

ARTICLES

Quantum Monte Carlo: Direct calculation of corrections to trial wave functions and their energies

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We report an improved Monte Carlo method for calculating the difference δ between a true wave function Ψ and an analytic trial wave function Ψ_0 . The method also produces a correction to the expectation value of the energy for the trial function. The nodes of the trial function are not corrected and the energy is corrected to the fixed-node energy of the trial function. Applications to several sample problems as well as to the water molecule are described. © 2000 American Institute of Physics. [S0021-9606(00)30921-7]

I. INTRODUCTION

We have previously described a quantum Monte Carlo (QMC) method for the direct calculation of corrections to trial wave functions.¹⁻³ We report here an improved method which is much simpler to use. Like its predecessors the improved method gives (for fixed nodes) the difference δ between a true wave function Ψ and a trial wave function Ψ_0 , but it gives in addition the difference between the true energy E and the expectation value of the energy E_{var} for the trial wave function.

The statistical or sampling errors associated with the Monte Carlo procedures as well as any systematic errors occur only in the corrections. Thus very accurate wave functions and energies may be corrected with very simple calculations.

For systems with nodes, the nodes are unchanged. The wave functions and energies for these systems are corrected to the fixed-node values—those corresponding to the exact solutions for the fixed nodes of the trial wave functions.

The method has the very desirable features of: good wave function in/better wave function out ... good energy in/better energy out.

II. THEORETICAL BASIS

The diffusion quantum Monte Carlo method is based on the simulation of the time-independent Schrödinger equation in imaginary time^{4,5} according to

$$\frac{\partial \Psi}{\partial \tau} = \frac{\hbar^2}{2m} \nabla^2 \Psi - V\Psi. \quad (1)$$

With incorporation of importance sampling⁶ based on a trial function Ψ_0 , the above equation becomes (in atomic units with m equal to the mass of the electron)

$$\frac{\partial f}{\partial \tau} = \frac{1}{2} \nabla^2 f - \nabla \cdot (f \nabla \ln \Psi_0) - \left(\frac{H\Psi_0}{\Psi_0} - E_{\text{ref}} \right) f, \quad (2)$$

where $f = \Psi\Psi_0$, the product of the true wave function and the trial wave function, and E_{ref} is a reference energy.

Making use of the difference $\delta = \Psi - \Psi_0$ and defining another function $g = \delta\Psi_0 = (\Psi - \Psi_0)\Psi_0$ we obtain²

$$\begin{aligned} \frac{\partial g}{\partial \tau} = & \frac{1}{2} \nabla^2 g - \nabla \cdot (g \nabla \ln \Psi_0) - \left(\frac{H\Psi_0}{\Psi_0} - E_{\text{ref}} \right) g \\ & + \left[- \left(\frac{H\Psi_0}{\Psi_0} - E_{\text{ref}} \right) \Psi_0^2 \right]. \end{aligned} \quad (3)$$

The term $H\Psi_0/\Psi_0$ is the local energy E_{loc} for the trial wave function. The last term in Eq. (3) is a distributed source term S , which may be positive or negative. It is convenient to introduce the expectation value of the energy E_{var} for the trial function and write S as a collection of terms

$$\begin{aligned} S = & [- (E_{\text{loc}} - E_{\text{var}}) \Psi_0^2]_p + [- (E_{\text{loc}} - E_{\text{var}}) \Psi_0^2]_n \\ & + [- (E_{\text{var}} - E_{\text{ref}}) \Psi_0^2] \end{aligned} \quad (4)$$

or

$$S = S_p + S_n + S_q, \quad (5)$$

where

$$\begin{aligned} S_p = & [- (E_{\text{loc}} - E_{\text{var}}) \Psi_0^2]_p, \\ S_n = & [- (E_{\text{loc}} - E_{\text{var}}) \Psi_0^2]_n, \\ S_q = & [- (E_{\text{var}} - E_{\text{ref}}) \Psi_0^2], \end{aligned}$$

and where the subscript p indicates a region of $E_{\text{loc}} < E_{\text{var}}$ and a positive particle feed, the subscript n indicates a region of $E_{\text{loc}} > E_{\text{var}}$ and a negative particle feed, and the subscript q indicates an additional particle feed, normally negative.

In the procedure used previously, Eq. (3) was simulated by g -particles fed continuously to the system according to the source terms; allowed to diffuse, drift, and multiply or disappear; and to cancel each other, positive with negative, regardless of position if beyond a specified age or elapsed

time since being fed. After an initial period to allow the system to approach steady state, the calculation was continued and the correction term g was determined by sampling the particle distribution. The energy was determined as equal to the reference energy required to maintain a fixed net weight of particles.

For the new procedure we consider the integrals of each of terms in Eq. (3) over all accessible space. Thus we define

$$I_g = \int g dV, \quad I_p = \int S_p dV, \quad I_n = \int S_n dV, \quad (6)$$

$$I_q = \int \Psi_0^2 dV,$$

and Eq. (3) becomes

$$\frac{\partial I_g}{\partial \tau} = \int \frac{1}{2} \nabla^2 g dV - \int \nabla \cdot (g \nabla \ln \Psi_0) dV$$

$$- \int (E_{\text{loc}} - E_{\text{ref}}) g dV + I_p + I_n - (E_{\text{var}} - E_{\text{ref}}) I_q. \quad (7)$$

Since the diffusion and drift terms merely move particles within the volume and the drift term prevents their crossing a nodal surface, they make no contribution to changes in I_g , and they are zero and may be eliminated. The multiplication term containing $(E_{\text{loc}} - E_{\text{ref}})$ is applicable to each particle fed to the system. An average growth factor \bar{f}_p , \bar{f}_n , \bar{f}_q for each type of particle during its lifetime in the system may be combined with the feed terms. Thus we obtain

$$\frac{\partial I_g}{\partial \tau} = I_p \bar{f}_p + I_n \bar{f}_n - (E_{\text{var}} - E_{\text{ref}}) I_q \bar{f}_q. \quad (8)$$

Since particles fed at any point in the system tend to the same distribution with increased time in the system, those of sufficient age may be cancelled in equal weights, positive with negative, regardless of their locations. For a steady state and for a complete cancellation of positive and negative particles at a fixed age we have $\partial I_g / \partial \tau = 0$, and the energy E is equal to E_{ref} which is given by (after rearrangement)

$$E = E_{\text{ref}} = E_{\text{var}} - \frac{I_p \bar{f}_p + I_n \bar{f}_n}{I_q \bar{f}_q} \quad (9)$$

or

$$E = E_{\text{ref}} = E_{\text{var}} - \frac{\frac{I_p}{I_q} \bar{f}_p + \frac{I_n}{I_q} \bar{f}_n}{\bar{f}_q}. \quad (10)$$

To determine the energy one then needs to obtain only the ratios of the integrals I_p/I_q and I_n/I_q rather than the individual values. Also needed are the values of \bar{f}_p , \bar{f}_n , and \bar{f}_q as well as E_{var} .

The ratios of the integrals may be determined by numerical integration, typically by Metropolis sampling of Ψ_0^2 with accumulation of average values of I_p/I_q and I_n/I_q . Their definition in terms of E_{var} ensures that the absolute values of these ratios be equal and uncertainty in their relative values

TABLE I. Results for harmonic oscillator.^{a,b}

$\psi_0 = \exp(-bx^2)$	$\psi = \exp(-ax^2)$
$b = 0.47$	$a = 0.50$
$E_{\text{var}} = 0.500\ 957$	$E_{\text{true}} = 0.500\ 000$
$I_p/I_q = -I_n/I_q = 0.014\ 983$	$f_p = 1.012\ 457$
	$f_n = 0.948\ 961$
	$f_q = 0.999\ 516$
$E_{\text{calc}} = E_{\text{var}} + E_{\text{corr}}$	
$= 0.500\ 957 - 0.000\ 957$	
$= 0.500\ 000$	
$E_{\text{true}} = 0.500\ 000$	
$b = 0.5001$	$a = 0.5000$
$E_{\text{var}} = 0.500\ 000\ 009\ 998$	$E_{\text{true}} = 0.500\ 000\ 000\ 000$
$I_p/I_q = -I_n/I_q = 0.000\ 048\ 389$	$f_p = 1.000\ 165\ 544$
	$f_n = 0.999\ 958\ 932$
	$f_q = 0.999\ 999\ 994$
$E_{\text{calc}} = E_{\text{var}} + E_{\text{corr}}$	
$= 0.500\ 000\ 009\ 998 - 0.000\ 000\ 009\ 998$	
$= 0.500\ 000\ 000\ 000$	
$E_{\text{true}} = 0.500\ 000\ 000\ 000$	

^aOne-dimensional by numeric integration. Not Monte Carlo.

^bAtomic units for all quantities with units.

is eliminated. Since an accurate value of E_{var} is required, an analytic integration to determine E_{var} is preferred.

The values of \bar{f}_p , \bar{f}_n , and \bar{f}_q are determined for sample feed particles obtained in the Metropolis integrations. These are selected with probabilities proportional (in addition to Ψ_0^2) to the absolute values of $[-(E_{\text{loc}} - E_{\text{var}})]_p$ for p , $[-(E_{\text{loc}} - E_{\text{var}})]_n$ for n , and unity for q . The particles are subjected to diffusion, drift, and multiplication (weight increase or decrease) for a period (age) sufficiently long to produce no further change in their average weights. Positive particles of type p , fed in regions of $E_{\text{loc}} < E_{\text{var}}$, give values of $\bar{f}_p > 1$. Negative particles of type n , fed in regions of $E_{\text{loc}} > E_{\text{var}}$, give values of $\bar{f}_n < 1$. Particles of type q normally give a value \bar{f}_q very close to unity.

The advantages of the new procedure may be seen with reference to Eq. (10). The energy E is given by the known value of E_{var} and a correction term. When Ψ_0 is a good approximation to the true wave function, the correction term is small and any error in the correction term is correspondingly small. As Ψ_0 approaches the true wave function the

TABLE II. Results for hydrogen atom.^{a,b}

$\psi_0 = \exp(-br)$	$\psi = \exp(-ar)$
$b = 0.90$	$a = 1.00$
$E_{\text{var}} = -0.495\ 000$	$E_{\text{true}} = -0.500\ 000$
$I_p/I_q = -I_n/I_q = 0.024\ 360\ 4\ (5)$	$f_p = 1.1220\ (2)$
	$f_n = 0.9178\ (2)$
	$f_q = 0.9896\ (0)$
$E_{\text{calc}} = E_{\text{var}} + E_{\text{corr}}$	
$= -0.495\ 000 - 0.005\ 027\ (6)$	
$= -0.500\ 003\ (6)$	
$E_{\text{true}} = -0.500\ 000$	

^aAtomic units for all quantities with units.

^bStandard deviation (1 sigma) in last digit indicated in parentheses.

TABLE III. Results for helium atom.^{a,b}

$\psi_0 = 189\text{-term Hylleraas}^c$	$\psi = \text{Morgan expression}^d$
$E_{\text{var}} = -2.903\ 724\ 376\ 180$	$E_{\text{true}} = -2.903\ 724\ 277\ 034$
$I_p/I_q = -I_n/I_q = 0.000\ 085\ 33\ (3)$	$f_p = 1.000\ 005\ 36\ (12)$
	$f_n = 0.999\ 995\ 32\ (19)$
	$f_q = 1.000\ 000\ 00\ (0)$
$E_{\text{calc}} = E_{\text{var}} + E_{\text{corr}}$	
$= -2.903\ 724\ 376\ 180$	
$-0.000\ 000\ 000\ 856\ (19)$	
$= -2.903\ 724\ 377\ 036\ (19)$	
$E_{\text{true}} = -2.903\ 724\ 377\ 034$	

^aAtomic units for all quantities with units.^bStandard deviation (1 sigma) in last digit indicated in parentheses.^cReference 9.^dReference 10.

ratios I_p/I_q and I_n/I_q approach zero and the values of \bar{f}_p , \bar{f}_n , and \bar{f}_q approach unity.

III. EXAMPLE: HARMONIC OSCILLATOR

The ground state of the harmonic oscillator in one dimension provides a simple example. We use atomic units throughout and define $\hbar=1$, $m=1$, and $V=\frac{1}{2}kx^2$ with $k=1$. The exact solutions are $\Psi = \exp(-ax^2)$ with $a=1/2$ and $E=1/2$. The trial wave function is $\Psi_0 = \exp(-bx^2)$ and its expectation value is $E_{\text{var}} = \frac{1}{2}(b+k/4b)$ with b variable.

This example may be treated by Monte Carlo methods or by direct numerical integration on a grid. For this one-dimensional problem \bar{f}_p , \bar{f}_n , and \bar{f}_q are most easily and accurately obtained with numerical integration, and we used a simple difference scheme⁷ for solving the diffusion equation for initial populations corresponding to the three feed terms. The grid was uniformly spaced with a step size $\Delta x = 0.005$ and a time step $\Delta\tau = 0.000\ 01$. The integral ratios I_p/I_q and I_n/I_q were obtained by numerical integration on the same grid.

The results for two different cases, one with a poor trial function and the other with a good trial function are listed in Table I. In each case the known correction E_{corr} to the energy is obtained with an error of less than one part in 1000.

The Monte Carlo procedure gave similar results with statistical error bars straddling the known corrections.

IV. EXAMPLE: HYDROGEN ATOM

The ground state of the hydrogen atom provides another simple example. In this case we used only the new Monte Carlo procedure. The trial wave function was $\Psi_0 = \exp(-br)$ with $b=0.90$ (inverse a.u.) for which the expectation value is known from analytic integration.

The integral ratios I_p/I_q and I_n/I_q were obtained by Metropolis integration based on sampling with weight Ψ_0^2 . The uncertainties in these ratios were estimated from the variance in values for repeated independent runs. These same integrations were used to generate the source terms, i.e., points (particles) sampled from S_p , S_n , and S_q . These starting configurations were chosen with probabilities pro-

portional to $[-(E_{\text{loc}} - E_{\text{var}})\Psi_0^2]_p$, $[-(E_{\text{loc}} - E_{\text{var}})\Psi_0^2]_n$, and $[\Psi_0^2]$, respectively, with appropriate consideration of signs.

Groups of starting particles of each type were subjected to diffusion, drift, and growth using the normal procedures for importance sampling.⁸ To improve the accuracies for the high drift velocities and rapid weight changes in the initial steps, the time step was begun at $\Delta\tau = 0.000\ 001$ (a.u.) and gradually increased to 0.0001 (a.u.). The time span required to approach a constant value of \bar{f}_p or \bar{f}_n was about 0.1 (a.u.).

In this case the reference energy could be set to the known value of the energy $E = -0.5$, but testing showed the resulting energy correction E_{corr} to be insensitive to small errors in E_{ref} . Since E_{corr} depends on the difference between \bar{f}_p and \bar{f}_n as indicated in Eq. (10) and since they are affected similarly by errors in E_{ref} , the effects on E_{corr} tend to cancel each other.

The results for the hydrogen atom are listed in Table II.

V. EXAMPLE: HELIUM ATOM

For the ground state of the helium atom we used as a trial wave function the 189-term Hylleraas function described by Schwarz⁹ which is accurate to about 10 digits. The true energy is known to at least 13 digits from the analytic variational calculation of Freund, Huxtable, and Morgan¹⁰ with a more complex trial function.

TABLE IV. Results for water molecule.^{a,b}

$\psi_0 = \text{simple SCF, no Jastrows}$	
$E_{\text{var}} = -75.560$	$E_{\text{true}} = -76.438\ (3)^c$
$I_p/I_q = -I_n/I_q = 1.513\ (2)$	$f_p = 0.724\ (5)$
	$f_n = 1.084\ (5)$
	$f_q = 0.909\ (7)$
$E_{\text{calc}} = E_{\text{var}} + E_{\text{corr}}$	
$= -75.560 - 0.599\ (10)$	
$= -76.16\ (1)$	
$E_{f_n} = -76.17\ (1)$ (fixed-node result)	
$E_{\text{true}} = -76.438\ (3)$	

^aAtomic units for all quantities with units.^bStandard deviation (1 sigma) in last digit indicated in parentheses.^cFrom experiment. Nonrelativistic. Reference 13.

The procedure used was essentially the same as that described for the hydrogen atom above. Results obtained with the new Monte Carlo procedure are listed in Table III.

VI. EXAMPLE: WATER MOLECULE

The water molecule presents the problem of nodes in the wave function as well as a much higher dimensionality. In this case the nodes are fixed in position by the use of fixed-node QMC procedures^{11,12} and the resulting energy obtained is the fixed-node energy for the nodes of the trial wave function. As in any fixed-node calculation the energy obtained is a variational upper bound to the true energy, and if the nodes are wrong the energy will be higher than the true energy.

The trial function for this case was a simple SCF function, consisting of a single 10×10 determinant of LCAO-MO terms of Slater-type orbitals without any Jastrow or other explicit electron correlation terms. The expectation value of the energy E_{var} and the fixed-node energy E_{fn} were determined independently by standard methods.

The procedure used was essentially the same as that used for hydrogen and helium. Results are listed in Table IV.

VII. DISCUSSION

The revised method offers improved energies from analytic variational calculations without the use of larger basis sets. Such calculations are made practical by the limitation of sampling errors to the correction itself rather than the total energy.

Earlier fixed-node QMC calculations for systems of ten or more electrons have used single-determinant trial wavefunctions with Jastrow terms. With the improved correction procedure the need for accurate expectation values for the trial function requires eliminating the Jastrow terms, but it may make practical the use of many more determinants in the trial function. This is likely to give improved node locations and lead to much lower node location errors. The sign problem of quantum Monte Carlo for large systems would not be eliminated but it might be significantly reduced.

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