

Improved quantum Monte Carlo calculation of the ground-state energy of the hydrogen molecule

Bin Chen^{a)} and James B. Anderson^{b)}

The Pennsylvania State University, University Park, Pennsylvania 16802

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We report an improved Green's function quantum Monte Carlo calculation of the nonrelativistic ground-state energy of the hydrogen molecule, without the use of the Born–Oppenheimer or any other adiabatic approximations. A more accurate trial function for importance sampling and the use of the exact cancellation method combine to yield an energy which is a factor of 10 more accurate than that of previous quantum Monte Carlo calculations. The energy is less accurate than that of recently improved analytic variational calculations. The calculated energy is $-1.164\,0239 \pm 0.000\,0009$ hartree. Expressed as the dissociation energy and corrected for relativistic and radiative effects, the result is $36\,117.84 \pm 0.20$ cm⁻¹, a value in agreement with the most recent experimental value $36\,118.11 \pm 0.08$ cm⁻¹ obtained by Balakrishnan *et al.* © 1995 American Institute of Physics.

I. INTRODUCTION

The hydrogen molecule H₂ is a basic arena for the confrontation of theory and experiment in fundamental molecular physics. It is the simplest molecular system which exhibits such important effects as electron correlation, the separation of electronic and nuclear motion, and related nonadiabatic effects, as well as relativistic and radiative effects.

There is a long history of increasingly accurate theoretical calculations of the energy of the hydrogen molecule and increasingly accurate experimental measurements of the ionization potential and the dissociation energy.^{1–3} The method of choice for theoretical predictions has most often been the analytic variational method, but the quantum Monte Carlo method has recently approached its accuracy for the hydrogen molecule.⁴

We report here improved quantum Monte Carlo calculations yielding an energy a factor of 10 more accurate than that of earlier quantum Monte Carlo calculations. The accuracies of analytic variational calculations have also been improved recently and the Monte Carlo energy remains less accurate, but it provides an independent check for the analytic variational energies. The accuracy of the new Monte Carlo energy is approximately equal to that of recent experimental measurements and it similarly provides an independent check for those results.

Each of the most recent theoretical predictions of the energy of H₂ is based on a variational solution of the Schrödinger equation for the electrons to obtain a Born–Oppenheimer potential curve. The Schrödinger equation for the protons in the potential is then solved to obtain the energy of the molecule. The potential curve or the energy determined from it may be corrected for various defects with the addition of (a) basis set corrections, (b) adiabatic corrections, (c) nonadiabatic corrections, (d) relativistic correc-

tions, and (e) radiative corrections. Their effects are to alter the ground-state energy of H₂ by

$$\begin{aligned} &-0.014 \text{ cm}^{-1} \quad (\text{typical basis set}), \\ &+114.5 \text{ cm}^{-1} \quad (\text{adiabatic}), \\ &-0.5 \text{ cm}^{-1} \quad (\text{nonadiabatic}), \\ &-2.4 \text{ cm}^{-1} \quad (\text{relativistic}), \\ &+0.747 \text{ cm}^{-1} \quad (\text{radiative}). \end{aligned}$$

The same effects alter the energy of two separated ground-state H atoms by

$$\begin{aligned} &\text{no error} \quad (\text{basis set}), \\ &+119.5 \text{ cm}^{-1} \quad (\text{adiabatic}), \\ &\text{no error} \quad (\text{nonadiabatic}), \\ &-2.9 \text{ cm}^{-1} \quad (\text{relativistic}), \\ &+0.54 \text{ cm}^{-1} \quad (\text{radiative}). \end{aligned}$$

The lowest-energy analytic variational calculations for clamped-nucleus H₂ are those reported by Cencek and Rychlewski⁵ in 1993 giving a Born–Oppenheimer dissociation energy of $38\,292.989$ cm⁻¹ adjusted to 1.4 bohr. The lowest-energy Born–Oppenheimer potential energy curve which has been used in calculating the energy of H₂ was reported in 1993 by Wolniewicz⁶ and has a Born–Oppenheimer dissociation energy of $38\,292.984$ cm⁻¹ at 1.4 bohr. Calculations by Wolniewicz⁶ for that curve give a dissociation energy (including all corrections except basis set corrections) of $36\,118.060$ cm⁻¹. In 1994 Kolos⁷ reported additional variational calculations giving Born–Oppenheimer dissociation energies as high as $38\,292.989$ cm⁻¹ at 1.4 bohr. Extrapolating to a basis set of infinite size Kolos estimated the true Born–Oppenheimer dissociation energy to be $38\,292.998$ cm⁻¹ at 1.4 bohr. If we add the indicated basis set correction of $+0.014$ cm⁻¹ to the dissociation energy reported by Wolniewicz we obtain a “best” predicted dissociation energy of $36\,118.074$ cm⁻¹.

Some of the uncertainties in the corrections are difficult to evaluate, but it appears that the combination of the uncer-

^{a)}Department of Physics, 104 Davey Laboratory.

^{b)}Department of Chemistry, 152 Davey Laboratory.

tainties in the corrections to the Born–Oppenheimer curve and in all the other corrections leads to an overall uncertainty of about 0.01 cm^{-1} in the theoretical dissociation energy. The values reported over the past decade have varied by as much as 0.1 cm^{-1} .

Uncertainties in the fundamental constants lead to an uncertainty of about 0.002 cm^{-1} in the predicted dissociation energy for the hydrogen molecule.⁸

The accuracies of experimental measurements of the dissociation energy for H_2 have been improved repeatedly in recent years. In 1987 McCormack and Eyler⁹ reported a value of $36\,118.1 \pm 0.2 \text{ cm}^{-1}$. In 1992 Balakrishnan *et al.*¹⁰ reported a value of $36\,118.11 \pm 0.08 \text{ cm}^{-1}$.

The Green's function quantum Monte Carlo (GFQMC) method was used by Traynor *et al.*⁴ in 1991 for solution of the full four-body nonrelativistic Schrödinger equation for the hydrogen molecule. The method has the advantage of eliminating the basis set correction, the adiabatic correction, and the nonadiabatic correction. The Schrödinger equation is solved without systematic error, but a sampling or statistical error, which is easily estimated, is introduced. Since the trial function used in these earlier calculations was extremely simple and the step sizes were very small, the statistical accuracy was limited to $\pm 2.0 \text{ cm}^{-1}$.

In the improved calculations reported here the gain in accuracy results from (a) larger step sizes made possible by the use of positive and negative walkers and exact cancellation¹¹ and (b) an improved importance sampling function with a lower variance in local energies. Nevertheless, because of the masses of the nuclei, the steps remain small. For calculations with small steps the high correlation of the energies of walkers in successive steps decreases the efficiency of the calculations, and lengthy calculations are required for high accuracies.

II. THEORETICAL BACKGROUND

In order to calculate the ground-state energy of H_2 without using the Born–Oppenheimer or a related approximation, one must solve the Schrödinger equation for the full four-body system,

$$-\sum_j^n \frac{\hbar^2}{2m_j} \nabla_j^2 \Psi(\mathbf{R}) + V(\mathbf{R}) \Psi(\mathbf{R}) = E \Psi(\mathbf{R}). \quad (1)$$

With a transformation $\mathbf{Q}_j = \sqrt{(m_j/m_e)} \mathbf{R}_j$, Eq. (1) becomes

$$-\frac{\hbar^2}{2m_e} \nabla_Q^2 \Psi(\mathbf{Q}) + V(\mathbf{Q}) \Psi(\mathbf{Q}) = E \Psi(\mathbf{Q}). \quad (2)$$

This equation may be rearranged to obtain

$$-\nabla_Q^2 \Psi(\mathbf{Q}) + k^2 \Psi(\mathbf{Q}) = k^2 \frac{V(\mathbf{Q})}{E} \Psi(\mathbf{Q}), \quad (3)$$

where $k^2 = -2m_e E / \hbar^2$. It has been shown that the integral form of Eq. (3) can be written as

$$\Psi(\mathbf{Q}) = \int d\mathbf{Q}' G_0(\mathbf{Q}, \mathbf{Q}') \frac{V(\mathbf{Q}')}{E} \Psi(\mathbf{Q}'), \quad (4)$$

with the Green's function given¹²

$$G_0(\mathbf{Q}, \mathbf{Q}') = (2\pi)^{-3N/2} (k|\mathbf{Q} - \mathbf{Q}'|)^{1-3N/2} \times K_{3N/2-1}(k|\mathbf{Q} - \mathbf{Q}'|), \quad (5)$$

where K is the Bessel function of imaginary argument. The solution of Eq. (4) by iteration, starting with a trial function ψ_0 , is given by

$$\psi_{n+1}(\mathbf{Q}) = \int d\mathbf{Q}' G_0(\mathbf{Q}, \mathbf{Q}') \frac{V(\mathbf{Q}')}{E} \psi_n(\mathbf{Q}'). \quad (6)$$

It is not difficult to show that the sequence defined in Eq. (6) converges to the state of lowest energy which is not orthogonal to ψ_0 . In implementation, the Green's function serves as a transition probability for the random walker to move from \mathbf{Q} to \mathbf{Q}' with the step size $|\mathbf{Q} - \mathbf{Q}'|$ given by¹²

$$\mathbf{Q} = \frac{1}{k} (1 - \xi^{2/(N-1)})^{1/2} \ln(\xi_1 \xi_2, \dots, \xi_N), \quad (7)$$

where the ξ_j 's are uniformly distributed random numbers in the interval $[0, 1]$. By rescaling \mathbf{Q} back to \mathbf{R} , we have

$$\mathbf{R}_j = \sqrt{\frac{m_e}{m_j}} \mathbf{Q}_j. \quad (8)$$

Using \mathbf{R}_j , one can sample the ground-state wave function in the original coordinates.

Importance sampling may be used to make the sampling more effective, i.e., instead of the true wave function, the mixed distribution $\Phi = \Psi \psi_0$ may be sampled. With this substitution Eq. (4) becomes

$$\Phi(\mathbf{R}) = \int d\mathbf{R}' \frac{\psi_0(\mathbf{R})}{\psi_0(\mathbf{R}')} G_0(\mathbf{R}, \mathbf{R}') \frac{V(\mathbf{R}')}{E} \Phi(\mathbf{R}'), \quad (9)$$

and the energy is given by

$$E = \frac{\int d\mathbf{R} \Phi(\mathbf{R}) H \psi_0(\mathbf{R}) / \psi(\mathbf{R})}{\int d\mathbf{R} \Phi(\mathbf{R})}, \quad (10)$$

$$= \frac{\sum_i W_i E_L(\mathbf{R})}{\sum_i W_i}, \quad (11)$$

where, in sampling, the integrals are replaced by summations for random walkers with weights W_i .

III. CALCULATION PROCEDURE

Computations were carried out using IBM SP1 and SP2 machines at the Maui High Performance Computing Center and the Penn State Center for Academic Computation. The program consisted of about 860 lines of FORTRAN code. The calculations were carried out in about 1000 independent runs. Each run was divided into blocks of 55 iterations. The number of random walkers was controlled at approximately 30 000 by random duplication or elimination at the first iteration of each block. The energies were recorded after the ensemble was equilibrated and the data from the first ten iterations of each block were discarded in order to avoid any bias due to renormalization.

Since there are no nodes in the H_2 wave function, the only negative walkers came from the V/E term of Eq. (9) and the cancellation was very effective in eliminating them. The cancellations were carried out only for walkers corre-

TABLE I. Calculated energy of the hydrogen molecule.

Energy of 2H atoms	-0.999 4556 hartree
Calculated energy of H ₂	
GFQMC, uncorrected	-1.164 0239±0.000 0009 hartree
Calculated dissociation energy	
GFQMC, uncorrected	0.164 5682±0.000 0009 hartree
Calculated dissociation energy ^a	36 118.56±0.20 cm ⁻¹ ^b
Relativistic correction	-0.52±0.03 cm ⁻¹
Radiative correction	-0.20 cm ⁻¹
Calculated dissociation energy corrected	36 117.84±0.20 cm ⁻¹ ^b

^aConversion factor: 219 474.631 cm⁻¹=1 hartree.^bIndicated uncertainty is one standard deviation.

sponding to configurations in which the electrons were in close proximity to the nuclei. At steady state, the ratio of positive to negative walkers was approximately 30 to 1. The explicit algorithm was as follows:

(1) For each walker i with weight W_i at position \mathbf{R}'_i , calculate a new weight according to $W'_i = W_i V(\mathbf{R}'_i)/E$.

(2) Make symmetry transformations to concentrate positive and negative walkers in the same region of configuration space for more effective cancellation.

(3) Divide the cancellation region into boxes, pair the positive (negative) walkers in each box with the nearest negative (positive) walkers in the same box, and identify the pairs.

(4) Sample the Green's function $G_0(\mathbf{R}, \mathbf{R}')$ for a new position \mathbf{R}_i for each walker and move each walker from \mathbf{R}'_i to \mathbf{R}_i . For a paired walker i , having a cancellation partner j , the weight is adjusted according to

$$W'_i = W'_i \frac{G_0(\mathbf{R}, \mathbf{R}'_i) W'_i \psi_0(\mathbf{R}'_j) - G_0(\mathbf{R}, \mathbf{R}'_j) W'_j \psi_0(\mathbf{R}'_i)}{G_0(\mathbf{R}, \mathbf{R}'_i) W'_i \psi_0(\mathbf{R}'_j)} \quad (12)$$

(5) Evaluate $\psi_0(\mathbf{R}_i)/\psi_0(\mathbf{R}'_i)$. If $\psi_0(\mathbf{R}_i)/\psi_0(\mathbf{R}'_i) \geq 1$, the move is accepted and the new weight becomes $W'_i \psi_0(\mathbf{R}_i)/\psi_0(\mathbf{R}'_i)$. If $\psi_0(\mathbf{R}_i)/\psi_0(\mathbf{R}'_i) < 1$, the move is accepted with a probability equal to $\psi_0(\mathbf{R}_i)/\psi_0(\mathbf{R}'_i)$.

(6) Divide each walker into m walkers of unit weight with m given by the integer part of $W'_i + u$, where u is a random number in the interval of $[0,1]$.

(7) Calculate the local energy. Add the weighted energy and the weight to the appropriate sums for computing final averages.

(8) Go back to (1).

IV. THE TRIAL FUNCTION

The trial wave function used is a product of four terms:

$$\psi_0 = \psi_1 \psi_2 \psi_3 \psi_4. \quad (13)$$

Each of the first two terms is simply the linear combination of atomic orbitals of an electron $i=1,2$ for the two nuclei $\alpha=A, B$,

$$\psi_1 = \exp(-ar_{1A}) + \exp(-ar_{1B}), \quad (14)$$

$$\psi_2 = \exp(-ar_{2A}) + \exp(-ar_{2B}). \quad (15)$$

The term ψ_3 is the Jastrow factor which accounts for both electron-electron and electron-nucleus correlation such that the cusp conditions are satisfied as $r_{12}, r_{i\alpha} \rightarrow 0$ for $i=1$ or 2 and $\alpha=A$ or B . It has the form

$$\psi_3 = \exp \left[\sum_{ij} \frac{a_{ij}^{(0)} r_{ij}}{1 + b_{ij}^{(0)} r_{ij}} + \sum_{ijkl} \frac{a_{ijkl}^{(1)} r_{ij} r_{kl}}{1 + b_{ijkl}^{(1)} r_{ij} r_{kl}} \right], \quad (16)$$

where ij and kl include the interactions 12, 1A, 1B, 2A, 2B. The last term ψ_4 is a harmonic oscillator term intended to include in part the effects of nuclear interaction, and it is given by

$$\psi_4 = \exp[-d(r_{AB} - c)^2]. \quad (17)$$

The variational parameters $a, d, c, a_{ij}^{(n)}, b_{ij}^{(n)}, a_{ijkl}^{(n)}, b_{ijkl}^{(n)}$ were optimized to minimize the variance of the local energy.

V. RESULTS AND DISCUSSION

The total energy given by the Monte Carlo calculation for the ground state of H₂ is $-1.164 0239 \pm 0.000 0009$ hartree. The dissociation energy, obtained by subtracting the cal-

TABLE II. Comparison of the dissociation energies obtained from nonadiabatic variational calculations, QMC calculations, and experimental measurements. All theoretical values include corrections for both relativistic and radiative effects.

Authors	Date	Type	Dissociation energy (cm ⁻¹)
Bishop and Cheung (Ref. 13)	1978	Four-body variational ^a	36 117.92
Wolniewicz (Ref. 14)	1983	BO variational ^b	36 118.01
Kolos <i>et al.</i> (Ref. 15)	1986	BO variational ^b	36 118.023
Kolos and Rychlewski (Ref. 16)	1993	BO variational ^b	36 118.049
Wolniewicz (Ref. 6)	1993	BO variational ^b	36 118.060
Best theoretical		adjusted, see the text	36 118.074
Traynor <i>et al.</i> (Ref. 4)	1991	DQMC	36 107±11 ^c
Traynor <i>et al.</i> (Ref. 4)	1991	GFQMC	36 117.9±2.0 ^c
Chen and Anderson		GFQMC, this work	36 117.84±0.20 ^c
McCormack and Eyler (Ref. 9)	1987	experiment	36 118.1±0.2
Balakrishnan <i>et al.</i> (Ref. 10)	1992	experiment	36 118.11±0.08

^aIncludes basis set correction.^bBorn-Oppenheimer with adiabatic and nonadiabatic corrections.^cIndicated uncertainty is one standard deviation.

culated energy from the energy of two free H atoms ($-0.499\,7278$ hartree each), is $0.164\,5682$ hartree. This corresponds to a dissociation energy of $36\,118.56 \pm 0.20$ cm^{-1} (uncorrected). Adding a relativistic correction of -0.5174 cm^{-1} and a radiative correction of -0.20 cm^{-1} as determined by Wolniewicz,⁶ we obtain a corrected value for the dissociation energy for H_2 of $36\,117.84 \pm 0.2$ cm^{-1} . The indicated uncertainty is statistical and corresponds to one standard deviation. These values are listed in Table I.

The predicted value is in agreement with the most recent experimental value $36\,118.11 \pm 0.08$ cm^{-1} . It is in approximate agreement with the best value obtained from analytic variational calculations $36\,118.074 \pm 0.01$ cm^{-1} . The sources of these values are discussed in Sec. I. They are listed in Table II along with several others for comparison.

The (uncorrected) energy from the Monte Carlo calculation may be compared with a similar (uncorrected) energy from a four-body analytic variational calculation carried out by Bishop and Cheung¹³ in 1978. Both are independent of adiabatic and nonadiabatic corrections. The variational calculation gave an upper bound of $-1.164\,0241$ hartree for the energy of H_2 and a corresponding lower bound to the dissociation energy (uncorrected) of $36\,118.60$ cm^{-1} . The total energy given by the Monte Carlo calculation is $0.000\,0002$ hartree higher than the variational result and its lower error bar is $0.000\,0007$ hartree lower than the variational result. The results of the two calculations are consistent with each other.

Another factor of 10 in the accuracy of the Monte Carlo calculations could be gained by extending the calculations by a factor of about 100. Since computer speeds have increased by a factor of more than 100 in each of the past five decades, we might expect a gain in accuracy of more than a factor of 10 per decade without any improvement in the method. However, earlier and greater gains in accuracy are likely to be obtained with still better trial functions for importance sampling.

As the theoretical methods and the experimental methods continue to be improved, the small effects such as the radiative and relativistic corrections, which are now larger than the experimental error, increase in importance.

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