High Precision Variational Calculations for the Born-Oppenheimer Energies of the Ground State of the Hydrogen Molecule

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Abstract

Born-Oppenheimer approximation Hylleraas (Hy) 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 −1.1744 7571 4220(1) hartree at R= 1.4 bohr, which is 4 orders of magnitude better than the best previous Hylleraas calculation, that of Wolniewicz[1]. This result agrees well with the best previous variational energy, −1.1744 7571 4216 hartree, of Cencek[2], obtained using Explicitly Correlated Gaussians (ECG) [3–5]. The uncertainty in our result is also discussed. The nonrelativistic energy is calculated to be −1.1744 7593 1399(1) hartree at the equilibrium R= 1.4011 bohr distance. This result also agrees well with the best previous variational energy, −1.1744 7593 1389 hartree, of Cencek and Rychlewski[6, 7], obtained using Explicitly Correlated Gaussians (ECG) [3–5].

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 [7]). 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 [8]. Following the work of Hylleraas [9] on the helium atom, they employed factors of r_{12} in the hydrogen molecule wave function (the full bibliography on H_2 calculations through 1960 is given in [10]) and established beyond a doubt the usefulness of including the interelectronic distance explicitly in the wave function. Kolos, Roothaan, and Wolniewicz [1, 11, 12] generalized the approach of James and Coolidge to get a more accurate description of dissociation. Wave functions using their "generalized James-Coolidge" wave functions are commonly referred to as Hylleraas (Hy) or more specifically Kolos-Wolniewicz (KW) wave functions [7]. In addition to Hy wave function calculations, the Hylleraas-Configuration Interaction (Hy-CI) technique (developed by us [13] and also independently by Woźnicki [14]) has been applied to diatomic molecules (including H_2) by Clary and coworkers [15–18] and Clementi and coworkers [19–24]. 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 [5] and Section 2.4 Rychlewski [7] for a discussion of Hy-CI wave functions). However the Clementi, et. al. calculations for H_2 did not achieve the accuracy of purely Hy calculations, the best of which were the KW calculations of Wolniewicz [1].

In this work we extend the work of Kolos, Roothaan, and Wolniewicz [1, 11, 12] to calculate 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 bohr to 6.0 bohr. We also determine the BO ground state energy more precisely than the best previous calculation [6, 7].

The calculations reported are similar to those described in the classic paper of Kolos and

Roothaan [11], (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 one employing exponentially correlated gaussian (ECG) functions [3–5, 7]. 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 calculation. Many authors have emphasized that the wave function should have a cusp-like behavior [25] at $r_{12} = 0$ such that

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

The ECG wave function cannot properly represent this behavior. However progress towards overcoming this defect has recently been made by Pachucki and Komasa [26, 27]. They add terms linear in r_i and r_{ij} to an ECG calculation to produce what they call a LECG (Linear ECG) basis.

II. WAVE FUNCTIONS

Since the time-independent, nonrelativistic electronic Schrödinger equation in the Born-Oppenheimer (BO) (or 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 [28] 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 [29] to allow multiple parameters, e.g., 132 in the calculation reported in Table 3). 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 bohr to 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 $\alpha = \bar{\alpha} = \alpha_1$, the other with $\alpha = \bar{\alpha} = \alpha_2$ (we refer to these as 2 alpha expansions).

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 $n+j \leq k$, and all $\bar{n}$ and $\bar{j}$ powers of ξ_2 and η_2, respectively, satisfying $\bar{n}+\bar{j} \leq k$. 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 $\leq \nu$. This and the value of α ($= \bar{\alpha}$) 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 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 8 lines are for adding successively high powers of r_{ij} with $\alpha_1 = 1.32075$, then terms corresponding to $\alpha_2 = 6.32075$ 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 distribution with a single non-linear parameter. In this connection, we note that the reordered 2 alpha expansion results presented in Table II exhibit no such

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) in hartrees	ΔE
0	11	10	1.32075	0	1491	-1.1615 1824 0453 5174	
1	10	10	1.32075	1131	2622	-1.1744 3703 3907 7737	-0.12918×10^{-1}
2	9	10	1.32075	790	3412	-1.1744 7526 7311 5136	-0.38233×10^{-4}
3	8	10	1.32075	535	3947	-1.1744 7570 6160 3207	-0.43884×10^{-6}
4	7	10	1.32075	346	4293	-1.1744 7571 3814 8606	-0.76545×10^{-8}
5	7	10	1.32075	346	4639	-1.1744 7571 4083 1845	-0.26832×10^{-9}
6	6	10	1.32075	214	4853	-1.1744 7571 4100 1853	-0.17000×10^{-10}
7	6	10	1.32075	214	5067	-1.1744 7571 4145 0115	-0.44826×10^{-10}
0	8	8	6.32075	535	5602	-1.1744 7571 4190 6843	-0.45672×10^{-10}
1	8	8	6.32075	535	6137	-1.1744 7571 4210 5233	-0.19839×10^{-10}
2	7	8	6.32075	346	6483	-1.1744 7571 4216 4017	-0.58783×10^{-11}
3	6	8	6.32075	214	6697	-1.1744 7571 4218 7116	-0.23099×10^{-11}
4	6	8	6.32075	214	6911	-1.1744 7571 4219 8181	-0.11065×10^{-11}
5	5	8	6.32075	123	7034	-1.1744 7571 4220 0755	-0.2574×10^{-12}

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, $E = -1.1744\ 7571\ 4220(1)$ 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

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; $\alpha_1 = 1.32075$, $\alpha_2 = 6.32075$

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μ	ΔN	N	Energy(E) in hartrees	ΔE
0		2026	-1.1615 2330 0229 8360	
1	1656	3682	-1.1744 3733 6488 6086	-0.12914×10^{-1}
2	1146	4828	-1.1744 7528 0326 4709	-0.37943×10^{-4}
3	749	5577	-1.1744 7570 6942 0231	-0.42661×10^{-6}
4	560	6137	-1.1744 7571 4069 2123	-0.71271×10^{-8}
5	469	6606	-1.1744 7571 4216 3899	-0.14717×10^{-9}
6	214	6820	-1.1744 7571 4219 9248	-0.35349×10^{-11}
7	214	7034	-1.1744 7571 4220 0755	-0.1507×10^{-12}

calculation reported in [6]. As communicated to us by Cencek [2], he gets $-1.1744\ 7571\ 4216$ hartree and then the numerical stability of the wave function deteriorates so that the last digit starts fluctuating. Which means the $-1.1744\ 7571\ 4223$ hartree reported in [6] 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 1.1744 7571 4220(1), two orders of magnitude better than the error estimate of the best previous calculations [2, 6] . In Table III we label our calculations with a single α as 1 alpha and those with both an α_1 and an α_2 as 2 alpha. The JC, KW, ECG and Hy-CI designations in this and following tables are those of Rychlewski[7].

In Kolos and Roothaan's original paper[11] the highest power of r_{12} used was 2. Terms with r_{12}^2 introduce the equivalent of $\pi(1)\pi(2)$ configuration interaction type terms. So only $\sigma-\sigma$ 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 8 digits (7 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 [31]. The energy calculated

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) in hartrees
many alpha	Kubacki and Komasa [29]	22 [a]	-1.1744 7477
JC	Bishop and Cheung [30]	249	-1.1744 7565
KW	Kolos (includes r_{12}^3) [12]	370	-1.1744 7568 5
1 alpha	This work (includes r_{12}^3)	3947	-1.1744 7570 6160
2 alpha	This work (includes r_{12}^3)	5577	-1.1744 7570 6942
KW	Wolniewicz (includes r_{12}^6) [1]	883	-1.1744 7571 3565
ECG	Cencek and Kutzelnigg [31]	1200	-1.1744 7571 4037
1 alpha	This work (includes r_{12}^5)	4639	-1.1744 7571 4083
1 alpha	This work (includes r_{12}^7)	5067	-1.1744 7571 4145
2 alpha	This work (includes r_{12}^5)	6606	-1.1744 7571 4216
ECG	Cencek[2]	2400	-1.1744 7571 4216
2 alpha	This work (includes r_{12}^7)	7034	-1.1744 7571 4220

[a] 132 nonlinear parameters

with the ECG wave function was obtained only after a very time-consuming optimization process in which 5 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 Equation 3 and the optimization of only the single parameter α. By going up to r_{12}^7 we effectively correlate up to $\phi(1)\phi(2)$ type products. Table III shows that a single nonlinear parameter is adequate for a 0.1 nanohartree 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 nanohartree 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 Cencek and Rychlewski wave function parallels the relationship of ECG to Hy at R = 1.4 bohr.

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

Technique	Author	N	Energy(E) in hartrees
Hy-CI	Clementi [22, 23]	586	-1.1744 7467
KW	Wolniewicz [1]	883	-1.1744 7593 0742
ECG	Rychlewski,Cencek, and Komasa [32]	700	-1.1744 7593 1197
ECG	Cencek and Rychlewski [6]	2400	-1.1744 7593 1389
2 alpha	This work (includes r_{12}^7)	7034	-1.1744 7593 1399 84

We find in this work that very good energies are obtained with our wave functions up to and including R = 6.0 bohr. 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 the 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 [1].

Drake[33] 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 10th digit (0.1 nanohartree 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

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 [7]) 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 1 α
1.0	-1.1245 3971 95	-1.1245 3971 9462 06
1.2	-1.1649 3524 33	-1.1649 3524 3354 69
1.4	-1.1744 7571 40	-1.1744 7571 4145 01
1.6	-1.1685 8337 33	-1.1685 8337 3287 03
1.8	-1.1550 6873 75	-1.1550 6873 7548 57
2.0	-1.1381 3295 70	-1.1381 3295 7074 81
3.0	-1.0573 2626 87	-1.0573 2626 8835 43
4.0	-1.0163 9025 28	-1.0163 9025 2933 31
6.0	-1.0008 3570 76	-1.0008 3570 7653 04

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 bohr to 6.0 bohr 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 nanohartree. We have not investigated this question for the other R values. In the table we give energies 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.

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

R	α_1	α_2	Energy(E) in hartrees	ΔE(α_2) $\times 10^{12}$
0.4	0.5075	0.98286	-0.1202 3034 1177 8644	285.9
0.5	0.605	1.28144	-0.5266 3875 8742 3172	152.1
0.6	0.6875	1.65	-0.7696 3542 9485 3568	118.1
0.7	0.78	2.0	-0.9220 2746 1527 0152	93.8
0.8	0.86125	2.445	-1.0200 5666 6360 1389	88.5
0.9	0.9395	3.0075	-1.0836 4323 9958 5087	86.6
1.0	1.0175	3.6794	-1.1245 3971 9546 5791	84.5
1.1	1.09325	4.445	-1.1500 5736 7738 2885	83.0
1.2	1.16	5.1975	-1.1649 3524 3440 0281	85.3
1.3	1.2275	5.945	-1.1723 4714 9037 7800	86.1
1.4	1.32075	6.32075	-1.1744 7571 4220 0755	75.0
1.5	1.39	6.945	-1.1728 5507 9578 1447	74.3
1.6	1.43	7.35125	-1.1685 8337 3370 9263	83.9
1.7	1.525	7.695	-1.1624 5872 6897 8088	72.6
1.8	1.625	7.82	-1.1550 6873 7610 8071	62.2
1.9	1.705	8.07	-1.1468 5069 7028 7210	58.2
2.0	1.775	8.32	-1.1381 3295 7131 5035	56.7
2.1	1.851	8.445	-1.1291 6383 6099 9721	53.8
2.2	1.94	8.44575	-1.1201 3211 6847 6391	48.9
2.3	1.985	9.07	-1.1111 8176 5202 6448	51.2
2.4	2.05	9.445	-1.1024 2260 6009 2978	49.9
2.5	2.125	9.57	-1.0939 3812 9953 5998	47.0
2.6	2.225	9.32	-1.0857 9123 7393 5887	40.4
2.7	2.2875	9.695	-1.0780 2848 4181 0479	40.2
2.8	2.35	9.82	-1.0706 8323 3478 4095	38.9

TABLE VI: – *continued from previous page*

R	α_1	α_2	Energy(E) in hartrees	ΔE(α_2) $\times 10^{12}$
2.9	2.425	10.07	-1.0637 7800 8802 7916	36.3
3.0	2.5	10.195	-1.0573 2626 8869 2439	33.8
3.1	2.6	9.945	-1.0513 3377 2264 4516	29.9
3.2	2.65	10.32	-1.0457 9966 1428 7338	29.0
3.3	2.75	10.07	-1.0407 1736 5347 5985	25.7
3.4	2.825	10.21	-1.0360 7539 5186 9195	23.7
3.5	2.875	10.695	-1.0318 5808 4851 2230	22.5
3.6	2.95	10.7575	-1.0280 4630 8375 8766	20.5
3.7	3.025	11.07	-1.0246 1818 8407 1472	18.6
3.8	3.115	10.82	-1.0215 4979 5529 9109	16.6
3.9	3.1675	11.32	-1.0188 1582 7692 8498	15.3
4.0	3.23	11.60125	-1.0163 9025 2947 1283	13.8
4.2	3.38	11.8825	-1.0123 5995 9679 9189	11.0
4.4	3.525	12.15	-1.0092 5651 6258 6632	8.7
4.6	3.6	13.32	-1.0068 9522 3820 1211	6.9
4.8	3.75	13.32	-1.0051 1600 6098 0952	5.3
5.0	3.9	13.195	-1.0037 8565 8581 9889	4.0
5.2	3.95	14.75	-1.0027 9681 6309 5431	3.2
5.4	4.1	14.00	-1.0020 6505 7208 2353	2.4
5.6	4.15	14.82	-1.0015 2525 1885 3549	1.9
5.8	4.2	15.57	-1.0011 2788 0851 3214	1.5
6.0	4.3	15.00	-1.0008 3570 7654 2279	1.2

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 Adamowicz, et.

al. [34]. This approach yields energies of about 10 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 VERSUS 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 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

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2\cos\theta_{12}. \tag{4}$$

For high precision, Hy wave functions [1, 8, 11, 12] 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,

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

where

$$\begin{aligned} p &= \xi_1^2 + \eta_1^2 + \xi_2^2 + \eta_2^2 - 2 - 2\xi_1\eta_1\xi_2\eta_2 \\ q &= [(\xi_1^2 - 1)(1 - \eta_1^2)(\xi_2^2 - 1)(1 - \eta_2^2)]^{\frac{1}{2}}. \end{aligned} \tag{6}$$

Expanding Equation 5, the first term is just a polynomial in $\xi_1, \eta_1, \xi_2, \eta_2$. Hence multiplying it by $\sigma(1)\sigma(2)$ just produces another $\sigma(1)\sigma(2)$ charge distribution with higher powers of n_i, j_i. The second term in Equation 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 just as good an answer with Hy-CI as Hy. Similar results apply for r_{12}^4 and r_{12}^6 (this same point was made by Clary[17]).

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 one 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.), then add to this each of the terms multiplied by r_{12}. But in general with different non-linear parameters. In particular, we note that where calculations have been done (CI for H_2, 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 Clementi, et. al. molecular Hy-CI calculations 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 [35]), an Hy-CI calculation should be able to achieve comparable or better energies than these results with shorter expansions.

Comparison with Experiment

For a review of the status of our knowledge of the dissociation energy of H_2 through the year 2000 (theoretical and experimental), see Stoicheff [36]. Currently the best experimental value for the dissociation energy D_0 for H_2 is 36118.062(10) cm^{-1} [37]. The best theoretical value is 36118.058 cm^{-1} [7]. The previous best theoretical values were 36118.069 cm^{-1} [38] and 36118.049 cm^{-1} [1], 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, [7]). Our results are good enough to pin down the theory to 0.001 wavenumber *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 wavenumber as the level of accuracy to shoot for. That is, an order of magnitude reduction in the current experimental uncertainties.

APPENDIX A: 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[11, 39] and references therein, and in particular the definitive paper of Rüdenberg [40].

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

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

by the inverse iteration method [41]. We solve this secular equation using our own portable parallel inverse iteration solver [42]. The generation of the matrices **H** and **S** is order N^2 while the solution of the secular equation Equation A1 is order N^3. Since for us N is large and interprocessor communication is only order N^2, the parallelization of the H and 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 H and 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)'s 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 Alan Miller's [43] quadruple precision package which we augmented to interface to other data types (where native quadruple precision exists complete agreement with Miller's package was always obtained). Much of the present code was developed on a conventional desktop 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 Yozo Hida[44]'s very efficient quadruple precision package (coded in C++) has become available.

We have our own, portable Fortran 90 version of this excellent package [42], 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 the Miller quadruple precision package, we made use of Richard Brent's arbitrary multiple precision floating point arithmetic package [45, 46] for the Rüdenberg ϕ [40] function, on which all integrals depend. The Rüdenberg ϕ function is computed in multiple precision using the Brent MP package interfaced to Fortran 90 using the user defined datatype mechanism with associated interface block definitions for the MP arithmetic operations and intrinsic functions.

The Rüdenberg ϕ function is

$$\begin{aligned}\phi_{nn'}^{Ml}(\alpha,\alpha') &= \phi_{n'n}^{Ml}(\alpha',\alpha) \\ &= (-1)^M \frac{(l-M)!}{(l+M)!} \int_1^\infty d\xi Q_l^M(\xi)(\xi^2-1)^{M/2} \\ &\times \{e^{-\alpha\xi}\xi^n \int_1^\xi dx P_l^M(x)(x^2-1)^{M/2} e^{-\bar{\alpha}x} x^{\bar{n}} \\ &+ e^{-\bar{\alpha}\xi}\xi^{\bar{n}} \int_1^\xi dx P_l^M(x)(x^2-1)^{M/2} e^{-\alpha x} x^n\},\end{aligned} \tag{A2}$$

where the P_l^M are Legendre polynomials and the Q_l^M are associated Legendre functions of the second kind (see [40], 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, 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,n' up to 81 were used. The recursion relations are unstable for all indices but for l is 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 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 [1, 12] 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, 0.5Gb 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 (AVIDD)and NIST (raritan). The parallelization proved extremely helpful not only for speeding the calculation up but also by spreading the total memory needed across the nodes of the cluster.

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