

## Quantum chemistry by random walk: Higher accuracy for H<sup>+</sup> 3

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# Quantum chemistry by random walk: Higher accuracy for $\text{H}_3^+$

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An improved quantum Monte Carlo calculation for the ground state of the molecular ion  $\text{H}_3^+$  gives higher accuracies than previously attained. The nonrelativistic electronic energy for the equilateral triangle configuration of side length 1.6500 bohrs is found to be  $-1.343\,835 \pm 0.000\,001$  hartrees.

## I. INTRODUCTION

Since Hirschfelder's<sup>1</sup> first analytic variational calculation of the electronic energy of the molecular ion  $\text{H}_3^+$ , there has been a succession of improved calculations which illustrate the advance of theoretical chemistry to higher and higher accuracies.<sup>2-41</sup> Calculations for the equilateral triangle nuclear configuration of  $\text{H}_3^+$  near the equilibrium internuclear distance of approximately 1.6500 bohrs are listed in Table I and their energies are plotted in Fig. 1. The progress of analytic variational calculations may be followed toward lower and lower energies, approaching with time the exact value. The progress of quantum Monte Carlo calculations may be followed toward the exact value with narrower and narrower error limits, approaching with time an uncertainty of zero.

We report here a new quantum Monte Carlo calculation of the nonrelativistic energy of  $\text{H}_3^+$  in the equilateral triangle configuration with an internuclear distance of 1.6500 bohrs. The accuracy obtained is better than that of any previous calculation. The gain in accuracy results from (a) the larger step sizes made possible by use of positive and negative psips along with cancellation; (b) an improved importance sampling function with a lower variance in local energies; and (c) the faster computation speed of a new computer.

## II. THEORETICAL BASIS

The Green's function quantum Monte Carlo method<sup>42</sup> provides solutions to the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(X) + V(X) \Psi(X) = E \Psi(X) \quad (1)$$

in the form of samples of the exact wave function  $\Psi(X)$ . Sampling is based on the property of the Green's function which relates the wave function to itself

$$\Psi(X) = \int G_0(X, X') \frac{V(X')}{E} \Psi(X') dX'. \quad (2)$$

Repeated application of Eq. (2) to an initially arbitrary wave function  $\Psi(X')$  leads to a wave function  $\Psi(X)$  which is the lowest-energy solution to the Schrödinger equation for the specified boundary conditions or other constraints.

We have previously reported, in detail, a simplified sampling procedure<sup>33</sup> for quantum Monte Carlo (QMC) calculations of wave functions for molecular systems without nodes. In that procedure, the wave function was maintained positive everywhere and changes in sign were prevented by

shifting the zero of potential energy such that  $V(X')$  and  $E$  were both negative. We recently described an exact quantum Monte Carlo method<sup>43</sup> for treating many-electron systems with nodes which is based on the partial cancellation of positive and negative wave function samples (psips) having overlapping Green's functions. As pointed out by Kalos,<sup>44</sup> the use of both positive and negative psips eliminates the need to keep  $V(X')$  negative. The zero of potential energy may then be adjusted to maximize the width of the Green's function and thus increase the average step size between successive samples to reduce the serial correlation and improve the efficiency of the calculations.

The Green's function  $G_0(X, X')$  is given by

$$G_0(X, X') = \left(\frac{1}{2\pi}\right)^{3N/2} (k |X - X'|)^{1-3N/2} \times K_{3N/2-1}(k |X - X'|), \quad (3)$$

where  $K_\nu$  is a modified Bessel function of the second kind and

$$k = \left(-\frac{2mE}{\hbar^2}\right)^{1/2}. \quad (4)$$

The average step size is proportional to  $k^{-1}$  and  $(-E)^{-1/2}$ . For large steps, the value of  $E$  should be chosen slightly below zero.

The theoretical basis for cancellation of positive and negative psips is described in Refs. 45 and 43. For the ground state of  $\text{H}_3^+$ , the wave function has no nodes and cancellation serves only to produce a stable, net positive population of psips. In the absence of cancellation, the wave function would be given by the small difference between large populations of positive and negative psips. With cancellation a stable, net positive population is easily maintained.

When importance sampling<sup>46</sup> is included, a guide function  $\Psi_G$  which is positive everywhere may be incorporated into the sampling process. A new function  $\Phi$  is defined as  $\Phi = \Psi \Psi_G$  the product of the exact wave function and the guide function, and Eq. (2) is replaced by

$$\Phi(X) = \int \frac{\Psi_G(X')}{\Psi_G(X')} G_0(X, X') \frac{V(X')}{E} \Phi(X') dX'. \quad (5)$$

The details of energy determination using importance sampling are given in Refs. 33 and 43. For the present case, the trial function  $\Psi_T$  is positive everywhere and the guide function  $\Psi_G$  is identical to  $\Psi_T$ . The exact energy  $E$  is given by

TABLE I. Quantum calculations for  $H_3^+$  in equilateral triangle configuration.

Reference	Date	$R$	Energy (a.u.)	Type
1 (Hirschfelder)	1938	1.790 0	− 1.292 9	CI-valence bond <sup>a</sup>
2 (Ellison, Huff, and Patel)	1963	1.760 0	− 1.338 3	Diatomics in molecules
3 (Conroy)	1964	1.680 0	− 1.357	MC variational
4 (Hoyland)	1964	1.680 0	− 1.272 6	CI-elliptical basis
5 (Christoffersen)	1964	1.657 5	− 1.332 64	CI-STO <sup>b</sup>
6 (Preuss)	1965	1.620 0	− 1.298 78	CI-GTO <sup>c</sup>
7 (Joshi)	1966	1.622 9	− 1.286 3	SCF-STO <sup>d</sup>
8 (Lester and Krauss)	1966	1.680 0	− 1.298 41	CI-GTO
9 (Pearson, Poshusta, and Browne)	1966	1.660 0	− 1.318 5	CI-GTO, 18 configurations
10 (Schwartz and Schaad)	1967	1.650 4	− 1.337 64	CI-GTO
11 (Kutzelnigg, Ahlrichs, Labib-Iskander, and Bingel)	1967	1.660 0	− 1.335 9	CI-GTO
12 (Grien and Chang)	1968	1.607 0	− 1.303 7	CI, SCF + $r_{12}$
13 (Christoffersen and Schull)	1968	1.657 5	− 1.299 2	SCF-NSO <sup>e</sup>
14 (Conroy)	1969	1.650 0	− 1.348	MC variational
15 (Csizmadia, Kari, Polanyi, Roach, and Robb)	1970	1.660 0	− 1.339 7	CI-GTO, > 120 configurations
16 (Borkman)	1970	1.638 5	− 1.339 181	CI-STO, 85 configurations
17 (Duben and Lowe)	1971	1.640 6	− 1.340 50	CI-GTO, 48 configurations
18 (Kawaoka and Borkman)	1971	1.650 0	− 1.340 50	CI-STO, 100 configurations
19 (Preston and Tully)	1971	1.730 0	− 1.356	Diatomics in molecules
20 (Salmon and Poshusta)	1973	1.650 0	− 1.343 35	CI, 15 polymal configurations
21 (Jaffe, Morokuma, and George)	1974	1.660 0	− 1.338 185	CI-GTO
22 (Carney and Porter)	1974	1.650 4	− 1.340 658	CI-GTO, 309 configurations
23 (Ahlrichs)	1975	1.660 0	− 1.337 93	CI-GTO
24 (Anderson)	1975	1.660 0	− 1.344 ± 0.013	QMC
25 (Dykstra, Gaylord, Gwinn, Swope, and Schaefer)	1978	1.650 4	− 1.342 784	CI-GTO, 1296 configurations
26 (Schinke, Dupuis, and Lester)	1980	1.660 0	− 1.340 229	CI-GTO, 606 configurations
27 (Mentch and Anderson)	1981	1.650 0	− 1.343 9 ± 0.000 2	QMC
28 (Preiskorn and Woznicki)	1982	1.650 4	− 1.342 03	CI, with $r_{12}$ , 36 configurations
29 (Wright and Borkman)	1982	1.650 0	− 1.340 22	CI-GTO
30 (Preiskorn and Woznicki)	1984	1.650 4	− 1.343 422	CI, with $r_{12}$ , 192 configurations
31 (Burton, Nagy-Felsobuki, Doherty, and Hamilton)	1985	1.650 41	− 1.342 72	CI-GTO
32 (Meyer, Botschwina, and Burton)	1986	1.650 4	− 1.343 40	CI-GTO
33 (Anderson)	1987	1.650 0	− 1.343 76 ± 0.000 03	QMC
34 (Traynor and Anderson)	1988	1.650 0	− 1.343 87 ± 0.000 05	QMC
35 (Urdaneta, Largo-Cabrerizo, Lievin, Lie, and Clementi)	1988	1.650 4	− 1.343 500	CI, with $r_{12}$
36 (Huang, Sun, and Lester)	1990	1.650 0	− 1.343 3 ± 0.000 5	QMC
37 (Frye, Preiskorn, Lie, and Clementi)	1990	1.650 0	− 1.343 827 9	CI, with $r_{12}$
38 (Alexander, Monkhorst, Roeland, and Szalewicz)	1990	1.650 0	− 1.343 822 0	CI-GTO, 700 configurations
39 (Röhse, Klopper, and Kutzelnigg)	1991	1.650 4	− 1.343 498	CI
40 (GAUSSIAN 88)	1991	1.650 0	− 1.332 21	CISD/6-31G** <sup>f</sup>
41 (Alexander, Coldwell, Monkhorst, and Morgan)	1991	1.650 0	− 1.343 820 ± 0.000 066	MC variational
This work	1992	1.650 0	− 1.343 835 ± 0.000 001	QMC

<sup>a</sup>CI denotes configuration interaction.<sup>b</sup>STO denotes Slater-type orbital.<sup>c</sup>GTO denotes Gaussian-type orbital.<sup>d</sup>SCF denotes self-consistent field.<sup>e</sup>NSO denotes natural spin-orbital.<sup>f</sup>CISD denotes single and double excitation configuration interactions.

$$E = \frac{\int \Phi (H\Psi_T/\Psi_T) dX}{\int \Phi dX}, \quad (6)$$

where  $\Phi = \Psi\Psi_T$  the product of the exact and the trial functions and  $(H\Psi_T/\Psi_T)$  is the local energy for the trial function.

The estimate of the energy obtained from Monte Carlo sampling is given by

$$E = \frac{\sum s_i W_i (H\Psi_T/\Psi_T)_i}{\sum s_i W_i}, \quad (7)$$

where  $s_i$  is the sign of a psip ( $\Phi$  based) and  $W_i$  is its weight. The uncertainty in the estimate of the energy depends on the accuracy of the trial function and the number of samples. It is directly proportional to this standard deviation  $\sigma_i$  in local energy and inversely proportional to the square root of the number of samples. Thus an accurate trial function and/or a large number of samples are desired.

### III. IMPORTANCE SAMPLING FUNCTION

The importance sampling function is similar to those of our previous calculations for  $\text{H}_3^+$ . The Jastrow part of the function is expanded to include terms suggested by several other workers.<sup>47-49</sup> As in all earlier work with importance sampling, the optimization of the coefficients was carried out by minimizing the variance in the local energy for a large sample of psips (e.g., Ref. 27).

The trial function is given by

$$\Psi_T = f_1 f_2 J, \quad (8)$$

where

$$\begin{aligned} f_1 &= \exp(-c_a r_{1A}) + \exp(-c_a r_{1B}) + \exp(-c_a r_{1C}), \\ f_2 &= \exp(-c_a r_{2A}) + \exp(-c_a r_{2B}) + \exp(-c_a r_{2C}), \\ J &= \exp(U), \end{aligned}$$

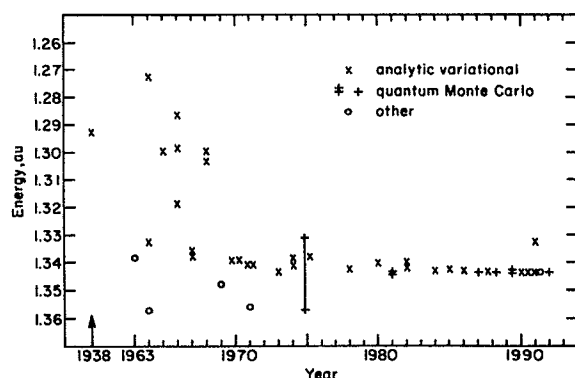


FIG. 1. A time-line history of quantum calculations of the electronic energy of  $\text{H}_3^+$  in equilateral-triangle nuclear configurations of side length approximately 1.6500 bohr. Data are listed in Table I. Error bars are indicated for quantum Monte Carlo calculations.

$$U = \sum_{k=1,20} \frac{b_k w_k}{1 + c_k w_k},$$

$$w_k = r_{1A}, r_{12}, r_{1A}^2, r_{12}^2, r_{1A}r_{12}, \text{ etc.}$$

The terms and their coefficients are listed in Table II.

For the optimized trial wave function, the standard deviation in local energy (from the exact value) is approximately 0.08 hartrees. This is a factor of 3 smaller than that for the trial function of our previous calculation.<sup>34</sup>

### IV. CALCULATION PROCEDURE

The calculation procedure was similar to that used in our earlier calculations with cancellation,<sup>43</sup> but it differs in several important details. It was not necessary to restrict the symmetry of the wave function and this simplified the calculations somewhat.

The calculations were carried out in 120 independent runs. Each run was started with 2000 positive psips increased in number by duplication at intervals of 55 iterations to 15 000 psips after four cycles of 55 iterations. The population was controlled at approximately 15 000 psips by random duplication or elimination at intervals of 55 iterations thereafter. Each run was terminated after 330 cycles of 55 iterations. Data for determining the energy were accumulated for iterations six to 55 of cycles six to 330. Data from iterations one to five following each renormalization were discarded in order to avoid any bias due to renormalization.

Each iteration began with psips of varying sign  $s_i$  and weight  $W'_i$  at positions  $X'_i$ . The weight of each was multiplied by  $V(X')/E$  to obtain a new weight  $W''_i$  and then divided into  $m$  psips of unit weight with  $m$  given by the integer part of  $(W''_i + u)$ , where  $u$  is a random number in the interval  $[0,1]$ .

The positions of selected psips were then transformed in order to concentrate all psips to the extent possible in a single region of electron configuration space. With the nuclear framework placed in the  $xy$  plane and symmetric to reflection in the  $xz$  plane, the electrons were reflected in either the  $xy$  plane or the  $xz$  plane or both to place electron 1 in the

TABLE II. Terms and coefficients of importance sampling trial wave function  $\Psi_T$ .

$f_1, f_2$	$c_a = 1.067$	
$w_1, \dots, w_6$	$r_{1A}, r_{1B}, r_{1C}, r_{2A}, r_{2B}, r_{2C}$	
	$b_k = -0.218$	$c_k = 0.015$
$w_7, \dots, w_{12}$	$r_{1A}^2, r_{1B}^2, r_{1C}^2, r_{2A}^2, r_{2B}^2, r_{2C}^2$	
	$b_k = 0.005$	$c_k = 1.455$
$w_{13}$	$r_{12}$	
	$b_k = 0.366$	$c_k = 0.276$
$w_{14}$	$r_{12}^2$	
	$b_k = 0.101$	$c_k = 1.256$
$w_{15}, \dots, w_{20}$	$r_{1A}r_{12}, r_{1B}r_{12}, r_{1C}r_{12}, r_{2A}r_{12}, r_{2B}r_{12}, r_{2C}r_{12}$	
	$b_k = 0.008$	$c_k = 0.167$

region of positive  $x$  and positive  $z$ .

The electron configuration space in the region of the nuclei was divided into 3125 boxes of side length 0.5–1.0 bohrs in each of the five dimensions  $x_1, y_1, x_2, y_2, z_2$ . The box number for each psip was determined and pairs of positive and negative psips in close proximity within each box were determined. Since the ratio of positive to negative psips

was large, most negative psips were paired and most positive psips were not.

Each psip was then moved to a new position selected from the distribution  $G_0(X, X')$  of Eq. (2). The psips of positive-negative pairs were then partially cancelled by their partners. The new weight of partner  $i$  of the  $ij$  pair was obtained from<sup>43</sup>

$$W_i(\text{new}) = \frac{\text{Max}\{[W_i(\text{old})G_0(X_i, X'_i) - W_j(\text{old})G_0(X_i, X'_j)\Psi_G(X'_i)/\Psi_G(X'_j)], 0\}}{G_0(X_i, X'_i)} \quad (9)$$

The new weight for partner  $j$  was obtained in a similar fashion.

The weight of each psip was then multiplied by the ratio of  $\Psi_G(X)/\Psi_G(X')$  to obtain a weight for the psip in distribution  $\Phi(X)$  as indicated in Eq. (5). An iteration was completed by adding the products of sign, weight, and local energy, etc. to the cumulative sums required for energy evaluation according to Eq. (7).

A series of preliminary runs was used to estimate the value of  $E$  for use in the multiplication  $V/E$  in Eq. (2) and the scaling of length in the function  $G_0(X, X')$ . The preliminary estimate of the energy of  $H_3^+$  was  $-1.343\,836$  hartrees. Combined with a shift of the zero of potential energy of  $+1.0$  hartrees and reduction by the nuclear repulsion energy of  $1.818\,182$  hartrees, this gave a value for  $E$  of  $-2.162\,018$  hartrees used in the final calculation.

The sensitivity of the calculated (output)  $E$  to the estimated (input)  $E$  was investigated in a separate set of calculations.

It was found that an input error of  $-0.004\,000$  hartrees resulted in an output error of about  $-0.000\,070$  hartrees. Thus, we expect that the actual input error of about  $-0.000\,001$  hartrees caused an error which is much smaller than  $\pm 0.000\,001$  hartrees and is insignificant.

## V. RESULTS

The result of the calculation for  $H_3^+$  in the equilateral triangle nuclear configuration of side length  $1.6500$  bohrs is an energy of very high accuracy:  $-1.343\,835 \pm 0.000\,001$  hartrees. The energy is the weighted average value of the energies of 120 runs of approximately equal weights having a standard deviation from the mean  $\sigma_i$  of  $0.000\,010$  hartrees. The uncertainty in the mean is estimated as  $\sigma_m = \sigma_i/\sqrt{N-1}$ , where  $N = 120$ .

## VI. DISCUSSION

Our calculated value is the most accurate to date. It lies  $0.000\,007$  hartrees below the lowest-energy analytic variational result ( $R = 1.6500$  bohr) of Frye, Preiskorn, Lie, and Clementi<sup>37</sup> and  $0.000\,013$  hartrees below the second lowest-energy result ( $R = 1.6500$  bohr) of Alexander, Monkhorst, Roeland, and Szalewicz.<sup>38</sup>

An extrapolation of the analytic variational energies obtained by Alexander *et al.*<sup>38</sup> using increasingly larger basis sets of 100, 200, ..., 700 Gaussian-type geminals gives  $-1.343\,830$  to  $-1.343\,845$  hartrees (our estimate). This is consistent with our result.

Results of these most recent calculations are plotted in Fig. 2. This plot is a dramatic example of the considerable progress in quantum chemistry in the past few years, not only in quantum Monte Carlo calculations, but also in analytic variational calculations.

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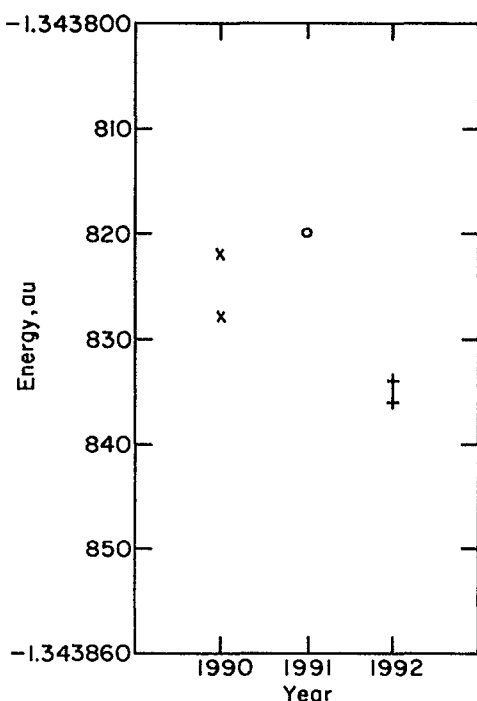


FIG. 2. An expanded section of Fig. 1. The energy scale is magnified by a factor of 2500.

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