BASIS QUANTUM MONTE CARLO IN THREE DIMENSIONS

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الخلاصـة :

يعمم المؤلف في هذا البحث نظرية مونتى — كارلو — والتى سبق للمؤلف نفسه وأن صاغها في بعد واحد — الى أبعاد ثلاثة . ويدخل تخالف الفيرميون في هذه النظرية بشكل ضمنى ، ولايلزم معرفة سابقة بدالة الموجة . وتسمح النظرية باستخدام حساب الاعداد الصحيحة بشكل كبير في الحسابات ، ولذلك تقدم هذه النظرية طريقة للحسابات أسرع من طريقة مونتى — كارلو الكمية الموجودة . وتطبق هذه الطريقة على اثنين من الفيرميونات التى لها حركة دورانية متوازية في جهد اهتزازى هارمونى في ثلاثة أبعاد كذلك تطبق في حالة آي^{3} أس لذرة الهليوم . وتعتبر النتائج التى تم الحصول عليها في أقل من ثلاثين دقيقة باستخدام جهاز آى بي ام ٣٠٣٣ صحيحة لاجزاء قليلة من الالف . ويمكن أن تطبق هذه النظرية وبشكل مباشر في حالة نظم مكونة من أربعة اليكترونات . وندرس في النهاية تطبيق هذه الطريقة على أنظمة أكثر اتساعا .

ABSTRACT

The Basis Quantum Monte Carlo Theory, previously formulated in one dimension by the author, is generalized to the three dimensional case. Fermion antisymmetry is implicit in the theory and no previous knowledge about the wave function is assumed. The theory allows the use of integer arithmetic to a large extent in the calculational procedure, thus rendering the method faster than existing Quantum Monte Carlo treatments. The method is applied to two Fermions with parallel spins moving in a three dimensional harmonic oscillator potential and to the I ^{3}S state of the He atom. The results obtained in less than 30 minutes of IBM 3033 CPU time are accurate to within a few parts in a thousand. Application to four electron systems is straightforward, and application to larger systems is discussed.

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1. INTRODUCTION

A good portion of the activity in the fields of quantum chemistry and atomic and molecular physics is focused on the solution of the time independent Schroedinger equation,

$$H\Psi = E\Psi \tag{1}$$

for the atomic or molecular system of interest. In the non-relativistic case and with the Born Oppenheimer approximation, H is a function of electronic coordinates $\mathbf{r}_i \equiv (x_i, y_i, z_i)$,

$$H = -\tfrac{1}{2}\sum \nabla_i^2 + V(\mathbf{r}_i)\,. \tag{2}$$

(All equations in this paper are written in atomic units; that is, $m_e = 1$, $q_e = 1$, $\hbar = 1$, etc.). Within these limitations and approximations, Equation (1) is a linear second order differential eigenvalue equation with appropriate boundary conditions on $\Psi(\mathbf{r}_i)$. The presence of interelectronic repulsion terms, $1/|\mathbf{r}_{ij}| = 1/[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}$, prevents decoupling of (1), and since 1925 sophisticated methods for approximate solutions, mainly through the use of perturbational and Rayleigh–Schroedinger type variational methods, have been developed [1]. The variational approach, especially the Configuration-Interaction (CI) method, has been more popular and successful. The CI method can be viewed as an attempt to solve (1) in a finite dimensional space with a basis set chosen from antisymmetrized products of one-electron functions called 'orbitals'. The products have to be antisymmetrized owing to the Fermion character of the electrons and these products, or symmetrically correct combinations of such products, are called 'configurations'; hence the name, 'Configuration Interaction'. Equation (1), then, becomes a matrix eigenvalue equation and Ψ is obtained as a linear combination of the 'configuration' basis set. Although successful, the CI method reaches a point of diminishing returns as the number of electrons, N, increases. A larger N means that more 'orbitals' must be included, and more orbitals require a larger number of configurations to be taken into account. The results are matrices of order 10^3–10^6, the elements of which are combinations of many-center integrals.

These difficulties have led researchers to keep searching for novel approximate solutions of (1). One approach which promises cheaper computations for larger N and certainly much less human effort is the Quantum Monte Carlo (QMC) method, which has recently attracted a great deal of interest [2–8]. The main shortcoming of the QMC methods developed to date has been their inability to include implicitly the antisymmetry requirement for the wave function. In CI and perturbative treatments, antisymmetry can be built in from the start by choosing antisymmetric bases of functions. In the QMC methods listed in [2–8], it is necessary either to determine the zeros of the wave function in advance or to use an analytic 'importance function' which is antisymmetric under the exchange of electron coordinates. Such approaches render the QMC dependent on CI type calculations, although this dependence is hoped to be minimized, that is, it is expected that simple CI functions will guide the QMC calculation to yield results with accuracies comparable or superior to those obtained from large CI treatments.

In a recent paper (hereafter referred to as I) [9], a new QMC method, called Basis Quantum Monte Carlo (BQMC), has been developed. In BQMC, the Monte Carlo simulation is carried out in the space of an antisymmetrized collocating basis set rather than over points in configuration space. Therefore, antisymmetry is built in from the start. In I, the method was successfully applied to two Fermions with parallel spins in one dimension, moving in a harmonic oscillator potential. This amounted to a complete solution of the antisymmetry problem for this simple system.

In this paper, BQMC, with its built-in antisymmetry, is extended to three dimensions and hence to real systems. The main difficulty in the path of QMC methods is thus overcome. Moreover, BQMC is found to be approximately twice as fast as the conventional QMC methods because the resulting algorithm uses integer arithmetic to a large extent—including the costly calculation of the potential. The method is successfully applied to two particles with parallel spins (in three dimensions) moving in a harmonic oscillator potential and to the lowest ^3S state of He.

For the details of the problem and a short review of conventional QMC methods, the reader is referred to I [9].

In Section 2 of this paper, the BQMC theory is

formulated in three dimensions. In Section 3, the antisymmetry problem is discussed and the solution is presented. In Section 4, the resulting algorithm is presented and applied to the two examples mentioned above. The relative probable error after MC runs of 30 minutes each on the IBM 3033 is four parts per thousand for the two-particle harmonic oscillator and five parts per thousand for the I ^{3}S state of He. In Section 5, the conclusions and a preliminary discussion for applications to larger systems are presented. Such applications are under way and will be presented in subsequent papers.

2. BASIS QUANTUM MONTE CARLO IN THREE DIMENSIONS

For two Fermions with parallel spins in three dimensional space, the spatial part of the wave function can be approximated by

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{i\sim j} c_{ij}P_{ij}(\mathbf{r}_1,\mathbf{r}_2), \tag{3a}$$

where

$$P_{ij}(\mathbf{r}_1,\mathbf{r}_2)=\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)-\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2) \tag{3b}$$

are the antisymmetrized collocating basis functions. The $\sim$ indicates an ordering of the indices, e.g., $i>j$ or $j>i$ or another rule, to ensure the linear independence of the basis; for example, P_{ij} and P_{ji} are not two linearly independent functions, but $P_{ij}=-P_{ji}$. The ϕ_i are collocating functions defined over a uniform mesh of knots $\mathbf{r}_i$ with mesh spacing b, that is, the function ϕ_i is centered on the knot $\mathbf{r}_i$. In this work, the ϕ_i are chosen to be the gaussians,

$$\phi_i(\mathbf{r})=\exp\left[-\frac{(\mathbf{r}-\mathbf{r}_i)^2}{2b^2}\right], \tag{4}$$

although any other collocating basis, e.g. cubic splines, could have been used. Here, $(\mathbf{r}-\mathbf{r}_i)^2\equiv(x-x_i)^2+(y-y_i)^2+(z-z_i)^2$. For an iterative solution of (1) for the ground state, Grimm and Storer's [2, 3] iteration operator, that is, the A_3 operator of I, is used:

$$\chi^{(n+1)}=A_3\chi^{(n)}$$

$$\lim_{n\to\infty}\chi^{(n)}=\chi^{(\infty)}, \tag{5}$$

where χ is defined by

$$\chi^{(n)}=e^{\frac{\varepsilon}{2}V}\Psi^{(n)}$$

$$\chi^{(\infty)}=e^{\frac{\varepsilon}{2}V}\Psi^{(\infty)}$$

and where $\Psi^{(n)}$ is the wave function after iteration n, and $\Psi^{(\infty)}$ is the ground state wave function. It has been shown in I that $\varepsilon\gg b^2$ is necessary for the formulation of the method and that $\varepsilon=3b^2$ is satisfactory. This equality is used throughout this paper. It is clear that the wave function as approximated by Equations (3) has built-in antisymmetry. V is the potential of Equation (2). $A_3=Te^{-\varepsilon V}$, where T is the integral operator

$$T(\mathbf{r}_1,\mathbf{r}_2,\mathbf{q}_1,\mathbf{q}_2)\equiv\frac{1}{(2\pi\varepsilon)^3}\int\int e^{-[(r_1-q_1)^2+(r_2-q_2)^2]/2\varepsilon}d\mathbf{q}_1\,d\mathbf{q}_2 \tag{6}$$

and the integrals are taken over the whole three dimensional space. With these definitions, we can repeat the steps of Öksüz [9] as given in Section 4 of paper I; after collocating the iteration equation (5) at the knots, we get the equivalent matrix equation:

$$\mathbf{TB}^{-1}\mathbf{LBc}^n=\mathbf{Bc}^{n+1}. \tag{7}$$

Here, $\mathbf{c}$ is the column vector (discrete, infinite dimensional: E_∞) carrying the coefficients of (3), and

$$B_{kl,ij}=\varphi_i(\mathbf{r}_k)\varphi_j(\mathbf{r}_l)-\varphi_j(\mathbf{r}_k)\varphi_i(\mathbf{r}_l). \tag{8}$$

Moreover,

$$L_{kl,ij}=L(\mathbf{r}_i,\mathbf{r}_j)\delta_{ik}\delta_{jl} \tag{9}$$

is the diagonal potential matrix, $L(\mathbf{r}_i,\mathbf{r}_j)=e^{-\varepsilon V(\mathbf{r}_i,\mathbf{r}_j)}$. Finally,

$$T_{kl,ij}=\left(\frac{b^2}{\varepsilon+b^2}\right)^3[e^{-(\mathbf{r}_k-\mathbf{r}_i)^2/2(\varepsilon+b^2)}e^{-(\mathbf{r}_l-\mathbf{r}_j)^2/2(\varepsilon+b^2)} -e^{-(\mathbf{r}_k-\mathbf{r}_j)^2/2(\varepsilon+b^2)}e^{-(\mathbf{r}_l-\mathbf{r}_i)^2/2(\varepsilon+b^2)}]. \tag{10}$$

The quantum heat matrix $\mathbf{U}$ is defined by $\mathbf{U}=\mathbf{TB}^{-1}$, and it is found that

$$T_{kl,ij}\cong\sum_{m\sim n}U_{kl,mn}[\varphi_m(\mathbf{r}_i)\varphi_n(\mathbf{r}_j)-\varphi_n(\mathbf{r}_i)\varphi_m(\mathbf{r}_j)], \tag{11}$$

where

$$U_{kl,mn}=\left(\frac{b^2}{2\pi\varepsilon}\right)^3[e^{-(\mathbf{r}_m-\mathbf{r}_k)^2/2\varepsilon}e^{-(\mathbf{r}_n-\mathbf{r}_l)^2/2\varepsilon} -e^{-(\mathbf{r}_m-\mathbf{r}_l)^2/2\varepsilon}e^{-(\mathbf{r}_n-\mathbf{r}_k)^2/2\varepsilon}]. \tag{12}$$

Finally, we arrive at Equation (17) of I in three dimensions:

$$\mathbf{ULd}^{(n)}=\mathbf{d}^{(n+1)} \tag{13}$$

where $\mathbf{d}=\mathbf{Bc}$.

This derivation, which may be overly compact as presented here, follows exactly the steps of the derivation in I with two changes: (1) the one dimensional coordinates, x, of I are replaced by the three dimen-

sional position vectors $\mathbf{r}$, and (2) the constants of I are readjusted for the three dimensional case.

Now, assume for a moment that $\mathbf{U}$ is a non-negative matrix satisfying the Markovian condition $\sum_{kl} U_{kl,mn}=1$. Then, the iteration in (13) can be simulated by a Monte Carlo game, the details of which are given in I. It was also shown in I that the resulting game coincides with that of the conventional QMC methods in the case of a single particle. The eigenenergy can be calculated from

$$a=\frac{\sum_{i\sim j} \mathrm{e}^{-\varepsilon V(\mathbf{r}_i,\mathbf{r}_j)} d_{ij}^{(\infty)}}{\sum_{i\sim j} d_{ij}^{(\infty)}}; \quad E=-\frac{1}{\varepsilon}\ln a. \tag{14}$$

Equation (14) for a is simply the average of $\mathrm{e}^{-\varepsilon V(\mathbf{r}_i,\mathbf{r}_j)}$ taken over the set of 'psips' in the Monte Carlo game:

$$a=\frac{\sum_{p} \mathrm{e}^{-\varepsilon V(p)}}{M_p} \tag{15}$$

where $\sum_p$ indicates the sum over 'psips' in a MC run and M_p is the total number of psips [3, 4].

If the Markovian condition is not satisfied, $\mathbf{U}$ must be renormalized. We define the diagonal matrix $\mathbf{S}$:

$$S_{mn,ij}=\left(\sum_{k\sim l} U_{kl,mn}\right)\delta_{im}\delta_{jn}=S_{ij}, \tag{16}$$

where $S_{ij}\cong\int\int \mathrm{d}\mathbf{r}_k \mathrm{d}\mathbf{r}_l U_{kl,ij}$ (see I) and integration is over all space. Inserting unity $\mathbf{I}=\mathbf{S}^{-1}\mathbf{S}$ in Equation (13):

$$\mathbf{U}\mathbf{S}^{-1}\mathbf{S}\mathbf{d}^{(n)}=\mathbf{d}^{(n+1)} \tag{17}$$

and carrying out the iteration using

$$\mathbf{U}'\mathbf{L}'\mathbf{d}^{(n)}=\mathbf{d}^{(n+1)}, \tag{18}$$

where $\mathbf{U}'=\mathbf{U}\mathbf{S}^{-1}$ and $\mathbf{L}'=\mathbf{S}\mathbf{L}$, the Markovian condition is once more satisfied. We then have

$$a'=\frac{\sum_{i\sim j} S_{ij}\mathrm{e}^{-\varepsilon V(\mathbf{r}_i,\mathbf{r}_j)} d_{ij}^{(\infty)}}{\sum_{i,j} d_{ij}^{(\infty)}}; \quad E=-\frac{1}{\varepsilon}\ln a' \tag{19}$$

and

$$a'=\frac{\sum_{p} S(p)\mathrm{e}^{-\varepsilon V(p)}}{M_p} \tag{20}$$

instead of (14) and (15).

The assumption that $\mathbf{U}$ or $\mathbf{U}'$ is non-negative is not true in general for $\mathbf{U}$ given by Equation (12) and this is the BQMC equivalent of the 'negative psip' problem encountered in fixed node MC calculations (see, for example, [7]).

3. THE ANTISYMMETRY PROBLEM

Equation (12) can be rewritten as:

$$U_{kl,mn}=\left(\frac{b^2}{2\pi\varepsilon}\right)^3 \mathrm{e}^{-(\mathbf{r}_m-\mathbf{r}_k)^2/2\varepsilon}\mathrm{e}^{-(\mathbf{r}_n-\mathbf{r}_l)^2/2\nu}\times [1-\mathrm{e}^{-(\mathbf{r}_k-\mathbf{r}_l)\cdot(\mathbf{r}_m-\mathbf{r}_n)/\nu}], \tag{21}$$

which becomes,

$$U_{kl,mn}=\left(\frac{b^2}{2\pi\varepsilon}\right)^3 \mathrm{e}^{-(x_m-x_k)^2/2\varepsilon}\mathrm{e}^{-(x_n-x_l)^2/2\varepsilon}\times [1-\mathrm{e}^{-(x_k-x_l)(x_m-x_n)/\varepsilon}] \tag{22}$$

for the one dimensional case.

The terms in the brackets in the above equations show a sharp decrease in the transition probabilities to states which correspond to two Fermions in the same vicinity. In fact, the probability vanishes for transition to a state which corresponds to the case of two Fermions on top of each other. This is clearly the 'Fermi Hole' effect. (Note that these conclusions are independent of the potential between the Fermions. They could even be attracting each other, and Fermi Hole avoidance would still be true.) If the ordering ($\sim$), which was not specified up to this point, is now chosen to mean $x_k>x_l$ and $x_m>x_n$ in Equation (22), then, $(x_k-x_l)(x_m-x_n)>0$ and the exponential in the brackets would always be less than unity, thus ensuring the non-negativity of $\mathbf{U}$. This is how the antisymmetry problem was completely solved in one dimension in I. The similar condition for Equation (21) is

$$(\mathbf{r}_k-\mathbf{r}_l)\cdot(\mathbf{r}_m-\mathbf{r}_n)>0, \tag{23}$$

that is, the dot product is positive. However, it is not possible to ensure this in two or three dimensions by a simple choice of ordering. The interpretation of the vectors in (23) is as follows: $\mathbf{r}_m$ and $\mathbf{r}_n$ are the positions of the electrons before a Markovian transition and $\mathbf{r}_k$ and $\mathbf{r}_l$ are the positions after the transition. Equation (23) is equivalent to the restriction that the angle between the initial difference vector $\mathbf{v}_i=\mathbf{r}_m-\mathbf{r}_n$ and the final difference vector $\mathbf{v}_f=\mathbf{r}_k-\mathbf{r}_l$ be less than $\pi/2$. Since only the angle between $\mathbf{v}_i$ and $\mathbf{v}_f$ is important in this discussion, it is possible to illustrate the situation by

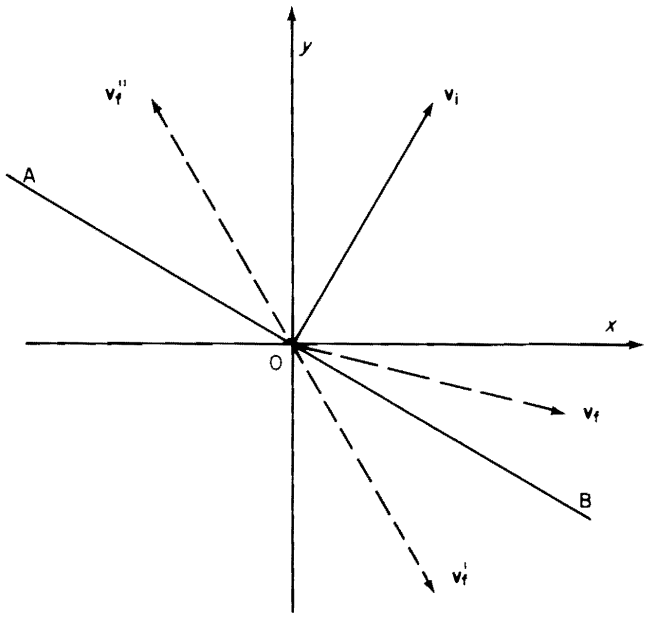

Figure 1. Initial and Final States in the Antisymmetric 'Difference Space'

translating $\mathbf{v}_i$ or $\mathbf{v}_f$ to the same origin. For simplicity, we have drawn $\mathbf{v}_i$ and $\mathbf{v}_f$ in two dimensions in Figure 1. We still have to impose an ordering ($\sim$), and this has been chosen as $x_m > x_n$ and $x_k > x_l$ in the figure. This means that, of the possible basis functions P_{ij} of Equation (3), only those with $x_i > x_j$ are included in the basis set and the collocation is performed only at points satisfying the same condition in configuration space. This is equivalent to stating that there can be no transitions to the left half of the plane in Figure 1. A transition to a Markov state represented by $\mathbf{v}_f$ will have a positive transition matrix element. This is true for all $\mathbf{v}_f'$, above the line $\overline{AB}$. On the other hand, a transition to a state such as $\mathbf{v}_f'$, that is, to a difference vector below $\overline{AB}$, will have a negative transition matrix element. The vector $\mathbf{v}_f''$ obtained by inverting $\mathbf{v}_f'$ through the origin falls outside the basis used with the present ordering. However, it is useful to note that the basis function P_{nm} corresponding to the Markov state occupied by $\mathbf{v}_f''$ is simply the negative of that for $\mathbf{v}_f'$: $P_{nm} = -P_{mn}$. We can thus study the problem from two equivalent points of view as follows.

(1) The difference vectors are restricted to the positive x half of the plane with final vectors above the line $\overline{OB}$ having positive transition matrix elements, and those between $\overline{OB}$ and the negative half of the y-axis having negative transition matrix elements.

(2) The transitions into the final difference vector are restricted to above the $\overline{AB}$ line with all transition matrix elements positive. (This would amount to changing the definition of the ordering for each transition.) But if the transition happens to be a $\mathbf{v}_f''$-like state on the left of the y-axis, we change the sign of the basis function corresponding to this state to get back to our ordered basis (therefore moving back to $\mathbf{v}_f'$, an equivalent result.

With these considerations in mind, a method for dealing with negative transitions suggests itself. Consider Equation (18) as,

$$\underbrace{\mathbf{U}'\mathbf{L}'\mathbf{U}'\mathbf{L}'\cdots\mathbf{U}'\mathbf{L}'}_{k}\mathbf{d}^{(n)} = \mathbf{d}^{(n+k)}. \tag{24}$$

In the Monte Carlo simulation of this matrix iteration, $\mathbf{d}^{(i)}$ is always a Markov 'state', that is, all elements of $\mathbf{d}^{(i)}$ are zero except for one which is unity. Let the non-zero element be z, and indicate the corresponding vector by $\mathbf{d}_z^{(i)}$. At each application of $\mathbf{U}'$, only the z^{th} column of $\mathbf{U}'$ has any effect, that is, only the elements $U_{\alpha z}$ play a role for each transition. Let us construct a diagonal matrix $\mathbf{X}(z)$ such that $X_{j\alpha} = \delta_{j\alpha}$ if $U_{\alpha z} > 0$ and $X_{j\alpha} = -\delta_{j\alpha}$ if $U_{\alpha z} < 0$. It is clear that $\mathbf{X}(z) = \mathbf{X}(z)^{-1}$ and $\mathbf{I} = \mathbf{X}(z)\mathbf{X}(z)^{-1} = \mathbf{X}(z)\mathbf{X}(z)$. If we insert this expression for $\mathbf{I}$ to the left of the appropriate $\mathbf{U}'$ in (24) we obtain

$$\begin{aligned}&\mathbf{X}(z_k)\mathbf{X}(z_k)\mathbf{U}'\mathbf{L}'\mathbf{X}(z_{k-1})\mathbf{X}(z_{k-1})\mathbf{U}'\mathbf{L}'\ldots\\ &\quad\ldots\mathbf{X}(z_1)\mathbf{X}(z_1)\mathbf{U}'\mathbf{L}'\mathbf{d}^{(n)} = \mathbf{d}^{(n+k)}\ .\end{aligned} \tag{25}$$

If we now define $\mathbf{U}'' = \mathbf{X}(z_i)\mathbf{U}'$, we get:

$$\begin{aligned}&\mathbf{X}(z_k)\mathbf{U}''\mathbf{L}'\mathbf{X}(z_{k-1})\mathbf{U}''\mathbf{L}'\ldots\\ &\quad\ldots\mathbf{X}(z_1)\mathbf{U}''\mathbf{L}'\mathbf{d}^{(n)} = \mathbf{d}^{(n+k)}.\end{aligned} \tag{26}$$

Now, the 'effective' row of $\mathbf{U}''$ is always non-negative. The $\mathbf{X}(z)$ matrices remaining in Equation (26) will have the effect of multiplying the Markov state $\mathbf{d}^{(i)}$ by -1 if a transition is made to a vector such as $\mathbf{v}_f'$ in Figure 1.

This procedure is reminiscent of Anderson's treatment of negative psips in his method of successive corrections and also of Ceperley and Alder's and Reynolds and others' treatments of node crossing [7, 8]. We change the sign of a psip which crosses the $\overline{OB}$ line (viewpoint (1)), or the sign of the psip which ends up in the negative x half plane (viewpoint (2)). The authors referred to above change the sign of a psip when it crosses a node or when it represents a negative correction to a starting function. It is, however, not possible to draw an exact parallel since their sign changes occur at predetermined hyperplanes in configuration space whereas ours are dependent only on relative positions of the Fermions and the initial and final states. Nevertheless, the same numerical problem arises in all three methods where psips are allowed to take both negative and positive values: the

number of negative and positive psips increase rapidly as the iteration proceeds. In the present method, this leads to a numerical instability in both the numerator and the denominator of Equation (20), both of which become the differences between two large numbers of similar magnitude. This causes unstable oscillations in a and E with an increasing number of iterations. The large number of psips also quickly overburdens the memory of the computer.

It has been suggested by Anderson [6] and Reynolds and others [7] that this problem may be overcome by letting negative and positive psips in the 'same region' annihilate each other. The analog of this suggestion seems to be called for in our problem. Yet, this proposal is not as attractive as it looks at first sight since it would involve a measurement of distance (in $3N$ dimensional space) between psips of different signs to determine which pairs are in the same 'region'. Probably, because of this difficulty, the suggestion has yet to be implemented in actual three dimensional calculations.

However, in BQMC, there exists an alternative solution. The first point to realize is that the initial and final configurations of states are in the same 'region'. For the one dimension, single particle case, the average distance between an initial and final Markov state is

$$\bar{x}=\left[\frac{1}{\sqrt{2\pi\varepsilon}}\int_{-\infty}^{\infty}x^2\mathrm{e}^{-x^2/2\varepsilon}\mathrm{d}x\right]^{1/2}=\varepsilon=\sqrt{3}b$$

if $\varepsilon^2=3b^2$. Therefore the 'parent' and 'daughter' psips of a transition are in the same vicinity. Therefore the solution is: Annihilate any psip which makes a transition into the negative region. (This conclusion reminds one of Reynolds' and others' [7] 'fixed node MC' approximation. However, in BQMC there are no predetermined nodes and therefore no errors in the nodal surfaces to be corrected.)

Another way of looking into this conclusion is as follows: consider the initial state $\mathbf{v}_i$ in Figure 2 which lies on the negative–positive border (viewpoint (2)). The circle indicates the range of possible transitions in one iteration, which is about $8b$ in our calculations. It is clear that the probabilities of transitions into the negative and positive zones are equal and such a psip could be dropped from our calculations if the potential in the region were slowly varying because contributions of all possible transitions to the value of a in Equation (20) would then cancel. If $\mathbf{v}_i$ were slightly to the right, annihilation of this state would be an 'over-kill' for positive contributions and if it were slightly to the left, dropping it would exaggerate the positive region. Therefore, if we let all states crossing the y-axis to the left disappear and let all psips approaching it but staying on the right survive, it would seem that we are introducing a bias in favor of the positive zone. That this conclusion is erroneous can be seen when we consider that for every transition to the negative region an inverse transition from the negative and into the positive region is equally probable. Of course, in our ordering scheme for basis functions, the inverse transition will also appear as a positive to negative jump. In terms of basis functions: for every transition $P_{kl}^{+}\rightarrow P_{mn}^{-}$ there is an inverse transition $P_{mn}^{-}\rightarrow P_{kl}^{+}$ which will appear in our calculations as $P_{nm}^{+}\rightarrow P_{lk}^{-}$, and any bias introduced in the annihilation of the state created by the first transition will be balanced by the opposite bias caused by the similar annihilation in the second. It is now seen that we can also lift the restriction to slowly varying potentials, since the bias introduced by the potential differences in the negative and positive halves of the transition range circle in Figure 2 would also be balanced by the equal and opposite bias brought by the inverse transition.

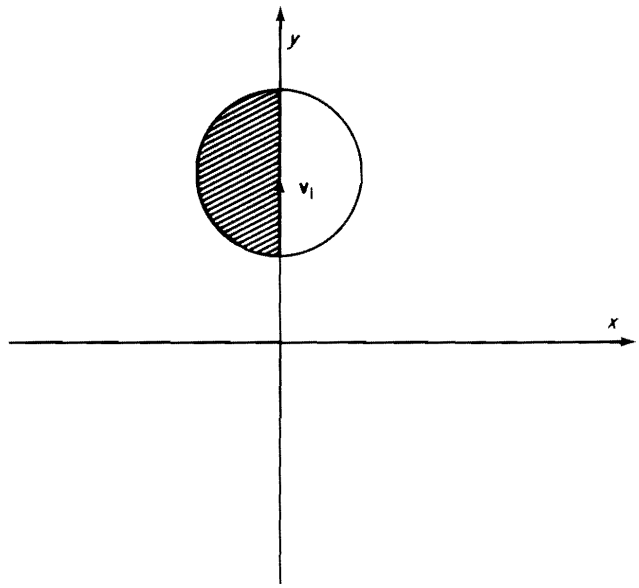

Figure 2. An Initial Difference Vector on the Negative–Positive State Border and the Range of Possible Final States for One Iteration

4. THE MONTE CARLO ALGORITHM AND RESULTS

After the choice of an ordering of the basis set (which is taken to be $x_k>x_l$ throughout this paper)

the BQMC algorithm for two Fermions in three dimensional space can be formulated:

(1) Start with any distribution of states $\{(\mathbf{r}_1, \mathbf{r}_2)_i\}$.
(2) For each state generate a random number R_i uniformly distributed between 0 and 1. Replace each state $(\mathbf{r}_1, \mathbf{r}_2)_i$ by m_i identical states with

$$m_i = [L_i'] + 1$$

if the fractional part of L_i' is greater than R_i and with

$$m_i = [L_i']$$

if otherwise. $[L_i']$ is the integer part of L_i'. (L_i' is the element of the diagonal matrix $\mathbf{L}'$ in Equation (18) corresponding to the position $(\mathbf{r}_1, \mathbf{r}_2)_i$.)
(3) For each surviving state (step 2 might cause some states to disappear) execute a Markovian transition between states with transition probabilities given by the elements of $\mathbf{U}''$. If the transition creates a negative state, annihilate that state.
(4) Calculate a' and E for this pass using Equation (20). Stop if satisfied with probable error limits. Otherwise go to step 2.

To keep to some predetermined number the quantity of states dealt with at each pass, all elements of $\mathbf{L}'$ can be multiplied by N_p/N at the beginning of each pass, where N_p is the predetermined number and N is the actual number of states present. The effect of this factor can be canceled at the end of each pass by multiplying the right-hand side of Equation (20) with N/N_p.

The method was first applied to two Fermions with parallel spins moving under the effect of the three dimensional harmonic oscillator potential:

$$v(\mathbf{r}_1, \mathbf{r}_2) = \tfrac{1}{2}(|\mathbf{r}_1|^2 + |\mathbf{r}_2|^2). \tag{27}$$

Eight computer runs were performed; each was over an average number of 500 states, and each required about 4 minutes on the IBM 3033 using double precision arithmetic. Each run started with $b = 0.16$ and this value was kept until the 1800th pass after which it was reduced to 0.02. The collection of data started at the 2000th pass and a' was calculated for every 1000 passes up to the 6000th pass. If each a' and each E computed from it is considered to be an independent statistical point, we thus obtain 48 data points. The resulting energy is 3.498 ± 0.015 au. The exact energy for this example is 3.5 au.

In order to apply the method to the lowest ^{3}S state of He, the singularity of the attractive coulomb potential at the origin (where we located the nucleus) must be considered:

$$V(\mathbf{r}_1, \mathbf{r}_2) = -\frac{2}{|\mathbf{r}_1|} - \frac{2}{|\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{28}$$

This is accomplished by taking the average of the coulomb potential in a cube centered at the origin with sides equal to b, and assigning this value of the potential to any electron stepping on the origin. In effect, this turns out to be equivalent to assigning $r_{\text{origin}} = 0.420168$. The number of points was again kept at about 500, and b was fixed at 0.12 au throughout. The first 2000 passes were not included in the calculations and each 1000 passes thereafter was considered to be an independent statistical data point. Fifty-six data points were thus collected. An energy of -2.171 ± 0.011 au was obtained. The exact energy is -2.175 au [10] (both values are reported before the reduced mass correction). The cost of the total calculation is slightly less than 30 minutes on the IBM 3033, using double precision. The apparent speed of the method is due to the use of integer arithmetic in a large portion of the program. It is clear that BQMC will lead to integer arithmetic for the harmonic oscillator potential where all terms are squares of distances, which in turn are integer multiples of b, the mesh spacing. For the coulomb potential, integer arithmetic can be used to calculate the squares of the distances, but it is then necessary to take square roots. However, it was realized that the squares of the distances in the denominators of Equation (28) hardly ever exceeded $150{,}000b^2$. Thus, a linear array of this length containing square roots was first calculated and stored on disk. This array is then read into the core at the beginning of the MC run at a cost of 20 seconds. The CPU time using the array was found to be 40% less than the time when each square root was calculated as needed. The important elements of the S matrix of Equation (16), a total of 158 values, and 90 values for the Fermi Hole term in Equation (22) are also kept in arrays and are not calculated during the MC run.

5. CONCLUSION

A quantum Monte Carlo procedure, the Basis Quantum Monte Carlo, is formulated for two Fermions with parallel spins in three dimensions. Antisymmetry is implicit in the method. There is no need for prior knowledge of node locations. The resulting algorithm is also faster than existing QMC methods owing to the possibility of using integer arithmetic in a large portion of the computer program. The results obtained for two particles moving in a three dimensional harmonic oscillator potential and for the I ^{3}S

state of He are satisfactory, and are accurate to a few parts in a thousand at comparatively short computer runs.

The present method is directly applicable to systems containing up to four electrons, in which two of the electrons have α and the other two have β spins, since the inter-pair interactions (that is, the interactions between electrons of opposite spin) may be assumed to be taking place between bosons, and QMC procedures lead to boson states of correct symmetry [3–5]. It is therefore possible to apply the present algorithm directly to, for example, LiH or Be.

Reduction of the mesh spacing will have the same effect as the reduction of ε, the time step size in other QMC methods [4, 5], through the relation $\varepsilon \gg b^2$ (actually $\varepsilon = 3b^2$ in this paper). Increasing mesh size should lead to systematic errors for the same reason. However, since an iteration operator accurate to the order ε^2 is being used, the effect of finite mesh size is not yet apparent in the present work, being probably masked by statistical error. This effect, however, should be taken into consideration when variance reducing techniques are applied to the BQMC algorithm.

The application of the method to larger systems requires the following approximation: there is a negligible frequency of occurrence of Markov states corresponding to three electrons with parallel spins within the range of each other's Fermi Holes (Equation (21)). It is clear that this approximation makes physical sense and it is helped not only by the Fermi Hole avoidance of the electrons but also by their coulomb repulsions. A large system will, of course, result in a very large number of knots, but this increase is just the analog of the increase of the size of the configuration space in other QMC methods. The variance of the potential energy within a given configuration space will probably be more important than the size of the space. BQMC calculations on B, LiH, NH_3, CH_4, and H_2O will be reported on shortly [11].

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