

**Quantum chemistry by random walk. H 2 P, H+ 3 D 3h 1 A'1, H2 3Σ+ u , H4 1Σ+ g , Be 1 S**

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# Quantum chemistry by random walk. $H^2P$ , $H_3^+ D_{3h}$ $^1A'$ , $H_2$ $^3\Sigma_u^+$ , $H_4$ $^1\Sigma_g^+$ , $Be$ $^1S$

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The random-walk method of solving the Schrödinger equation for molecular wavefunctions is extended to incorporate the effects of electron spin in several one- to four-electron systems. Improved calculation procedures reduce computation requirements for high accuracy by a factor of about 10. Results are given for the systems  $H^2P$ ,  $H_3^+ D_{3h}$   $^1A'$ ,  $H_2$   $^3\Sigma_u^+$ , linear equidistant  $H_4$   $^1\Sigma_g^+$ , and  $Be$   $^1S$ .

## I. INTRODUCTION

The random-walk method<sup>1</sup> of solving the Schrödinger equation consists of a simple game of chance involving the random movement of particles in space subject to a variable probability of multiplication or disappearance. In an earlier investigation<sup>2</sup> of the use of the method in determining the ground-state energy of the molecular ion  $H_3^+$  we found computation requirements to be 20–50 times those of existing LCAO–MO–SCF–CI variational methods of similar accuracy. However, we estimated that computation requirements of the random-walk method might be reduced as much as a factor of 10 by improved procedures. We indicated that the method might be most useful for systems of four or more electrons provided the effects of electron spin (or particle indistinguishability) could be properly accounted for.

In this paper we report improved computation procedures which allow a greater time-step size and reduce computation efforts by a factor of about 10 for a given level of accuracy. We also report the development of methods for treating electron spin in simple atomic and molecular systems. These developments are examined in applications to several one-, two-, and four-electron systems.

In addition to those reported here there are a number of alternate approaches which may be used to improve the accuracy and reduce the computation requirements of the random walk method. Formulation of the problem in terms of a trial wavefunction  $\psi_0$  such that a difference  $\delta = \psi - \psi_0$  is calculated is an especially attractive possibility. Given a trial wavefunction from any source, even from accurate variational calculations, the difference  $\delta$  may, in principle, be calculated and used to correct the trial wavefunction. Successive calculations offer the possibility of further corrections and wavefunctions of unlimited accuracy. The systematic errors associated with use of a finite step size are absent in a Monte Carlo method developed by Kalos<sup>3</sup> for solution of the Schrödinger equation in integral form. Following this approach Kalos, Levesque, and Verlet<sup>4</sup> have shown that use of a trial wavefunction allows eigenvalues to be estimated without statistical error.

## II. THE RANDOM-WALK METHOD

The random-walk method is most easily described for a one-dimensional system. The Schrödinger equation in imaginary time  $\tau = it$  for a single particle restricted to a line is given, in atomic units, by

$$\frac{\partial \psi(x, \tau)}{\partial \tau} = \frac{1}{2} \frac{\partial^2 \psi(x, \tau)}{\partial x^2} - (V - V_{\text{ref}}) \psi(x, \tau), \quad (1)$$

in which  $V$  is the local potential and  $V_{\text{ref}}$  is an arbitrary reference potential. The equation has solutions for large  $\tau$  consisting of a spatial part  $\psi(x)$  multiplying exponentially in time:

$$\psi(x, \tau) = \psi(x) e^{-(E - V_{\text{ref}})\tau}. \quad (2)$$

When integration is carried out to large values of  $\tau$  the spatial part of the wavefunction approaches that for a solution to the time-independent Schrödinger equation with the eigenvalue  $E$ .

The (normalized) solution  $\psi(x)$  of the time-independent equation is independent of the initial conditions  $\psi(x, 0)$  and the reference potential  $V_{\text{ref}}$ . The eigenvalue  $E$  is lowest energy corresponding to the prescribed symmetry of the solution.

In the random-walk method Eq. (1) is simulated by a process of movement, multiplication, and disappearance of imaginary particles initially distributed arbitrarily on the line. To avoid confusion with the particles of the physical system we refer to the imaginary particles as “psips.” The behavior of a collection of psips may be described by the diffusion equation to which a first-order rate term is added:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC, \quad (3)$$

where  $C$  is the concentration of psips,  $D$  is the diffusion coefficient and  $k$  rate constant for disappearance (negative for multiplication). With an appropriate choice of constants Eq. (3) may be made identical to Eq. (1). Thus, the time-dependent Schrödinger equation may be simulated by a process of diffusion, multiplication, and disappearance of psips. As time is advanced one step  $\Delta\tau$  each psip is moved at random right or left a distance determined by  $D$ . Then each psip is allowed to multiply or disappear with a probability depending on the value of  $k$  (or  $V - V_{\text{ref}}$ ) determined by the local potential energy. The process is repeated until the distribution of psips approaches a fluctuating steady-state distribution from which the eigenvalue  $E$  may be evaluated.

In Ref. (2) we have provided a full description of computation procedures: details of the generalization to multidimensional systems, choice of step size, control of the total number of psips by varying  $V_{\text{ref}}$ , evaluation of  $E$ , and so forth. For the calculations re-

ported here the procedures were essentially identical to those of Ref. (2), except as indicated. Initial distributions of psips in the multidimensional configuration space of electrons were obtained by random placement of electrons in the vicinity of the nuclei. The approach to steady state required a time  $\tau$  of at least several times the relaxation time for diffusion  $L^2/D$ , in which  $L$  is the approximate physical size (length) of the molecular system and  $D$  is the diffusion coefficient. The reference potential was adjusted to maintain a fixed number of psips and had no effect on the rate of approach to steady state.

### III. MODIFICATIONS FOR LARGER TIME STEPS

The accuracy in determining an eigenvalue  $E$  by the random-walk method is limited primarily by the statistical error associated with the random nature of the process and by the error introduced by use of a finite time step  $\Delta\tau$ . The statistical error in the calculated energy may be reduced by averaging  $E$  over a long time interval. For small values of  $\Delta\tau$  this requires a large number of time steps. If the process can be modified to allow larger values of  $\Delta\tau$  without introducing error, then the number of time steps and the computation requirements for a given accuracy can be reduced. Three such modifications are described below.

#### A. Integration over the time step

The multiplication or disappearance of a psip is governed by the first-order rate constant  $k$ , which is set equal to the quantity  $(V - V_{\text{ref}})$ . The differential change in concentration due to multiplication or disappearance is given by

$$\frac{\delta C}{\delta t} = -kC \equiv -(V - V_{\text{ref}})C. \quad (4)$$

For  $k > 0$  the probability of disappearance for a psip in an infinitesimal interval  $\delta t$  is  $k\delta t$ . For  $k < 0$  the probability of multiplication (to two psips) of a psip is  $-k\delta t$ .

In our earlier study<sup>2</sup> we used the terms  $P_b$  and  $P_d$  for the probability of birth of a new psip and disappearance of a psip, respectively, at the end of a time step. These were taken as the simple difference expressions for the first-order rate process implied by Eq. (1):

$$\begin{aligned} P_b &= -(V - V_{\text{ref}})\Delta\tau, & V < V_{\text{ref}}, \\ P_b &= 0, & V > V_{\text{ref}}, \\ P_d &= (V - V_{\text{ref}})\Delta\tau, & V > V_{\text{ref}}, \\ P_d &= 0, & V < V_{\text{ref}}. \end{aligned} \quad (5)$$

After each time step, a random number  $N_R$  in the interval  $(0, 1)$  was compared with  $P_b$  (or  $P_d$ ) for each psip and if smaller than  $P_b$  (or  $P_d$ ) then a birth (or disappearance) was completed. This procedure is accurate only in the limit of a small time step.

Greater accuracy with large time steps may be obtained by use of the first order birth or disappearance expressions integrated over the time step:

$$d\psi = -(V - V_{\text{ref}})\psi d\tau, \quad (6)$$

$$\psi_{\tau+\Delta\tau} = \psi_{\tau} \exp[-(V - V_{\text{ref}})\Delta\tau], \quad (7)$$

or

$$\Delta\psi = \psi \{\exp[-(V - V_{\text{ref}})\Delta\tau] - 1\}. \quad (8)$$

The corresponding expressions for  $P_b$  and  $P_d$  for each psip are

$$\begin{aligned} P_b &= \exp[-(V - V_{\text{ref}})\Delta\tau] - 1, & V < V_{\text{ref}}, \\ P_b &= 0, & V > V_{\text{ref}}, \\ P_d &= 1 - \exp[-(V - V_{\text{ref}})\Delta\tau], & V > V_{\text{ref}}, \\ P_d &= 0, & V < V_{\text{ref}}. \end{aligned} \quad (9)$$

After each time step the value of  $P_b$  or  $P_d$  is computed for each psip. The birth term  $P_b$  will in general consist of an integer  $n=0, 1, 2, \dots$  plus a fraction  $f$  less than unity. For multiplication ( $V < V_{\text{ref}}$ ) of a psip  $n$  new psips are added and one more psip is added if  $f$  is greater than a random number selected in the interval  $(0, 1)$ . For disappearance ( $V > V_{\text{ref}}$ ) of a psip a random number in the interval  $(0, 1)$  is selected and if less than  $P_d$  the psip is removed.

The revised expressions are exact in the limit of small  $\Delta\tau$  as are the original expressions. However, in the absence of psip movement or for constant  $V$  the new expressions are also exact for large  $\Delta\tau$ . Since psip movement does occur and thus  $V$  may change with time, the overall process of simulating the Schrödinger equation remains exact only in the limit of small  $\Delta\tau$ , but the new expressions may be expected to reduce the error associated with finite values of  $\Delta\tau$ .

A comparison of results with the original and the revised expressions is given for the molecular ion  $\text{H}_3^+$  in Sec. V.

#### B. Average potential for electrons near a nucleus

Use of the integrated birth term of Eq. (9) can produce a very high multiplication rate for psips corresponding to configurations with an electron near a nucleus. Allowances may be made in computation for handling a large increase in the number of psips, but since the potential energy approaches negative infinity as the electron approaches a nucleus, the possibility of exceeding storage capacity cannot be eliminated. We found that placing an upper limit on  $P_b$  of twice the average number of psips had no detectable effect on the computed energy values for H atoms. However, it is more reasonable to use an average potential energy for electrons near a nucleus. Thus, for electrons within a radius  $r_c$  of a nucleus having charge  $c$  the potential was taken as the average over the volume enclosed by a shell of radius  $r_c$ :

$$\langle V \rangle = -\frac{3}{2}cr_c^{-1}. \quad (10)$$

The value of  $r_c$  was adjusted to give an upper limit of 1000 for  $P_b$ . For the H atom with  $\Delta\tau = 0.010$  a.u., this occurs with  $r_c = 0.0022$  a.u.

This modification in procedure was used in all new calculations reported in Sec. V.

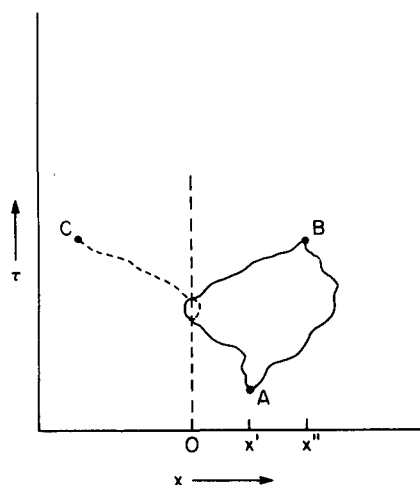


FIG. 1. Example of psip movement near a node.

### C. Node crossing and recrossing

Wavefunctions for excited atomic or molecular states and for systems containing electrons of the same spin contain nodes on which  $\psi = 0$ .<sup>2</sup> For the random-walk method these nodes may be regarded as sinks for psips—any psip moving across a node is caused to disappear. With use of a finite time step  $\Delta\tau$  the movement of psips occurs in finite steps of variable size  $\Delta x$ . For a psip located near a node and found on the allowed side of the node at both the beginning and end of a time step, there is a possibility that the psip may have crossed and recrossed the node in the interval of the time step. In the limit of small  $\Delta\tau$  this possibility becomes negligible, but for finite step sizes the failure to eliminate psips subject to disappearance if their complete path were determined may cause an appreciable error.

The probability of this cross/recross behavior is a function of distances  $x'$  and  $x''$  from a node at the beginning and end of the time step. Shown schematically in Fig. 1 are two paths for a psip moving from  $x'$  to  $x''$ , from point A to point B. One path crosses and recrosses the node; the other does not. The probability of motion from  $x'$  to  $x''$  is given by

$$P_B = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{(x'' - x')^2}{2\sigma^2}\right) \quad (11)$$

where  $\sigma$  is standard deviation in  $x$  for the time interval. The probability of motion to a point C, the image of point B in the plane of the node is given by

$$P_C = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{(x'' + x')^2}{2\sigma^2}\right). \quad (12)$$

Since the probabilities of ending the step at points B and C once the node is reached must be equal, the probability  $P_C$  is equal to the probability of movement to point B by a path crossing and recrossing the node. The probability of crossing and recrossing the node in attaining point B is then given by  $P_x$ , the ratio of  $P_C$  to  $P_B$ , which may be expressed as

$$P_x = \exp\left(-\frac{4x'x''}{2\sigma^2}\right). \quad (13)$$

In executing a random-walk calculation for a system with nodes located symmetrically in the configuration space of the electrons consideration is limited to a single region of space partially bounded by nodes. At the end of each time step psips outside the region are eliminated. The cross/recross probability  $P_x$  is incorporated in the calculation by retaining the values  $x'$  and  $x''$  and computing  $P_x$  at the end of each time step for psips inside the allowed region. If  $P_x$  for a given psip is greater than a random number selected in the interval (0, 1), then that psip is eliminated.

Equation (13) and the calculation procedure indicated above apply to the case of a single plane nodal surface. In the case of multiple plane surfaces (which may or may not intersect) Eq. (13) may be used to determine independently the probability of crossing and recrossing each of the nodal surfaces. The probability of a psip movement without crossing and recrossing a specific node  $i$  is given by  $(1 - P_x)_i$  and the probability of movement without crossing and recrossing any nodes is given by the product of these factors for all nodes. In the random-walk calculation a psip near a node is retained with this probability. The behavior with multiple planar nodes and with intersecting planar nodes is then estimated correctly.

These procedures were used in calculations for  $H\ 2p_x$ ,  $H_2\ ^3\Sigma_u^+$  and  $H_4\ ^1\Sigma_g^+$  as reported in Sec. V. In the case of "smooth" but nonplanar nodal surfaces, such as the spherical surfaces encountered for  $Be\ ^1S$ , Eq. (13) is exact only in the limit of small  $\Delta\tau$ . In the calculations for  $Be\ ^1S$  the formula and calculation procedures for plane surfaces were used with the simple substitution of radial distances for  $x'$  and  $x''$ . This represents an approximation, which is satisfactory for  $Be\ ^1S$ , but it may be unsatisfactory for other cases involving nonplanar nodes.

When a nodal surface passes through a nucleus or through a region in which there is a large variation in potential energy with electron positions, the cross/recross correction terms are inaccurate for large time steps. Similarly, the use of an average potential energy  $\langle V \rangle$  for electrons near a nucleus is inaccurate in this situation. Thus it remains necessary to check the effect of time-step size by repeating calculations with different step sizes.

A comparison of results for  $H\ 2p_x$  calculated with and without the recrossing correction is given in Sec. V. These procedures were used in all other calculations reported in Sec. V except those for  $H_3^+$  which has no node in the ground-state wavefunction.

## IV. ELECTRON SPIN AND EXCITED STATES

To be useful in determining the electronic energies of complex chemical systems any method of solving the Schrödinger equation must provide for the effects of electron spin. For the simplest case, in which the electrons are assumed to be noninteracting, the Pauli exclusion principle may be applied directly: No two electrons can have the same set of quantum numbers. For interacting electrons satisfactory solutions are

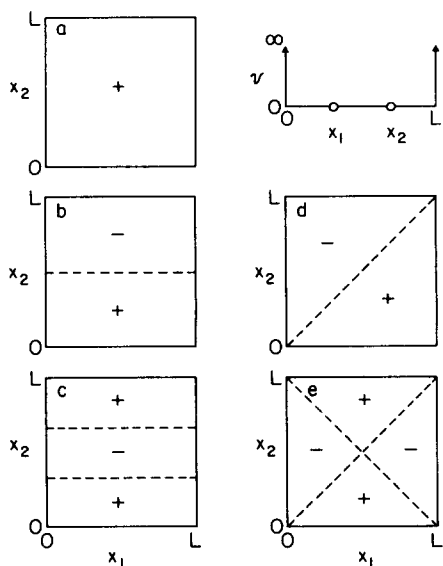


FIG. 2. Wavefunctions for two particles in a one-dimensional well. Distinguishable: (a)  $n_1=1, n_2=1$ ; (b)  $n_1=1, n_2=2$ ; (c)  $n_1=1, n_2=3$ . Indistinguishable: (d)  $n_1=1, n_2=2$ ; (e)  $n_1=1, n_2=3$ .

obtained by requiring the spatial part of the wavefunction to be antisymmetric to the exchange of electrons of like spin. In variational calculations this is most easily accomplished by the use of Slater determinants which restrict the form of the solution.

In the random-walk method the analytic form of the solution for the wavefunction cannot be specified in advance. However, boundary conditions can be imposed in a manner to require the solution to be antisymmetric to the exchange of electrons of like spin. If the electron configuration space is divided in a symmetric fashion by one surface of  $\psi=0$ , i. e., a node, for each possible pair of electrons of like spin, the solution obtained will have the appropriate antisymmetry when the sign of the wavefunction is chosen positive on one side and negative on the other side of each node.

The idea is easily illustrated with the case of two noninteracting particles confined in a potential well or one-dimensional box as illustrated in Fig. 2. For a one-particle system the spatial part of the wavefunction is given by

$$\psi_i(j) = A \sin(n_i \pi x_j / L), \quad (14)$$

and the lowest-energy wavefunction is obtained with the quantum number  $n_1$  equal to unity. For two distinguishable particles a satisfactory overall wavefunction is given by the product  $\psi_{12} = \psi_1(1)\psi_2(2)$  without restrictions on the quantum numbers  $n_1$  and  $n_2$ . The form of such solutions is indicated in Fig. 2, parts (a), (b), and (c), for  $n_1=1$  and  $n_2=1, 2$ , and  $3$ , respectively.

If the two particles are indistinguishable then wavefunctions with the required antisymmetry may be obtained by use of a determinant,

$$\psi_{12} = \psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1) \quad (15)$$

The form of such solutions is indicated in Fig. 2, parts (d) and (e), for  $n_1=1$  and  $n_2=2, 3$ , respectively. The lowest-energy solution is that corresponding to part (d)

in which the configuration space of the particles is divided by a line on which  $\psi=0$ . The same solution could be obtained by imposing the boundary condition  $\psi=0$  for  $x_1=x_2$  and finding the lowest-energy solution on one side of the boundary or by requiring that the wavefunction be non-existent or zero when  $x_1=x_2$ . The same energy is also obtained by requiring that  $x_1$  be less than  $x_2$  and setting  $\psi=0$  for  $x_1 > x_2$ .

The prescription for incorporating indistinguishability effects in a random-walk calculation is thus very simple: Divide the configuration space in half by a symmetric surface of  $\psi=0$  once for each possible pair of indistinguishable particles and limit the solution to any one of the separate regions of configuration space. For excited states add more symmetric surfaces of  $\psi=0$ .

There is, for systems of interacting particles, no reason to believe that an arbitrary symmetric division of configuration space will lead to the lowest-energy solution. A mathematically valid solution will be obtained but it is not necessarily the physically admissible, lowest-energy solution. There are, however, qualitative arguments that suggest the division for the lowest-energy solution is obtained when the surface-to-volume ratio of the separated regions is smallest. Then, too, there is available a large amount of information on the nature of molecular wavefunctions from variational calculations. Most authors have not reported sufficient details of their variational wavefunctions to allow a quick determination of the location of the nodes, but the information is, in principle, available.

The molecule  $H_2$  in the triplet state  ${}^3\Sigma_u^+$  has two electrons of like spin. The variational calculations of James, Coolidge, and Present<sup>5</sup> give a reasonably accurate value for the energy of this state when the internuclear distance is 1.6 a. u. Their calculations were made with configuration interaction for a number of different sets of terms. In Fig. 3 the location of the nodes in the electron configuration space is shown for two of these calculations. In each case the location of the protons and one of the electrons is shown. The sign of the wavefunction is indicated according to the position of the second electron. For the functions used by James, Coolidge, and Present<sup>5</sup> this sign is a function only of the position of the second electron along the axis of the molecule and its radial distance from the axis. Thus, a set of two-dimensional plots is sufficient for locating the node. We note for the calculation identified as F [Fig. 3, parts (a)–(d)] there is considerable curvature in the nodal surface when the first electron is outside the region between the protons, but within this region the surface is given approximately by  $\psi=0$  for  $z_1=z_2$  where  $z_i$  is the distance along the axis for electron  $i$ . For calculation H, which gives a slightly lower energy, the phenomenon is more evident.

(We speculate that current methods for variational calculations might be improved by use of trial wavefunctions which specify node locations. Once a crude unrestricted variational calculation has been done, the node locations will be evident on examination of the wavefunction. Then each term in the wavefunction may

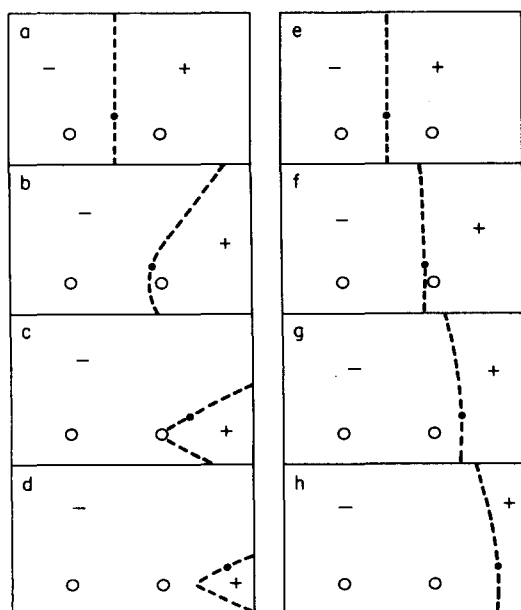


FIG. 3. Node locations in calculations of James, Coolidge, and Present<sup>3</sup> for  $H_2 \ ^3\Sigma_u^+$ . The protons are indicated by open circles, the first electron by a filled circle and the node by a dashed line. The sign of the wavefunction is indicated according to the position of the second electron. Calculation F: (a)–(d). Calculation H: (e)–(h).

be modified analytically to reproduce the node locations and no terms would be wasted simply to position the nodes. For example, in the calculations of James, Coolidge, and Present<sup>5</sup> for  $H_2 \ ^3\Sigma_u^+$ , modifying the terms of the trial wavefunction to require that  $\psi = 0$  for  $z_1 = z_2$  is likely to give a more accurate energy with fewer terms.)

For the lowest triplet state of the helium atom  $He \ 1s2s$  Kostin and Steiglitz<sup>6</sup> have found that a satisfactory energy is obtained when the six-dimensional configuration space is cut by a nodal surface corresponding to equal electron–nucleus radii, i. e.,  $r_1 = r_2$ . This is a plane in the orientation independent space  $(r_1, r_2, \theta)$  in which  $\theta$  is the angle between the radii.

Wavefunctions for electronic states of atoms and molecules are characterized by different symmetries in the configuration space of the electrons. For a particular set of states specified by the symmetry of its wavefunctions, as for  $H_2$  the  $^3\Sigma_u^+$  states, the lowest-energy state is that with the least number of nodal surfaces. States of the same symmetry but with more nodes have higher energies. In specifying node locations for random-walk calculations, one may restrict the choices to conform to a particular symmetry and number of nodes, thus specifying a particular electronic state. In a random-walk calculation, as in a variational calculation, the node locations must be varied subject to these restrictions to determine the lowest energy and, hence, the energy of the state considered.

In the absence of more definite rules for locating the nodal surfaces, we must consider random-walk calculations as variational in nature when determining the

energies of molecules with electrons of like spin. The use of arbitrary nodal surfaces does not necessarily lead to a physically admissible solution of the Schrödinger equation having continuous derivatives of the wave function across the nodal surfaces. Although we find the calculated energies to be insensitive to small changes in node positions, the variation principle must be applied in determining accurate energies for systems with unspecified nodes. For the molecular states considered in Sec. V the node locations are specified in advance. For more complex systems the locations are not known and it will be necessary to vary node positions for assurance that energies are not lower than those calculated. However, examination of wavefunctions for these more complex systems may reveal simple criteria for locating nodes.

## V. RESULTS

As noted previously the calculation procedures used in determining the eigenvalues for the systems treated are described in Ref. 2. In each calculation the total number of psips was maintained near 1000 by variation of  $V_{ref}$ . The other variable quantities—time step size  $\Delta\tau$  and steady-state time span for evaluating energy—are given below. The probable error indicated with each reported energy is the probable statistical error as determined from the variance in calculated energy over the time span and excludes systematic error. Since the computer storage requirements for determining average psip concentrations within a multidimensional configuration space were prohibitive, detailed examinations of wavefunctions and comparisons with those determined by other methods were not possible.

### A. $H_3 \ D_{3h} \ ^1A_1'$

We have repeated our earlier calculations<sup>2</sup> for the ground state of the system  $H_3^+$  using the birth and disappearance terms given by Eq. (9) and an average potential for an electron near a nucleus given by Eq. (10). Except for these changes the method used is identical to that used previously.<sup>2</sup> A single configuration of  $H_3^+$  was examined in each study—the equilateral triangle with side length 1.66 a.u. The earlier calculations gave an energy of  $-1.344 \pm 0.013$  a.u. which may be compared to the lowest-energy variational result of  $-1.343$  a.u. determined by Salmon and Poshusta.<sup>7</sup>

The effect of time-step size in the earlier calculations is indicated in Fig. 4 by the open circles. The error bars shown indicate the probable statistical error in the energy as determined by repetition of the calculations.

Also shown in Fig. 4 is the effect of time-step size with the revised expressions for  $P_b$  and  $P_d$  for step sizes up to 0.020 a.u. The error introduced by a step size of 0.020 a.u. appears to be negligible in comparison to the statistical error. The point at  $\Delta\tau = 0.020$  was determined from a set of 30 calculations, each with a transient time span of 9 a.u. followed by a span of 12 a.u. from which the energy was determined. The average energy is  $-1.3414$  a.u. with a probable sta-

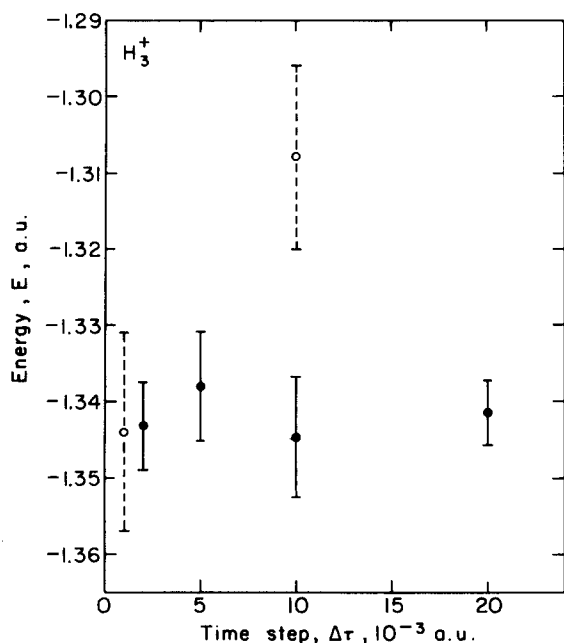


FIG. 4. Variation of calculated total energy for  $H_3^+$  with time-step size. Open circles: original method, from Ref. 2. Filled circles: revised method.

tistical error of 0.0043 a. u. as determined from the variance of the energies in the 30 independent runs.

The total computation time for the point at  $\Delta\tau=0.020$  a. u. was 73 min on the IBM 370-168 computer used. In our previous study similar accuracy was estimated to require 625 min. Variational calculations of comparable accuracy by Duben and Lowe<sup>8</sup> and by Csizmadia *et al.*<sup>9</sup> required 30 min on an IBM 360-67 and 15 min on an IBM 7094II, respectively. These correspond roughly to 30 min and 7-8 min on an IBM 370-168. Thus, the new birth and death terms cut the computation requirements of the random-walk method by a factor of about 10. While comparisons of computation effort are somewhat uncertain, especially when further optimization of computer programs is possible, it is apparent that the random-walk method is nearly competitive with variational methods for the two-electron  $H_3^+$  system.

### B. $H^2p$

The wavefunction for the  $2p_x$  state of the H atom contains a single nodal plane at  $x=0$  in the Cartesian coordinate system with the origin at the proton. Random-walk calculations were carried out for this system using the birth and disappearance terms and the average potential terms described in Sec. II. Several sets of calculations were made with the cross/recross procedure of Sec. II and, for comparison, several were made without it.

The calculation method was essentially the same as that for  $H_3^+$  except that the available configuration space was limited to the region with  $x>0$ . Psips crossing the plane  $x=0$  were eliminated. Additional psips were eliminated with probability  $P_x$  when the cross/recross correction was used.

The energies computed are shown in Fig. 5. The

open circles indicate values of  $E$  for four runs without the cross/recross correction. It may be seen that there is a significant trend with increasing  $\Delta\tau$  away from the exact analytical result of  $-0.125$  a. u. The cross/recross term was incorporated in two runs at  $\Delta\tau=0.020$  a. u. and  $0.050$  a. u. indicated by the filled circles. For  $\Delta\tau=0.020$  a. u. the energy determined over a span of 500 a. u. is  $-0.12575 \pm 0.00068$  a. u. For  $\Delta\tau=0.050$  a. u. the energy from a span of 700 a. u. is  $-0.12303 \pm 0.00041$  a. u.

The results show a marked improvement in accuracy is obtained by introducing the cross/recross terms. For  $\Delta\tau=0.050$  there remains a significant error due to step size as indicated by the absolute error of 0.00197 a. u. compared to the probable statistical error of 0.00041 a. u. However, it appears the use of the correction term allows  $\Delta\tau$  to be increased by a factor of 10 without a sacrifice in accuracy.

### C. $H_2^3\Sigma_u^+$

Calculations of the lowest triplet state of  $H_2$ , the  $^3\Sigma_u^+$  state, were carried out for an internuclear separation of 1.4 a. u. The node location was specified as  $\psi=0$  for  $z_1=z_2$ , where  $z_i$  is position along the axis of the molecule for electron  $i$ . The three corrections for large time steps outlined in Sec. II were incorporated in the calculations.

Two time-step sizes were used:  $\Delta\tau=0.010$  a. u. and  $\Delta\tau=0.020$  a. u. The total time span for evaluating the energy was in each case 70 a. u. The calculated energies were  $-0.7851 \pm 0.0036$  a. u. for  $\Delta\tau=0.010$  a. u. and  $-0.7799 \pm 0.0041$  a. u. for  $\Delta\tau=0.020$  a. u. These values may be compared with the essentially exact value  $-0.7831$  a. u. determined by Kolos and Roothaan.<sup>10</sup>

### D. Linear symmetric $H_4^1\Sigma_g^+$

Calculations for linear, symmetric, equidistant  $H_4$  were carried out with an internuclear spacing of 1.67 a. u. Node locations in the configuration space of the

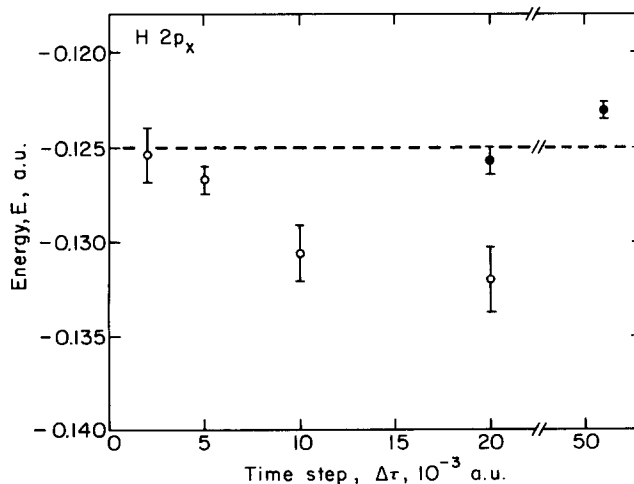


FIG. 5. Variation of calculated energy for  $H 2p_x$  with time-step size. Open circles: calculated without node recrossing correction. Filled circles: with node recrossing correction.

four electrons were specified as  $\psi=0$  for  $z_1=z_2$  and  $\psi=0$  for  $z_3=z_4$  with the protons lying on the  $z$  axis. This corresponds to a  $^1\Sigma_g^+$  state. Two step-sizes were used. The total time spans and computed energies are as follows:  $\Delta\tau=0.010$  a. u., span=200 a. u.,  $E=-2.2408 \pm 0.0340$  and  $\Delta\tau=0.020$ , span=200 a. u.,  $E=-2.2612 \pm 0.0212$  a. u.

These energies may be compared with the lowest-energy variational result,  $-2.2615$  a. u., determined by Bender and Schaefer.<sup>11</sup> With a correction of  $0.0175$  a. u., twice the error in calculations for  $H_2^+ \Sigma_g^+$  at  $1.42$  a. u. by Bender and Schaefer with the same basis set, the true energy may be roughly estimated to be  $-2.2790$  a. u.

Our  $H_4$  program was checked with calculations for two hydrogen molecules  $^1\Sigma_g^+$  at  $1.4$  a. u. separated by  $100$  a. u. The energy calculated with  $\Delta\tau=0.010$  a. u. and a time span of  $100$  a. u. was  $-2.3286 \pm 0.0159$  a. u. This is  $0.0204$  a. u. higher than the exact value of  $-2.3490$  a. u.<sup>10</sup>

### E. Be X $^1S$

For the ground-state beryllium atom we chose the node locations as  $\psi=0$  at  $r_1=r_2$  and  $\psi=0$  at  $r_3=r_4$  where  $r_i$  is the electron-nucleus distance. Calculations were carried out with two time-step sizes. For  $\Delta\tau=0.005$  a. u. a total span of  $80$  a. u. gave an energy of  $-14.596 \pm 0.060$  a. u. For  $\Delta\tau=0.010$  a. u. with the same span the energy was  $-14.894 \pm 0.045$  a. u. These values may be compared with the value determined from spectroscopic measurements,<sup>12</sup>  $-14.669$  a. u. (adjusted to a reduced mass of unity for the electron in the Be atom). The corresponding Hartree-Fock energy<sup>13</sup> is  $-14.573$  a. u. and a recent variational calculation by Nesbet<sup>14</sup> yields  $-14.665$  a. u. (without a relativistic correction).

## VI. DISCUSSION

While the results given in Sec. V represent no advance in knowledge for the several systems considered, they do indicate, in general, that the random-walk method can be successfully utilized in determining energies of these systems. Neither variational methods nor the random-walk method can compete with direct analytic solution in the case of the H atom. For  $H_2$  and Be the random-walk method is unlikely to compete with existing variational methods such as those used by Kolos and Roothaan<sup>10</sup> for  $H_2$  and by Nesbet<sup>14</sup> for Be. For  $H_3^+$  we estimate the calculation effort for random-walk calculations is now only two to five times that for variational calculations of similar accuracy.

For linear  $H_4$  the comparison of variational and random-walk methods is clouded by the uncertainty in the exact value of the energy. Both the random-walk calculations and the variational calculations<sup>11</sup> give energies about  $0.02$  a. u. higher than the roughly estimated true energy. The random-walk result for  $H_2 + H_2$  with the same program is also  $0.02$  a. u. higher than the exact result, but this error is approximately

equal to the probable statistical error. Further calculations to reduce the statistical error in the random-walk results may resolve these questions (or perhaps indicate a systematic error in the  $H_4$  and  $H_2 + H_2$  calculations).

Applications of the random-walk method to systems more complex than those considered here will require a detailed knowledge of node positions. The general requirements for physically admissible wavefunctions were outlined in terms of electron spin and symmetry properties in 1925–26 by Pauli,<sup>15</sup> Dirac,<sup>16</sup> and Heisenberg.<sup>17</sup> These requirements were placed in the framework of group theory in 1927–28 by Wigner,<sup>18</sup> Hund,<sup>19</sup> and Heitler.<sup>20</sup> In this period node locations and properties were carefully considered. With the advent of Slater determinants<sup>21</sup> in 1929 the problem of node locations was effectively solved for variational calculations. It was then unnecessary to consider the details of node structure in solving the Schrödinger equation. For the random-walk method to succeed in its present form node structure must again be considered in detail.<sup>22</sup>

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