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Quantum chemistry by random walk: Higher accuracy

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The random walk method of solving the Schrödinger equation is extended to allow the calculation of eigenvalues of atomic and molecular systems with higher accuracy. The combination of direct calculation of the difference δ between a true wave function ψ and a trial wave function ψ_0 with importance sampling greatly reduces systematic and statistical error. The method is illustrated with calculations for ground-state hydrogen and helium atoms using trial wave functions from variational calculations. The energies obtained are 20 to 100 times more accurate than those of the corresponding variational calculations.

We have examined previously a simple random walk method of simulating the Schrödinger equation to determine wave functions and energies for atomic and molecular species.¹⁻³ The direct calculation of the difference between a true wave function and a trial wave function was found to increase greatly the accuracy of the results.⁴ We report here still further increases in accuracy obtained by a combination of this difference method with importance sampling.⁵ The improved method is illustrated with calculations for hydrogen and helium atoms.

The time-dependent Schrödinger equation,

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

may be transformed to an ordinary differential equation with real variables with the use of imaginary time $\tau = it/\hbar$,

$$\frac{\partial \psi}{\partial \tau} = \frac{\hbar^2}{2\mu} \nabla^2 \psi - V\psi. \quad (2)$$

This equation is similar in form to the diffusion equation modified by the addition of a first-order rate term to describe a system of particles undergoing diffusion and reaction.

As shown in Ref. 1 use of imaginary time allows the Schrödinger equation to be simulated by a random walk game in which particles or "psips" are caused to diffuse and multiply or disappear. With increasing time an arbitrary initial distribution of psips approaches a fluctuating "steady-state" distribution corresponding to the wave function for a solution of the time-independent Schrödinger equation with the eigenvalue E .

The method has the advantage of extreme simplicity but requires lengthy calculations for accurate determinations of eigenvalues. In Ref. 4 we described a modification to allow direct calculation of the difference δ between the true wave function ψ and a trial wave function ψ_0 ,

$$\delta = \psi - \psi_0. \quad (3)$$

Substitution into Eq. (1) yields, in atomic units,

$$\frac{\partial \delta}{\partial \tau} = \frac{1}{2} \nabla^2 \delta - (V - V_{\text{ref}}) \delta + \left[\frac{1}{2} \nabla^2 \psi_0 - (V - V_{\text{ref}}) \psi_0 \right], \quad (4)$$

where the terms in brackets correspond to a distributed source fixed in time and the potential energy V is defined

relative to a reference potential energy V_{ref} . With this "difference method," accuracy is greatly increased for a given calculation effort when ψ_0 approximates the true wave function.

Kalos *et al.*⁵ showed theoretically and practically that improved accuracy could be obtained by importance sampling, that is, by introducing a trial function ψ_0 and then sampling an equation for $\psi_0 \psi$ rather than for ψ itself. Ceperley⁶ has pointed out how importance sampling could be used to obtain a differential equation similar to Eq. (2). Multiplying Eq. (2) by a trial function ψ_0 and letting $f = \psi \psi_0$ yields

$$\frac{\partial f}{\partial \tau} = \frac{1}{2} \nabla^2 f - \nabla \cdot (f \nabla \ln \psi_0) - \left(\frac{H\psi_0}{\psi_0} - V_{\text{ref}} \right) f. \quad (5)$$

Since the third term corresponds to a drift of particles in a fluid of velocity $\nabla \ln \psi_0$, this equation may be simulated by a random walk process with drift and reaction. When the trial function ψ_0 approximates the true wave function, the local energy $H\psi_0/\psi_0$ is nearly constant and particle multiplication is minimized. The variance in computed values of E is thus reduced.

The two procedures for improving the accuracy may be combined. Replacing f of Eq. (5) with a new difference function,

$$g = (\psi - \psi_0) \psi_0, \quad (6)$$

yields upon rearrangement

$$\begin{aligned} \frac{\partial g}{\partial \tau} = & \frac{1}{2} \nabla^2 g - \nabla \cdot (g \nabla \ln \psi_0) - \left(\frac{H\psi_0}{\psi_0} - V_{\text{ref}} \right) g \\ & + \left[- \left(\frac{H\psi_0}{\psi_0} - V_{\text{ref}} \right) \psi_0^2 \right]. \end{aligned} \quad (7)$$

This equation may be simulated by the diffusion, drift, multiplication, and feed of particles. When ψ_0 approaches the true wave function and V_{ref} approaches E , the multiplication and the feed of particles both approach zero.

The calculation procedure employed for simulating Eq. (7) for hydrogen and helium atoms was essentially the same as that of Ref. 4 with several modifications. Particles were assigned weights W that increased or decreased with time according to the multiplication term. At each time step, three particles were fed to the system according to the source term. The bracketed feed term of Eq. (7) may be rewritten as

$$S_{10c} = V_{\text{con}} \psi_0^2 - \left(\frac{H\psi_0}{\psi_0} - E_{\text{var}} \right) \psi_0^2, \quad (8)$$

where the control potential $V_{\text{con}} = V_{\text{ref}} - E_{\text{var}}$ is the difference between the reference potential and the expectation value E_{var} of the energy given by a variational calculation for ψ_0 . Particles were fed as suggested by Eq. (8). One particle selected with probability ψ_0^2 was fed with sign and weight proportional to the integral of $V_{\text{con}} \psi_0^2$ over space. One particle of positive sign selected with probability $(H\psi_0/\psi_0 - E_{\text{var}})\psi_0^2$ from regions of space with $(H\psi_0/\psi_0 - E_{\text{var}}) < 0$ was fed with weight proportional to the integral of $(H\psi_0/\psi_0 - E_{\text{var}})\psi_0^2$ over all such regions. One particle of negative sign selected in the same way from regions with $(H\psi_0/\psi_0 - E_{\text{var}}) > 0$ was fed with the same weight.

Given sufficient time to diffuse, drift, and multiply, particles fed to the system at any point tend to the same distribution. Thus, if a particle's age is defined as the time elapsed since the feed of the particle or its ancestor, particles of infinite age may be combined without loss of accuracy. In practice, it was found convenient to divide the configuration space into regions and combine particles of age greater than τ_{old} within each region. The effect of using a finite value for τ_{old} was determined by varying τ_{old} .

The calculations were begun with a feed of three particles at time $\tau = 0$. At each successive time step $\Delta\tau$, three more particles were fed. At the end of a time step the weight of each particle was multiplied by the factor $\exp[-(H\psi_0/\psi_0 - V_{\text{ref}})\Delta\tau]$. Each particle was then moved in each dimension a step Δx chosen from a Gaussian distribution with a standard deviation $(\Delta\tau)^{1/2}$. Each particle was then moved a distance given by the product of drift velocity and time step $(\nabla \ln \psi_0)\Delta\tau$. Any allowed combinations were then executed, and the cycle was repeated. The reference potential was adjusted at each time step to produce a net weight of particles of approximately zero. Energies were evaluated from the average reference potential for a period of time after steady state was reached.

For the hydrogen atom, calculations were carried out with the two trial wave functions listed in Table I. The random walk game was executed with a time step $\Delta\tau$ of 0.010 a.u. for a period of 105 a.u. with accumulation of V_{ref} averages beginning at 5 a.u. The computation required 1800 sec on an IBM 370 System 3033 for each case. The configuration space was divided into nine regions with electron-nucleus distances r in intervals of 0.1 a.u. up to 0.9 a.u. and one region with r greater than 0.9 a.u. Combination of particles was carried out within these regions for particles of age greater than $\tau_{\text{old}} = 2$ a.u. Repeated runs with $\tau_{\text{old}} = 1$ a.u. showed no effect of varying τ_{old} and thus indicated no significant error in the choice of $\tau_{\text{old}} = 2$ a.u. For configurations with r less than 0.13 a.u., the time step was reduced by a factor of 10.

The random-walk energies E_{rw} obtained are listed in Table I together with E_{var} for the trial wave functions used and the exact value of the energy. The probable sampling error listed (approximately one standard deviation) was evaluated from the variance in the average V_{ref} for 5 a.u. inter-

TABLE I. Computed energies for H and He.

Hydrogen	
$\psi_0 = e^{-0.98r}$	$\psi_0 = e^{-0.999r}$
$E_{\text{var}} = -0.4998$	$E_{\text{var}} = -0.4999995$
$E_{\text{rw}} = -0.499995$ ± 0.000004	$E_{\text{rw}} = -0.500000007$ ± 0.00000010
$E_{\text{exact}} = -0.5$	$E_{\text{exact}} = -0.5$
Helium $s = r_1 + r_2 \quad t = r_1 - r_2 \quad u = r_{12}$	
$\psi_0 = e^{-1.6875s}$	$\psi_0 = e^{-1.616s} (1 + 0.13t^2 + 0.30u)$
$E_{\text{var}} = -2.84765625$	$E_{\text{var}} = -2.902412618$
$E_{\text{rw}} = -2.9044$ ± 0.0012	$E_{\text{rw}} = -2.903649$ ± 0.000060
$E_{\text{exact}} = -2.903724377$	$E_{\text{exact}} = -2.903724377$

vals of time and excludes any systematic error. Repeat runs with $\Delta\tau = 0.005$, 0.010, and 0.020 a.u. gave similar results.

For helium, the two Hylleraas wave functions of Table I were used as trial wave functions. The time step $\Delta\tau$ was 0.005 a.u. For combination of old particles, the electron configuration space was divided into regions with r_1 and r_2 in five intervals of 0.2 a.u. and r_{12} in ten intervals of 0.2 a.u. with allowance for permutation of r_1 and r_2 . Combination was carried out for particles of age greater than 2 a.u. Results are listed in Table I for runs of 30 a.u. duration. The calculated energies may be compared with the "exact" value obtained by Schwartz⁷ in variational calculations with a 189 term wave function. Runs with time steps of 0.010 and 0.020 a.u. showed an appreciable systematic error for large time-step sizes (0.00025 a.u. at $\Delta\tau = 0.020$ a.u.).

The results for both hydrogen and helium show energy improvements by factors of 20 to 100 over the expectation values of the energies for the trial wave functions used. While this is certainly unimportant for these two systems, it demonstrates the power of the improved random walk method and illustrates the potential of the method for more complex molecular systems.

The method offers improved energies for variational calculations without the necessity of larger basis sets. Electron interaction effects are incorporated completely. Thus, in principle, the accuracy of any variational calculation may be improved by use of the random walk method. In practice, the complexity of trial wave functions for many-electron systems may (or may not) limit the usefulness of the method.

For systems of two or more electrons of the same spin or for excited states, the node structure of the computed wave function is that of the trial wave functions. Although it has been found⁸ for several simple systems that energies are insensitive to minor variations in reasonable node structure, there is no solid evidence to support such an insensitivity for complex systems. Variation of node locations will be required to minimize the computed energies to obtain exact results

for such systems. Applications to the methane system are under investigation.

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