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High precision variational calculations for H_2^+

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Abstract

A double basis set in Hylleraas coordinates is used to obtain improved variational upper bounds for the nonrelativistic energy of the 1^1S ($v = 0$, $R = 0$), 2^1S ($v = 1$, $R = 0$) and 2^3P ($v = 0$, $R = 1$) states of H_2^+ . This method shows a remarkable convergence rate for relatively compact basis set expansions. A comparison with the most recent work is made. The accuracy of the wavefunctions is tested using the electron–proton Kato cusp condition.

1. Introduction

The hydrogen molecular ion H_2^+ is a fundamental three-body quantum system. This ion presents the complexities associated with multi-centred systems while still remaining amenable to high precision calculation. The recent theoretical and experimental interest in this ion comes from two fronts. The first is due to the precision measurement of the dipole polarizability for H_2^+ , as determined by an analysis of the Rydberg states of H_2 , by Jacobson *et al* [1, 2]. This experiment revealed a discrepancy with theory of about $0.0007 a_0^3$, where a_0 is the first Bohr radius. This discrepancy was only partially removed by including the Breit α^2 corrections to the nonrelativistic Hamiltonian [3], where $\alpha \approx 137^{-1}$ is the fine structure constant. There are, in addition, other unexplained experimental results [4, 5] that would benefit from further theoretical study. The second is due to the possible improvement in the accuracy of the proton to electron mass ratio by an order of magnitude. The possibility of a precise determination of this fundamental mass ratio through the use of two-photon high resolution spectroscopy in H_2^+ was pointed out almost a decade ago [6]. In order for such an experiment to be used for metrological purposes, however, the relativistic and QED corrections to the energy levels involved in the measured transition frequencies must be known to order α^5 , in atomic units. The feasibility of this experiment was recently shown by Hilico *et al* [7], and is currently being carried out [8].

The motivation for the present work lies in the fact that if corrections to the nonrelativistic energy levels of H_2^+ are required to order $\alpha^5 \approx 10^{-10}$, then the wavefunctions must be accurate, at least, to this same level. The wavefunctions, however, are typically accurate to

less than half as many significant figures as the energy; hence, relativistic and QED corrections calculated from these wavefunctions suffer the same reduction in accuracy. This implies that the nonrelativistic energies need to be accurate to order 10^{-20} or better in order to take full advantage of the experimental accuracy.

To date, the most accurate calculations for H_2^+ have employed two types of basis set expansions [9–11]. In the first approach, the trial function is expanded in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^n a_i \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}) \pm (\text{exchange}), \quad (1)$$

where r_j is the distance of the electron from the j th proton, r_{12} is the inter-protonic coordinate and α_i , β_i and γ_i are real (or complex) numbers chosen in a so-called quasi-random manner from a small number of real intervals. This method, as described in [9, 10, 12], has yielded very accurate upper bounds for the ground state energy and geometrical properties for a wide variety of three-body systems.

In the second approach, the trial function is expanded in Hylleraas coordinates as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{q=1}^m \sum_{i,j,k}^{i+j+k \leq \Omega} a_{ijk}^{(q)} r_1^i r_2^j r_{12}^k \exp(-\alpha^{(q)} r_1 - \beta^{(q)} r_2) \pm (\text{exchange}), \quad (2)$$

where $\Omega \geq j_{\min} \approx 35$, and q is an integer that partitions the basis set into m sectors with distinct scale factors $\alpha^{(q)}$ and $\beta^{(q)}$. In such a calculation, a complete optimization is performed with respect to all nonlinear parameters. This method yielded an upper bound to the ground state energy comparable to expansion (1), but with half as many terms, as well as a new upper bound to the first triplet P-state [11].

The present paper extends previous results for H^- and Ps^- [13], using a double basis set [14], to cover a wider range of bound three-body systems, including H_2^+ . It was found that including higher powers of r_{12} and an extra exponential scale factor $\exp(-\gamma r_{12})$ was essential, since this allows the vibrational modes along the inter-protonic coordinate to be well represented. The result is a new lowest upper bound for the first three states of H_2^+ , i.e. the $(v=0, R=0)$, $(v=0, R=1)$ and $(v=1, R=0)$ vibronic states (see table 1 of [15] for a discussion of the correspondence between atomic and molecular notation).

2. Calculations

After isolating the centre-of-mass motion, the Hamiltonian for H_2^+ may be written (in reduced mass atomic units) as

$$H = -\frac{1}{2} \nabla_{r_1}^2 - \frac{1}{2} \nabla_{r_2}^2 - \frac{\mu}{m_e} \nabla_{r_1} \cdot \nabla_{r_2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}, \quad (3)$$

where μ is the reduced electron mass; the electron has been chosen to be at the origin of the coordinate system. The main task now is to solve the Schrödinger equation

$$H\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (4)$$

for the stationary states of the Hamiltonian H .

For our modified double basis set, the trial function for S-states is given by

$$\Psi^S(\mathbf{r}_1, \mathbf{r}_2) = \sum_{p=1}^2 \sum_{i,j=0}^{\Omega_1} \sum_{k=\Omega_{\text{low}}}^{\Omega_{\text{high}}} a_{ijk}^{(p)} r_1^i r_2^j r_{12}^k \exp(-\alpha^{(p)} r_1 - \beta^{(p)} r_2 - \gamma^{(p)} r_{12}) \pm (\text{exchange}), \quad (5)$$

where $\Omega_1 \geq i + j$, that is, Ω_1 is the maximum sum of powers of r_1 and r_2 ,

$$\begin{aligned}\Omega_{\text{low}} &= \mathcal{M} - \Omega_1 + (i + j), \\ \Omega_{\text{high}} &= \mathcal{M} + \Omega_1 - (i + j),\end{aligned}$$

and the integer $\mathcal{M} > \Omega_1$ is an adjustable parameter; and for states with $L > 0$,

$$\Psi^{L>0}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\text{ang}} \Psi^S(\mathbf{r}_1, \mathbf{r}_2) \mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2), \quad (6)$$

where $\mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ is a vector-coupled product of spherical harmonics [16] and \sum_{ang} means that all distinct angular couplings are included according to the scheme in [17].

Normally, all distinct combinations of powers $\{i, j, k\}$ would be included in expansions (5) and (6); however, in order to avoid problems of near linear dependence for S-states, all terms with $i > j$ are omitted only in (5). In addition, we employed a form of truncation first introduced by Kono and Hattori [18] in which terms with $i + j + |\mathcal{M} - k| - |l_1 - l_2| + |j - i| > \Omega_1$ are avoided.

For a given state, \mathcal{M} is varied until a minimum in the energy is found for the largest basis set used. The value of \mathcal{M} is then held at this value for all basis set sizes N as Ω_1 is increased. The inclusion of $r_{12}^k \exp(-\gamma r_{12})$ in (5) and (6), where k is a large integer, allows the trial functions to effectively represent a nuclear vibrational wavefunction, which is known from the Born–Oppenheimer approximation to be Gaussian [19, 20]. The condition $\gamma \approx \mathcal{M}/2$ of [19] naturally appears in this calculation upon optimization of E with respect to γ . It was found that $\mathcal{M} = 39, 38, 37$ give the minimum energy (and good convergence) for the three lowest states of H_2^+ .

After constructing the basis set, the principal computational step is to solve the generalized eigenvalue problem $(\mathbf{H} - E\mathbf{O})\mathbf{x} = 0$. The Hamiltonian matrix \mathbf{H} and the overlap matrix \mathbf{O} have elements $H_{ab} = \langle \phi_a | H | \phi_b \rangle$, and $O_{ab} = \langle \phi_a | \phi_b \rangle$, respectively, where

$$\phi = r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2 - \gamma r_{12}), \quad (7)$$

is any member of the basis set, and a (and b) represents a specific combination of radial powers $\{i, j, k\}$.

The optimization of $\alpha^{(p)}$, $\beta^{(p)}$ and $\gamma^{(p)}$ is accomplished by simultaneously calculating the first derivatives of the energy with respect to the nonlinear parameters:

$$\frac{\partial E}{\partial \alpha^{(p)}} = -2 \frac{\langle \Psi | (H - E) r_1 | \Psi^{(p)} \rangle}{\langle \Psi | \Psi \rangle}, \quad (8)$$

where $\Psi^{(p)}$ denotes the part of the wavefunction that depends explicitly on $\alpha^{(p)}$, and similarly for the $\beta^{(p)}$ and $\gamma^{(p)}$ derivatives. There is no contribution to these derivatives from variations of the $a_{ijk}^{(p)}$ because of the variational stability of the wavefunction. The final step is then to change $\alpha^{(p)}$, $\beta^{(p)}$ and $\gamma^{(p)}$ in the directions indicated by the derivatives, resolve the generalized eigenvalue problem, recalculate the derivatives and locate their zeros by Newton's method.

All calculations were done in quadruple precision (about 32 decimal digits) arithmetic on SHARCnet's *Tiger* cluster of Compaq Alpha ES40 workstations.

3. Results

We present our results in tables 1–5. The value used for the proton mass was $m_p = 1836.152\,701$ [21], in atomic units¹. Tables 1, 3 and 4 show the convergence pattern for

¹ In order to facilitate a comparison with other results, the more recent value of $m_p = 1836.152\,672\,61$ [22] was not used.

Table 1. Convergence study for the ground state of H_2^+ . $\Omega (=M + \Omega_1)$ is the highest power of r_{12} and N is the total number of terms in the basis set. Atomic units are used.

Ω	N	$E(\Omega)$	Ratio ^a
42	33	-0.597 138 979 257 696 807 296 095	
43	57	-0.597 139 061 191 160 229 487 982	
44	90	-0.597 139 062 954 250 154 856 869	46.47
45	134	-0.597 139 063 120 531 138 258 260	10.60
46	190	-0.597 139 063 123 316 985 447 178	59.69
47	260	-0.597 139 063 123 402 568 522 508	32.55
48	345	-0.597 139 063 123 404 987 310 249	35.38
49	447	-0.597 139 063 123 405 072 038 078	28.55
50	567	-0.597 139 063 123 405 074 674 920	32.13
51	707	-0.597 139 063 123 405 074 825 966	17.46
52	868	-0.597 139 063 123 405 074 834 205	18.33
53	1052	-0.597 139 063 123 405 074 834 331	65.43
Extrapolation		-0.597 139 063 123 405 074 834 338(3)	19.80
^b	2200	-0.597 139 063 123 405 0740	
^c		-0.597 139 063 123 405 076(2)	
^d	3500	-0.597 139 063 123 405 074 83	
^e	1330	-0.597 139 063 123 405 0741	
^f		-0.597 139 063 123 405 074 5(4)	

^a Ratio is the ratio of successive differences $[E(\Omega - 1) - E(\Omega - 2)]/[E(\Omega) - E(\Omega - 1)]$.

^b Korobov variational bound [10].

^c Korobov extrapolation [10].

^d Bailey and Frolov variational bound [9].

^e Yan *et al* variational bound [11].

^f Yan *et al* extrapolation [11].

the ground state and the first two excited states of H_2^+ and comparisons with other calculations. The ratios given in the last column of each table are defined by

$$R(\Omega) = \frac{E(\Omega - 1) - E(\Omega - 2)}{E(\Omega) - E(\Omega - 1)}, \quad (9)$$

where $\Omega = M + \Omega_1$, and thus give the values of the ratios of successive differences in the energies. If $R(\Omega)$ were constant, the extrapolated value of the energy would simply be the series limit of a geometric series. Since this is not the case, we fit the ratios to the form a/Ω^b and sum the series of differences to obtain the extrapolated value. The final quoted uncertainty is thus determined from the uncertainty in the parameters a and b . For the three states calculated, the largest basis set gives the lowest upper bound to date. However, all the results agree to within their estimated uncertainties.

The wavefunction for each state may be reproduced immediately using the optimized scale factors listed in table 5. Carrying out a complete optimization of all nonlinear parameters naturally partitions the basis set into two distinct sectors: one describing the asymptotic behaviour of the wavefunction, and the other describing the short-range behaviour. This partitioning preserves the numerical stability of the calculations within standard quadruple precision arithmetic for the basis set sizes listed.

A useful test of the accuracy of the wavefunctions near a two-particle coalescence point is the Kato cusp condition [23, 24]

$$v_{ij} = \frac{\langle \delta(\mathbf{r}_{ij}) \cdot \frac{\partial}{\partial r_{ij}} \rangle}{\langle \delta(\mathbf{r}_{ij}) \rangle}, \quad (10)$$

Table 2. Convergence study for the electron–proton cusp condition ν_{ep} for the 1 ¹S and 2 ¹S states in atomic units.

1 ¹ S		2 ¹ S	
N^a	ν_{ep}	N	ν_{ep}
33	−1.000 019 529 846	20	−1.004 119 449 150
57	−0.999 672 587 190	40	−1.001 983 322 004
90	−0.999 487 499 090	70	−0.999 731 407 353
134	−0.999 469 240 363	112	−0.999 540 780 459
190	−0.999 459 218 417	168	−0.999 467 185 612
260	−0.999 456 326 808	240	−0.999 459 647 216
345	−0.999 455 752 544	330	−0.999 456 274 413
447	−0.999 455 687 556	440	−0.999 455 794 843
567	−0.999 455 684 622	572	−0.999 455 713 857
707	−0.999 455 679 856	728	−0.999 455 686 394
868	−0.999 455 679 492	910	−0.999 455 681 786
987	−0.999 455 679 464	1015	−0.999 455 679 820
		1240	−0.999 455 679 502
		1496	−0.999 455 679 491
ν_{ep}^b	−0.999 455 679 432	ν_{ep}^b	−0.999 455 679 432

^a Using $\mathcal{M} = 40$ in expansion (5).^b Exact value as given by equation (13).**Table 3.** Convergence study for the 2 ¹S state of H₂⁺. Ω ($=\mathcal{M} + \Omega_1$) is the highest power of r_{12} and N is the total number of terms in the basis set. Atomic units are used.

Ω	N	$E(\Omega)$	Ratio ^a
39	20	−0.587 151 043 016 274 880 167	
40	40	−0.587 155 435 230 538 473 190	
41	70	−0.587 155 671 003 177 129 307	18.63
42	112	−0.587 155 678 540 275 385 079	31.28
43	168	−0.587 155 679 208 721 236 702	11.28
44	240	−0.587 155 679 212 575 658 166	173.42
45	330	−0.587 155 679 212 741 279 834	23.27
46	440	−0.587 155 679 212 746 648 696	30.85
47	572	−0.587 155 679 212 746 807 755	33.75
48	728	−0.587 155 679 212 746 811 406	43.56
49	910	−0.587 155 679 212 746 812 118	5.13
50	1015	−0.587 155 679 212 746 812 191	9.65
51	1240	−0.587 155 679 212 746 812 205	5.57
52	1496	−0.587 155 679 212 746 812 211	2.03
Extrapolation		−0.587 155 679 212 746 812 212(2)	6.18
^b		−0.587 155 679 212(1)	
^c		−0.587 155 679 2127	
^d		−0.587 155 679 213 6(5)	

^a Ratio is the ratio of successive differences $[E(\Omega - 1) - E(\Omega - 2)]/[E(\Omega) - E(\Omega - 1)]$.^b Hilico *et al* [15].^c Moss variational bound [26].^d Taylor *et al* [27].

where \mathbf{r}_{ij} is any inter-particle coordinate. The exact values of the cusps are known to be

$$\nu_{ij}^{\text{exact}} = q_i q_j \frac{m_i m_j}{m_i + m_j}, \quad (11)$$

Table 4. Convergence study for the 2^3P state of H_2^+ . Ω ($=\mathcal{M} + \Omega_1$) is the highest power of r_{12} and N is the total number of terms in the basis set. Atomic units are used.

Ω	N	$E(\Omega)$	Ratio ^a
40	39	-0.596 872 821 718 250 761 31	
41	82	-0.596 873 728 191 903 938 74	
42	149	-0.596 873 738 113 177 432 23	91.37
43	244	-0.596 873 738 822 338 108 35	13.99
44	373	-0.596 873 738 832 029 635 19	73.17
45	540	-0.596 873 738 832 750 200 25	13.45
46	751	-0.596 873 738 832 762 355 10	59.28
47	1010	-0.596 873 738 832 764 668 79	5.25
48	1323	-0.596 873 738 832 764 729 56	38.07
49	1694	-0.596 873 738 832 764 734 80	11.60
Extrapolation		-0.596 873 738 832 764 734 96(5)	32.92
^b		-0.596 873 738 832 8(5)	
^c		-0.596 873 738 832 8	
^d		-0.596 873 738 832 764 733(1)	

^a Ratio is the ratio of successive differences $[E(\Omega - 1) - E(\Omega - 2)]/[E(\Omega) - E(\Omega - 1)]$.

^b Taylor *et al* [27].

^c Moss variational bound [26].

^d Yan *et al* extrapolation [11].

where q_i and q_j are the charges and m_i and m_j are the masses of the particles. In the chosen coordinate system, and in atomic units, the electron–proton cusp is

$$v_{\text{ep}} = \frac{\langle \delta(\mathbf{r}_1) \cdot \frac{\partial}{\partial r_1} \rangle}{\langle \delta(\mathbf{r}_1) \rangle}, \quad (12)$$

with the exact value

$$v_{\text{ep}}^{\text{exact}} = -\frac{m_p}{m_p + 1} = -0.999\,455\,679\,432\,931. \quad (13)$$

The results of this calculation are shown in table 2.

4. Discussion

The results of this paper demonstrate that a double basis set in Hylleraas coordinates can be easily constructed to give highly accurate nonrelativistic energies for H_2^+ . Compared with other methods, this approach produces lower upper bounds using basis sets with fewer or the same number of terms. For the basis set sizes presented here, the numerical stability of the calculation is excellent, and so does not require the use of extended precision arithmetic.

One notable feature of this calculation is the large values and scatter of the ratio, especially for the 2^1S state, given in the last column of tables 1, 3 and 4. Although this would normally reduce the confidence in the stability of a calculation, it is here a result of a combination of effects: a change in the location of the lowest minimum on the energy surface (see figure 2(a) of [15]), a strong dependence of the energy on the range of powers of r_{12} included in the basis set and a related even/odd alternation in the values of the ratio with Ω [25]. As a simple illustration, one may note that the largest value for the ratio in table 3 occurs for $\Omega = 44$ which is preceded by a corresponding jump in the optimized scale factor $\beta^{(2)}$ listed in table 5. Further investigation of this, however, is still required.

Table 5. Optimized scale factors for the three lowest states of H_2^+ . Units are $\mu/(m_e a_0)$, where a_0 is the Bohr radius and μ is the reduced electron mass.

N	$\alpha^{(1)}$	$\beta^{(1)}$	$\gamma^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	$\gamma^{(2)}$
1^1S						
33	1.298 28	0.407 35	18.325 44	1.153 75	0.418 33	19.539 86
57	1.221 68	0.500 00	19.395 75	1.173 89	0.430 97	18.863 71
90	1.257 81	0.895 63	18.472 11	1.167 91	0.483 40	19.375 37
134	1.311 40	0.594 18	20.289 73	1.188 48	0.382 26	19.579 10
190	1.171 08	0.858 52	20.037 17	1.108 34	0.507 81	19.788 76
260	1.250 67	1.020 69	19.286 25	1.166 26	0.482 97	18.987 00
345	1.552 86	1.034 36	19.294 43	1.191 77	0.370 36	18.999 33
447	1.543 88	1.121 52	19.184 94	1.178 28	0.368 96	19.313 42
567	1.561 65	1.289 79	18.935 79	1.166 69	0.392 82	19.413 27
707	1.625 18	1.409 12	19.105 22	1.225 89	0.441 89	18.634 83
868	1.703 25	1.459 29	19.806 95	1.206 54	0.429 32	19.418 52
1052	1.718 81	1.471 98	19.984 99	1.192 87	0.425 05	17.587 71
2^1S						
20	1.446 66	0.194 21	16.939 94	1.071 29	0.300 90	17.510 99
40	1.219 73	0.373 60	16.521 73	1.104 80	0.388 55	18.238 34
70	1.529 42	0.360 84	16.595 21	1.158 02	0.359 80	18.129 58
112	1.465 09	0.286 93	16.856 57	1.297 97	0.344 54	17.879 27
168	1.166 99	0.718 99	17.654 54	1.130 68	0.594 79	17.733 70
240	1.307 74	0.811 04	17.186 04	1.181 15	0.601 38	17.444 89
330	1.531 86	0.931 95	16.537 48	1.162 90	0.586 06	17.150 76
440	1.730 41	0.985 84	16.496 95	1.167 66	0.560 06	17.844 85
572	1.646 24	1.027 95	18.023 19	1.109 80	0.568 73	18.673 34
728	1.572 94	1.071 66	20.452 64	1.121 64	0.573 85	18.974 49
910	1.556 15	1.060 24	20.235 23	1.133 61	0.580 02	19.176 27
1015	1.854 06	1.161 50	20.277 28	1.133 00	0.581 05	19.166 02
1240	1.844 67	1.156 62	20.254 94	1.135 19	0.584 11	19.188 42
1496	1.825 93	1.144 84	20.045 78	1.146 73	0.590 21	19.387 57
2^3P						
39	1.320 92	0.360 35	18.009 83	0.790 34	0.692 75	18.090 76
82	1.254 88	0.442 32	18.609 19	0.703 31	0.558 35	18.896 85
149	1.369 38	0.512 70	17.930 54	0.812 81	0.651 79	17.989 99
244	1.183 53	0.698 00	18.510 25	1.001 65	0.709 29	18.479 31
373	1.289 61	0.694 76	18.655 88	1.056 34	0.792 30	18.554 69
540	1.325 07	0.764 34	18.638 00	0.908 45	0.735 66	18.963 75
751	1.536 62	0.826 97	18.446 84	0.882 32	0.716 98	18.716 86
1010	1.528 87	0.831 18	18.532 29	0.878 36	0.719 06	18.633 06
1323	1.536 50	0.833 92	18.619 51	0.874 21	0.715 70	18.545 72
1694	1.536 07	0.851 56	18.824 04	0.864 07	0.713 99	18.344 18

The 20-, 21- and 24-figure accuracies of the nonrelativistic energy eigenvalues presented above, although more than sufficient for comparison with experiment, lay a firm foundation for the calculation of higher order relativistic and QED corrections to the nonrelativistic energy levels of H_2^+ . The 10-figure accuracy of the electron–proton cusp quoted here represents, to our knowledge, an improvement of about five orders of magnitude over the best available value in the literature [12, 20]. This further shows the reliability of the wavefunctions to compute observables, other than the energy, to high precision, and especially the highly singular operators that appear in the relativistic and QED corrections.

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