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Simplified sampling in quantum Monte Carlo: Application to H_3^+

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A new procedure for sampling molecular wave functions in quantum Monte Carlo calculations is used to determine energies for a number of configurations of the molecular ion H_3^+ . With the Green's function fixed by use of a trial energy and with no drift terms required for importance sampling the procedure is both simple and efficient. For the equilibrium configuration of H_3^+ the energy is found to be $-1.343\,76 \pm 0.000\,03$ a.u. (i.e., ± 0.02 kcal/mol).

I. INTRODUCTION

There are perhaps a dozen known ways in which random sampling can be used to solve the Schrödinger equation for small molecules.¹⁻⁶ The most promising of these involve random walks in the configuration space of the electrons and are based either on the diffusion equation or, more generally, on a Green's function approach. Applications to date include those to H_3^+ ,⁷ H_2 , H_4 , and Be ,⁸ LiH ,⁹ H_3 ,¹⁰⁻¹² H_2O ,¹³ CH_4 ,¹⁴ and Ne .¹⁵ For these and similar molecules success has come first with random walk simulation⁷ (often called diffusion Monte Carlo or DMC), then extension to incorporate the effects of electron spin (fixed node),⁸ applications to excited states,⁸ improvement with importance sampling,¹⁶⁻¹⁸ release of node locations¹¹ as well as faster algorithms.^{8,11,19,20} For systems of ten or more electrons statistical error has continued to limit the usefulness of these methods,^{3,4} but there remain a number of possibilities for improving accuracies and/or reducing computation time. Among these are, e.g., a scheme for determining corrections to trial wave functions,²¹ use of multiple trial wave functions,²² a method for energy differences between similar systems,²³ taking optimal advantage of array-processing computers¹⁵ and use of pseudopotentials to eliminate inner-shell electrons.

We describe here a variation of the Green's function Monte Carlo method originated by Kalos²⁴ with modifications to incorporate the importance sampling techniques originated by Grimm and Storer.¹⁶ In this variation it is possible to simplify earlier procedures and to eliminate one of the steps which is computationally expensive for systems of ten or more electrons. Two approximations are required, but neither one introduces serious error.

The procedure is tested in calculations of the energy of the H_3^+ molecular ion in several configurations. Comparison is made with results of prior random walk and variational calculations and indirectly with experimental measurements of infrared spectra of H_3^+ and its isotopic variants.

II. THEORETICAL BASIS

The new sampling procedure is a method for obtaining a set of points with approximately equal weights from the distribution $\psi\psi_0$, the product of the true wave function ψ , and an approximate wave function ψ_0 , in the coordinate space of the electrons.

For a molecular system of N electrons and an arbitrary number of fixed nuclei the time-independent Schrödinger equation is

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

where m is mass of an electron and ∇^2 is based on the physical coordinates X of all the electrons. The equation may be expressed in the form

$$-\nabla^2\psi(X) + \left(-\frac{2mE}{\hbar^2}\right)\psi(X) = -\frac{2mV(X)}{\hbar^2}\psi(X) \quad (2a)$$

or

$$-\nabla^2\psi(X) + k^2\psi(X) = k^2\frac{V(X)}{E}\psi(X), \quad (2b)$$

where

$$k^2 = -\frac{2mE}{\hbar^2}. \quad (3)$$

Since k^2 must be positive the energy E must be negative, a requirement met by adjusting the potential energy reference.

The Green's function for Eq. (2) which satisfies appropriate boundary conditions for the Schrödinger equation ($\psi \rightarrow 0$ as $X \rightarrow \infty$) is known and is given by²⁴⁻²⁶

$$G_0(X, X') = \left(\frac{1}{2\pi}\right)^{3N/2} (k|X - X'|)^{1-3N/2} \times K_{3N/2-1}(k|X - X'|), \quad (4)$$

where K_ν is the Bessel function of imaginary argument. Sampling is based on the property of the Green's function which relates the wave function to itself,

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

Repeated application of Eq. (5) 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.²⁴ A point in the distribution $\psi(X')$ may be transferred to the distribution $\psi(X)$ by multiplying its weight by $V(X')/E$, sampling the distribution $G_0(X', X)$, and moving the point to its new position. Repetition for an initially arbitrary set of points leads to a set which is a sample of points from the lowest-energy wave function. Additional repetition continues the sampling.

The sampling described above is (with exceptions) useful only when $V(X')$ remains negative throughout the repetition. Otherwise the weights of points become either positive or negative and the wave function is given by the small difference between positive and negative distributions. Kalos²⁴ and Ceperley¹⁹ have devised schemes for avoiding this problem. In this work we use the simple approach of setting the zero of potential energy sufficiently high such that, except in rare cases, $V(X')$ remains negative. [The problem of nodes, which may be treated by specifying regions in which $V(X') \rightarrow +\infty$, is discussed below.]

In sampling, the value of E affects the step-size distribution in the physical coordinate system X as well as the multiplication of point weights. Since points of high weight may be subdivided at any time without changing the properties of a sample, the effect of E on multiplication presents no difficulties. However, a small negative value of E is desired for large step-sizes ΔX to decrease the correlation between successive samples.

Both $V(X')$ and E depend on the arbitrary value of $V(X' \rightarrow \infty)$ selected for a molecular system with electrons removed to infinity. If this potential energy is fixed near zero or lower E will be negative and $V(X')$ will be positive only for points corresponding to configurations with short inter-electron distances. For example, in the case of ground state helium with $V(X' \rightarrow \infty)$ set at -10.0 a.u., E is -12.9 a.u. and only configurations with the interelectron distance less than 0.10 a.u. can have $V(X')$ greater than zero. These represent a small fraction of the configurations likely to be sampled.

If $V(X' \rightarrow \infty)$ is set at a sufficiently low value the potential energy $V(X')$ may be truncated at $V(X') = 0$ without introducing significant error. Use of an average potential energy for electrons in close proximity to limit $V(X')$ is probably more satisfactory. In this case the potential energy for the interaction of two electrons may be specified as

$$V_{ij} = \frac{1}{r_{ij}}, \quad r_{ij} > r^*; \\ V_{ij} = \frac{3}{2} \frac{1}{r^*}, \quad r_{ij} < r^*. \quad (6)$$

In deriving Eq. (6) the wave function is assumed constant in the region $r_{ij} < r^*$.

The value of the energy E required in the sampling described above is in most cases of interest not known exactly and is usually the quantity sought. However, a good estimate E_e of the energy is often available and may be used. The sampling of the wave function is then used to obtain a better value for E . In principle one should repeat the calculation until the value of E generated matches the value of E_e used. We find the calculated value of E to be insensitive to small errors in the estimated value. Convergence is thus extremely rapid.

Importance sampling¹⁶ may be included with use of an approximate wave function ψ_0 from which local energies $E_{loc} = H\psi_0/\psi_0$ are determined. For fixed nodes, the energy is given exactly by

$$E = \frac{\int \Psi \Psi_0 (H\Psi_0/\Psi_0) dX}{\int \Psi \Psi_0 dX} \quad (7)$$

and for Monte Carlo sampling by

$$E = \lim_{I \rightarrow \infty} \frac{\sum_{i=1,I} W_i (H\Psi_0/\Psi_0)_i}{\sum_{i=1,I} W_i} \quad (8)$$

when points are chosen with a probability proportional to the quantity $(\Psi\Psi_0/W)_i$ and have weights W_i . For high efficiency in estimating E it is necessary that the weights be approximately equal. Multiplying both sides of Eq. (5) by $\Psi_0(X)$ and designating the product $\Psi(X)\Psi_0(X)$ as $\phi(X)$ we obtain

$$\phi(X) = \int \frac{\Psi_0(X)}{\Psi_0(X')} G_0(X, X') \frac{V(X')}{E} \phi(X') dX'. \quad (9)$$

In the same way that Eq. (5) is the basis for an iterative procedure for sampling $\Psi(X)$, Eq. (9) is the basis for sampling $\phi(X)$.

III. CALCULATION PROCEDURE

In sampling $\phi(X)$ as suggested by Eq. (9) there are several alternatives which differ in detail. We have found the procedure described below convenient for the H_3^+ ion.

Given a distribution of points with weights W'_i and positions X'_i new weights W''_i are calculated according to

$$W''_i = W'_i \frac{V(X')}{E_e}. \quad (10)$$

Each of the points is divided into m points 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 value of m may be zero.

For each of the resulting points a step ΔX_i is selected at random²⁷ from the distribution G_0 of Eq. (4). A trial position $X_i = X'_i + \Delta X_i$ is determined and $\Psi_0(X_i)$ is calculated. If $\Psi_0(X_i)/\Psi_0(X'_i) \geq 1.0$ the move to the trial position is accepted and the point is assigned a weight $W_i = \Psi_0(X_i)/\Psi_0(X'_i)$. If $\Psi_0(X_i)/\Psi_0(X'_i) < 1.0$ the move is accepted with a probability equal to $\Psi_0(X_i)/\Psi_0(X'_i)$ and the point is assigned a weight $W_i = 1.0$. If the move is not accepted the point is eliminated.

The result many iterations after the start is a new set of points having weights approximately equal to unity and distributed, when weights are taken into account, according to the product $\Psi\Psi_0$. The procedure is continued to generate additional points for calculating the energy as given by Eq. (8).

The number of points is not constant and may vary widely in the course of several thousand iterations. If E_e is far from the true value of E a noticeable systematic growth or shrinkage in the number of points occurs. Care must be taken to avoid any action which might introduce bias into the selection or retention of points.

IV. THE MOLECULAR ION H_3^+

We reviewed earlier work in two previous papers^{7,28} on H_3^+ and several others²⁹⁻³² have reviewed both experimental and theoretical work within the past year. The H_3^+ ion is the simplest polyatomic molecule (or molecular ion) and for that reason has served as a test species for developing theo-

retical methods in quantum mechanics. The potential energy surface of ground state H_3^+ is required for the prediction of the rates and molecular dynamics of the reaction $H^+ + H_2 \rightarrow H_2 + H^+$ and for the prediction of the rotation-vibration states of H_3^+ .

Spectra for transitions of H_3^+ or its isotopic equivalents H_2D^+ , D_2H^+ , and D_3^+ were not (knowingly) observed until 1980 when Oka³³ and Shy, Farley, Lamb, and Wing³⁴ measured rotation-vibration transitions of H_3^+ and D_3^+ . The wavelengths of the observed lines were in excellent agreement with the prior theoretical predictions of Carney and Porter.³⁵ Since then many more rotation-vibration lines and two pure rotation lines have been observed (see Ref. 32 for citations). An emission line from interstellar space has been detected³⁶ at the wavelength for a pure rotation transition of H_2D^+ , one of the species important in interstellar chemistry.

The best variational calculations of the electronic energy of ground-state H_3^+ at or near its lowest-energy configuration, an equilateral triangle of side length 1.6500–1.6510 a.u., are those of Meyer, Botschwina, and Burton³⁰; Salmon and Poshusta³⁷; Dykstra and Swope³⁸; Burton, von Nagy-Felsobuki, Doherty, and Hamilton²⁹; and Carney and Porter.^{39,40} Our earlier random-walk calculations^{7,28} gave a lower, more-accurate value for the absolute electronic energy than these variational calculations. Differences in energy for nearby points on the potential energy surface, the information needed for predicting spectra, were given more accurately by the variational calculations. Some details of these calculations are listed in Table I.

V. CALCULATIONS FOR H_3^+

The calculations for H_3^+ were made in order to test the new procedure as well as to provide more accurate electronic energies for several configurations of interest in predicting the spectra. The configurations are the same five we considered earlier⁷ and match almost exactly points chosen by Carney and Porter³⁹ (geometry numbers 1, 3, 5, 18, and 24), Dykstra and Swope,³⁸ and Salmon and Poshusta.³⁷

The trial wave functions for all configurations were of the modified product type with a Jastrow term and an added Gaussian expression,

$$\Psi_0 = (f_1 f_2 + C_3 f_3)(1.0 + C_4 f_4) f_J, \quad (11)$$

where

$$f_1 = \exp[-C_1 r_{1A}] + \exp[-C_1 r_{1B}] + \exp[-C_1 r_{1C}],$$

$$f_2 = \exp[-C_1 r_{2A}] + \exp[-C_1 r_{2B}] + \exp[-C_1 r_{2C}],$$

$$f_3 = \exp[-C'_3(r_{1A} + r_{2A})] + \exp[-C'_3(r_{1B} + r_{2B})]$$

$$+ \exp[-C'_3(r_{1C} + r_{2C})],$$

$$f_4 = \exp[-C'_4(r_{1xy}^2 + r_{2xy}^2) - C''_4(r_{1z}^2 + r_{2z}^2)],$$

$$f_J = \exp[C_b r_{12}/(1.0 + C_c r_{12})].$$

The symbols above are conventional except for r_{ixy} and r_{iz} which represent the distance of electron i from the nuclear center of mass in the plane and normal to the plane of nuclei, respectively.

The coefficients of the Jastrow function were fixed at $C_b = C_c = 0.5$ and other coefficients were optimized for each of the five nuclear configurations to give a minimum variance in E_{loc} for approximately 5000 points distributed in electron configuration space approximately as $\Psi\Psi_0$. The optimized coefficients for the equilateral triangle of side length 1.65 a.u. were $C_1 = 1.130$; $C_3 = -0.491$; $C'_3 = 1.113$; $C_4 = 3.12$; $C'_4 = 0.175$; $C''_4 = 0.165$ (in a.u. as required). For the other configurations the coefficients had similar values. The standard deviation in E_{loc} was 0.12–0.15 a.u.

Since nuclear motion is not considered the internuclear interactions do not play a direct role and are not to be included in the energy E and potential energy V of Sec. II. (However, in giving results for the energy of the molecule, we will continue to include the internuclear energy.) For the calculations the potential energy was adjusted to give a value $V_x = 12$ a.u. for separation of the electrons to infinity. Thus, V is based on

$$V = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{1C}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} - \frac{1}{r_{2C}} - \frac{1}{r_{12}} + V_x \quad (12)$$

and E is similarly based, so that if the equilateral triangle configuration of H_3^+ has an internuclear potential energy of 3/1.65 or 1.818 18 a.u. and a molecular energy of $-1.343\ 76$ a.u. the energy of the electrons in the field of the nuclei is taken as $(-12 - 1.343\ 76 - 1.818\ 18)$ or $-15.161\ 94$ a.u.

TABLE I. Selected *ab initio* calculations for H_3^+ .

Authors	Method	R (a.u.)	E (a.u.)
Salmon and Poshusta (Ref. 37) (1973)	CI,18 Singer P	1.6500	-1.343 35
Carney and Porter (Ref. 40) (1976)	CI,21 FSGO	1.6500	-1.339 36
Dykstra and Swope (Ref. 38) (1979)	CI,63 CGTO	1.6504	-1.342 78
Schinke <i>et al.</i> (Ref. 41) (1980)	CI,42 CGTO	1.6531	-1.340 23
Burton <i>et al.</i> (Ref. 29) (1985)	CI,108 PNO	1.6525	-1.342 72
Meyer <i>et al.</i> (Ref. 30) (1986)	CI,104 CGTO	1.6504	-1.343 40
Anderson (Ref. 7) (1975)	Random walk	1.6500	-1.344 ± 0.015
Mentch and Anderson (Ref. 28) (1981)	Random walk	1.6500	-1.343 9 ± 0.000 2
This work	Random walk	1.6500	-1.343 76 ± 0.000 03

TABLE II. Results for H_3^+ .

	Configuration R_{AB}, R_{AC}, R_{BC} (a.u.)	Energy E (a.u.)
	1.6500, 1.6500, 1.6500	- 1.343 76 ± 0.000 03
1	2.0500, 2.0500, 2.0500	- 1.319 13 ± 0.000 05
2	1.2500, 1.2500, 1.2500	- 1.286 41 ± 0.000 09
3	1.9000, 1.5402, 1.5402	- 1.336 15 ± 0.000 07
4	1.4496, 1.7581, 1.7581	- 1.336 74 ± 0.000 08

In order to keep the value of V less than zero the term $1/r_{12}$ of Eq. (12) was modified according to Eq. (6) with r^* equal to 0.08 a.u. The estimated values of E for the five cases were those given by our previous calculations.²²

The sampling calculations were begun with sets of 2500 points selected to approximate the correct $\Psi\Psi_0$ distribution. Each was subjected to 6000 iterations with data collection begun after the first 1000 iterations. With 2500 points at the start for each set the variation in the number of points presented no particular difficulties, although the number in a set ranged as low as zero and as high as 9000. From 5 to 20 sets of points were used for each of the H_3^+ configurations. Results are listed in Table II. Discussion is deferred to Sec. VI.

Two additional calculations were made in order to assess the sensitivity of the calculated energies to variations in the approximate energies used as inputs. Both were for the case of the 1.6500 a.u. internuclear distance. For these the value of V_x was kept at - 12 a.u. and the values of E raised by 1.000 00 a.u. and lowered by 0.100 00 a.u. from - 15.162 10 to - 14.162 10 and - 15.262 10 a.u. The errors introduced were found to be $0.000\,05 \pm 0.000\,13$ and $0.000\,01 \pm 0.000\,05$ a.u., respectively. Since the actual errors in the approximate energies for the main calculations

were only about 0.000 20 a.u., we estimate the errors in the calculated energies due to this cause to be less than 0.000 001 a.u.

The sampling or statistical error in the calculated energies was determined from the variance in energies for results grouped into blocks of about 2000 iterations.

VI. RESULTS FOR H_3^+

The energies listed in Table II are a factor of 7 more accurate than those of our previous calculations.²⁸ The uncertainty in the energy for the 1.65 a.u. equilateral triangle is reduced to 0.000 03 a.u. or 0.02 kcal/mol. The energy is 0.000 40 a.u. below the lowest variational energy (see Table I).

Relative energies, the elevations with respect to the minimum for the same basis set in variational calculations for the various configurations, are listed in Table III along with the comparable energies from the current calculations. Very minor interpolations for the data of Refs. 38 and 39 to the exact configurations listed are described in Ref. 28. The agreement of energies from the several calculations is strikingly good and indicates the accuracies of relative energies by both variational and random-walk methods. The excellent agreement of predicted vibrational levels with experimental measurements is an additional confirmation.^{30-32,35}

Since the energies from the random-walk calculations are more accurate in terms of total energy, a potential energy surface based on them would be globally more accurate than one from existing variational calculations. With such a surface the prediction of the higher vibration-rotation levels would be facilitated.

VII. DISCUSSION

From the results it is evident that the simplified sampling method can be used in calculating energies of very high accuracy and for systems such as H_3^+ can yield results not yet available from variational calculations. The improved accuracy results from a lower variance in local energy for the trial function, a greater number of points sampled, and elimi-

TABLE III. Comparison of energies for H_3^+ .

Configuration*	Energy, a.u. (Energy relative to minimum, a.u.)			
	1	2	3	4
Carney and Porter ^b	- 1.3146	- 1.2819	- 1.3317	- 1.3324
(ACI)	(0.0248)	(0.0575)	(0.0077)	(0.0069)
Dykstra and Swope ^c	- 1.3180	- 1.2850	- 1.3352	- 1.3362
	(0.0248)	(0.0578)	(0.0076)	(0.0066)
Salmon and Poshusta ^d	- 1.3355
	(0.0057)
Random walk	- 1.3191	- 1.2864	- 1.3362	- 1.3367
This work	(0.0247)	(0.0574)	(0.0077)	(0.0071)
	± 0.0001	± 0.0001	± 0.0001	± 0.0001

* See Table II.

^b Reference 33.

^c Reference 32.

^d Reference 31.

nation of problems associated with time-step error.

Serial and parallel correlation of local energies for individual points lowers the accuracies obtained. For the equilibrium configuration with $R_{AB} = R_{AC} = R_{BC} = 1.6500$ a.u., the standard deviation σ_i from the mean value of E_{loc} for individual points is 0.14 a.u. and the total number of points used in estimating the energy is about 10^8 . If there were no point-to-point correlation the uncertainty σ_m in the estimated energy would be 0.000 014 a.u. rather than 0.000 03 a.u. as given by analysis of results for uncorrelated blocks. Although a non-Gaussian distribution of local energies may account for a part of the difference, it is apparent that there is significant correlation. The average step size (length) in one dimension for the distribution $G_0(X, X')$ with $E = -15$ a.u. is 0.18 a.u., a value for which correlation may be expected.

In the case of H_3^+ the efficiency of the simplified method appears to be similar to that of the scheme devised by Ceperley.¹¹ For $E = -15$ a.u. the mean square step size is 0.024 a.u.² which corresponds to a time-step size of 0.024 a.u. In the case of H_3 Ceperley has used a time step factor of 10 larger, which results in a distance step a factor of 3 larger, but each step requires more computation effort, perhaps a factor of 3 larger. We plan to examine the efficiencies in detail for several other problems.

For the more general case of molecules with two or more electrons of like spin the use of the fixed-node approximation requires the removal of sample points which have crossed a node. This is the equivalent of a point's crossing into a region of infinite potential energy and if a large region of high potential energy occurs truncation is not acceptable. With the released-node technique¹¹ this problem does not occur. Although we have not yet made trials it appears that released nodes are compatible with the current sampling method. There is, of course, the intermediate course of "partially released nodes" in which sign changes occur on crossings of the tentative node and potential energy is set higher for points with an odd number of crossings.

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