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Quantum chemistry by random walk: A faster algorithm

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Two extensions of the fixed-node random walk method of solving the Schrödinger equation are described. A simple iterative procedure is found to reduce time-step error and the use of two trial wave functions in place of one for importance sampling is found to reduce computation effort. In combination the two modifications reduce computation effort for a fixed accuracy by a factor of about 10.

With the random walk method of solving the Schrödinger equation it is now possible to calculate the potential energy of several small molecular systems with accuracies of 0.1 kcal/mol or better.[1] The use of importance sampling has reduced greatly the computation requirements for such calculations. We report here two modifications which reduce the computation requirements still further—by at least a factor of 10. These modifications are (1) use of an iterative procedure to eliminate in part the error introduced by finite time-step size and (2) the use of two trial wave functions, one a simple function for guiding particle drift and the other a more accurate function for determining energies. The first allows greater time-step sizes and the second allows sampling for energy determination at greater intervals of time.

The basic random walk method and the introduction of importance sampling have been described previously.[1-3] With importance sampling the Schrödinger equation in imaginary time is simulated by the diffusion, drift, and multiplication of wave function particles or psips in the configuration space of the electrons. The resulting density of psips is proportional to the product $f = \psi \psi_T$ of the true wave function ψ and a trial wave function ψ_T. The electronic energy of the system is given by the average of the local energy $E_{\text{loc}} = H\psi_T/\psi_T$ for all psips. High accuracies are obtained by accumulating values of E_{loc} for long intervals of time.

In practice the simulation requires the use of time steps of finite size and, as a result, the introduction of time-step error. Extrapolation of energies to a time step of zero is one possible way of eliminating this error; but it is not certain that, in the presence of an attractive Coulomb singularity, the result is exact even in the limit of small time steps. This question has been discussed by Moskowitz *et al.*[4] If the Coulomb potential is modified[4,5] for very small electron–nucleus distances the procedure may be made exact in the limit of small time steps. (An alternative for the elimination of time-step error is the sampling of the corresponding Green's function for particle movement.[6])

In many cases the validity of extrapolation to zero time-step size has been established empirically. Shown in Fig. 1 is the effect of time-step size on the energy calculated for the H-atom system with a trial wave function $\psi_T = \exp(-0.98r)$. In the simplest case a psip at position x at time τ is moved a distance Δx given by the sum of a random diffusion step Δx_{diff}, $\langle \Delta x_{\text{diff}}^2 \rangle = \Delta\tau$, and a drift step $\Delta x_{\text{drift}} = v_x \Delta\tau$, where the velocity $v_x = -(\partial/\partial x)\ln \psi_T$ is evaluated at point x. Since v_x is not constant over the time interval $\Delta\tau$ an error in the path of a psip is introduced.

We investigated several ways of reducing the error in the path. These included use of first and higher derivatives in v_x with position, the use of an average of v_x values for τ and $\tau + \Delta\tau$, and various combinations. These methods are well known for the integration of the classical equations of motion of particles as in, e.g., the trajectory calculations of molecular dynamics. Rothstein and Vrbik[7] have reported the use of a similar method in random walk calculations. We find the most efficient method of those we investigated to be that of simple iteration. The diffusion step Δx_{diff} is selected; the velocity v_x is calculated at x; a velocity v_x' is calculated at $x' = x + \Delta x_{\text{diff}} + v_x \Delta\tau$; the new position is taken as $x = x + \Delta x_{\text{diff}} + \frac{1}{2}(v_x + v_x')\Delta\tau$. Additional iterations were not more efficient than use of smaller time-step sizes. The reduction in time-step error with the single iteration is indicated in Fig. 1. The calculation effort for a time step of 0.010 a.u. with the iterative procedure is roughly equal to that for 0.005 a.u. without iteration but the time-step error is about a factor of 3 lower. Similar behavior was observed for the case of the He atom with simple trial functions.

The second improvement is based on the use of two trial wave functions in importance sampling. The combination has been used recently by Ceperley and Alder[8] in variable-node Monte Carlo calculations. With a single function the energy is given by

$$E = \frac{\displaystyle\int \frac{H\psi_T}{\psi_T}\psi\psi_T\,d\bar{r}}{\displaystyle\int \psi\psi_T\,d\bar{r}} \cong \frac{\displaystyle\sum_{\text{all }i}\left(\frac{H\psi_T}{\psi_{T_i}}\right)}{\displaystyle\sum_{\text{all }i} 1},\qquad(1)$$

where the summations are for all psips after a "steady state" has been reached. The energy may also be given by

$$E = \frac{\displaystyle\int \frac{H\psi_T}{\psi_T}\frac{\psi_T}{\psi_G}\psi\psi_G\,d\bar{r}}{\displaystyle\int \frac{\psi_T}{\psi}\psi\psi_G\,d\bar{r}} \cong \frac{\displaystyle\sum_{\text{all }i}\left(\frac{\psi_T}{\psi_G}\right)_i\left(\frac{H\psi_T}{\psi_T}\right)_i}{\displaystyle\sum_{\text{all }i}\left(\frac{\psi_T}{\psi_G}\right)_i},\qquad(2)$$
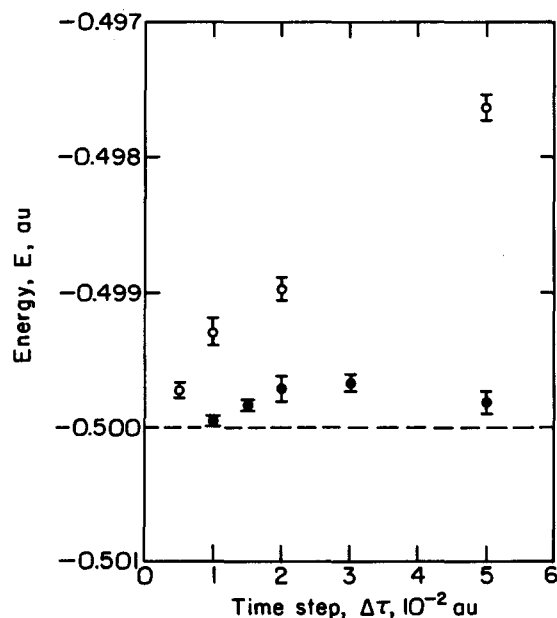
FIG. 1. Variation of calculated energy with time-step size for the hydrogen atom. Open circles: no iteration. Closed circles: single iteration.

TABLE I. Computation times and energy uncertainties for varied sampling intervals.

Sampling interval n	Uncertainty in energy σ_b (10^{-6} a.u.)	Computation time	
		Per block t_b (s)	Relative[a] t_{rel}
1	4.0	2 200	1.8
2	4.4	1 200	1.2
5	5.8	600	1.0
10	8.0	400	1.3
20	10.5	300	1.6
50	16.4	240	3.2
A	4.0	4 000	3.2
B	4.0	20 000	16.0

[a] Relative time required for a fixed uncertainty in energy.

where ψ_G is a second trial function. The variance in the energy given by the summation terms in Eq. (2) is lowest when the samples i are independent; but, for small step sizes successive values of the local energy for individual psips are strongly correlated. When the trial wave function ψ_T is complex most of the calculation effort goes into evaluating the derivatives of ψ_T for determining the drift velocity and the local energy. Use of a second, simpler function ψ_G allows the psips to be moved and multiplied with less effort. With use of Eq. (2) for evaluating the energy the advantage of higher accuracy (and lower variance) in energy may be retained while sampling for energy determination is made at larger time intervals. Thus, one may use a simple ψ_G trial function with time steps of 0.005 a.u. but the energy may be calculated from Eq. (2) using E_{loc} for a complex ψ_T at intervals of 0.050 a.u.

We tested the idea in applications to the hydrogen and helium atoms. For the helium atom the simple function was a three-term Hylleras expression $\psi_G = e^{-1.816s}(1 + 0.13t^2 + 0.30u)$ where $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12}$ and the complex function was a similar function of 189 terms given by Schwartz.[9] The basic time-step size was 0.005 a.u. and the single iteration procedure described above was used. Calculations were made with 100 psips for a time of 40 a.u. after steady state. Energies were calculated for blocks of 2 a.u. and the standard deviation of block energies σ_b from the "exact" value ($-2.903\ 7244$ a.u.) determined by Schwartz was used in comparing the effects of sampling at varied time intervals.

Results are listed in Table I. The sampling interval n indicates the energy was evaluated using Eq. (2) at every nth time step. The standard deviations σ_b in energies for the 2 a.u. blocks and computation times t_b (Prime

750 computer) are shown together with relative computation times t_{rel} for the same overall accuracy in extended calculations. The standard deviation σ_b may be seen to increase slowly with n for low n and rapidly at high n. The computation time decreases with increasing n. Since the standard deviation of the mean energy for an extended calculation varies inversely with the square root of the number of blocks, the computation time for a fixed accuracy is proportional to $t_b\sigma_b^2$. This value divided by that for $n = 5$ is listed as t_{rel}.

Also listed in Table I are values for (A) the use of a single 189-term trial function with $\Delta\tau = 0.005$ a.u. and iterative path correction and (B) the use of single 189-term trial function with $\Delta\tau = 0.001$ a.u. which is estimated to give a similar time-step error. It may be seen that t_{rel} is lowest for a sampling interval $n = 5$ and that it is lower by a factor of about 16 than for the conventional case (B).

The two modifications described above have been tested on only a few problems but the advantages of their use appear to be general. The iterative procedure is expected to yield similar gains for all systems. The advantages in use of two trial functions may vary significantly with the nature of the trial wave function ψ_T and the extent of correlation of E_{loc} with position in configuration space. A number of extensions, such as adjustment of psip multiplication to give equal weights ψ_T/ψ_G in Eq. (2), may lead to further improvements.

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