **123**, 104306 (2005)]. Expectation values of the interparticle distances are evaluated. Similar results for ³HeH⁺ are also presented.

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The hydrogen-helium ion ⁴HeH⁺, a four-body Coulombic system consisting of (α^+ , p^+ , e^- , e^-), is an important molecule which has attracted a great deal of attention (see [1] and references therein). In a recent paper by Pavanello *et al.* [1], the pure vibrational spectrum of ⁴HeH⁺ was studied nonadiabatically, using a variational method in an explicitly correlated Gaussian basis. Very accurate vibrational energy levels up to $v=11$ have been determined. The characteristic of this type of calculation is to put all charged particles on the same footing without using the Born-Oppenheimer approximation. The vibrational modes are reflected by simply including higher powers of the internuclear distance in the basis set. This approach is exact in the sense that it solves the complete eigenvalue problem of a molecular Hamiltonian. The ground-state energy of ⁴HeH⁺ has been calculated by them to about nine-digit accuracy, which is the best result reported so far.

Recently we [2,3] performed high-precision nonadiabatic calculations on some three- and four-body molecular systems, such as hydrogen molecular ions and muonium hydride (MuH), using Hylleraas coordinates, which have been traditionally used in solving variational eigenvalue problems of few-body atomic systems. The purpose of this paper is to report the variational upper bounds for the ground-state energies of ⁴HeH⁺ and ³HeH⁺ calculated using Hylleraas coordinates. In this work, the following masses of the ³HeH⁺ nucleus, the ⁴HeH⁺ nucleus, and the proton are adopted [4]:

$$m_{3\text{He}} = 5495.885\,269(11)m_e, \quad (1)$$

$$m_{4\text{He}} = 7294.299\,536\,3(32)m_e, \quad (2)$$

$$m_p = 1836.152\,672\,61(85)m_e, \quad (3)$$

where m_e is the electron mass. Atomic units (a.u.) are used throughout, where the unit of energy is $E_h = e^2/a_0$ and the unit of length is $a_0 = \hbar^2/(m_e e^2)$.

In order to transform a four-body Hamiltonian to an effective three-body one-center Hamiltonian, we first separate the center-of-mass motion out and then neglect its coordinate \mathbf{X} ; this is because the transformed Hamiltonian does not contain \mathbf{X} and thus \mathbf{X} can be ignored [3,5]. The resulting Hamiltonian, which describes the internal motion of HeH⁺, is

$$H = -\frac{1+m_{\text{He}}}{2m_{\text{He}}}(\nabla_1^2 + \nabla_2^2) - \frac{m_p + m_{\text{He}}}{2m_p m_{\text{He}}}\nabla_3^2 - \frac{1}{m_{\text{He}}}(\nabla_1 \cdot \nabla_2 + \nabla_2 \cdot \nabla_3 + \nabla_3 \cdot \nabla_1) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_{12}} - \frac{1}{r_{23}} - \frac{1}{r_{31}}, \quad (4)$$

where \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 are, respectively, the position vectors of the two electrons and the proton relative to the helium nucleus. This Hamiltonian (up to the mass polarization terms) can be thought of as one describing three “effective particles” moving relative to the heaviest particle, the helium nucleus, located at the origin. This one-center effective three-body problem, however, is a two-center problem in nature due to the presence of the two heavy particles, the helium nucleus and the proton. It is, therefore, crucial to build the vibrational degrees of freedom into the trial wave function, according to the picture of the Born-Oppenheimer approximation. The simplest way to achieve this is to use a Gaussian-like function [2,6] $r_3^n e^{-br_3}$ in the basis set, where n is a large integer, as demonstrated by our previous work [2,3] for H₂⁺ and MuH, where for H₂⁺, for example, convergence up to 20 or even more [7] digits can generally be achieved for lower-lying vibrational energy eigenvalues. Thus, the basis set can be constructed in Hylleraas coordinates according to (for the case of nonrotational states)

$$r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \quad (5)$$

with $j_3 \geq j_{3\min}$. In the present work, we set $j_{3\min}$ to be 50 and 40 for ⁴HeH⁺ and ³HeH⁺, respectively. All terms in (5) are included such that for each given integer Ω not smaller than $j_{3\min}$,

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega, \quad (6)$$

except that terms with $j_1 > j_2$, as well as terms with $j_1 = j_2$ and $j_{23} > j_{31}$, are excluded in the basis set in order to avoid a near-linear dependence problem. We then divide this generated basis into several blocks each having its own set of nonlinear parameters α , β , and γ . The number of blocks N_B increases as Ω increases and is determined by $N_B = \Omega - j_{3\min} + 1$. The n th block includes all the terms satisfying the following relation for the powers $j_3^{(n)}$ of r_3 :

TABLE I. Convergence of the nonrelativistic ground-state energy of ${}^4\text{HeH}^+$. N denotes the number of terms in the basis set and $R(\Omega)$ is the ratio of two successive differences in energy. Units are atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$
54	120	-2.970 842 869 11	
55	256	-2.971 050 388 65	
56	502	-2.971 074 362 87	8.65
57	918	-2.971 077 848 85	6.87
58	1589	-2.971 078 352 12	6.92
59	2625	-2.971 078 451 37	5.07
60	4172	-2.971 078 467 40	6.19
61	6412	-2.971 078 469 41	7.97
62	9576	-2.971 078 469 56	13.3
∞		-2.971 078 469 8(3)	
[1]		-2.971 078 459 4	

$$g_1 \leq j_3^{(1)} \leq g_2,$$

$$g_n < j_3^{(n)} \leq g_{n+1}, \quad n = 2, \dots, N_B, \quad (7)$$

with

$$g_n = \text{int} \left(j_{3\text{min}} + \frac{\Omega - j_{3\text{min}}}{N_B} (n - 1) \right), \quad (8)$$

where $\text{int}(x)$ stands for the integer part of x . Thus, the largest powers of r_1 , r_2 , and r_3 for the case of $\Omega=61$ are 5, 11, and 61, respectively. An optimization is performed with respect to N_B sets of nonlinear parameters by minimizing the energy eigenvalues. This involves the calculation of first- and second-order energy derivatives ($\partial E/\partial\alpha$) and ($\partial^2 E/\partial\alpha^2$) with respect to each nonlinear parameter, where ($\partial E/\partial\alpha$) can be evaluated analytically [8], whereas ($\partial^2 E/\partial\alpha^2$) can be estimated by finite differencing from two successive calculations.

TABLE II. Nonlinear parameters for the case of $\Omega=61$ of ${}^4\text{HeH}^+$.

Block index	α	β	γ
1	1.691650	1.691772	35.201599
2	2.615784	2.615784	37.004028
3	2.241943	2.011841	33.162048
4	1.345886	2.249329	33.757141
5	1.247131	2.334534	31.948730
6	1.882263	1.881531	40.661499
7	6.298279	7.614990	37.792725
8	3.602844	7.109436	38.398987
9	2.225769	8.284851	38.678406
10	2.091675	4.064331	39.077576
11	2.072937	4.073364	39.076477
12	2.083435	4.075256	39.075806

TABLE III. Expectation values of various powers of the inter-particle distances for ${}^4\text{HeH}^+$ and ${}^3\text{HeH}^+$. Units are atomic units.

Quantity	${}^4\text{HeH}^+$	${}^3\text{HeH}^+$
$\langle r_1^{-2} \rangle$	5.836 880(2)	5.836 212 (1)
$\langle r_1^{-1} \rangle$	1.660 181 99(1)	1.660 046 280 (2)
$\langle r_1 \rangle$	0.935 568 7(2)	0.935 741 95(1)
[1]	0.935 6	
$\langle r_1^2 \rangle$	1.180 895 5(5)	1.181 482 04(2)
[1]	1.180 9	
$\langle r_3^{-2} \rangle$	0.448 599 4(3)	0.448 016 23(1)
$\langle r_3^{-1} \rangle$	0.666 113 0(2)	0.665 560 53(1)
$\langle r_3 \rangle$	1.517 663 0(2)	1.519 458 65(2)
[1]	1.517 7	
$\langle r_3^2 \rangle$	2.328 282 6(7)	2.334 605 7(1)
[1]	2.328 3	
$\langle r_{12}^{-1} \rangle$	0.940 704 3(2)	0.940 558 61(2)
$\langle r_{12} \rangle$	1.405 160 2(2)	1.405 481 456(1)
[1]	1.405 2	
$\langle r_{12}^2 \rangle$	2.410 698 (3)	2.411 957 5(1)
[1]	2.410 7	
$\langle r_{23}^{-1} \rangle$	0.787 179 5(5)	0.786 472 727 (1)
$\langle r_{23} \rangle$	1.561 943 9(2)	1.563 608 88(2)
[1]	1.561 9	
$\langle r_{23}^2 \rangle$	2.777 494 (4)	2.783 673 6(1)
[1]	2.777 5	

The basic integrals that appear in our calculation are of the form

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \times Y_{\ell_1 m_1}^*(\mathbf{r}_1) Y_{\ell_2 m_2}^*(\mathbf{r}_2) Y_{\ell_3 m_3}^*(\mathbf{r}_3) Y_{\ell_1 m_1}(\mathbf{r}_1) \times Y_{\ell_2 m_2}(\mathbf{r}_2) Y_{\ell_3 m_3}(\mathbf{r}_3) \quad (9)$$

with $j_{12} \geq -1$, etc. Computational details, together with the reduction of Hamiltonian matrix elements into the basic integrals, may be found in [9]. Table I lists a convergence study for the ground-state energy of ${}^4\text{HeH}^+$, as the size of the basis set increases. In the table, $R(\Omega)$ is defined by

$$R(\Omega) = \frac{E(\Omega - 2) - E(\Omega - 1)}{E(\Omega - 1) - E(\Omega)}, \quad (10)$$

which can be used to monitor the rate of convergence and to extrapolate the energy eigenvalue to $\Omega \rightarrow \infty$. The uncertainty is taken to be $E(62) - E(\infty)$. The extrapolated value of the energy is therefore estimated to be accurate at the level of 1 part in 10^{10} , a factor of 30 improvement over the previous result of Pavanello *et al.* [1]. A similar calculation was also performed for ${}^3\text{HeH}^+$ with the calculated ground-state energy being $-2.970 725 444 1(2)$ a.u. Table II lists all the nonlinear parameters for the case of $\Omega=61$ of ${}^4\text{HeH}^+$. However, a full optimization of nonlinear parameters would be extremely

time consuming for larger basis sets. Table III presents expectation values of various powers of the interparticle distances for $^4\text{HeH}^+$ and $^3\text{HeH}^+$ together with the results of Pavanello *et al.* [1]. Their results are in perfect agreement with ours to the last digits of their values.

In summary, the ground-state energies of $^4\text{HeH}^+$ and $^3\text{HeH}^+$ have been calculated to higher precision nonadiabatically using one-center atomic approach with appropriate

building-in of vibrational modes. It would be interesting to explore higher vibrational and rotational excited states.

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