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Calculations of energies of the hydrogen molecular ion

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We report high precision calculations of nonrelativistic energies of the hydrogen molecular ion H_2^+ in some low-lying states, using a variational method in multiple Hylleraas basis sets. For the ground state, for example, the energy is established to an accuracy of 8 parts in 10^{30}, which represents 8 orders of magnitude improvement over the best previous value of Cassar and Drake [J. Phys. B **37**, 2485 (2004)]. Our calculations lay a firm foundation for studying higher-order relativistic and QED effects.

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I. INTRODUCTION

Recently the hydrogen molecular ion H_2^+ has been sympathetically cooled to mK temperatures with Be^+ by Schiller's group [1,2], which could lead to improved spectroscopic measurements by 4 orders of magnitude or more [1]. Since the two-photon transition energies between the lowest vibrational states of H_2^+, such as $(J,v)=(0,0)\rightarrow(0,1)$, are approximately scaled [3] as $(m_p/m_e)^{-1/2}$, where m_p and m_e are the proton and electron masses, respectively, it is therefore possible to derive an improved determination of the electron-proton mass ratio m_e/m_p, as first suggested by Nez *et al.* [4] a decade ago, provided that the high-order relativistic and QED corrections to the energy levels can be calculated to sufficiently high precision. The present CODATA value [5] for m_e/m_p is accurate to about 5 parts in 10^{10}. In order to obtain an improved value for m_e/m_p by one order of magnitude in precision, the theory and experiment must be accurate at least to a few parts in 10^{12} or better, according to $\delta E/E \sim (1/2)(\delta\epsilon/\epsilon)$, where $\epsilon=m_e/m_p$. In other words, the relativistic and QED corrections must at least be included up to order α^5 or even α^6 atomic units, which is a very challenging task. So far, only the lowest-order relativistic and QED effects of α^2 and α^3 atomic units have been calculated [6–8] for H_2^+ and HD^+. Since the variational principle is stationary with respect to the energies, not to the wave functions, it is therefore necessary to obtain the nonrelativistic energy eigenvalues at the level of a few parts in 10^{24} or better to ensure the desired accuracy in the wave functions.

Precision calculations for the nonrelativistic energies of H_2^+ have been performed by many authors in the past decade. Moss and co-workers [9–11] have done a series of nonadiabatic calculations for H_2^+ and its isotopomers in the frame of the traditional molecular physics method. A similar approach has also been used by Taylor *et al.* [12,13] in their calculations of energies and polarizabilities of H_2^+ and D_2^+. Using perimetric coordinates, Hilico and co-workers [3,14,15] calculated energies and many other properties for H_2^+, D_2^+, and HD^+. Another nonadiabatic approach includes the finite element method by Shertzer and Greene [16].

In addition to the above mentioned methods, there have been a number of high-precision works for H_2^+ reported recently using correlated Hylleraas coordinates. One approach [17,18] is to use the following basis set:

$$\exp(-\alpha r_{12} - \beta r_{23} - \gamma r_{31}), \tag{1}$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ is the distance between two particles and α, β, and γ are nonlinear parameters determined quasirandomly. This method has been applied to H_2^+, as well as other three-body Coulombic systems, and precise energy eigenvalues have been obtained.

The second approach, originally proposed by Bhatia and Drachman [19] and further developed by Yan *et al.* [20], is to apply the basis set

$$r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2), \tag{2}$$

where r_1 and r_2 are the distances of the electron and one proton relative to the second proton located at the origin of the reference frame. The vibrational modes of the system can be well represented by $r_2^j e^{-\beta r_2}$, where $j_2 \geqslant j_{\min}$ with $j_{\min}$ being a nonzero integer. For the ground state of H_2^+, for example, it is taken to be 35. This method has been employed to the energy calculations of many rotationally excited states of H_2^+ and its isotopomers [20,21] at the level of a few parts in 10^{17} to 10^{20}.

To date, the most accurate calculations for H_2^+ have been performed by Cassar and Drake [22] who employed the double basis set expansion in Hylleraas coordinates. Their trial wave function for an S state is given by

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{p=1}^{2}\sum_{i,j=0}^{\Omega_1}\sum_{k=\Omega_{\rm low}}^{\Omega_{\rm high}} a_{ijk}^{(p)} r_1^i r_2^j r_{12}^k \times\exp(-\alpha^{(p)}r_1-\beta^{(p)}r_2-\gamma^{(p)}r_{12}) \pm (\text{exchange}), \tag{3}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the two protons relative to the electron, and the exchange term is for the two protons. The ground state energy of H_2^+ has been calculated by them to an accuracy of a few parts in 10^{24}, about three

TABLE I. Convergence for the nonrelativistic energy of H_2^+ in the ground state $1\,^1S$. N denotes the number of terms in the basis set and $R(\Omega)$ is the ratio of two successive differences in energy. The proton-electron mass ratio m_p/m_e=1836.152 701 is used. In atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$
42	124	−0.597 138 953 453 237 785 045 976 830 389	
43	175	−0.597 139 053 111 307 839 929 434 959 843	
44	240	−0.597 139 062 528 105 695 808 532 422 882	10.58
45	321	−0.597 139 063 082 331 171 153 394 239 752	16.99
46	420	−0.597 139 063 120 045 448 702 148 121 141	14.69
47	539	−0.597 139 063 123 138 505 907 171 751 120	12.19
48	680	−0.597 139 063 123 387 781 203 768 459 892	12.40
49	845	−0.597 139 063 123 403 938 893 896 323 109	15.42
50	1036	−0.597 139 063 123 404 993 139 853 200 418	15.32
51	1255	−0.597 139 063 123 405 062 553 388 319 457	15.18
52	1504	−0.597 139 063 123 405 073 866 273 274 907	6.13
53	1785	−0.597 139 063 123 405 074 767 253 435 857	12.55
54	2100	−0.597 139 063 123 405 074 830 248 095 239	14.30
55	2451	−0.597 139 063 123 405 074 833 661 581 044	18.45
56	2840	−0.597 139 063 123 405 074 834 100 198 770	7.78
57	3269	−0.597 139 063 123 405 074 834 130 004 786	14.71
58	3740	−0.597 139 063 123 405 074 834 133 639 660	8.20
59	4255	−0.597 139 063 123 405 074 834 134 046 373	8.93
60	4816	−0.597 139 063 123 405 074 834 134 090 546	9.20
61	5425	−0.597 139 063 123 405 074 834 134 095 348	9.20
62	6084	−0.597 139 063 123 405 074 834 134 095 875	9.10
63	6795	−0.597 139 063 123 405 074 834 134 095 987	4.69
64	7560	−0.597 139 063 123 405 074 834 134 096 014	4.22
65	8381	−0.597 139 063 123 405 074 834 134 096 021	3.94
Extrap.		−0.597 139 063 123 405 074 834 134 096 026(5)	

orders of magnitude improvement over the best previous result of Bailey and Frolov [18]. They have also obtained the energies for the $2\,^1S$ and $2\,^3P$ states with the 21- and 20-figure accuracies, respectively.

The purpose of this paper is to report three variational energy upper bounds for H_2^+ in the $1\,^1S$, $2\,^1S$, and $2\,^3P$ states, using our modified basis sets in Hylleraas coordinates. Our calculations have dramatically improved the results of Cassar and Drake [22] by 6 to 8 orders of magnitude. Discrepancies have been found for the $1\,^1S$ and $2\,^3P$ states.

II. COMPUTATIONAL METHOD

Atomic units are used throughout this paper. After separating the center of mass degrees of freedom, the Hamiltonian for H_2^+ becomes [20]

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

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the electron and one proton, relative to the other proton located at the origin, and $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$. The energy eigenvalue problem can be solved variationally in the following Hylleraas basis set:

$$\phi_{ijk}(\mathbf{r}_1,\mathbf{r}_2) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1-\beta r_2}\mathcal{Y}^{LM}_{l_1l_2}(\mathbf{r}_1,\mathbf{r}_2), \tag{5}$$

where $\mathcal{Y}^{LM}_{l_1l_2}(\mathbf{r}_1,\mathbf{r}_2)$ is the vector coupled product of spherical harmonics for the electron and the proton forming a common eigenstate of $\mathbf{L}^2$, L_z, and the parity operator Π with the corresponding eigenvalues of $L(L+1)\hbar^2$, $M\hbar$, and $(-1)^{l_1+l_2}$, respectively,

$$\mathcal{Y}^{LM}_{l_1l_2}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{m_1m_2}\langle l_1l_2m_1m_2|LM\rangle Y_{l_1m_1}(\mathbf{r}_1)Y_{l_2m_2}(\mathbf{r}_2). \tag{6}$$

In (5), the lowest power of r_2 is set to be $j_{\min}$=35 [20], and the basis set is generated according to

$$i+j+k\leqslant\Omega \tag{7}$$

with Ω being an integer not smaller than $j_{\min}$. In order to enhance the rate of convergence for the energy, we further divide the generated basis set into multiple blocks each having its own nonlinear parameters α and β; this is because different values of (α,β) reflect different distance scales in the wave function. For the S symmetry, we divide the basis set into eight blocks, where the nth block includes all the terms fulfilling the following relation for the powers j_n of r_2,

TABLE II. Convergence for the nonrelativistic energy of H_2^+ in the $2\,^1S$ state. N denotes the number of terms in the basis set and $R(\Omega)$ is the ratio of two successive differences in energy. The proton-electron mass ratio $m_p/m_e = 1836.152\,701$ is used. In atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$
42	124	−0.587 153 607 002 006 418 200 220 763 0	
43	175	−0.587 155 426 254 101 377 535 322 880 2	
44	240	−0.587 155 661 339 102 062 270 242 865 6	7.73
45	321	−0.587 155 677 869 116 686 795 888 201 5	14.22
46	420	−0.587 155 679 113 072 173 107 795 553 9	13.28
47	539	−0.587 155 679 204 157 196 270 104 659 2	13.65
48	680	−0.587 155 679 212 003 787 996 828 814 2	11.60
49	845	−0.587 155 679 212 683 704 022 973 271 0	11.54
50	1036	−0.587 155 679 212 743 594 739 072 455 9	11.35
51	1255	−0.587 155 679 212 746 290 920 242 352 7	22.21
52	1504	−0.587 155 679 212 746 773 930 182 684 6	5.58
53	1785	−0.587 155 679 212 746 808 402 509 860 1	14.01
54	2100	−0.587 155 679 212 746 811 737 892 060 5	10.33
55	2451	−0.587 155 679 212 746 812 174 792 934 1	7.63
56	2840	−0.587 155 679 212 746 812 208 287 636 9	13.04
57	3269	−0.587 155 679 212 746 812 211 568 313 5	10.20
58	3740	−0.587 155 679 212 746 812 211 848 704 0	11.70
59	4255	−0.587 155 679 212 746 812 211 878 636 8	9.36
60	4816	−0.587 155 679 212 746 812 211 880 910 6	13.16
61	5425	−0.587 155 679 212 746 812 211 881 121 6	10.77
62	6084	−0.587 155 679 212 746 812 211 881 176 1	3.87
63	6795	−0.587 155 679 212 746 812 211 881 188 8	4.26
64	7560	−0.587 155 679 212 746 812 211 881 191 7	4.50
65	8381	−0.587 155 679 212 746 812 211 881 192 6	3.03
66	9260	−0.587 155 679 212 746 812 211 881 192 9	2.87
Extrap.		−0.587 155 679 212 746 812 211 881 193 5(6)	

$$g_1 \leqslant j_1 \leqslant g_2,$$

$$g_n < j_n \leqslant g_{n+1}, \quad n = 2, \ldots, 8 \tag{8}$$

with

$$g_n = \mathrm{int}\left[j_{\min} + \frac{\Omega - j_{\min}}{8}(n-1) \right], \tag{9}$$

and int$[x]$ stands for the integer part of x. The size of each block is controlled by the same Ω. The basis set such constructed can sufficiently represent the vibrational modes in the wave function and thus it forms a complete set. We found, however, that if some lower power terms of r_2 are included in the basis set, the rate of convergence, as well as the numerical stability in the wave function, can further be significantly enhanced. We thus augment our basis set by including another independent block with $j_{\min}=0$. Therefore, for the $1\,^1S$ and $2\,^1S$ states, the total number of blocks is nine where the corresponding size-controlling parameters are $\Omega_i = \Omega$ for $i=1$ to 8, and $\Omega_9 = \Omega - 41$. For the P symmetry, the independent angular momentum configurations of (l_1, l_2) are (0,1) and (1,0). Since the (0,1) is the dominant configuration, we similarly divide it into five blocks. Thus, the number of blocks for the P symmetry is six, where the first five blocks have the same Ω, whereas for the sixth block, it is $\Omega - 4$. In addition to these blocks, a block with $j_{\min}=0$, $(l_1, l_2) = (0,1)$, and the size-controlling parameter $\Omega - 39$ is added. The total number of blocks is thus seven for the P symmetry. A complete optimization is then performed with respect to α and β in each block by calculating the first-order derivatives analytically according to

$$\frac{\partial E}{\partial \gamma} = 2\left\langle \Psi \middle| H \middle| \frac{\partial \Psi}{\partial \gamma} \right\rangle - 2E\left\langle \Psi \middle| \frac{\partial \Psi}{\partial \gamma} \right\rangle, \tag{10}$$

and the second-order derivatives numerically by finite differencing, where γ represents any nonlinear parameter, E is the energy eigenvalue, and $\langle \Psi | \Psi \rangle = 1$ is assumed, and then locating the zeros of the derivatives by Newton's method. The basic integrals that are required in our variational calculations are of the form

TABLE III. Convergence for the nonrelativistic energy of H_2^+ in the $2\ ^3P$ state. N denotes the number of terms in the basis set and $R(\Omega)$ is the ratio of two successive differences in energy. The proton-electron mass ratio m_p/m_e=1836.152 701 is used. In atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$
40	58	−0.596 850 365 915 207 389 186 931 95	
41	92	−0.596 872 089 202 616 230 223 486 20	
42	140	−0.596 873 628 303 259 134 286 858 06	14.11
43	205	−0.596 873 731 183 374 223 030 799 84	14.96
44	290	−0.596 873 738 143 255 742 013 985 95	14.78
45	398	−0.596 873 738 790 503 736 649 759 71	10.75
46	532	−0.596 873 738 829 537 214 288 682 09	16.58
47	695	−0.596 873 738 832 506 925 627 336 08	13.14
48	890	−0.596 873 738 832 744 700 045 335 52	12.48
49	1120	−0.596 873 738 832 763 542 918 001 24	12.61
50	1388	−0.596 873 738 832 764 553 664 320 28	18.64
51	1697	−0.596 873 738 832 764 720 665 923 69	6.05
52	2050	−0.596 873 738 832 764 735 106 499 64	11.56
53	2450	−0.596 873 738 832 764 735 844 672 06	19.56
54	2900	−0.596 873 738 832 764 735 912 671 55	10.85
55	3403	−0.596 873 738 832 764 735 919 690 55	9.68
56	3962	−0.596 873 738 832 764 735 920 592 51	7.78
57	4580	−0.596 873 738 832 764 735 920 715 92	7.30
58	5260	−0.596 873 738 832 764 735 920 738 73	5.40
59	6005	−0.596 873 738 832 764 735 920 743 47	4.80
60	6818	−0.596 873 738 832 764 735 920 744 59	4.21
61	7702	−0.596 873 738 832 764 735 920 744 86	4.25
62	8660	−0.596 873 738 832 764 735 920 744 93	3.49
63	9695	−0.596 873 738 832 764 735 920 744 96	2.75
Extrap.		−0.596 873 738 832 764 735 920 744 98(2)	

TABLE IV. Convergence for the nonrelativistic energy of H_2^+ in the ground state $1\ ^1S$, where the block with $j_{\min}=0$ is excluded. N denotes the number of terms in the basis set and $R(\Omega)$ is the ratio of two successive differences in energy. The proton-electron mass ratio m_p/m_e=1836.152 701 is used. In atomic units.

Ω	N	$E(\Omega)$	$R(\Omega)$
42	120	−0.597 138 962 416 725 533 971 429 7	
43	165	−0.597 139 054 447 816 826 202 237 5	
44	220	−0.597 139 062 578 934 282 825 265 7	11.31
45	286	−0.597 139 063 081 839 631 781 106 5	16.16
46	364	−0.597 139 063 119 932 782 836 785 6	13.20
47	455	−0.597 139 063 123 115 876 312 138 4	11.96
48	560	−0.597 139 063 123 377 556 029 004 1	12.16
49	680	−0.597 139 063 123 403 045 708 806 3	10.26
50	816	−0.597 139 063 123 404 898 852 206 2	13.75
51	969	−0.597 139 063 123 405 048 434 288 8	12.38
52	1140	−0.597 139 063 123 405 071 697 755 2	6.42
53	1330	−0.597 139 063 123 405 074 322 889 9	8.86
54	1540	−0.597 139 063 123 405 074 735 817 2	6.35
55	1771	−0.597 139 063 123 405 074 820 366 1	4.88
56	2024	−0.597 139 063 123 405 074 828 867 4	9.94
57	2300	−0.597 139 063 123 405 074 833 194 3	1.96
58	2600	−0.597 139 063 123 405 074 833 869 0	6.41
59	2925	−0.597 139 063 123 405 074 834 076 1	3.25
60	3276	−0.597 139 063 123 405 074 834 126 3	4.12
61	3654	−0.597 139 063 123 405 074 834 129 6	15.53
62	4060	−0.597 139 063 123 405 074 834 132 6	1.06

TABLE V. Optimized nonlinear variational parameters for the case of Ω=63, Ω=63, and Ω=59 for the $1\ ^1S$, $2\ ^1S$, and $2\ ^3P$ wave functions, respectively. In atomic units.

Block index	α	β
	$1\ ^1S$	
1	3.1612548828	22.3286743164
2	1.8020629882	19.6459350585
3	2.0606079101	22.3659057617
4	1.4689941406	20.8551025390
5	1.3847656250	21.1079101562
6	1.2354125976	25.1978759765
7	1.5448608398	22.3665771484
8	1.3237304687	37.9212646484
9	3.5509033203	8.0480957031
	$2\ ^1S$	
1	2.8723754882	21.0615844726
2	1.9583129882	19.5808715820
3	1.6140136718	19.2453613281
4	1.5167846679	19.8361816406
5	1.5820922851	19.7752685546
6	1.4572753906	20.9851074218
7	1.4785156250	28.2769165039
8	1.5940551757	33.4921875000
9	3.6137084960	6.8052978515
	$2\ ^3P$	
1	2.9519653320	19.6304321289
2	1.6480102539	20.1096801757
3	1.4729614257	21.0721435546
4	1.4372558593	22.4479980468
5	1.5366210937	22.9940185546
6	1.8576660156	20.5938720703
7	3.4689331054	7.2451782226

$$\int d\mathbf{r}_1 d\mathbf{r}_2 [\mathcal{Y}^{L'M'}_{l_1'l_2'}(\mathbf{r}_1,\mathbf{r}_2)^*]\mathcal{Y}^{LM}_{l_1l_2}(\mathbf{r}_1,\mathbf{r}_2) r_1^a r_2^b r_{12}^c e^{-\alpha r_1-\beta r_2}, \tag{11}$$

which can be evaluated analytically [23] using Perkins expansion for r_{12}^c. The final result can be expressed in terms of the hypergeometric function ${}_2F_1(a,b,c;x)$.

III. RESULTS

Tables I–III show the convergence studies for the nonrelativistic energies of H_2^+ in the $1\ ^1S$, $2\ ^1S$, and $2\ ^3P$ states, as the size of the basis set increases progressively. In the calculations, the older proton-electron mass ratio m_p/m_e =1836.152 701 is adopted, in order to facilitate a meaningful comparison with most of the high precision results. Also in the tables, the ratio $R(\Omega)$ is defined by

$$R(\Omega) = \frac{E(\Omega-2)-E(\Omega-1)}{E(\Omega-1)-E(\Omega)}, \tag{12}$$

which can be considered as a measure for the rate of convergence. The extrapolations to $N\rightarrow\infty$ were done based on

TABLE VI. Comparison of the nonrelativistic energies of H_2^+ in the $1\,^1S$, $2\,^1S$, and $2\,^3P$ states. The proton-electron mass ratio $m_p/m_e=1836.152\,701$ is used. In atomic units.

Author (Year)	Reference	Energy
$1\,^1S$		
Rebane and Filinsky (1997)	[25]	−0.597 139 063 123 40
Saavedra *et al.* (1998)	[26]	−0.597 139 063 123
Grémaud *et al.* (1998)	[27]	−0.597 139 063 123(1)
Taylor *et al.* (1999)	[12]	−0.597 139 063 123 9(5)
Moss (1999)	[10]	−0.597 139 063 123 4
Korobov (2000)	[17]	−0.597 139 063 123 405 074
Hilico *et al.* (2000)	[14]	−0.597 139 063 123 40(1)
Bailey and Frolov (2002)	[18]	−0.597 139 063 123 405 074 83
Yan *et al.* (2003)	[20]	−0.597 139 063 123 405 074 5(4)
Cassar and Drake (2004)	[22]	−0.597 139 063 123 405 074 834 338(3)
This work		−0.597 139 063 123 405 074 834 134 096 026(5)
$2\,^1S$		
Taylor *et al.* (1999)	[12]	−0.587 155 679 213 6(5)
Moss (1999)	[10]	−0.587 155 679 212 7
Hilico *et al.* (2000)	[14]	−0.587 155 679 212 75(1)
Cassar and Drake (2004)	[22]	−0.587 155 679 212 746 812 212(2)
This work		−0.587 155 679 212 746 812 211 881 193 5(6)
$2\,^3P$		
Taylor *et al.* (1999)	[12]	−0.596 873 738 832 8(5)
Moss (1999)	[10]	−0.596 873 738 832 8
Hilico *et al.* (2000)	[14]	−0.596 873 738 83(1)
Yan *et al.* (2003)	[20]	−0.596 873 738 832 764 733(1)
Cassar and Drake (2004)	[22]	−0.596 873 738 832 764 734 96(5)
This work		−0.596 873 738 832 764 735 920 744 98(2)

these ratios. Our calculated energy eigenvalues for the $1\,^1S$, $2\,^1S$, and $2\,^3P$ states of H_2^+ are estimated to be accurate at the level of 8 parts in 10^{30}, 1 part in 10^{27}, and 3 parts in 10^{26}, respectively. In order to maintain numerical stability, especially for larger sizes of basis sets, we employed the multiple precision arithmetic QD developed by Bailey *et al.* [24], which has 64 decimal digits. To demonstrate the importance of the lower power block, a convergence study is presented in Table IV for the $1\,^1S$ state, where the ninth block with $j_{\min}=0$ is not included. One can see that the convergence pattern starts to deteriorate at an early stage around $N=2300$, as indicated by the erratic change in ratio $R(\Omega)$. At $N=4060$, $R(\Omega)$, the rate of convergence, becomes very small. The overall number of significant figures obtained for the ground state energy is only 23, in comparison with the 30-figure accuracy when the ninth block is included. Furthermore, if one examines the wave function coefficients, i.e., the linear variational parameters, they can be as large as 10^{30} without this block; whereas if one includes this block, these large wave function coefficients are greatly reduced to 10^{10} or below, a manifestation of significant improvement on the numerical stability of the wave function. Table V lists all optimized nonlinear parameters α and β for some selected basis sets. For the last block, a typical trend for α and β is that they increase almost monotonically as the size of basis set increases. Table VI presents comparisons with some of the recent calculations. For the ground state energy, our value agrees with the one of Cassar and Drake [22] within the first 21 digits. Our value, however, is in disagreement with theirs after the twenty-first digit. Although we do not know the exact reason for this discrepancy at this moment, one obvious difference is that, in our calculations, the 64-digit multiple precision arithmetic QD was used; whereas their calculations were done in quadruple precision arithmetic which has only 32 digits. For the $2\,^1S$ state, our result, which is in good accord with the value of Cassar and Drake,

TABLE VII. The nonrelativistic energies of H_2^+ in the $1\,^1S$, $2\,^1S$, and $2\,^3P$ states. The more recent value [5] of $m_p/m_e=1836.152\,672\,61$ is used. In atomic units.

State	Energy
$1\,^1S$	−0.597 139 063 079 392 297 758 825 121 655(5)
	−0.597 139 063 079 39[a]
$2\,^1S$	−0.587 155 679 096 189 579 601 871 099 2(6)
	−0.587 155 679 096 19[a]
$2\,^3P$	−0.596 873 738 784 713 077 838 580 80(2)
	−0.596 873 738 784 71[a]

[a] Karr and Hilico [15].

represents an improvement over theirs by about 6 orders of magnitude. For the $2\,^3P$ state, our result disagrees with the result of Cassar and Drake at the level of 1 part in 10^{18}. Finally, Table VII lists the energy eigenvalues of the $1\,^1S$, $2\,^1S$, and $2\,^3P$ states using the more recent value [5] of $m_p/m_e=1836.152\,672\,61$, together with the calculations of Karr and Hilico [15] for further comparison.

In summary, we have established the variational upper bounds for the three states $1\,^1S$, $2\,^1S$, and $2\,^3P$ of H_2^+ at the level of 30-, 27-, and 26-digit accuracy, respectively, which represent 6 to 8 orders of magnitude improvement over the best previous calculations. Our method can be extended to higher angular momentum states [21], as well as other low-lying vibrational states which are relevant to current high precision measurements. The obtained theoretical precision for H_2^+ is also achievable for other hydrogen molecular ions, in particular, HD^+ and D_2^+. Our truly accurate results can not only serve as a benchmark for other computational methods, but can also be used reliably in the calculation of higher-order relativistic and QED effects.

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