PHYSICAL REVIEW A **90**, 032516 (2014)

Variational energy bounds for the hydrogen molecular ion

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(Received 14 April 2014; published 30 September 2014)

We report a high-precision calculation for the hydrogen molecular ion H_2^+ by using a variational method in Hylleraas coordinates. The calculated nonrelativistic ground-state energy is accurate to 2 parts in 10^{34}, which represents a more than 3 orders of magnitude improvement over the best previous value of Hijikata *et al.* [J. Chem. Phys. **130**, 024102 (2009)]. For the first excited states of S and P symmetries, the achieved precision is about 2 parts in 10^{31} and 3 parts in 10^{29}, respectively. Comparison with other calculations are made.

DOI: 10.1103/PhysRevA.90.032516 PACS number(s): 31.15.ac, 31.15.xt

I. INTRODUCTION

The hydrogen molecular ion H_2^+ is the simplest stable molecule which is versatile in physical, chemical, and astrophysical environments. In recent years, significant advances have been made in the studies of the hydrogen molecular ion and its isotopes, both theoretically [1,2] and experimentally [3–5], with a purpose of determining the proton-electron mass ratio, or the mass ratios between different nuclei [6]. Such an idea comes from the scaling relationships between transition frequencies and mass ratios embodied in fundamental vibrational and rotational transitions, such as $\nu_{\text{vib}} \sim \sqrt{m_e/\mu}\, R_\infty c$ and $\nu_{\text{rot}} \sim (m_e/\mu) R_\infty c$, where μ denotes the reduced mass of the two nuclei and R_∞ is the Rydberg constant.

In the past several decades, we have witnessed progressive improvement of precision for nonrelativistic energies of H_2^+ performed by many authors. Figure 1 shows selected values for the nonrelativistic ground-state energy determined over the past 40 years. In 2000, Korobov [7] performed a variational calculation and achieved a precision of 18 significant digits. Two years later, this precision was improved by two orders of magnitude by Bailey and Frolov [8], using an exponential variational basis set in perimetric coordinates. In 2004, Cassar and Drake [9] obtained improved eigenvalues for the ground and some low-lying excited states. Based on an earlier work of Yan *et al.* [10], Li *et al.* [11] in 2007 further improved the Cassar and Drake's values, in which the ground-state energy was improved by about 8 orders of magnitude. In the calculations of Yan *et al.* [10] and Li *et al.* [11], the Hylleraas coordinates were used containing only two nonlinear parameters in the exponential function:

$$r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2) Y_{LM}^{\ell_1 \ell_2}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2). \tag{1}$$

In the above, one proton is set to be at the origin, $\mathbf{r}_1$ is then the position vector of the electron and $\mathbf{r}_2$ is the position vector of the other proton. In order to simulate the vibrational modes of the two nuclei, $j \geqslant 35$ and $\beta \sim 15-20$, as first suggested by Bhatia and Drachman [12]. To accelerate the rate of convergence, the base set was divided into eight blocks each having different α and β. Optimization was performed for all nonlinear parameters.

Up to now, the most precise calculation on H_2^+ has been from the work of Hijikata *et al.* in 2009 [13], using the free iterative complement interaction method. This method is based on the idea that the exact wave function can be obtained by a function of the Hamiltonian $f(H)$ operating on some function ψ_0,

$$\psi_{\text{exact}} = f(H)\psi_0. \tag{2}$$

When this is applied to a scaled Schrödinger equation, a manageable iteration procedure can be formed:

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n, \tag{3}$$

where g is introduced to suppress the singularity that is intrinsic to the Coulomb systems. For the ground state, the energy eigenvalue was determined by them at the level of 4 parts in 10^{31}.

The purpose of this paper is to report new variational energy upper bounds for the ground state $1\,^1S$ and the two lowest excited states $2\,^1S$ and $2\,^3P$ of H_2^+, using the approach of Cassar and Drake [9]. Our calculations have significantly improved the best previous results of Li *et al.* [11] and Hijikata *et al.* [13]. Atomic units are used throughout.

II. COMPUTATIONAL METHOD

In the center of mass frame, setting the position of the electron at the origin of the coordinate system, the Hamiltonian of H_2^+ can be written as

$$H = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{m_p}{1+m_p}\nabla_{r_1}\cdot\nabla_{r_2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}, \tag{4}$$

where m_p is the mass of the proton, r_1 and r_2 are, respectively, the positions of the two protons relative to the origin, and r_{12} is the distance between the two protons. For an S state where the total angular momentum of the system is zero, the wave function can be expanded in a doubled base set, according to Cassar and Drake [9]:

$$\Psi^S(\mathbf{r_1},\mathbf{r_2}) = \sum_{p=1}^{2} \sum_{i,j=0}^{i+j\leqslant\Omega} \sum_{k=\Omega_{\text{low}}}^{\Omega_{\text{high}}} a_{ijk}^{(p)} r_1^i r_2^j r_{12}^k \times \exp\left(-\alpha^{(p)} r_1 - \beta^{(p)} r_2 - \gamma^{(p)} r_{12}\right) \pm (1 \leftrightarrow 2), \tag{5}$$

with

$$\begin{aligned} \Omega_{\text{low}} &= N_p - \Omega + (i+j), \\ \Omega_{\text{high}} &= N_p + \Omega - (i+j). \end{aligned} \tag{6}$$

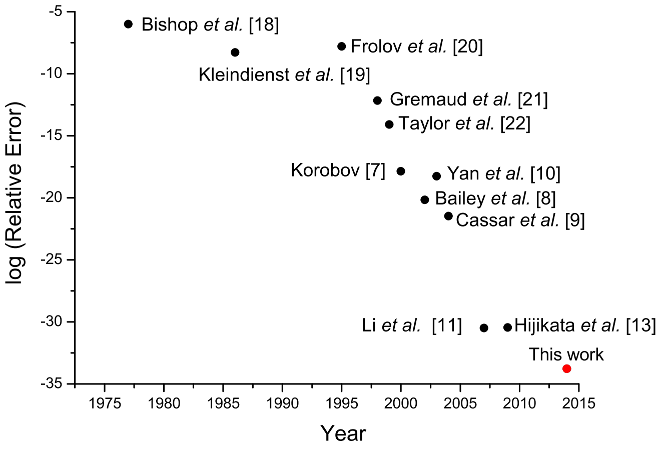

FIG. 1. (Color online) Progress of theoretical calculations of the ground-state energy of H_2^+.

Here N_p was used to optimize the scope of the base set in Ref. [9]. In this work, however, since the base set can be very large, we fix the value of N_p to be 37. We only adjust Ω to control the size of the base set.

Compared with Eq. (1), Eq. (5) contains one more exponential term, which gives rise to some difference in computing matrix elements of the Hamiltonian. The basis in Eq. (5) is more powerful in enhancing the rate of convergence. On the other hand, it is more likely to cause the problem of near linear dependence when the size of the basis set becomes large. In our construction of the basis set certain truncations are applied to reduce near linear dependence, according to Kono and Hattori [14]. As suggested by Bhatia and Drachman [12], the nonlinear parameter $\gamma^{(p)}$ is chosen to be about 10 times bigger than $\alpha^{(p)}$ and $\beta^{(p)}$.

For states with the total angular momentum $L > 0$, we need to introduce the angular coupling part of the two protons $(\ell_1,\ell_2;LM)$, defined below, into our basis set [15]:

$$(\ell_1,\ell_2;LM) = r_1^{\ell_1} r_2^{\ell_2} \sum_{m_1 m_2} \langle \ell_1 \ell_2 m_1 m_2 | LM\rangle Y_{\ell_1}^{m_1}(\hat{\mathbf{r}}_1) Y_{\ell_2}^{m_2}(\hat{\mathbf{r}}_2). \tag{7}$$

For a given L, the coupling terms necessary for forming a complete basis set are

$$(0,L;LM),(1,L-1;LM),\ldots,([L/2],L-[L/2];LM), \tag{8}$$

where $[x]$ denotes the integer part of x. To achieve a better convergence, an optimization for the nonlinear parameters $\alpha^{(p)}$, $\beta^{(p)}$, and $\gamma^{(p)}$ was done using Newton's method. The first-order derivative of energy with respect to $\alpha^{(p)}$, for example, can be calculated using the following analytical formula:

$$\frac{\partial E}{\partial \alpha^{(p)}} = -2\frac{\langle \Psi|(H-E)r_1|\Psi^{(p)}\rangle}{\langle \Psi|\Psi\rangle}, \tag{9}$$

where $\Psi^{(p)}$ denotes the part of the wave function containing explicitly $\alpha^{(p)}$. Table I lists all optimized values for the nonlinear parameters used for the largest sizes of basis sets in this work. In order to maintain numerical stability, especially for large sizes of basis sets, the standard 32-digit quadruple precision arithmetic, and even the 64-digit multiple precision arithmetic QD developed by Bailey [16], were employed. We also parallelized our codes using the message passing interface (MPI) .

III. RESULTS AND DISCUSSION

Our results are presented in Tables II–IV. For the sake of consistency in comparison, the 1986 CODATA [17] value of the proton-electron mass ratio of $m_p/m_e = 1836.152\,701$, which has been used in many recent calculations, was adopted. In these tables, the ratio $R(\Omega)$ is defined by

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

which may be considered as a measure for the rate of convergence. The extrapolation to $\Omega \to \infty$ was done based on these ratios. Ideally, if $R(\Omega)$ were a constant, then the series would converge as a geometric series, to the value,

$$E(\Omega) = E(\Omega_{\max}) + \frac{E(\Omega_{\max}) - E(\Omega_{\max}-1)}{R-1}. \tag{11}$$

In practice, we can still get an extrapolated energy in the limit $\Omega \to \infty$ provided R varies smoothly enough with respect to Ω. The convergence study for the ground-state energy eigenvalue is listed in Table II. One can see that, as the size of the basis set increases progressively, the energy eigenvalue reaches a precision of 2 parts in 10^{34}. The extrapolated value was obtained by assuming that the ratio $R(\Omega)$ be 8 as $\Omega \to \infty$. Also in Table V, a comparison with some previous calculations is made. We can see that the result of Cassar and Drake [9] seems to converge in a wrong direction, after the 21st digit, which may imply the existence of numerical instability in their calculation for large basis sets. On the other hand, the results of Li *et al.* [11], Hijikata *et al.* [13], and the present work agree perfectly well with each other until the 29th decimal place. Although Hijikata *et al.* have claimed that their result for the ground state has 31 digits of precision (not including the digit 0 before the decimal point), a comparison with the present calculation shows that their value is only accurate up to the

TABLE I. Nonlinear parameters for the wave functions of $1\,^1S$, $2\,^1S$, and $2\,^3P$ states.

$1\,^1S$			$2\,^1S$			$2\,^3P$		
α	β	γ	α	β	γ	α	β	γ
1.931 417	4.773 601	15.567 74	4.306 412	3.261 670	15.581 84	1.324 138	0.556 385	18.830 92
0.213 388	0.953 530	19.426 45	0.308 493	1.109 355	19.887 26	2.484 564	2.615 623	20.109 25
						1.204 844	0.531 492	19.749 15

TABLE II. Nonrelativistic energy for the ground state of H_2^+.

Ω	No. of terms	$E(\Omega)$ (a.u.)	$R(\Omega)$
3	32	– 0.597 138 982 249 839 766 674 228 437 022 897	
4	58	– 0.597 139 062 095 593 487 466 938 942 979 182	
5	94	– 0.597 139 063 075 853 406 303 378 173 871 251	81.45
6	144	– 0.597 139 063 122 676 395 625 438 654 740 649	20.93
7	208	– 0.597 139 063 123 384 395 608 334 606 353 522	66.13
8	290	– 0.597 139 063 123 404 506 047 653 790 245 369	35.20
9	390	– 0.597 139 063 123 405 064 624 580 206 465 343	36.00
10	512	– 0.597 139 063 123 405 074 540 495 404 209 463	56.33
11	656	– 0.597 139 063 123 405 074 824 265 899 599 489	34.94
12	826	– 0.597 139 063 123 405 074 833 826 471 754 663	29.68
13	1022	– 0.597 139 063 123 405 074 834 129 700 384 551	31.52
14	1248	– 0.597 139 063 123 405 074 834 133 821 134 784 73	73.58
15	1504	– 0.597 139 063 123 405 074 834 134 092 642 376 75	15.17
16	1794	– 0.597 139 063 123 405 074 834 134 095 975 150 09	81.46
17	2118	– 0.597 139 063 123 405 074 834 134 096 025 192 00	66.59
18	2480	– 0.597 139 063 123 405 074 834 134 096 025 843 47	76.81
19	2880	– 0.597 139 063 123 405 074 834 134 096 026 176 93	1.95
20	3322	– 0.597 139 063 123 405 074 834 134 096 026 188 92	27.81
21	3806	– 0.597 139 063 123 405 074 834 134 096 026 189 87	12.64
∞		– 0.597 139 063 123 405 074 834 134 096 026 189 9(1)	

29th digit. Therefore, our result for the ground-state energy has improved the value of Hijikata *et al.* by more than 3 orders of magnitude, which now represents the most precise value for this state. As for the first excited state 2 ^1S, our calculation has improved the best previous value of Li *et al.* [11], which is accurate to 6 parts in 10^{28}, by a factor of 3×10^3. The corresponding value of Hijikata *et al.* [13], which is accurate to about 1 part in 10^{26}, is absent from the table for a direct comparison because they used a more recent mass ratio for this state. For 2 ^3P, the present calculation has improved over the best previous value of Li *et al.* [11] by a factor of 2.5×10^2 and over the second best previous value of Hijikata *et al.* [13] by a factor of 5×10^3. Table VI lists the energy eigenvalues of the 1 ^1S, 2 ^1S, and 2 ^3P states using the 2006 CODATA value for the proton-electron mass ratio $m_p/m_e = 1836.152\,672\,47$ [24], together with a comparison with the results of Hijikata *et al.* [13]. We can see that similar improvements have been achieved.

TABLE III. Nonrelativistic energy for 2 ^1S of H_2^+.

Ω	No. of terms	$E(\Omega)$ (a.u.)	$R(\Omega)$
2	16	– 0.587 111 463 446 186 724 988 214 552 952 1	
3	32	– 0.587 155 150 140 016 063 020 158 386 095 0	
4	58	– 0.587 155 588 439 363 271 394 698 468 988 3	99.67
5	94	– 0.587 155 678 508 313 535 260 517 739 136 6	4.86
6	144	– 0.587 155 679 195 915 604 532 422 557 689 4	130.9
7	208	– 0.587 155 679 212 345 249 044 607 148 490 5	41.85
8	290	– 0.587 155 679 212 728 577 388 514 285 008 1	42.86
9	390	– 0.587 155 679 212 746 497 897 440 649 300 5	21.39
10	512	– 0.587 155 679 212 746 804 597 179 270 865 2	58.43
11	656	– 0.587 155 679 212 746 812 105 379 714 192 4	40.84
12	826	– 0.587 155 679 212 746 812 208 888 525 788 0	72.53
13	1022	– 0.587 155 679 212 746 812 211 760 281 300 6	36.04
14	1248	– 0.587 155 679 212 746 812 211 876 394 450 9	24.73
15	1504	– 0.587 155 679 212 746 812 211 881 048 935 1	24.94
16	1794	– 0.587 155 679 212 746 812 211 881 185 064 5	34.19
17	2118	– 0.587 155 679 212 746 812 211 881 193 000 9	17.15
18	2480	– 0.587 155 679 212 746 812 211 881 193 129 9	61.54
19	2880	– 0.587 155 679 212 746 812 211 881 193 139 4	13.51
20	3322	– 0.587 155 679 212 746 812 211 881 193 140 2	11.28
∞		– 0.587 155 679 212 746 812 211 881 193 140 3(1)	

TABLE IV. Nonrelativistic energy for 2 ^3P of H_2^+.

Ω	No. of terms	$E(\Omega)$ (a.u.)	$R(\Omega)$
3	45	– 0.596 870 537 101 185 385 627 600 417 73	
4	84	– 0.596 873 730 141 682 760 071 190 192 29	
5	138	– 0.596 873 738 607 576 740 548 687 862 88	377.2
6	213	– 0.596 873 738 814 866 278 128 138 371 89	40.84
7	309	– 0.596 873 738 832 571 860 772 152 694 11	11.70
8	432	– 0.596 873 738 832 749 121 655 904 053 78	99.88
9	582	– 0.596 873 738 832 764 413 721 857 842 55	11.59
10	765	– 0.596 873 738 832 764 724 516 223 571 35	11.59
11	981	– 0.596 873 738 832 764 735 843 735 789 21	27.43
12	1236	– 0.596 873 738 832 764 735 918 838 265 11	150.8
13	1530	– 0.596 873 738 832 764 735 920 633 962 28	41.82
14	1869	– 0.596 873 738 832 764 735 920 735 564 15	17.67
15	2253	– 0.596 873 738 832 764 735 920 743 742 07	12.42
16	2688	– 0.596 873 738 832 764 735 920 744 875 46	7.21
17	3174	– 0.596 873 738 832 764 735 920 744 969 40	12.06
18	3717	– 0.596 873 738 832 764 735 920 744 983 96	6.45
19	4317	– 0.596 873 738 832 764 735 920 744 985 04	61.54
20	5706	– 0.596 873 738 832 764 735 920 744 985 09	19.22
∞		– 0.596 873 738 832 764 735 920 744 985 11(2)	

IV. CONCLUSION

In this work, we have developed a set of well-tested MPI Fortran codes incorporated with the multiprecision software QD to perform high-precision calculations of the nonrelativistic energy eigenvalues of the hydrogen molecular ion H_2^+ in some low-lying states. The established results for 1 ^1S, 2 ^1S, and 2 ^3P states can serve as a benchmark

TABLE V. Comparison of nonrelativistic energies of H_2^+ in the 1 ^1S, 2 ^1S, and 2 ^3P states.

Author (year)	Ref.	Energy (a.u.)
	1 ^1S	
Bishop and Cheung (1977)	[18]	– 0.597 138 460
Kleindienst and Hoppe (1986)	[19]	– 0.597 139 06(3)
Frolov and Smith Jr. (1995)	[20]	– 0.597 139 053 69
Grémaud *et al.*	[21]	– 0.597 139 063 123(1)
Taylor *et al.* (1999)	[22]	– 0.597 139 063 123 9(5)
Korobov (2000)	[7]	– 0.597 139 063 123 405 074
Hilico *et al.* (2000)	[23]	– 0.597 139 063 123 40(1)
Bailey and Frolov (2002)	[8]	– 0.597 139 063 123 405 074 83
Yan *et al.* (2003)	[10]	– 0.597 139 063 123 405 074 5(4)
Cassar and Drake (2004)	[9]	– 0.597 139 063 123 405 074 834 338(3)
Li *et al.* (2007)	[11]	– 0.597 139 063 123 405 074 834 134 096 026(5)
Hijikata *et al.* (2009)	[13]	– 0.597 139 063 123 405 074 834 134 096 025 974 142
This work		– 0.597 139 063 123 405 074 834 134 096 026 189 9(1)
	2 ^1S	
Taylor *et al.* (1999)	[22]	– 0.587 155 679 213 6(5)
Hilico *et al.* (2000)	[23]	– 0.587 155 679 212 75(1)
Cassar and Drake (2004)	[9]	– 0.587 155 679 212 746 812 212(2)
Li *et al.* (2007)	[11]	– 0.587 155 679 212 746 812 211 881 193 5(6)
This work		– 0.587 155 679 212 746 812 211 881 193 140 3(1)
	2 ^3P	
Taylor *et al.* (1999)	[22]	– 0.596 873 738 832 8(5)
Hilico *et al.* (2000)	[23]	– 0.596 873 738 83(1)
Yan *et al.* (2003)	[10]	– 0.596 873 738 832 764 733(1)
Cassar and Drake (2004)	[9]	– 0.596 873 738 832 764 734 96(5)
Li *et al.* (2007)	[11]	– 0.596 873 738 832 764 735 920 744 98(2)
Hijikata *et al.* (2009)	[13]	– 0.596 873 738 832 764 735 920 744 893
This work		– 0.596 873 738 832 764 735 920 744 985 11(2)

TABLE VI. The nonrelativistic energies of H_2^+ in the $1\,^1S$, $2\,^1S$, and $2\,^3P$ states, where $m_p/m_e = 1836.152\,672\,47$ [24] is used. The second entries for each state are the corresponding values from Hijikata *et al* [13].

State	Energy (a.u.)
$1\,^1S$	– 0.597 139 063 079 175 256 939 382 100 937 586 2(1)
	– 0.597 139 063 079 175 256 939 382 100 935 311
$2\,^1S$	– 0.587 155 679 095 614 799 300 630 047 602 2(1)
	– 0.587 155 679 095 614 799 300 630 460 069
$2\,^3P$	– 0.596 873 738 784 476 120 029 013 155 63(1)
	– 0.596 873 738 784 476 119 983

for other theoretical methods. The current method can in principle be applied to calculate other excited states with different ro-vibrational quantum numbers. Furthermore, the extension of the current work to other isotopomers of H_2^+ can readily be made, with some slight modifications of basis parameters.

ACKNOWLEDGMENTS

Research support from the Natural Sciences and Engineering Research Council of Canada and from the Canadian computing facilities of SHARCnet and ACEnet is gratefully acknowledged.

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