High precision variational calculations for the Born-Oppenheimer energies of the ground state of the hydrogen molecule

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Born-Oppenheimer approximation Hylleraas variational calculations with up to 7034 expansion terms are reported for the $^1\Sigma_g^+$ ground state of neutral hydrogen at various internuclear distances. The nonrelativistic energy is calculated to be $-1.174\,475\,714\,220(1)$ hartree at $R=1.4$ bohr, which is four orders of magnitude better than the best previous Hylleraas calculation, that of Wolniewicz [J. Chem. Phys. **103**, 1792 (1995)]. This result agrees well with the best previous variational energy, $-1.174\,475\,714\,216$ hartree, of Cencek (personal communication), obtained using explicitly correlated Gaussians (ECGs) [Cencek and Rychlewski, J. Chem. Phys. **98**, 1252 (1993); Cencek *et al.*, *ibid.* **95**, 2572 (1995); Rychlewski, Adv. Quantum Chem. **31**, 173 (1998)]. The uncertainty in our result is also discussed. The nonrelativistic energy is calculated to be $-1.174\,475\,931\,399(1)$ hartree at the equilibrium $R=1.4011$ bohr distance. This result also agrees well with the best previous variational energy, $-1.174\,475\,931\,389$ hartree, of Cencek and Rychlewski [Rychlewski, *Handbook of Molecular Physics and Quantum Chemistry*, edited by S. Wilson (Wiley, New York, 2003), Vol. 2, pp. 199–218; Rychlewski, *Explicitly Correlated Wave Functions in Chemistry and Physics Theory and Applications*, edited by J. Rychlewski (Kluwer Academic, Dordrecht, 2003), pp. 91–147.], obtained using ECGs. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2173250]

I. INTRODUCTION

Variational methods based on explicitly correlated wave functions are known to give the most accurate upper bounds to energy states, and hence the inclusion of terms containing the interelectronic distance r_{ij} in the wave function has become increasingly common, at least for few-electron atomic systems ($N \leq 4$) (so common, in fact, that a book dealing entirely with explicitly correlated functions has recently been produced[1]). The milestone in the theory of the hydrogen molecule, the simplest molecular system containing an electron pair bond, is the work of James and Coolidge.[2] Following the work of Hylleraas[3] on the helium atom, they employed factors of r_{12} in the hydrogen molecule wave function (the full bibliography on H_2 calculations until 1960 is given in Ref. 4 and established beyond a doubt the usefulness of including the interelectronic distance explicitly in the wave function. Kolos and co-worker[5,6] and Wolniewicz[7] generalized the approach of James and Coolidge to get a more accurate description of dissociation. Wave functions using their "generalized James-Coolidge (JC)" wave functions are commonly referred to as Hylleraas (Hy) or more specifically Kolos-Wolniewicz (KW) wave functions.[1] In addition to Hy wave function calculations, the Hylleraas-configuration interaction (Hy-CI) technique (developed by us[8] and also independently by Woźnicki[9]) has been applied to diatomic molecules (including H_2) by Clary and co-worker[10–13] and

Clementi and co-workers.[14–19] In Hy-CI calculations the wave function is expanded as a linear combination of correlated configuration state functions (CSFs), where the unique part of each CSF is a product of orbitals (σ, π, δ, etc.) and at most one r_{ij} raised to some power (See the review article by Rychlewski[20] and Sec. 2.4 of Rychlewski[1] for a discussion of Hy-CI wave functions). However, the calculations of Clementi *et al.* for H_2 did not achieve the accuracy of purely Hy calculations, the best of which were the KW calculations of Wolniewicz.[7]

In this work we extend the work of Kolos and co-worker[5,6] and Wolniewicz[7] to calculate the energies of $^1\Sigma_g^+$ states of H_2 using expansions in confocal elliptical coordinates with explicit inclusion of interelectronic distance coordinates up through r_{12}^7. We calculate Born-Oppenheimer (BO) energies for various internuclear distances in the range of 0.4–6.0 bohr. We also determine the BO ground state energy more precisely than the best previous calculation.[1,21]

The calculations reported are similar to those described in the classic paper of Kolos and Roothaan[5] (see this paper for algorithmic details of our calculations) but go far beyond those as a reflection of the improved capability of modern computers. We also note that the best previous calculation to date on the H_2 ground state is neither Hy (KW) nor Hy-CI but the one employing exponentially correlated Gaussian (ECG) functions.[1,20,22,23] While the results that have been obtained with this technique have been impressive, this technique suffers from the same inability to represent the electron cusp behavior at $r_{ij}=0$ as a strictly orbital CI calcula-

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TABLE I. Calculations of the BO energy of the ground state of the H_2 molecule at internuclear distance R =1.4 bohr. See text for what is tabulated in each column.

μ	k	ν	α	ΔN	N	Energy (E) (hartree)	ΔE
0	11	10	1.320 75	0	1491	−1.161 518 240 453 517 4	
1	10	10	1.320 75	1131	2622	−1.174 437 033 907 773 7	−0.129 18 × 10⁻¹
2	9	10	1.320 75	790	3412	−1.174 475 267 311 513 6	−0.382 33 × 10⁻⁴
3	8	10	1.320 75	535	3947	−1.174 475 706 160 320 7	−0.438 84 × 10⁻⁶
4	7	10	1.320 75	346	4293	−1.174 475 713 814 860 6	−0.765 45 × 10⁻⁸
5	7	10	1.320 75	346	4639	−1.174 475 714 083 184 5	−0.268 32 × 10⁻⁹
6	6	10	1.320 75	214	4853	−1.174 475 714 100 185 3	−0.170 00 × 10⁻¹⁰
7	6	10	1.320 75	214	5067	−1.174 475 714 145 011 5	−0.448 26 × 10⁻¹⁰
0	8	8	6.320 75	535	5602	−1.174 475 714 190 684 3	−0.456 72 × 10⁻¹⁰
1	8	8	6.320 75	535	6137	−1.174 475 714 210 523 3	−0.198 39 × 10⁻¹⁰
2	7	8	6.320 75	346	6483	−1.174 475 714 216 401 7	−0.587 83 × 10⁻¹¹
3	6	8	6.320 75	214	6697	−1.174 475 714 218 711 6	−0.230 99 × 10⁻¹¹
4	6	8	6.320 75	214	6911	−1.174 475 714 219 818 1	−0.110 65 × 10⁻¹¹
5	5	8	6.320 75	123	7034	−1.174 475 714 220 075 5	−0.257 4 × 10⁻¹²

tion. Many authors have emphasized that the wave function should have a cusplike behavior[24] at $r_{12}=0$ such that

$$\left(\frac{1}{\Psi}\frac{\partial\Psi}{\partial r_{12}}\right)_{r_{12}=0}=\frac{1}{2}. \tag{1}$$

The ECG wave function cannot properly represent this behavior. However, progress towards overcoming this defect has recently been made by Pachucki and Komasa.[25,26] They add terms linear in r_i and r_{ij} to an ECG calculation to produce what they call a linear ECG (LECG) basis.

II. WAVE FUNCTIONS

Since the time-independent, nonrelativistic electronic Schrödinger equation in the Born-Oppenheimer (BO) (or the so-called clamped nuclei) approximation is not separable in the electron coordinates, basis sets which incorporate the r_{12} interelectronic coordinate are most efficient. The wave function we use for the H_2 ground state is

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{K=1}^{N}C_K\Phi_K(\mathbf{r}_1,\mathbf{r}_2). \tag{2}$$

The terms Φ_K have the form

$$\Phi_K(\mathbf{r}_1,\mathbf{r}_2)=(1+P_{12})[r_{12}^{\mu}\xi_1^{n}\eta_2^{j}\xi_1^{\bar n}\eta_2^{\bar j}e^{-(\alpha\xi_1+\bar\alpha\xi_2)}], \tag{3}$$

where ξ and η are confocal elliptic coordinates[27] and n, j, $\bar n$, $\bar j$, α, $\bar\alpha$, and μ must be specified for each expansion term K. For $^1\Sigma_g^+$ states, $j+\bar j$ must be even. Terms in the KW wave function differ from ours in that they include exponential factors $e^{-(\beta\eta_1+\bar\beta\eta_2)}$ in η_1 and η_2 providing proper asymptotic behavior of the wave function at large internuclear distance R (recently the KW approach has been extended by Kubacki and Komasa[28] to allow multiple parameters, e.g., 132 in the calculation reported in Table III). Setting $\beta=\bar\beta=0$ in the KW wave function limits the range of R for which high precision energies can be obtained. For us that range turns out to be 0.4–6.0 bohr (we could handle $R<0.4$ with the current basis if we used normalized orbitals, but even then, for technical reasons our existing code would not allow R to approach 0).

In practice for the ground state one can let $\alpha=\bar\alpha$ in each term K as James and Coolidge originally did. Thus our wave function has $\alpha=\bar\alpha$ for each K, but to speed up convergence we use two sets of terms Φ_K and Φ_K', one set with $\alpha=\bar\alpha=\alpha_1$ and the other with $\alpha=\bar\alpha=\alpha_2$ (we refer to these as two alpha expansions).

A. Results and discussion

In Table I we give the results of a 7034 term calculation for $R=1.4$ bohr. In the table we show in each row the results of adding to the previous calculation terms with an r_{ij} power given by μ and containing all n and j powers of ξ_1 and η_1, respectively, that satisfy $n+j\leqslant k$ and all $\bar n$ and $\bar j$ powers of ξ_2 and η_2, respectively, satisfying $\bar n+\bar j\leqslant k$. In addition for a $^1\Sigma_g^+$ state $j+\bar j$ must be even, so terms with odd $j+\bar j$ are not included. The last term selection criterion is that n, $\bar n$, j, and $\bar j$ must be $\leqslant\nu$. This and the value of $\alpha(=\bar\alpha)$ for each line *completely specifies the wave function expansion in sufficient detail that the calculation can be repeated*, in contrast to any of the previous large scale calculations on H_2. This is one reason why we made no attempt to further select the terms being used (it then becomes difficult to specify the final wave function terms in print without giving a detailed list).

The first eight lines are for adding successively high powers of r_{ij} with $\alpha_1=1.320\,75$ and then terms corresponding to $\alpha_2=6.320\,75$ are added. Energies for each expansion length N are tabulated as well as the improvement over the previous level.

We note that ΔE for $\mu=7$ is greater then that for $\mu=6$, whereas one might expect a monotone decrease as the power of r_{12} is raised. However, the terms in our expansion are of two types: those with even powers of r_{12}, which are basically (complicated) CI-type terms, and those with odd powers of r_{12}, which treat electron-electron interactions in an essentially different fashion. The ΔE contributions from both of these term types are indeed monotone decreasing as expected but there is nothing that requires the combination to be similarly monotone decreasing, especially since one has reached the point where it is getting difficult to describe the electron

TABLE II. Calculations of the BO energy of the ground state of the H_2 molecule at $R=1.4$ bohr expressed in hartrees. Terms are organized by r_{ij} power μ; $\alpha_1 = 1.320\,75$ and $\alpha_2 = 6.320\,75$.

μ	ΔN	N	Energy (E) (hartree)	ΔE
0		2026	$-1.161\,523\,300\,229\,836\,0$	
1	1656	3682	$-1.174\,437\,336\,488\,608\,6$	$-0.129\,14 \times 10^{-1}$
2	1146	4828	$-1.174\,475\,280\,326\,470\,9$	$-0.379\,43 \times 10^{-4}$
3	749	5577	$-1.174\,475\,706\,942\,023\,1$	$-0.426\,61 \times 10^{-6}$
4	560	6137	$-1.174\,475\,714\,069\,212\,3$	$-0.712\,71 \times 10^{-8}$
5	469	6606	$-1.174\,475\,714\,216\,389\,9$	$-0.147\,17 \times 10^{-9}$
6	214	6820	$-1.174\,475\,714\,219\,924\,8$	$-0.353\,49 \times 10^{-11}$
7	214	7034	$-1.174\,475\,714\,220\,075\,5$	$-0.150\,7 \times 10^{-12}$

distribution with a single nonlinear parameter. In this connection, we note that the reordered two alpha expansion results presented in Table II exhibit no such anomalous behavior.

Based on the rate of convergence that is observed here, we conclude that the energy has converged to 12 decimal places and the 13th digit is 0 or 1, i.e., $E = -1.174\,475\,714\,220(1)$ hartree. Optimization of α at the 7034 term level changes things only in the 15th decimal (16th digit), i.e., the energy surface in α space is very flat. Varying the expansion terms beyond 7034 systematically gave energy improvements occurring only in the 13th and 14th decimal places, further evidence that our result has converged to 13 digits.

In Table II we again give results for the 7034 term calculation but with terms reordered to show the energy contribution of each power of r_{ij} (μ). Energies for each expansion length N are tabulated as well as the improvement over the previous level.

Our final energy is also listed in Table III and compared with previous results. The 2400 ECG result in Table III has been communicated to us by W. Cencek to correct his calculation reported in Ref. 21. As communicated to us by Cencek,[29] he gets $-1.174\,475\,714\,216$ hartree and then the numerical stability of the wave function deteriorates so that the last digit starts fluctuating. Which means that the $-1.174\,475\,714\,223$ hartree reported in Ref. 21 is not a true last digit upper bound since the last digits suffer from

numerical instabilities. Cencek's error estimate is 1×10^{-10} hartree. As stated previously, we believe that our result has converged to 1.174 475 714 220(1), two orders of magnitude better than the error estimate of the best previous calculations.[21,29] In Table III we label our calculations with a single α as one alpha and those with both an α_1 and an α_2 as two alphas. The JC, KW, ECG, and Hy-CI designations in this and following tables are those of Rychlewski.[1]

In Kolos and Roothaan's original paper[5] the highest power of r_{12} used was 2. Terms with r_{12}^2 introduce the equivalent of $\pi(1)\pi(2)$ CI-type terms. So only σ-σ type terms were explicitly correlated in Kolos and Roothaan's original study. r_{12}^3 factors will introduce the equivalent of $\pi(1)\pi(2)r_{12}$ terms. In Table III it can be seen that using only a single α, we are able to compute the energy to eight digits (seven decimal places) with $r_{12} \leq 3$. It is interesting that with $r_{12} \leq 5$ [r_{12}^5 puts in $\delta(1)\delta(2)r_{12}$] we are able to do better than all previous Hy calculations employing many terms with high powers of ξ_1 and ξ_2 as well as the accurate 1200 term ECG calculation of Cencek and Kutzelnigg.[30] The energy calculated with the ECG wave function was obtained only after a very time-consuming optimization process in which five nonlinear parameters per basis function (which means 6000 parameters for the 1200 term wave function) were optimized. In contrast the optimization for our single α wave function is based on the selection of the terms of the form of Eq. (3) and the optimization of only the single parameter α. By going up to r_{12}^7 we effectively correlate up to

TABLE III. Comparison with previous explicitly correlated calculations for the BO energy of the ground state of the hydrogen molecule ($R=1.4$ bohr) expressed in hartrees.

Technique	Author	N	Energy (E) (hartree)
Many alphas	Kubacki and Komasa (Ref. 28)	22[a]	$-1.174\,474\,77$
JC	Bishop and Cheung (Ref. 45)	249	$-1.174\,475\,65$
KW	Kolos (includes r_{12}^3) (Ref. 6)	370	$-1.174\,475\,685$
One alpha	This work (includes r_{12}^3)	3947	$-1.174\,475\,706\,160$
Two alphas	This work (includes r_{12}^3)	5577	$-1.174\,475\,706\,942$
KW	Wolniewicz (includes r_{12}^6) (Ref. 7)	883	$-1.174\,475\,713\,565$
ECG	Cencek and Kutzelnigg (Ref. 30)	1200	$-1.174\,475\,714\,037$
One alpha	This work (includes r_{12}^5)	4639	$-1.174\,475\,714\,083$
One alpha	This work (includes r_{12}^7)	5067	$-1.174\,475\,714\,145$
Two alphas	This work (includes r_{12}^5)	6606	$-1.174\,475\,174\,216$
ECG	Cencek (Ref. 29)	2400	$-1.174\,475\,174\,216$
Two alphas	This work (includes r_{12}^7)	7034	$-1.174\,475\,174\,220$

[a]132 nonlinear parameters.

TABLE IV. BO energy for the ground state of the hydrogen molecule at $R=1.4011$ bohr.

Technique	Author	N	Energy (E) (hartree)
Hy-CI	Frye *et al.* (Refs. 17 and 18)	586	−1.174 474 67
KW	Wolniewicz (Ref. 7)	883	−1.174 475 930 742
ECG	Rychlewski *et al.* (Ref. 46)	700	−1.174 475 931 197
ECG	Cencek and Rychlewski (Ref. 21)	2400	−1.174 475 931 389
Two alphas	This work (includes r_{12}^7)	7034	−1.174 475 931 399 84

$\phi(1)\phi(2)$-type products. Table III shows that a single nonlinear parameter is adequate for a 0.1 nhartree level of accuracy, but is not as good as the 2400 term ECG wave function. By adding a second α at the r_{12}^5 level we were able to exceed our single α r_{12}^7 result as well as the 2400 ECG result. Going up to r_{12}^7 with α_1 and r_{12}^5 with α_2 achieves an 0.001 nhartree level of accuracy.

Table IV summarizes previous results at the equilibrium bond distance $R=1.4011$ bohr. The improvement of this wave function over the ECG 2400 term wave function of Cencek and Rychlewski parallels the relationship of ECG to Hy at $R=1.4$ bohr.

We find in this work that very good energies are obtained with our wave functions up to and including $R=6.0$ bohrs. The fact that we do so well for such large R values without a β nonlinear parameter in the wave function is presumably because we have numerous terms with high powers of η_1 and η_2. In Table V we show that the comparison of single α results versus ECG results holds not only for a single internuclear distance but for a whole range of R using the 5067 term single α wave function. We are basically assuming that the expansion terms used for $R=1.4$ will be adequate for other R values. We are also assuming that since α_1 and α_2 are not tightly coupled, we can use the α_1 values from Table VI for a good single nonlinear parameter calculation. It is striking how well these results agree with the 1200 term ECG results, which are better than the best previous Hy results, the KW results of Wolniewicz.[7]

Drake[31] has pointed out the practical need for "doubling" basis sets so there is a natural partition of the basis set into two distinct distance scales: one appropriate to the complex correlated motion near the nucleus and the other appropriate for further out. Drake uses just two sets of orbitals to

accelerate convergence. In our He calculations we found that the importance of the second orbital exponent came in around the 13th digit. In our present calculations we found it difficult to get the tenth digit (0.1 nhartree accuracy) without taking into account the detailed description of the wave function near the protons by incorporating elliptical orbitals with large orbital exponents to describe the charge distribution near the nucleus. This effect did not enter in the He calculations until we wanted more than 13 decimal places. The greater need for two scale parameters is probably to be expected in H_2 where much of the electron correlation energy is associated with the region far from the nuclei, unlike He where the space close to the nucleus is energetically important for both electron-electron and electron-nucleus interactions.

In Table VI we give our final results (7034 term wave functions) for the BO energy of the ground state of the H_2 molecule at internuclear distances ranging from 0.4 to 6.0 bohrs using two nonlinear parameters, α_1 and α_2. In Table VI we also tabulate the contribution of all the α_2 terms versus R [the column labeled $\Delta E(\alpha_2)\times 10^{12}$]. As previously discussed, we estimate the error in the energy at the internuclear distance $R=1.4$ bohr to be no more than 0.001 nhartree. We have not investigated this question for other R values. In the table we give energies up to 16 digits for the record and also for the benefit of anyone wanting to repeat a calculation. The table is very interesting, showing clearly how as R increases the electrons interact less and less, particularly around the nuclei. Each nucleus has an electron and the probability for both being around the same nucleus is small, as one would expect. Being able to demonstrate this is a side effect of our way of choosing the wave function. In a calculation with lots of nonlinear parameters one would not be able to see this so clearly.

In this paper we have restricted our calculations to the BO energies. Recently there has been much interest in a direct nonadiabatic (which is non-BO) variational approach using correlated Gaussian basis sets. The best result using this approach is that of Cafiero *et al.*[32] This approach yields energies of about ten digits accuracy. However, the feasibility of this approach to systems with more than two electrons has not been demonstrated. And for the two-electron case, we have been able to obtain results using traditional methods that yield energies to about 13 digit accuracy.

III. Hy VS Hy-CI

As there is a close relationship between the Hy wave functions we use and an essentially equivalent Hy-CI treatment, these Hy results can provide insight into what is

TABLE V. BO energy (in hartrees) of the ground state of the hydrogen molecule at selected internuclear distances (expressed in bohr) calculated using the 1200 ECG wave function (Table 2.8 in Ref. 1) and our 5067 term single α wave function (terms defined in Table I, lines 1–8). The α_1 values used here are those presented in Table VI.

R	1200 term ECG	5067 term one α
1.0	−1.124 539 719 5	−1.124 539 719 462 06
1.2	−1.164 935 243 3	−1.164 935 243 354 69
1.4	−1.174 475 714 0	−1.174 475 714 145 01
1.6	−1.168 583 373 3	−1.168 583 373 287 03
1.8	−1.155 068 737 5	−1.155 068 737 548 57
2.0	−1.138 132 957 0	−1.138 132 957 074 81
3.0	−1.057 326 268 7	−1.057 326 268 835 43
4.0	−1.016 390 252 8	−1.016 390 252 933 31
6.0	−1.000 835 707 6	−1.000 835 707 653 04

TABLE VI. BO energy of the ground state of the H_2 molecule at internuclear distances R from 0.4 to 6.0 bohrs. $N=7034$. See text for Table I for what is tabulated in each column.

R	α_1	α_2	Energy (E) (hartree)	$\Delta E(\alpha_2) \times 10^{12}$
0.4	0.507 5	0.982 86	−0.120 230 341 177 864 4	285.9
0.5	0.605	1.281 44	−0.526 638 758 742 317 2	152.1
0.6	0.687 5	1.65	−0.769 635 429 485 356 8	118.1
0.7	0.78	2.0	−0.922 027 461 527 015 2	93.8
0.8	0.861 25	2.445	−1.020 056 666 360 138 9	88.5
0.9	0.939 5	3.007 5	−1.083 643 239 958 508 7	86.6
1.0	1.017 5	3.679 4	−1.124 539 719 546 579 1	84.5
1.1	1.093 25	4.445	−1.150 057 367 738 288 5	83.0
1.2	1.16	5.197 5	−1.164 935 243 440 028 1	85.3
1.3	1.227 5	5.945	−1.172 347 149 037 780 0	86.1
1.4	1.320 75	6.320 75	−1.174 475 714 220 075 5	75.0
1.5	1.39	6.945	−1.172 855 079 578 144 7	74.3
1.6	1.43	7.351 25	−1.168 583 373 370 926 3	83.9
1.7	1.525	7.695	−1.162 458 726 897 808 8	72.6
1.8	1.625	7.82	−1.155 068 737 610 807 1	62.2
1.9	1.705	8.07	−1.146 850 697 028 721 0	58.2
2.0	1.775	8.32	−1.138 132 957 131 503 5	56.7
2.1	1.851	8.445	−1.129 163 836 099 972 1	53.8
2.2	1.94	8.445 75	−1.120 132 116 847 639 1	48.9
2.3	1.985	9.07	−1.111 181 765 202 644 8	51.2
2.4	2.05	9.445	−1.102 422 606 009 297 8	49.9
2.5	2.125	9.57	−1.093 938 129 953 599 8	47.0
2.6	2.225	9.32	−1.085 791 237 393 588 7	40.4
2.7	2.287 5	9.695	−1.078 028 484 181 047 9	40.2
2.8	2.35	9.82	−1.070 683 233 478 409 5	38.9
2.9	2.425	10.07	−1.063 778 008 802 791 6	36.3
3.0	2.5	10.195	−1.057 326 268 869 243 9	33.8
3.1	2.6	9.945	−1.051 333 772 264 451 6	29.9
3.2	2.65	10.32	−1.045 799 661 428 733 8	29.0
3.3	2.75	10.07	−1.040 717 365 347 598 5	25.7
3.4	2.825	10.21	−1.036 075 395 186 919 5	23.7
3.5	2.875	10.695	−1.031 858 084 851 223 0	22.5
3.6	2.95	10.757 5	−1.028 046 308 375 876 6	20.5
3.7	3.025	11.07	−1.024 618 188 407 147 2	18.6
3.8	3.115	10.82	−1.021 549 795 529 910 9	16.6
3.9	3.167 5	11.32	−1.018 815 827 692 849 8	15.3
4.0	3.23	11.601 25	−1.016 390 252 947 128 3	13.8
4.2	3.38	11.882 5	−1.012 359 959 679 918 9	11.0
4.4	3.525	12.15	−1.009 256 516 258 663 2	8.7
4.6	3.6	13.32	−1.006 895 223 820 121 1	6.9
4.8	3.75	13.32	−1.005 116 006 098 095 2	5.3
5.0	3.9	13.195	−1.003 785 658 581 988 9	4.0
5.2	3.95	14.75	−1.002 796 816 309 543 1	3.2
5.4	4.1	14.00	−1.002 065 057 208 235 3	2.4
5.6	4.15	14.82	−1.001 525 251 885 354 9	1.9
5.8	4.2	15.57	−1.001 127 880 851 321 4	1.5
6.0	4.3	15.00	−1.000 835 707 654 227 9	1.2

needed in Hy-CI calculations. This can be seen by considering what a $\sigma(1)\sigma(2)r_{12}^2$ term expands out to using

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}. \tag{4}$$

For high precision, Hy wave functions[2,5–7] must have the r_{12} power $k>1$, whereas Hy-CI wave functions need only have r_{12} raised to at most the first power.

In elliptical coordinates,

$$r_{12}^2 = \left(\frac{R}{2}\right)^2 [p - 2q\cos(\phi_1 - \phi_2)], \tag{5}$$

where

$$p = \xi_1^2 + \eta_1^2 + \xi_2^2 + \eta_2^2 - 2 - 2\xi_1\eta_1\xi_2\eta_2,$$

$$q = [(\xi_1^2 - 1)(1 - \eta_1^2)(\xi_2^2 - 1)(1 - \eta_2^2)]^{1/2}. \tag{6}$$

Expanding Eq. (5), the first term is just a polynomial in ξ_1, η_1, ξ_2, and η_2. Hence multiplying it by $\sigma(1)\sigma(2)$ just produces another $\sigma(1)\sigma(2)$ charge distribution with higher powers of n_i and j_i. The second term in Eq. (5) is proportional to $q\cos(\phi_1 - \phi_2)$. But $q\cos(\phi_1 - \phi_2)$ is a linear combination of $\pi(1)\pi(2)$ products with $M=0$ (but without the exponential factors). This gets multiplied by the $\sigma(1)\sigma(2)$ part (which does have the exponential factors). The $\pi(1)\pi(2)$ term gets multiplied by the $\sigma(1)\sigma(2)$ part of the $\sigma(1)\sigma(2)r_{12}^2$ term, so the final result is a special linear combination of $\sigma\sigma$ and $\pi\pi$ CI configurations. As long as the powers of ξ and η in the CI part of Hy-CI are greater than or equal to powers of ξ and η in the r_{12}^2 term in the Hy expansion for both $\sigma\sigma$ and $\pi\pi$, one will get an Hy-CI answer just as good as an answer with Hy. Similar results apply for r_{12}^4 and r_{12}^6 (this same point was made by Clary[12]).

Although other (radial) factors will be different in the two methods, they are essentially equivalent methods (for two-electron problems). We note that an equivalent Hy-CI calculation would have orbitals up to and including δ with r_{12} raised to at most the first power. A really good Hy-CI for H_2 would start out with a CI calculation including all the different term types ($\sigma\sigma, \pi\pi, \delta\delta, \phi\phi$, etc.) and then add to this each of the terms multiplied by r_{12} but in general with different nonlinear parameters. In particular, we note that where calculations have been done (CI for H_2 and Hy-CI for He) orbital exponents tend to increase at least for $\pi\pi$ (pp for He) terms resulting in significantly improved convergence of the expansion.

In this paper we go beyond both the molecular Hy-CI calculations of Clementi et al. and the purely Hy calculations to achieve the best results for both types of calculations. Since the Hy and Hy-CI methods are computationally equivalent for all practical purposes for two-electron molecular systems (we have demonstrated this for the helium atom[33]), a Hy-CI calculation should be able to achieve comparable or better energies than these results with shorter expansions.

A. Comparison with experiment

For a review of the status of our knowledge of the dissociation energy of H_2 until the year 2000 (theoretical and experimental), see Stoicheff.[34] Currently the best experimental value for the dissociation energy D_0 for H_2 is 36 118.062(10) cm^{-1}.[35] The best theoretical value is 36 118.058 cm^{-1}.[1] The previous best theoretical values were 36 118.069 cm^{-1} (Ref. 36) and 36 118.049 cm^{-1},[7] respectively. These theoretical values are obtained starting from accurate values for the Born-Oppenheimer (BO) electronic energies for the ground state of the H_2 molecule over a range

of internuclear distances R. This defines a BO potential energy (PE) curve. The results presented in Table VI are the definitive values for these BO energies defining the PE curve. These can be used with separate calculations of adiabatic, relativistic, and radiative (QED) corrections to obtain a theoretical dissociation energy (see, for example, Ref. 1). Our results are good enough to pin down the theory to 0.001 wave number *if* one can calculate the other corrections accurately enough. As new values of adiabatic, relativistic, and QED corrections are obtained, they can be combined with our BO energies to obtain new theoretical values. So maybe the experiment needs to be redone using 0.001 wave number as the level of accuracy to shoot for, that is, an order of magnitude reduction in the current experimental uncertainties.

APPENDIX: SPECIAL FEATURES OF THE CALCULATION

For a discussion of integral techniques needed to solve the H_2 electronic secular equation using ellipsoidal coordinates, see Kolos and Roothaan[5,37] and references therein and, in particular, the definitive paper of Rüdenberg.[38]

A parallel eigensolver proved essential for obtaining results over a range of R from 0.4–6.0 bohrs. This involves solving the N-dimensional generalized eigenvalue problem

$$\mathbf{HC} = \lambda \mathbf{SC} \tag{A1}$$

by the inverse iteration method.[39] We solve this secular equation using our own portable parallel inverse iteration solver.[40] The generation of the matrices $\mathbf{H}$ and $\mathbf{S}$ is of order N^2 while the solution of the secular equation Eq. (A1) is of order N^3. Since for us N is large and the interprocessor communication is only of order N^2, the parallelization of the $\mathbf{H}$ and $\mathbf{S}$ matrices is largely a matter of convenience (since no restructuring of the code is required, just a suitable selection of columns by each process). We calculated the basic integrals on each process, since this takes up only a small fraction of the total time, but parallelized the $\mathbf{H}$ and $\mathbf{S}$ matrix construction since that allows the total memory needed to be spread across the processors and eliminates a need to communicate matrix elements between processors. The result was that the whole process is almost "embarrassingly parallel" with near linear "speedup." For example, for a 4190 term wave function we achieved a factor of 30 speedup on 32 processors for the order N^3 step running on the National Institute of Standards and Technology (NIST) 147 processor cluster of Pentium (the identification of any commercial product or trade name does not imply endorsement or recommendation by either the National Institute of Standards and Technology or Indiana University), Athlon, and Intel processors running REDHAT LINUX.

Almost all results reported in this paper were obtained using quadruple precision ($\sim$30+ digits) floating point subroutines written in FORTRAN 90 using Miller's[41] quadruple precision package which we augmented to interface to other data types (where native quadruple precision exists and complete agreement with Miller's package was always obtained). Much of the present code was developed on a conventional desktop personal computer (PC) running WINDOWS 98 and using FORTRAN compilers that did not include quadruple precision as a native FORTRAN data type. It was here that Miller's package proved extremely useful. Recently Hida's[42] very efficient quadruple precision package (coded in C++) has become available. We have our own portable FORTRAN 90 version of this excellent package,[40] but there was no need in this work to switch from the Miller package which we have been using from the very beginning.

In addition to Miller's quadruple precision package, we made use of Brent's arbitrary multiple precision (MP) floating point arithmetic package[43,44] for the Rüdenberg ϕ function[38] on which all integrals depend. The Rüdenberg ϕ function is computed in multiple precision using Brent's MP package interfaced to FORTRAN 90 using the user defined data-type mechanism with associated interface block definitions for the MP arithmetic operations and intrinsic functions.

The Rüdenberg ϕ function is

$$\phi_{nn'}^{Ml}(\alpha, \alpha') = \phi_{n'n}^{Ml}(\alpha', \alpha)$$

$$= (-1)^M \frac{(l-M)!}{(l+M)!} \int_1^\infty d\xi Q_l^M(\xi)(\xi^2 - 1)^{M/2}$$

$$\times \left\{ e^{-\alpha\xi} \xi^n \int_1^\xi dx P_l^M(x)(x^2 - 1)^{M/2} e^{-\bar{\alpha}x} x^{\bar{n}} \right.$$

$$\left. + e^{-\bar{\alpha}\xi} \xi^{\bar{n}} \int_1^\xi dx P_l^M(x)(x^2 - 1)^{M/2} e^{-\alpha x} x^n \right\}, \tag{A2}$$

where the P_l^M are Legendre polynomials and the Q_l^M are associated Legendre functions of the second kind (see Ref. 38, footnote 4 for detailed definitions).

Rüdenberg gives complicated recursion schemes for raising n, n', l, and M starting from ϕ_{00}^{00}. Upper limits on n and n' depend on the values of l and M required, which in turn depend on the expansion basis being used (maximum powers of ξ and η). In the present work values of l up to 40 and n and n' up to 81 were used. The recursion relations are unstable for all indices, but for l they are particularly pathological involving the loss of one to two decimal digits of

accuracy each time l is raised by 1. Raising M from 0 to its maximum value of 7 (in this work) involves only minor loss of accuracy through differencing. Conversion back to quadruple precision was then done and the r_{ij}^{μ} integrals were evaluated in quadruple precision. To address these differencing problems we systematically increased the number of decimal digits used for only the ϕ part of the calculation up to a maximum of 160 decimal digits.

We note that Kolos and Wolniewicz[6,7] worked in double precision and evaluated the r_{ij} integrals numerically using an efficient charge distribution scheme (also introduced by Rüdenberg). This numerical approach is not applicable in this work due to the general need for higher precision values for all the basic integrals.

The code development used a desktop PC (Athlon, 0.5 Gbyte memory, WINDOWS 98) until the memory capacity of the system was exceeded, at which time we moved over to larger systems with more memory and somewhat later, parallelized the code to run on cluster systems at Indiana University [analysis and visualization of instrument-driven data (AVIDD)] and NIST (Raritan). The parallelization proved extremely helpful not only for speeding the calculation but also by spreading the total memory needed across the nodes of the cluster.

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