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A random-walk simulation of the Schrödinger equation: H₃⁺

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A simple random-walk method for obtaining *ab initio* solutions of the Schrödinger equation is examined in its application to the case of the molecular ion H₃⁺ in the equilateral triangle configuration with side length $R = 1.66$ bohr. The method, which is based on the similarity of the Schrödinger equation and the diffusion equation, involves the random movement of imaginary particles (psips) in electron configuration space subject to a variable chance of multiplication or disappearance. The computation requirements for high accuracy in determining energies of H₃⁺ are greater than those of existing LCAO–MO–SCF–CI methods. For more complex molecular systems the method may be competitive.

I. INTRODUCTION

The progress of chemistry is severely limited by the difficulty of solving the Schrödinger equation to determine energies of complex molecular systems. While variational methods have been remarkably successful, the problem is of sufficient importance that alternate methods ought to be developed and examined. We report here initial studies of an entirely different approach which appears to have merit. To our knowledge this is the first application to a chemical multicenter problem.

The time-dependent Schrödinger equation for a single particle in one dimension,

$$-i\hbar\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2\mu}\frac{\partial^2\psi}{\partial x^2} - \mathcal{V}\psi,\tag{1}$$

is similar in form to the diffusion equation

$$\frac{\partial C}{\partial t} = \mathcal{D}\frac{\partial^2 C}{\partial x^2}.\tag{2}$$

In the course of a study of dye dispersion in water,[1] it became apparent that rather than using the diffusion equation to simulate the random-walk dispersion process, one might use the random-walk process to simulate the diffusion equation. By including a first-order rate process, one may simulate the Schrödinger equation in the same way.

The idea is not new. Its use has been discussed by Metropolis and Ulam,[2] who attribute it to Fermi, by King,[3] by Donsker and Kac,[4] by Metropolis,[5] and by Ulam.[6] Further, the similarity of the related Boltzmann transport equation and the Schrödinger equation has also been recognized and examined in detail.[7] Other numerical methods and Monte Carlo techniques have also been used in various schemes for solving the Schrödinger equation[8] but these are essentially unrelated to the present method. The random-walk method is, of course, well known in direct simulation of physical processes: Brownian motion, neutron diffusion, rarefied gas dynamics, statistical mechanics.

In this paper we report an application of the random-walk method in determining the ground state energy of the molecular ion H₃⁺ in the absence of spin–spin and spin–orbit interaction. This system is relatively simple and since the two electrons are of opposite spin does not require use of the Pauli exclusion principle. How-ever, the problem is not trivial, and it offers the opportunity for comparison of computation requirements and accuracy with a number of recent calculations using LCAO–MO–SCF–CI methods.

II. THEORY

The diffusion of a dye occurs physically by a random-walk process. Molecules of dye are subject to random motion, moving in a time interval Δt a distance Δx in one direction or the other. The behavior of the dye system may be determined (a) by experiment, (b) by solution of a differential equation, Eq. (2), or (c) by simulation of the physical process with a game of chance, in this case a random-walk game. The solutions by any of the methods are equivalent.

In the case of the Schrödinger equation, one customarily attempts to predict (a) the result of experiment by (b) solution of a differential equation, Eq. (1). Use of the third method, (c), simulation by a game of chance, requires invention of the game. Although the game must predict the result of experiment directly, it is easier to visualize the relationship of the game to the differential equation. When the diffusion equation, Eq. (2), is modified by the addition of the first-order rate term, as for a chemically reactive system, we have

$$\frac{\partial C}{\partial t} = \mathcal{D}\frac{\partial^2 C}{\partial x^2} - kC.\tag{3}$$

A game of chance simulating this equation is a random-walk game for particles which are subject to disappearance (or multiplication) with a probability proportional to k ($-k$).

A transformation to imaginary time τ, defined as $it/\hbar$, converts Eq. (1) to an ordinary differential equation with real variables

$$\frac{\partial\psi}{\partial\tau} = \frac{\hbar^2}{2\mu}\frac{\partial^2\psi}{\partial x^2} - \mathcal{V}\psi.\tag{4}$$

This is identical in form to Eq. (3). With an appropriate choice of constants, the modified random walk game for Eq. (3) may also be used for Eq. (4).

The Schrödinger equation in imaginary time has solution at large τ of the type

$$\psi(x,\tau) = \psi(x)e^{-E\tau}\tag{5}$$

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consisting of a spatial part $\psi(x)$ multiplying exponentially in time. The equation may thus be integrated in imaginary time to large values of τ yielding as the spatial part of the wavefunction a solution to the time-independent Schrödinger equation corresponding to the eigenvalue E.

The random-walk game for solving the Schrödinger equation in one dimension may thus be envisioned as follows: An initial collection of particles (hereafter, ψ particles or psips) is distributed on a line. Time is advanced one step Δt and each psip is moved right or left at random one step Δx. Then each psip gives birth to a new psip with a probability $P_b = -k\Delta t = -\upsilon\Delta t$ if k is negative or disappears with a probability $P_d = k\Delta t = \upsilon\Delta t$ if k is positive. Time is advanced another step and the process is repeated. The step sizes Δt and Δx are related to the diffusion coefficient by the Einstein equation, [9]

$$\frac{1}{2}\frac{(\Delta x)^2}{\Delta t} = \mathfrak{D} . \qquad (6)$$

When there is a net growth in the number of psips, the normalized distribution of psips approaches with increasing time a "steady-state" distribution which fluctuates about an average steady-state distribution, corresponding to the lowest energy wavefunction satisfying the time-independent Schrödinger equation.

The method is readily generalized to any number of dimensions and appears to be most useful for problems in which the number of dimensions is large. The calculation of electronic wavefunctions and eigenvalues for atomic and molecular systems is an example.

Use of the random-walk method for problems involving electrons of the same spin or other indistinguishable particles requires a restatement of the Pauli exclusion principle. Considering the Schrödinger equation as simply a differential equation, we note that the solutions to the equation can be easily restricted by the imposition of boundary conditions of the type $\psi = 0$. In the case of two identical noninteracting particles in a one-dimensional potential well, one obtains a valid solution for the energy of the lowest state, if one requires that the wavefunction be nonexistent (i.e., zero) when one particle is, for example, to the left of the other. Thus we have $\psi = 0$ if the coordinates of the two particles are equal, impose a boundary condition, and limit the solution to one-half the previously available configuration space. For the He atom with unpaired electrons ($1s2s$), this approach is entirely appropriate. [53] We have explored this restatement of the exclusion principle in detail for several more complex problems, and we wish to point out its usefulness in solving the Schrödinger equation when the form of the wavefunction is otherwise unrestricted.

Similar boundary conditions may be employed to obtain solutions of the wave equation for certain excited states. For the H atom, ψ may be set at zero in the $x = 0$ plane passing through the origin at the proton. The lowest-energy solution, subject to this imposed boundary condition and restricted to the region $x > 0$ (or $x < 0$), is that of the $2p_x$ state. Other excited states may be investigated in the same way for alternate or additional symmetrical boundary conditions imposed on the wave-

function.

In developing and examining the random-walk method, we have applied it to the simple problems of particles in a box, harmonic oscillator, the H and He atoms, the molecular ion H_2^+, and the molecule H_2. We explored several variations of the method, including use of psip growth and shrinkage, fixed and variable step sizes Δx, and adjustments in the time step $\Delta\tau$. The calculation procedure reported here for the molecular ion H_3^+ is probably the most efficient of those investigated, but it should not be regarded as the result of an exhaustive investigation of all possibilities.

III. CALCULATION PROCEDURE

The time-dependent wave equation for the two-electron system H_3^+ with fixed protons is given, in atomic units, by

$$\partial\psi/\partial\tau = \tfrac{1}{2}\nabla_1^2\psi + \tfrac{1}{2}\nabla_2^2\psi - (\upsilon - \upsilon_{\mathrm{ref}})\psi = -(E - \upsilon_{\mathrm{ref}})\psi , \qquad (7)$$

where $\tau = it/\hbar$ and is measured in terms of $\hbar^2/me^4$. With the electrons labeled 1 and 2 and the three protons labeled A, B, and C, the potential υ, exclusive of internuclear terms, is

$$\upsilon = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{1C}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} - \frac{1}{r_{2C}} + \frac{1}{r_{12}} , \qquad (8)$$

where r_{1A} is the distance between electron 1 and proton A and so forth. In terms of the diffusion equation we then have $\mathfrak{D} = 1/2$ and $k = (\upsilon - \upsilon_{\mathrm{ref}})$.

The random walk in six dimensions was executed with nonuniform step sizes in each dimension selected at random from a Gaussian distribution with weights W given by

$$W(\Delta x) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{(\Delta x)^2}{2\sigma^2}\right) , \qquad -\infty < \Delta x < \infty , \qquad (9)$$

with $\sigma = (2\mathfrak{D}\Delta\tau)^{1/2}$. The probability of birth of a new particle was taken as

$$P_b = -k\Delta t = -(\upsilon - \upsilon_{\mathrm{ref}})\Delta\tau , \qquad \upsilon < \upsilon_{\mathrm{ref}} ,$$
$$= 0 , \qquad \upsilon \geq \upsilon_{\mathrm{ref}} , \qquad (10)$$

and the probability of disappearance or death as

$$P_d = k\Delta t = (\upsilon - \upsilon_{\mathrm{ref}})\Delta\tau , \qquad \upsilon > \upsilon_{\mathrm{ref}} ,$$
$$= 0 , \qquad \upsilon \leq \upsilon_{\mathrm{ref}} . \qquad (11)$$

After each time interval a random number N_R in the interval (0, 1) for each psip was compared with P_b (or P_d) and if smaller than P_b (or P_d) then a birth (or death) was completed.

The calculations were begun with a collection of 1000 psips corresponding to identical electron configurations with the electrons near the center of the nuclear system. An initially large time step was used in order to give a rapid approach to a steady-state psip distribution. The size of the time step was decreased as time progressed to improve the accuracy of the results.

To maintain the total number of psips at approximately 1000 the arbitrary reference potential, υ_{ref} for electrons at infinite separation was adjusted at the end of each time

step according to

$$v_{ref} = \bar{v} - \frac{N - 1000}{1000 \Delta \tau} ,$$ (12)

where $\bar{v}$ is the average potential energy of the psips (configurations).

At steady-state, the energy E corresponding to a wavefunction ψ may be evaluated according to Eq. (7), restated as

$$E - v_{ref} = - \frac{1}{\psi} \frac{\partial \psi}{\partial \tau} .$$ (13)

For a given psip distribution, the wavefunction is proportional to the total number of psips N and we have

$$\frac{1}{N} \frac{\partial N}{\partial \tau} = \frac{1}{\psi} \frac{\partial \psi}{\partial \tau} .$$ (14)

Since the total number of psips is not directly affected by the diffusion terms in Eq. (7) but changes according to

$$\frac{\partial N}{\partial \tau} = - \sum_1^N (v - v_{ref}) ,$$ (15)

the energy may be evaluated from the average potential $\bar{v}$,

$$E - v_{ref} = - \frac{1}{N} \frac{\partial N}{\partial \tau} = \frac{1}{N} \sum_1^N (v - v_{ref}) = \bar{v} - v_{ref} .$$ (16)

Thus, the energy corresponding to a psip distribution was calculated at each time step followed during the evolution of the steady-state distributions. At steady state, the energies at each time step were retained for averaging to obtain an accurate value of the energy.

There are five important sources of error in the calculation of wavefunctions by the random-walk method: (a) statistical variations associated with the random nature of the process, (b) the use of a finite time step $\Delta \tau$,
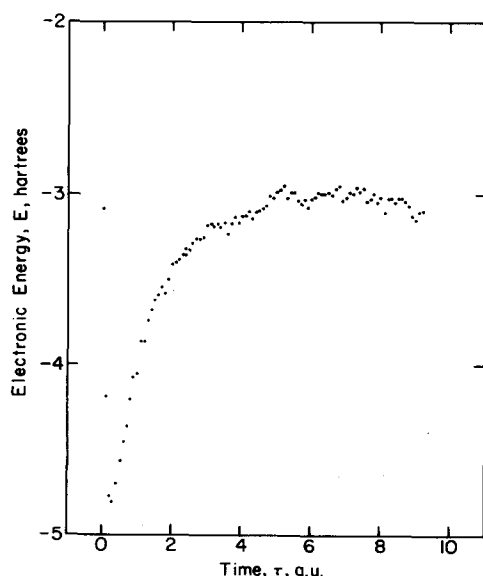

FIG. 1. Evolution of electronic energy with time, 1000 particles, group A. Points within time intervals of 0.010 a.u. not shown.

TABLE I. Energies calculated for H_3^+ ($R = 1.66$ bohr).

Step size $\Delta \tau$, a.u.	Number of steps	Energy E, hartree[a] Each batch	Average
0.001	400	−3.1376	
		−3.1441	
		−3.2125	
		−3.1107	−3.151 ± 0.013[b]
		−3.1896	
		−3.1121	
0.002	200	−3.1932	
		−3.1159	
		−3.1384	
		−3.0918	−3.141 ± 0.013[b]
		−3.1185	
0.005	80	−3.1675	
		−3.0473	
		−3.1719	
		−3.1749	−3.137 ± 0.015[b]
		−3.1537	
		−3.1072	
0.010	40	−3.1547	
		−3.1242	
		−3.0851	
		−3.1620	−3.115 ± 0.012[b]
		−3.0850	
		−3.0832	

[a]Excludes nuclear repulsion.
[b]Probable statistical error, excludes systematic errors.

(c) numerical error, (d) imperfect random number quality, (e) failure of the distributions to reach steady state in a finite time. Since successive distributions in a single calculation are not statistically independent, it was necessary to repeat calculations from the initial distribution using different sets of random numbers to estimate the variance of the energy in a single calculation. The effects of a finite time step were evaluated by repeating calculations using time steps of different sizes. Numerical error was evaluated by making several runs with double-precision arithmetic. Random number quality was tested in calculations of distributions without birth or death terms. Attempts to estimate the errors associated with terminating calculations at a finite time were made by comparing energies for different times.

IV. RESULTS

Twenty-four statistically independent sets of calculations, six in each of four groups terminated with different time-step sizes, were carried out for collections of 1000 psips in the time interval 0–9.2 a.u. The time-step size was decreased in sequence for each group as follows: (A) $\tau = 0-5$, $\Delta \tau = 0.050$; $5-7$, 0.020; $7-8$, 0.010; $8-8.5$, 0.005; $8.5-8.7$, 0.002; $8.7-9.2$, 0.001; (B) $\tau = 0-8.5$, same as A; $8.5-9.2$, 0.002; (C) $\tau = 0-8$, same as A; $8-9.2$, 0.005; (D) $\tau = 0-7$, same as A; $7-9.2$, 0.010. The evolution of the calculated energy E with time was similar for each set and is illustrated in Fig. 1 for one set in group A. The average energies in the final steps of each set, calculated in the time interval $8.8-9.2$, are listed in Table I.

For group A, with the smallest final step size $\Delta \tau$

$= 0.001$, the average electronic energy for the six sets is -3.151 hartree. The average deviation from the mean for the six results is 0.033 hartree, which corresponds to a probable statistical error[10] of the mean of 0.013 hartree. As shown in Table I, the mean energies for the other groups are higher and the probable statistical errors are similar.

The effect of varying final step size, which may be seen as a trend in the data of Table I, is shown in Fig. 2. Because the indicated probable error is approximately the same as the differences in energy values, extrapolation to $\Delta\tau = 0$ is questionable, but a trend to a lower value of E with decreasing $\Delta\tau$ is clearly indicated.

Comparison of average energies calculated for the time interval $8.0-8.4$ with those in the interval $8.8-9.2$ for groups B, C, and D gave no indication of a trend in the average energy with increasing time beyond $\tau = 8.0$. Thus, the error introduced by use of a finite time is probably small compared with the statistical error for these calculations. The checks for error in random number quality and numerical error were negative; i.e., any errors were undetectable in the presence of the statistical error.

The calculations were performed with an IBM-370-168 computer using the FORTRAN H programming language. The program size was about 75 statements. The computation time required was about 5 min for a set of calculations in group A (1000 psips, 1000 time steps, 10^6 psip movements). Other groups required fewer time steps per set: group B, 750; C, 540; D, 420.

V. DISCUSSION

Accuracy and computation requirements are the two important items to be considered in comparing the random-walk method with existing methods of solving the Schrödinger equation. Both methods require increased
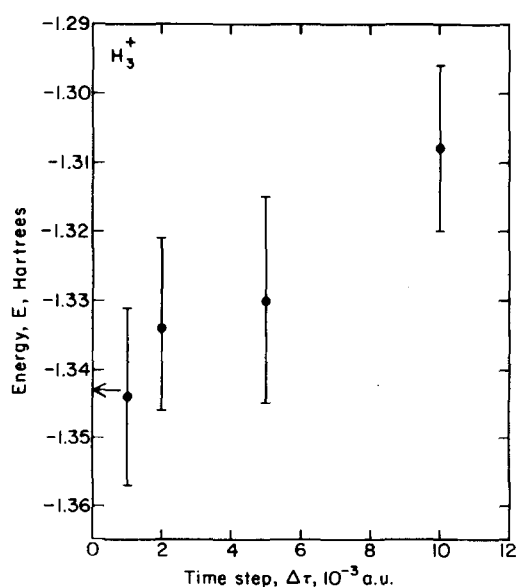

FIG. 2. Variation of total energy with time-step size. The arrow indicates the energy of the lowest variational calculation (Salmon and Poshusta, Ref. 19).

TABLE II. Comparison with variational calculations.

Author	Reference	R(bohr)	E(hartree)
Hirschfelder (1938)	11	1.79	-1.293
Christofferson (1964)	12	1.66	-1.333
Lester and Krauss (1966)	13	$\cdots$	-1.298
Kutzelnigg et al. (1967)	14	1.66	-1.336
Schwartz and Schaad (1967)	15	1.65	-1.338
Csizmadia et al. (1970)	16	1.66	-1.340
Duben and Lowe (1971)	17	1.64	-1.341
Bauschlicher et al. (1973)	18	1.66	-1.340
Salmon and Poshusta (1973)	19	1.65	-1.343
Jaffe et al. (1974)	20	1.66	-1.338
This work		1.66	-1.344

computation for increased accuracy and we must then compare computation requirements for the same accuracy or accuracies for the same computation effort.

Listed in Table II are the energies determined in several variational calculations for H_3^+ in the equilateral triangle configuration with $R = 1.64-1.66$ bohr, with one exception. The slight differences in R near 1.65 bohr are not important in comparing energies since the configuration is that corresponding to the bottom of a potential well. The energies listed for the variational calculations are the lowest calculated energies, not the lowest estimated energies given by several authors, which range $0.001-0.003$ hartree lower. The lowest variational energy is that by Salmon and Poshusta[19] at -1.343 hartree. The value for the group A (smallest $\Delta\tau$) random-walk calculations is -1.344 hartree, which with a statistical uncertainty of 0.013 hartree overlaps this lowest variational result.

Computation requirements are given for the study by Csizmadia et al.[16] as 15 min per energy on an IBM-7094 II computer. Duben and Lowe[17] required about 30 min per energy on an IBM-360-67 for their study.[21] These times roughly correspond to $7-8$ min and 30 min on the IBM-370-168 used in the present study. Error, as judged by energy above the lowest variational energy,[19] is $0.002-0.003$ hartree. For group A of the present calculations, the total computation time was 30 min and the probable statistical error is 0.013 hartree.

It is estimated that computation requirements could be reduced in the random-walk calculation as much as a factor of 10 by clever programming, use of a more efficient step selection procedure, and eliminating the requirement for total statistical independence of separate calculations. It seems unlikely that much more than a factor of 10 could be achieved.

The statistical error in the present calculations is approximately proportional to $N_s^{-1/2}$, where N_s is the number of sets of calculations performed. To reduce the statistical error to a value of $0.002-0.003$ hartree, the apparent error in the variational calculations cited above would require about 125 sets of calculations at 5 min each, or 625 min. Thus, even if one assumes the calculations could be done in one-tenth the time, 60 min, and one ignores the question of systematic error at $\Delta\tau = 0.001$ a.u., the method still requires $2-5$ times the effort for a variational calculation of similar accuracy.

But, what about molecular systems of more than two electrons? The random-walk calculations involve two time-consuming procedures: calculation of the potential energy for each configuration and random movement in configuration space. The number of terms in the potential energy equation, Eq. (5), is given by $[\frac{1}{2} n_e(n_e - 1) + n_e n_n]$, in which n_e is the number of electrons and n_n is the number of nuclei. This will be roughly $\frac{1}{2} n_e^2$ for many problems. The computation effort for random movement is directly proportional to n_e. Thus, we expect the total effort required to be proportional to n_e^s with s between one and two. In practice, we find that for the four-electron H_4 system, using a program nearly identical to that for the two-electron H_3^+ system, the computation time is a factor of 2.3 higher for the same number of time steps.

The computation times for CI calculations vary with the third or fourth power of the number of basis sets used, which is in turn proportional to the number of electrons for about the same accuracy in the energies. Thus, total computational effort required is proportional to n_e^s with s equal to three or four. One may then expect the random-walk method to be competitive with variational methods for systems of four or more electrons.

Computation time is, of course, not the only consideration for calculations to achieve a given level of accuracy. The human effort required appears to be considerably less for the random-walk method. There are no complicated integrals, no basis sets, no determinants, no matrices—nothing but a few simple equations and a short computer program.

However, there remain a number of questions which bear significantly on the utility of the random-walk method. Limitations on the time-step size for systems with inner- and outer-shell electrons have not been established. Methods of treating electron-spin effects must be investigated further. In general, not enough is known for confident assessment of the merits of the method, but initial results are encouraging.

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