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Quantum Chemistry by Random Walk: Method of Successive Corrections

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The random-walk method of solving the Schrödinger equation is reformulated to allow the direct calculation of the difference δ between a true wavefunction ψ and a trial wavefunction ψ_0. For a trial wavefunction from any source the difference δ may be calculated and used to correct the trial wavefunction. Successive calculations offer the possibility of further corrections and wavefunctions of unlimited accuracy. The calculation of δ is illustrated for the cases of the particle-in-a-box and the hydrogen atom. Energies are determined directly from the random-walk calculations and indirectly from computation of the expectation values for the corrected wavefunctions.

I. INTRODUCTION

We have described previously [1-3] the use of a random-walk method to solve the Schrödinger equation for several one- to four-electron molecular systems. The method is extremely simple. Nevertheless, lengthy computations are required for high accuracy in determining wavefunctions and energies for complex molecular systems.

An additional difficulty is caused by the necessity that nodes in a wavefunction must be specified in advance. While nodes may be determined *a priori* by symmetry requirements for a few simple systems, symmetry requirements are not sufficiently restrictive for the determination of nodes in complex systems [2, 4]. As pointed out by Klein and Pickett [4] nodal surfaces may be obtained from approximate wavefunctions and used in calculating improved wavefunctions with the same nodal surfaces. The energy determined in this way is then an upper bound to the true energy for the state considered. The technique has been found successful in the case of the H_4 square [3]. In general, however, optimization of node locations greatly expands the computation effort required.

We report here a reformulation of the method which allows the direct calculation of the difference δ between a true wavefunction ψ and a trial wavefunction ψ_0 for a fixed set of node locations. Calculation effort for a specified accuracy in the wavefunction or the energy is significantly reduced. This increases the number of node structures which can be examined with a given computation effort and facilitates the use of the method for complex molecular systems. We note the similar use of trial wave-

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functions in a somewhat-different Monte Carlo method described by Kalos, Levesque and Verlet [5].

In succeeding sections we describe the method and illustrate its use in applications to the simple problems of the particle-in-a-box and the hydrogen atom. Energies are derived both from the random-walk calculations and by computation of the expectation values of the energy for the corrected wavefunctions.

II. THE DIFFERENCE δ

The random-walk method for the direct determination of a wavefunction ψ consists of a simple game designed to simulate the time-dependent Schrödinger equation,

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

which is identical in form to the diffusion equation to which a first-order rate term is added,

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

With the substitution of imaginary time $\tau = it/\hbar$ Eq. (1) becomes

$$\frac{\partial \psi}{\partial \tau} = \frac{\hbar^2}{2\mu} \nabla^2 \psi - V\psi. \tag{3}$$

The equation has solutions at large τ of the type

$$\psi(x, \tau) = \psi(x)\, e^{-E\tau} \tag{4}$$

consisting of a spatial part $\psi(x)$ multiplying exponentially in time. Integration to large τ yields as the spatial part $\psi(x)$ a solution to the time-independent Schrödinger equation with the eigenvalue E.

To simulate Eq. (3) [or Eq. (2)] an initial collection of ψ particles (or psips) is caused to diffuse and multiply in a random-walk computation. As time is advanced one step $\Delta\tau$ each psip is moved at random a step Δx in each dimension and caused to multiply (or disappear) with a probability dependent on $V\Delta\tau$. With adjustments to maintain a fixed number of psips the distribution of psips approaches with increasing time a fluctuating "steady-state" distribution which corresponds to the lowest-energy wavefunction satisfying the time-independent Schrödinger equation. The process has been described in detail in earlier papers [1-3].

The calculation of the difference δ between a true wavefunction ψ and a trial wavefunction ψ_0 is similar. With ψ_0 fixed in time we have

$$\delta(x, \tau) = \psi(x, \tau) - \psi_0(x). \tag{5}$$

Substitution for ψ in Eq. (3) gives

$$\frac{\partial \delta}{\partial \tau} = \frac{\hbar^2}{2\mu} \nabla^2 \delta - V\delta + \left[\frac{\hbar^2}{2\mu} \nabla^2 \psi_0 - V\psi_0\right]. \tag{6}$$

The equation is similar to Eq. (3), containing a diffusion term and a first-order rate term; but, it contains in addition the term in brackets which corresponds to a distributed source fixed in time but varying with position. The source term may be positive or negative.

It is convenient to define the potential energy V relative to a reference potential V_{ref}. Thus, Eq. (6) becomes

$$\begin{aligned} \frac{\partial \delta}{\partial \tau} &= \frac{\hbar^2}{2\mu} \nabla^2 \delta - (V - V_{\text{ref}})\, \delta + S, \\ S(x) &= \left[\frac{\hbar^2}{2\mu} \nabla^2 \psi_0 - (V - V_{\text{ref}})\, \psi_0\right]. \end{aligned} \tag{7}$$

The source term S has the desirable property that as ψ_0 approaches the true solution and V_{ref} is adjusted to equal the eigenvalue E the term approaches zero.

The random-walk game for determining δ is the same as that for determining ψ directly except that additional psips are fed to the system as required by the source term. The δ psips of an arbitrary initial distribution are moved at random according to $\overline{(\Delta x)^2} = 2D\Delta\tau$. Each psip is caused to multiply or disappear with a probability $-V\Delta\tau$. Additional psips are fed to the system with the probability $|\, S \,|\, \Delta\tau$ at each point. The psips fed may be positive- or negative-valued depending on the sign of S. When the reference potential is adjusted to maintain a constant net (positive-negative) number of psips the distribution approaches in time a steady-state distribution corresponding to that of the function δ.

In executing such a calculation it is advantageous to make use of a cancellation of positive and negative psips occurring at the same point. For multidimensional systems it is advantageous to cancel positive and negative psips occurring in the same region of space provided each has had time to be representative of a steady-state distribution within the region.

The energy corresponding to a steady-state distribution may be evaluated according to

$$\frac{\partial \psi}{\partial \tau} = -(E - V_{\text{ref}})\, \psi \tag{8}$$

or

$$\frac{\partial \delta}{\partial \tau} = -(E - V_{\text{ref}})(\psi_0 + \delta). \tag{9}$$

Summing for all psips gives

$$\sum \frac{\partial \delta}{\partial \tau} = (E - V_{\text{ref}}) \sum (\psi_0 + \delta) \tag{10}$$

or

$$\frac{dN_\delta}{d\tau} = -(E - V_{\text{ref}})(N_0 + N_\delta), \tag{11}$$

where N_δ is the net number of psips and N_0 is the equivalent number for ψ_0. With V_{ref} adjusted to give a constant N_δ the energy is given by

$$E = V_{\text{ref}}. \tag{12}$$

An accurate value of E is obtained from an average of V_{ref} for a large number of time steps.

Accurate energies may also be obtained by use of the variational principle. An upper bound to E is the expectation value $\langle E \rangle$ given by

$$\langle E \rangle = \frac{\int \psi H \psi \, dx}{\int \psi \psi \, dx} \tag{13}$$

or

$$\langle E \rangle = \frac{\int \psi_0 H \psi_0 \, dx + 2 \int \delta H \psi_0 \, dx + \int \delta H \, \delta \, dx}{\int \psi_0 \psi_0 \, dx + 2 \int \delta \psi_0 \, dx + \int \delta \delta \, dx} \tag{14}$$

In many cases, including those in which ψ_0 is obtained from variational calculations, the integrals involving ψ_0 only may be obtained analytically. The function δ may be obtained in analytic form by a fit to the psip distribution. If this function is simple the integrals involving δ may, in some cases, be obtained analytically. In other cases it is necessary to evaluate these integrals by any one of a variety of numerical methods. The integral $\int \delta H \psi_0 \, dx$ may be obtained directly from the psip distribtion without an analytic function for δ. Where δ is small compared to ψ_0 the integrals $\int \delta H \delta dx$ and $\int \delta \delta dx$ are small and need not be evaluated accurately to obtain accurate expectation values for the energy.

The extensions for successive corrections $\delta_1, \delta_2, \delta_3 \cdots$ are similar. In the examples given below we have utilized two of the methods of determining energies described here.

III. PARTICLE-IN-A-BOX, WITHOUT ψ_0

For later comparisons the case of a particle in a one-dimensional box was investigated with a calculation of the complete wavefunction ψ. The trial wavefunction was set equal to zero to give no source term. The problem was specified in atomic units with $\hbar^2/2\mu = \frac{1}{2}$ and a box length $L = 1$ with a potential energy $V = 0$ for $0 < x < L$ and $V = \infty$ for $x \leqslant 0$ and $x \geqslant L$. The exact analytic solution is $\psi = \sin \pi x/L$ with the eigenvalue $E = \pi^2/2 = 4.93480$.

Psip positions were restricted to evenly spaced points at interval in x of 0.01 units. The random walk was executed with a time step of 0.0001 units and distance steps of -0.02, -0.01, 0.00, $+0.01$, $+0.02$ with probabilities $\frac{1}{16}$, $\frac{4}{16}$, $\frac{6}{16}$, $\frac{4}{16}$, $\frac{1}{16}$, respectively, to give $\overline{(\Delta x)^2} = 0.0001$. At each time step each psip with $0 < x < L$ was allowed to multiply to two psips with the probability $P_B = \exp(V_{\text{ref}}\, \Delta\tau) - 1$. Psips with $x \leqslant 0$ or $x \geqslant L$ were caused to disappear. In addition, psips found within the interval $0 < x < L$ at the beginning and end of a time step were removed with the cross/recross probability P_x described in Ref. [2]. The reference potential V_{ref} was adjusted at each time step to maintain the number of psips at approximately 1000.

The calculation was begun at $\tau = 0$ with 1000 psips placed at random within the box and allowed to proceed to $\tau = 0.2$ to reach "steady-state." The distribution of psips and the values of V_{ref} were accumulated for a time span of 1.0 from $\tau = 0.2$ to $\tau = 1.2$ for the determination of ψ and E. The distribution obtained is shown in Fig. 1. The average value of V_{ref} and thus E was 4.9515 with a probable error in sampling of 0.0626 as determined from the variance in E for intervals of 0.1 time units.

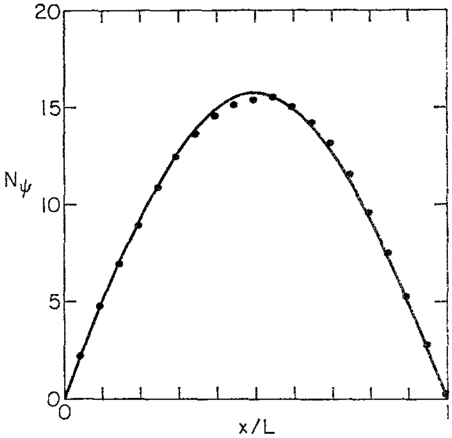

Fig. 1. Comparison of calculated psip distribution (points) with exact wavefunction (line) for the particle-in-a-box.

IV. Particle-in-a-Box, Sawtooth ψ_0

The difference formulation was investigated first for the particle-in-a-box with the sawtooth trial wavefunction shown in Fig. 2. The calculation was carried out with the same box length, step-sizes, and so forth as described in Section III. The trial function was

$$\begin{aligned} \psi_0 &= 2Ax, \qquad 0 \leqslant x \leqslant 0.5, \\ &= 2A(1 - x), \qquad 0.5 \leqslant x \leqslant 1 \end{aligned} \tag{15}$$

with

$$A = 18{,}000 \tag{16}$$

and

$$N_0 = \int_0^1 \psi_0 \, dx = 9000. \tag{17}$$

The expectation value of the energy given by Eq. (13) for ψ_0 is $\langle E \rangle = 6$.

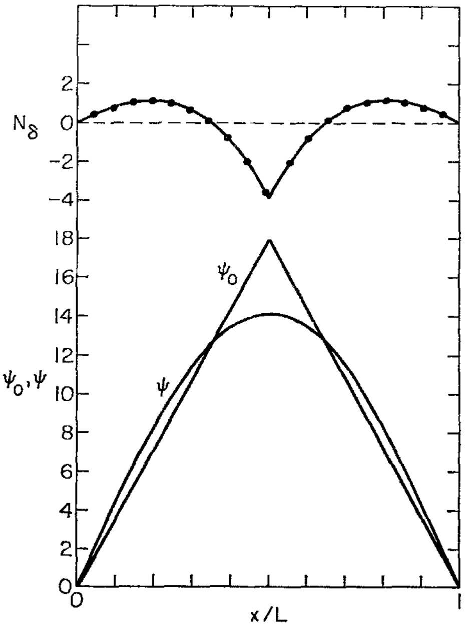

FIG. 2. Sawtooth trial wavefunction ψ_0, exact wavefunction ψ, computed psip distribution N_δ (points) and exact difference function (line) for particle-in-a-box.

The source term S consisted of a delta function for negative psips at a rate of $2A$ per unit time at $x = 0.5$ and a sawtooth function for positive psips at a total rate of $\frac{1}{2}A\ V_{\mathrm{ref}}$ per unit time distributed in proportion to ψ_0. Pairs of positive and negative psips occupying the same position were removed from the system. Multiplication and disappearance of psips were treated in the same way as described in Sec. III. The reference potential V_{ref} was adjusted at each time step to maintain the net (positive-negative) number of psips at approximately zero.

The initial distribution was set with 10 each of positive and negative psips at $\tau = 0$. At $\tau = 0.2$ the system had reached an apparent steady-state with approximately 500 psips of each type. The energy and psip distributions were evaluated in a time span of 1.0 from $\tau = 0.2$ to $\tau = 1.2$. The calculated distribution (or function δ) is compared to the exact value of δ in Fig. 2. The energy obtained as the average value of V_{ref} is $4.9279 + 0.0108$ (probable sampling error).

V. PARTICLE-IN-A-BOX, SKEWED-SINE ψ_0

The difference formulation was also investigated for the particle-in-a-box with the skewed-sine trial wavefunction of Fig. 3 which represents a better approximation to the true wavefunction than does the sawtooth function. The trial function was

$$\psi_0 = A\sin(\pi x/L)(1 + bx), \qquad 0 \leqslant x \leqslant L, \tag{18}$$

with

$$N_0 = A\frac{L}{\pi}(2 + bL). \tag{19}$$

Calculations were carried out for the skewed-sine trial function with $A = 80{,}000$, $b = 0.1$ and $A = 400{,}000$, $b = 0.02$. The procedure was essentially identical to that for the sawtooth function with a steady-state time span of one unit and approximately 1000 particles in each case. The energies obtained as the average values of V_{ref} were $E = 4.9356 + 0.0025$ for $b = 0.1$ and $E = 4.9343 + 0.0004$ for $b = 0.02$. The expectation values $\langle E \rangle$ as given by Eq. (13) for the trial wavefunctions are 4.93933 for $b = 0.1$ and 4.93499 for $b = 0.02$. Figures 3 and 4 show the calculated difference functions δ compared to the exact difference functions given by $\psi - \psi_0$.

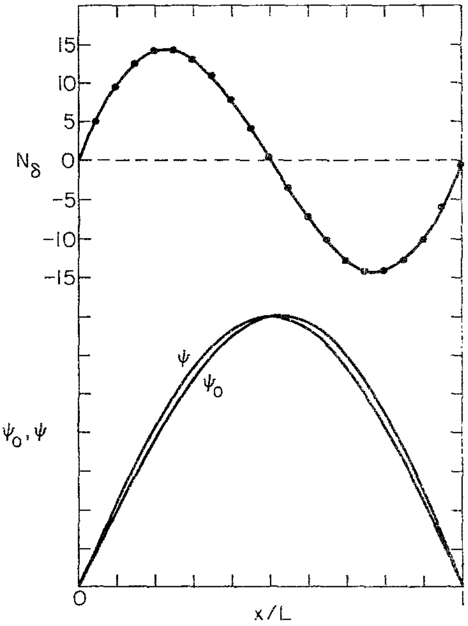

FIG. 3. Skewed-sine trial wavefunction ψ_0 (shown for $b = 0.3$ to exaggerate the difference for clarity), exact wavefunction ψ, computed psip distribution (points) and exact difference function (line) for particle-in-a-box with $b = 0.1$.

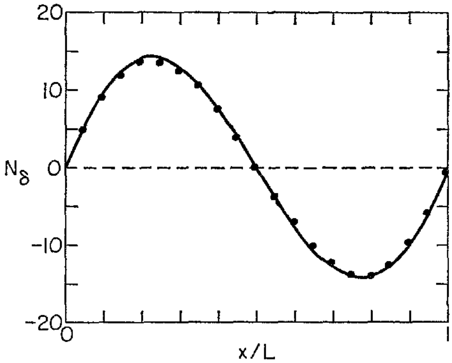

FIG. 4. Computed psip distribution (points) and exact difference function (line) for skewed-sine trial wavefunction with $b = 0.02$.

Results for the several treatments of the problem of the particle-in-a-box are listed in Table I. It may be seen that use of the difference method greatly increases the accuracy of the energy determined when the trial function approximates the true wavefunction.

TABLE I

Results for the Particle-in-a-Box

	Energies	
Trial function, ψ_0	Calculated by random walk[a]	Expectation value $\langle E \rangle$ for ψ_0
None, $\psi_0 = 0$	4.9515 ± 0.0626[b]	—
Sawtooth	4.9279 ± 0.0108	6
Skewed-sine, $b = 0.1$	4.9356 ± 0.0025	4.93933
Skewed-sine, $b = 0.02$	4.9343 ± 0.0004	4.93499
Exact, $\psi_0 = \sin(\pi x/L)$		4.93480

[a] Computation efforts are approximately equal. In each case about 1000 psips were followed through 10,000 time steps.

[b] Probable statistical error, excludes any systematic error.

VI. HYDROGEN ATOM, WITHOUT ψ_0

For later comparisons and to provide a first trial function for successive corrections a direct calculation of the wavefunction and energy with $\psi_0 = 0$ was made for the hydrogen atom. The problem was specified in atomic units with $\hbar^2/2\mu = \frac{1}{2}$ and $V = -1/r$ where r is the proton-electron distance. The exact solution is $\psi = e^{-r}$ with the eigenvalue $E = -\frac{1}{2}$.

The calculation procedure was identical to that described in Ref. [2]. The random walk was executed in three dimensions with a time step of 0.010 a.u. and distance steps selected from a set of twenty steps approximating a Gaussian distribution and having $\overline{(\Delta x)^2} = 0.010$. Each psip was subjected to multiplication or disappearance according to the potential energy corresponding to its electron position. The probability of multiplication was [2]

$$P_b = \exp[-(V - V_{\text{ref}})\,\Delta\tau] - 1, \; V < V_{\text{ref}}, \tag{20}$$

and of disappearance was [2]

$$P_d = 1 - \exp[-(V - V_{\text{ref}})\,\Delta\tau], \; V > V_{\text{ref}}. \tag{21}$$

To prevent exceeding the storage capacity of the computer system on multiplication of psips with r near zero an average potential energy for $0 < r < 0.01$ was used for $r < 0.01$. The reference potential V_{ref} was adjusted at each step to maintain approximately 1000 psips in the system.

An initial period of 10 a.u. was allowed for the system to reach steady-state. This was followed by a time span of 50 a.u. for determination of the energy and the psip distribution. The sampling error in the energy was estimated from the variation in the averages of V_{ref} for five 10-a.u. spans. The distribution of psips for the 50-a.u. span

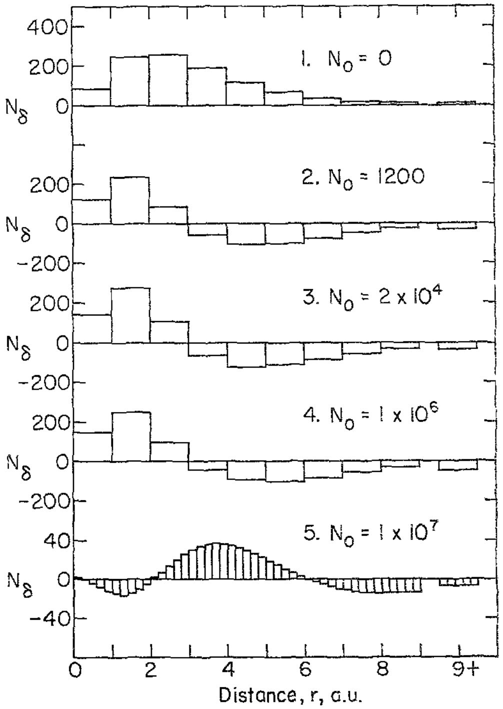

FIG. 5. Histograms of psip distributions obtained in successive corrections for the H atom.

was determined as the number of psips at each time step having r within intervals of 1 a.u. from 0 to 9 a.u. A tenth interval with $r > 9$ a.u. was also used.

The energy, determined as the average value of V_{ref}, was -0.507 ± 0.004 a.u. The psip distribution obtained is shown at the top of Fig. 5. Since the distribution is that for intervals of r rather than for intervals of volume in configuration space it should be compared to r^2e^{-r}, the exact wavefunction weighted by r^2. A comparison indicates approximate agreement.

VII. Hydrogen Atom, Successive Corrections

The difference method was applied to the case of the hydrogen atom with five successive corrections δ to the initial trial wavefunction ψ_0. The first run was that with $\psi_0 = 0$, described above, to generate a first correction δ_1. The second run with a trial function $\psi_1 = \psi_0 + \delta_1$ generated a second correction δ_2 to yield $\psi_2 = \psi_0 + \delta_1 + \delta_2$. The process was repeated to yield after five runs a wavefunction $\psi_5 = \psi_0 + \delta_1 + \cdots + \delta_5$. The energies obtained directly from the random-walk calculations and indirectly from the expectation values of the energy for the trial functions were determined for each run.

The correction δ to be applied for a succeeding trial function was expressed as a simple analytic function giving an approximate fit to the δ distribution generated in each run. The initial correction to $\psi_0 = 0$ was fit with the expression $\delta_1 = e^{-0.98r}$. Further corrections were fit with expressions of the type $\delta_i = Ae^{-ar}(1 + br + cr^2)$.

The calculation procedure was similar to that described in Sec. VI except for the additional requirements of the source term and the cancellation of positive and negative psips.

The source term S was obtained in analytic form with use of Eq. (7). Psips were fed to the system with probabilities given by the local value of the source term. At each time step N_f feed positions were chosen with r in the range 0 to $r_{\max}$. With the local feed rate per unit volume given by $S(r)$ the feed probability at each position chosen was given by

$$P_f = \frac{1}{N_f} \mid S \mid 4\pi r^2 r_{\max} \Delta\tau. \qquad (22)$$

The feed probability consisted in general of an integer n plus a fraction f less than unity. Psips having the sign of S were fed at each position as either n psips (probability $1 - f$) or $n + 1$ psips (probability f).

Cancellation of psips of opposite sign was carried out for pairs occurring in the same region of configuration space, i.e., having similar r values. The r-space was divided into $N_r - 1$ intervals of size Δr beginning at $r = 0$ plus a last region extending to infinity. To allow the opportunity for newly-fed psips and their descendants to approach equilibrium distributions within the regions the time elapsed since initial feed (family age) was followed for all psips. Psips with a family age less than a specified age τ_{old} were not subjected to cancellation. Pairs of positive and negative psips, each one with family age greater than τ_{old}, occurring in the same interval of r were removed from the system.

The difference calculations were executed with a time step of 0.010 a.u. with a span of 10 a.u. to approach steady-state and a span of 50 a.u. for determining energies and distributions. The reference potential was adjusted to give a net (positive-negative) number of psips of zero and the trial wavefunction was scaled to yield a total of approximately 1000 psips. Several combinations of the interval size Δr and the minimum family age for cancellation τ_{old} were investigated. These included Δr of 1 a.u. for r up to 10 a.u. and τ_{old} in the range of 0 to 1 a.u. Results were found insensitive to variations in these choices. For the results reported here $\Delta r = 0.1$ a.u. in 99 intervals up to $r = 9.9$ a.u. and $N_{old} = 0.1$ a.u.

Figure 5 shows histograms of the psip distributions obtained. These indicate the average net number of psips within r intervals of 1 a.u. (0.1 a.u. for Run 5). Shown also is the equivalent number of psips N_0, defined as $4\pi \int \psi_0 r^2\, dr$, for the trial wavefunction. Although the total number of psips remains constant at about 1000 for the five runs, the number relative to N_0 and, thus, the relative size of the correction is markedly decreased in successive runs.

The successive trial functions given in analytic form are listed in Table II. As indicated, δ_1 was fit by a simple exponential expression. For Runs 2-4 the corrections δ_i were adequately fit by the expression $\bar{e}^{0.99r}\,(1 - 0.33r)$ with successively smaller scaling constants. For Run 5 an exponential term multiplied by a quadratic expression in r was required.

TABLE II

Successive Corrections for the H Atom

Run no.	Trial function	Difference function
1.	$\psi_0 = 0$	$\delta_1 = e^{-0.98r}$
2.	$\psi_1 = e^{-0.98r}$	$\delta_2 = 0.058\, e^{-0.99r}\,(1 - 0.33r)$
3.	$\psi_2 = e^{-0.98r} + 0.058\, e^{-0.99r}\,(1 - 0.33r)$	$\delta_3 = 0.0044\, e^{-0.99r}\,(1 - 0.33r)$
4.	$\psi_3 = e^{-0.98}r + 0.0624\, e^{-0.99r}(1 - 0.33r)$	$\delta_4 = 0.000080\, e^{-0.99r}(1 - 0.33r)$
5.	$\psi_4 = e^{-0.98r} + 0.062480\, e^{-0.99r}(1 - 0.33r)$	$\delta_5 = 0.000002\, e^{-1.25r}(1 - 2.5r + r^2)$
–	$\psi_5 = e^{-0.98r} + 0.062480\, e^{-0.99r}(1 - 0.33r)$ $+ 0.000002\, e^{-1.25r}(1 - 2.5r + r^2)$	

Table III lists the energies calculated. The sampling error in the value of $\bar{V}_{ref}$ is reduced by about a factor of ten in each run and reaches a value in the fifth run of four parts in 10^7. The error in the energy as given by the expectation value for a trial function is reduced by a factor of about 10^2 in each run and reaches a value of four parts in 10^{13}.

TABLE III

Energies Calculated for the H Atom[a]

Run no.	Trial function	Random walk $E = \bar{V}_{\text{ref}}$		Expectation value $\langle E \rangle$
1.	ψ_0	-0.507	± 0.004[b]	–
2.	ψ_1	-0.5003	± 0.0003	-0.4998
3.	ψ_2	-0.49999	± 0.00002	-0.49999903
4.	ψ_3	-0.500003	± 0.000004	-0.49999999969
5.	ψ_4	-0.49999996	± 0.0000002	$-0.5 + 2.3\ E\text{-}12$
–	ψ_5	—		$-0.5 + 2.1\ E\text{-}13$

[a] Atomic units.

[b] Probable statistical error, excludes any systematic error.

VIII. DISCUSSION

It is clear that the random-walk method as reformulated is successful in generating the difference function δ for the simple systems treated. Further, the direct calculation of δ rather than ψ itself greatly improves the accuracy of the energy determined by reducing both systematic and random (sampling) errors. Wavefunctions and eigenvalues, both of high accuracy, may be determined in this manner.

In principle, application of the difference method to more complex systems, requiring psip movement in a space with a greater number of dimensions, is straight forward. No new concepts are required. With energies determined directly from the random-walk calculation there are no integrals to evaluate. Only the first and second derivatives of the trial wavefunctions are required.

In practice, application to more complex systems may be limited by the complexity of expressions required to represent accurate wavefunctions. As the trial wavefunction gains more terms its derivatives gain more terms and the computation effort for evaluating the source term S becomes greater. The cancellation of positive and negative psips is an essential requirement for successful use of the method. In systems of a large number of dimensions cancellation may be infrequent unless allowed to occur within relatively large regions. The use of a family age requirement may, however, allow large regions to be used without a sacrifice in accuracy.

Since terms involving inter-electron distances explicitly can be incorporated in the trial wavefunctions of a random-walk calculation, the expressions required may be much less complex than those of variational calculations. If this is the case, the use of the difference method with successive corrections may be simpler and more accurate than use of variational methods.

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