

## Quantum chemistry by random walk: Exact treatment of manyelectron systems

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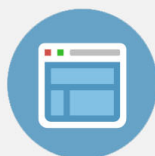
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# Quantum chemistry by random walk: Exact treatment of many-electron systems

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We report an improved Monte Carlo method for quantum chemistry which permits the exact treatment of many-electron systems. The method combines many of the best features of earlier fixed-node, released-node, and positive/negative cancellation methods with new ideas for relocation after node crossing, self-cancellations, multiple cancellations, maximum use of symmetry in promoting cancellations, and rigorous evaluation of energies using importance sampling with trial wave functions. The method is illustrated with applications to the problems of the first excited state of a particle in a two-dimensional box, the two-electron system of excited  $\text{H}_2$   $^3\Sigma_u^+$ , and the three-electron system of linear symmetric HHH, the intermediate for the reaction  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ .

## INTRODUCTION

Random-walk methods of solving the Schrödinger equation, including diffusion Monte Carlo (DMC) and Green's-function Monte Carlo (GFMC) methods, offer an attractive alternative to analytical variational methods for many systems, but for many other systems these methods have been limited by "the node problem" or "the sign problem in fermion Monte Carlo."<sup>1</sup> For a system of either bosons or fermions the wave function must have the correct properties of symmetry and antisymmetry. Except in the simplest cases the wave function is positive and negative in different regions of configuration space separated by one or more nodal hypersurfaces which cannot be specified except by solution of the Schrödinger equation.

One solution to the problem is the fixed-node method developed by Anderson<sup>1</sup> which allows the treatment of ground and excited states of fermion systems with use of approximate nodal surfaces which act as sinks for diffusing particles (psips). The fixed-node method has been found to be remarkably successful in many cases;<sup>2</sup> but, unless the nodal surfaces are exactly correct the method yields only an upper bound to the true energy and is not an exact method.

In an alternative method, devised by Ceperley and Alder<sup>3</sup> and applied in a number of cases,<sup>3,4</sup> the nodes are released to obtain a "transient estimate" of the wave function. This transient-estimate method is limited in its applications because the wave function for the fermion ground state is obtained as the difference in two populations of the lower-energy boson ground state which originate in different regions of the configuration space. Since these populations grow much more rapidly than their difference, the method is numerically unstable and a large, often prohibitive, computational effort is required for high accuracy. The applications of the transient-estimate method are thus restricted to cases with characteristics especially favorable for the method.

In another alternative method, cancellation of positive and negative psips in close proximity is used to stabilize the populations. Arnou, Kalos, Lee, and Schmidt<sup>5</sup> devised an exact cancellation method for GFMC in which partial cancellations are made on the basis of overlapping distributions of positions for pairs of positive and negative psips. Coker and Watts<sup>6</sup> used a cancellation of psips in close proximity in DMC to obtain stable populations of positive and negative psips. In each of these studies, the cases treated included as many as three particles in three dimensions. Zhang and Kalos<sup>7</sup> recently described a different type of cancellation method.

For completeness, we mention three other methods, which have been found to be useful in several applications: a combination of the ground-state method with a local-mode approximation,<sup>8(a)</sup> useful for molecular vibrations; a combination of the transient-estimate method with subspace projection methods,<sup>8(b)</sup> also useful for molecular vibrations; and a mirror potential method,<sup>9</sup> with possible applications to electronic systems.

Here, we report a new cancellation method which incorporates many of the best features of the earlier fixed-node, released-node, and cancellation methods. We make use of new ideas for taking advantage of symmetry and antisymmetry, for self-cancellation of psips, for multiple collective cancellations, and for the rigorous evaluation of energies using importance sampling with approximate wave functions. The new method is exact in that it requires no mathematical approximations and no physical approximations beyond those of the Schrödinger equation. As in most Monte Carlo methods there is a statistical or sampling error which is readily estimated.

We illustrate the method in detail for the easily visualized case of a particle in a two-dimensional box. We also report applications to the case of excited-state  $\text{H}_2$   $^3\Sigma_u^+$  and to the case of ground-state linear symmetric  $\text{H}_3$ , which is an intermediate for the reaction  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ .

## THEORETICAL BACKGROUND

Although the cancellation scheme we report here may be applied in diffusion Monte Carlo calculations, the major applications are more likely to be in Green's-function Monte Carlo calculations in which the problems associated with time steps are avoided. Thus we describe it in terms of GFMC, originated by Kalos<sup>10</sup> for nodeless systems and modified to incorporate the importance sampling techniques originated by Grimm and Storer.<sup>11</sup>

We use a simplified sampling variation of GFMC which we have used previously.<sup>12</sup> We describe it first without a guide or importance sampling function and then indicate the modifications required for importance sampling.

For a molecular system of  $N$  electrons and an arbitrary number of fixed nuclei the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(X) + V(X) \Psi(X) = E \Psi(X), \quad (1)$$

where  $m$  is mass of an electron and  $\nabla^2$  is based on the physical coordinates  $X$  of all the electrons. The equation may be expressed in the form

$$-\nabla^2 \Psi(X) + k^2 \Psi(X) = k^2 \frac{V(X)}{E} \Psi(X), \quad (2)$$

where

$$k^2 = -2mE/\hbar^2. \quad (3)$$

Since  $k^2$  must be positive the energy  $E$  must be negative, a requirement met by adjusting the potential-energy reference.

The Green's function for the left-hand side of Eq. (2) which satisfies appropriate boundary conditions for the Schrödinger equation ( $\Psi \rightarrow 0$  as  $X \rightarrow \infty$ ) is known and is given by

$$G_0(X, X') = \left( \frac{1}{2\pi} \right)^{3N/2} (k |X - X'|)^{1-3N/2} \times K_{3N/2-1}(k |X - X'|), \quad (4)$$

where  $K_\nu$  is the modified Bessel function of the second kind. Sampling is based on the property of the Green's function which relates the wave function to itself,

$$\Psi(X) = \int G_0(X, X') \frac{V(X')}{E} \Psi(X') dX'. \quad (5)$$

Repeated application of Eq. (5) to an initially arbitrary wave function  $\Psi(X')$  leads to a wave function  $\Psi(X)$  which is the lowest-energy solution to the Schrödinger equation for the specified boundary conditions. A point in the distribution  $\Psi(X')$  may be transferred to the distribution  $\Psi(X)$  by multiplying its weight by  $V(X')/E$ , sampling the distribution  $G_0(X, X')$ , and moving the point to its new position. Repetition for an initially arbitrary set of points leads to a set which is a sample of points (psips) from the lowest-energy wave function subject to whatever constraints may be applied. Additional repetition continues the sampling.

To avoid the inefficiency which might occur for the wide spread in the distribution of weights after a number of iterations, the psips are subjected to a killing/splitting operation

after their weights are multiplied by  $V(X')/E$ . Each psip, having weight  $W$ , is divided into  $m$  psips of unit weight with  $m$  given by the integer part of  $(W + u)$ , where  $u$  is random number in the interval  $[0, 1]$ . The value of  $m$  may be zero, in which case the psip is eliminated.

Importance sampling may be included with use of a guide function  $\Psi_G$  which is positive everywhere. The guide function may or may not be the same as an approximate or trial wave function  $\Psi_T$  subsequently used in determining energies. Multiplying both sides of Eq. (5) by  $\Psi_G$  and defining a new function

$$\phi(X) = \Psi(X) \Psi_G(X), \quad (6)$$

the product of the true wave function and the guide function, we obtain

$$\phi(X) = \int \frac{\Psi_G(X)}{\Psi_G(X')} G_0(X, X') \frac{V(X')}{E} \phi(X') dX'. \quad (7)$$

In the same way that Eq. (5) is the basis for an iterative procedure for sampling  $\Psi(X)$ , Eq. (7) is the basis for sampling  $\phi(X)$ . Samples from the distribution  $\phi(X)$  are used in determining the energy of the system.

With use of the guide function the weight  $W$  of a psip in the distribution  $\phi(X')$  is multiplied by  $V(X')/E$  and the psip is transferred to a new position  $X$  sampled from the distribution  $G_0(X, X')$ . The weight is then multiplied by the ratio  $\Psi_G(X)/\Psi_G(X')$  to produce a new weight  $W$  in the distribution  $\phi(X)$ . The effect of  $\Psi_G(X')$  must also be considered in cancellations.

## CANCELLATION OF POSITIVE AND NEGATIVE PSIPS

In general, a wave function and thus the psips representing a wave function may be positive or negative in various regions of the configuration space of the particles of the system. In the released-node method the difference in numbers of positive and negative psips may remain constant but numbers of each increase and the calculation is unstable. A pair of psips in the two populations could be cancelled if they occupied identical positions, but the probability of such an occurrence is so low that an exact method based on such cancellations is not possible. However, as shown by Arnow *et al.*,<sup>5</sup> the probability distributions for positions of a pair of psips at the end of their next moves may overlap and partial cancellations may be made on that basis.

We consider two different, but related, procedures for carrying out cancellations. For this discussion it is convenient to assign separately weights  $W$  (positive only,  $W \geq 0$ ) and signs  $s$  ( $s = +1$  or  $-1$ ) for each psip.

The first procedure is that of Arnow *et al.*<sup>5</sup> in a slightly revised form. For psips with equal weights  $W_i$  at positions  $X'_1$  and  $X'_2$  separated by a distance  $R$  the overlap  $O_{lap}$  of their distribution functions is defined as

$$O_{lap} = \int \text{Min}(G_1, G_2) dX, \quad (8)$$

where  $\text{Min}(G_1, G_2)$  is the smaller of  $G_0(X, X'_1)$  and  $G_0(X, X'_2)$ . If  $R$  is zero the overlap is unity and as  $R$  increases the overlap approaches zero. If the two psips have

opposite signs they may be cancelled to the extent of the overlap prior to their moves by reducing the weight of each, i.e.,  $W_i \rightarrow W_i(1 - O_{\text{lap}})$ . The distribution of new positions must be altered to account for effect of partial cancellation. This is accomplished with a rejection process. A new position  $X$  for the first psip may be selected from the distribution  $G_0(X, X')$  in the normal way, but the move is then accepted with a probability given by

$$P_a = \frac{G_0(X, X'_1) - G_0(X, X'_2)}{G_0(X, X'_1)} \quad (9)$$

If  $P_a$  is less than zero,  $P_a$  is replaced by zero, and if the move is rejected the selection process is repeated. The selection of a move for the second psip may be carried out in a similar fashion.

For this work we have devised a second procedure which facilitates multiple cancellations, eliminates the overlap integral, and eliminates the computationally expensive conditional acceptance of moves. For two psips 1 and 2 with signs (+) and (−), weights  $W_1$  and  $W_2$ , and positions  $X'_1$  and  $X'_2$ , the combined distribution of moves is given by a weight  $W$  and sign  $s$ ,

$$sW = W_1 G_0(X, X'_1) - W_2 G_0(X, X'_2), \quad (10)$$

or, introducing  $G_1$  and  $G_2$ ,

$$sW = W_1 G_1 - W_2 G_2. \quad (11)$$

We select a new position  $X_1$  for psip 1 as the normal way from the distribution  $G_0(X, X'_1)$ . The new weight is given by

$$W_1(\text{new}) = \text{Max}\{[W_1 G_1 - W_2 G_2], 0\} / G_1. \quad (12)$$

The new position  $X_2$  for psip 2 is selected independently from the distribution  $G_0(X, X'_2)$  and the new weight is given by

$$W_2(\text{new}) = \text{Max}\{[W_2 G_2 - W_1 G_1], 0\} / G_2. \quad (13)$$

The procedure reproduces the distribution  $W$  in the positive region since

$$W_1(\text{new}) G_1 = W_1 G_1 - W_2 G_2 = W. \quad (14)$$

Similarly, in the negative region,

$$W_2(\text{new}) G_2 = W_2 G_2 - W_1 G_1 = W. \quad (15)$$

Two psips of the same weight and opposite sign at the same location cancel completely. Two psips far apart keep their original weights.

## PROCEDURE FOR FERMION SYSTEMS

For the ground state of a system of electrons (or, more generally, fermions) the requirement of antisymmetry for the exchange of electrons of the same spin leads to a division of the configuration space into two equivalent regions. In one the wave function is positive, in the other it is negative, and the two meet at the nodal hypersurface in which the wave function is zero. Equivalent regions are geometrically similar or can be made similar by one or more symmetry operations. The requirement of antisymmetry for exchange of electrons of the same spin is not, except in a few special cases such as  $1s2s\ ^3S$  He, sufficient to determine the nodal hypersurface but merely limits its form.

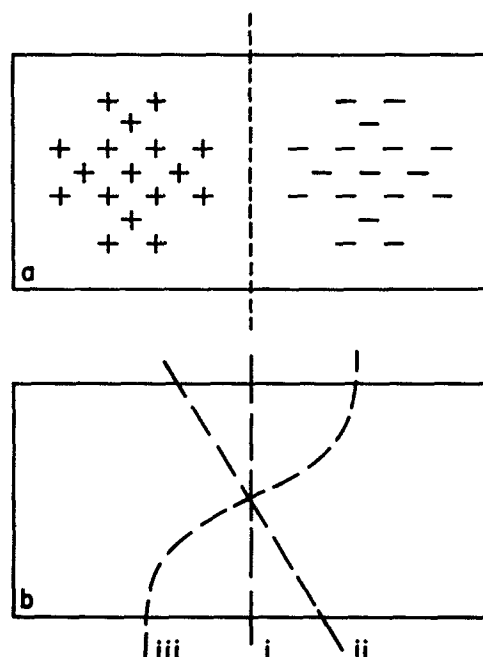


FIG. 1. (a) Wave function for the first excited state of a particle in a two-dimensional box. The exact node location is indicated by the dashed line. (b) Dividing lines which are antisymmetric to inversion through a point at the center of the box.

The case of the first excited state of a single particle in a two-dimensional rectangular box has similar characteristics and we use it to illustrate the calculation procedure. The exact wave function is shown as positive and negative in the regions left and right of the exact node line in Fig. 1(a). The wave function is antisymmetric to inversion through a point at the center of the box. We will divide the space into two regions using a dividing line which has the same symmetry. If we specify inversion symmetry any one of the dividing lines of Fig. 1(b)—the correct node  $i$ , the straight line  $ii$ , or the “yin-yang” line  $iii$ —has the specified symmetry.

A quantum Monte Carlo calculation for the excited state can be carried out with positive and negative psips initially separated left and right, respectively. The two populations spread across the node line and mix. With efficient cancellation and a control to maintain equal populations the result is a net positive population on the left, a net negative population on the right, and a net population of zero (average) at the exact node line as illustrated in Fig. 2. The steady-state averages of positive and negative populations are equivalent: one is the inverse of the other, after sign changes for the psips. Similarly, the regions left and right of any of the symmetric dividing lines of Fig. 1(a) are equivalent: one is the inverse of the other, after sign changes for the psips.

If left and right regions are equivalent one need not determine both. One may take advantage of the equivalent regions and carry out a calculation for a single region with both positive and negative particles. For this calculation is started with positive psips on one side of a symmetry-allowed dividing line and any psip crossing the dividing line is returned to the region by inverting its position and changing its sign as illustrated in Fig. 3. Cancellations may be carried

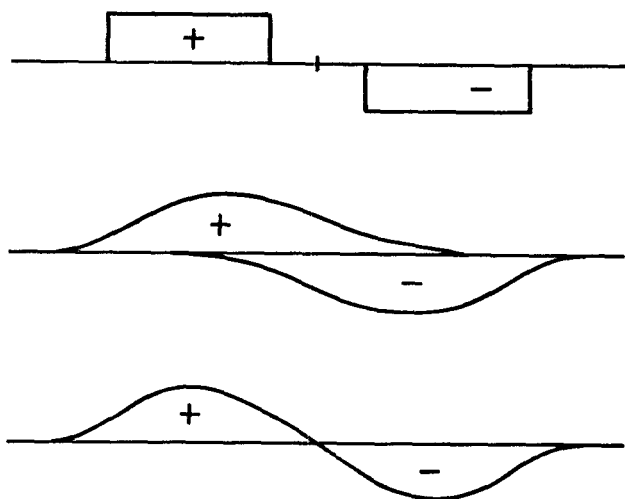


FIG. 2. Illustration of a partial cancellation of positive and negative psip populations to produce an excited-state wave function.

out between positive and negative particles within the occupied region.

For the ground state of a system of fermions the procedure is the same except that inversion is replaced by exchange of electrons of the same spin. The exchange-symmetric dividing surface is most easily specified as the nodal hypersurface of an approximate wave function  $\Psi_D$  which may be the same wave function as that used in importance sampling. Since the exact node structure is produced by the calculation, the dividing surface need not match either the true nodal hypersurface or that of the importance sampling wave function.

Thus as many as four wave functions may be considered: the true wave function  $\Psi$ , the guide wave function  $\Psi_G$  for importance sampling, the trial wave function  $\Psi_T$  for energy determination, and the wave function  $\Psi_D$  which specifies the dividing surface.

## SELF-CANCELLATION

For systems having a configuration space divided into equivalent regions a self-cancellation procedure may be carried out. Even if the positions of psips are limited to a single

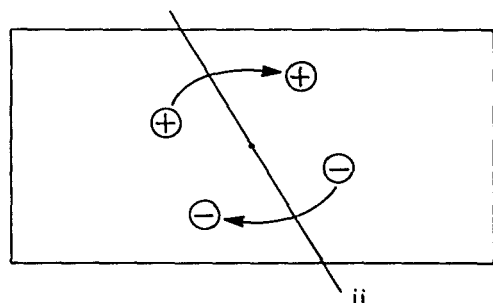


FIG. 3. Illustration of a return of a psip crossing a dividing surface by inversion and a sign change. The positive psip crossing the line *ii* is replaced by a negative psip at the inverse of its position.

region a psip in one region may be partially cancelled by a duplicate of itself of opposite sign at the corresponding position in another region. Thus, in the case of a reflection symmetry a psip may be partially cancelled by its image. The extent of cancellation increases to unity as the psip approaches the reflection plane and the revised distribution of moves prevents any move across the reflection plane. (We note that this is a way of using a Green's function for an unbounded system to solve a differential equation for a system with boundaries.)

Self-cancellation is found especially useful for fermion systems. The permutation of any two electrons of the same spin leaves the remaining electrons unchanged so that the distance in configuration space separating the original psip from its permuted partner is simply the square-root-of-two times the distance between the two electrons. This distance is often small enough for an appreciable cancellation effect.

## MULTIPLE CANCELLATIONS

As noted above our new procedure for cancellation of pairs of psips facilitates multiple cancellations. These may be carried out with a relatively simple extension of that procedure.

For a collection of  $N$  psips the configuration space may be divided into  $N$  or fewer regions, each including only the space for which the product of weight and Green's function [ $W_i G_i$  of Eqs. (10) and (11)] for one psip is greater than that for any of the other psips.

Within each region the value  $sW$  for the distribution of moves of all psips is given by

$$sW = \sum_{j=1,N} s_j W_j G_j. \quad (16)$$

The integral of  $sW$  for region  $i$ , in which  $W_i G_i$  is the greatest, is given by

$$\int_i sW dX = \int_i \frac{sW}{W_i G_i} W_i G_i (X, X') dX. \quad (17)$$

The term  $W_i G_i (X, X') dX$  may be sampled in the same way as for a psip move without cancellation, and the summation for moves of other psips to that position may be determined from their signs and weights and their Green's functions for moves to the same position.

The computation procedure is straightforward and is carried out without iterative sampling. First, a group of psips for multiple cancellation is selected. The current positions, weights, and signs of the psips are stored and their new positions are determined in the usual way by sampling  $G_0(X, X')$  for each. For each psip the value of  $G_i W_i$  is calculated for its new position  $X_i$ , and the values of  $G_j W_j$  for all the other psips considered are calculated for the same new position  $X_i$ . If any of these other psips has a value  $G_j W_j$  greater than  $G_i W_i$ , the new weight for psip  $i$  is reduced to zero. If  $G_i W_i$  is greater than  $G_j W_j$  for all other psips, the new weight and sign is given by

$$(sW)_i = \frac{s_i W_i + \sum_{\text{all } j \text{ in } i} s_j W_j}{s_i W_i}. \quad (18)$$

The summation is over all psips other than  $i$  in region  $i$ . Once

the value of  $(sW)_i$  has been found the weight is chosen positive and the sign is adjusted appropriately. This procedure is repeated for all psips in a multiple cancellation group.

We found it useful to divide the configuration space into cells and select groups of psips for cancellation from those within the same cell. This eliminated the computation effort associated with small partial cancellations of psips far apart in configuration space. Also, to avoid the combination of many psips of the same sign into a single psip of large weight, we determined for each cell the sums of the weights for positive psips and for negative psips and selected for the cancellation group all those of the sign of lesser weight and a sufficient number of the opposite sign to provide an equal weight.

### MAXIMUM USE OF SYMMETRY

The cancellation rate can be increased by using symmetry operations to concentrate positive and negative psips in the same regions of configuration space. There are several ways in which this can be done.

Electrons of the same spin can be ordered spatially by even numbers of exchanges without changing the sign of the corresponding psip. Thus, a positive psip with spin-up electrons 1,2,3 having  $x(3) < x(1) < x(2)$  can be changed to  $x(1) < x(2) < x(3)$  by exchanging 1,3 and 2,3 to be closer in configuration space to a negative psip having  $x(1) < x(2) < x(3)$ .

If the nuclear framework has symmetry the electrons can be subjected to symmetry operations to concentrate psips in a subregion of configuration space. Thus, in the case of  $H_2^+ \Sigma_u^+$ , which has rotational symmetry about the internuclear axis (the  $z$  axis), all configurations can be rotated to place electron 1 in the  $xz$  plane with  $y(1) = 0$  and  $x(1) \geq 0$ , and they may then be reflected in the  $xz$  plane to place electron 2 in the region  $y(2) \geq 0$ .

### ENERGY DETERMINATION

Although the energy of the system may be determined from the growth rate for the psip population, importance sampling methods are likely to produce more accurate values. Importance sampling may be included with use of an approximate wave function  $\Psi_T$  from which local energies  $E_{loc} = H\Psi_T/\Psi_T$  are determined. The energy is given exactly by

$$E = \frac{\int \Psi \Psi_T (H\Psi_T/\Psi_T) dX}{\int \Psi \Psi_T dX}. \quad (19)$$

With use of the everywhere-positive guide function  $\Psi_G$  and the product  $\phi = \Psi\Psi_G$  this becomes

$$E = \frac{\int \phi (\Psi_T/\Psi_G) (H\Psi_T/\Psi_T) dX}{\int \phi (\Psi_T/\Psi_G) dX}. \quad (20)$$

In Monte Carlo sampling of positive and negative psips the product  $\Psi\Psi_G$  is given by the net density of psips (positive — negative). The estimate of the energy is thus given by

$$E = \frac{\sum s_i W_i (\Psi_T/\Psi_G)_i (H\Psi_0/\Psi_0)_i}{\sum s_i W_i (\Psi_T/\Psi_G)_i}. \quad (21)$$

### EXAMPLE: PARTICLE IN A TWO-DIMENSIONAL BOX

For a first application we consider the problem of determining the energy of the first excited state of a particle in a two-dimensional box for which the wave function is separable and exact solutions are known. The mass of the particle is that of the electron and the potential energy is that for intersecting channels of finite depth, shown in Fig. 4, as given by (in atomic units of length and energy):

$$\begin{aligned} V &= V_x + V_y, \\ V_x &= 0, \quad -1 < x < +1, \\ V_x &= 20, \quad x < -1 \text{ or } +1 < x, \\ V_y &= 0, \quad -0.5 < y < +0.5, \\ V_y &= 20, \quad y < -0.5 \text{ or } +0.5 < y. \end{aligned} \quad (22)$$

The exact wave function is the product  $\Psi = \Psi_x \Psi_y$  with separate solutions having energies  $E_x$  and  $E_y$  and a total energy  $E = E_x + E_y$ . The exact energy of the ground state is 3.7323 a.u. and the exact energy of the first excited state, which has a node at  $x = 0$ , is 6.4606 a.u.

For simplicity and to avoid making use of a knowledge of the solution we set  $\Psi_G = 1$  and we used an excited-state importance sampling wave function  $\Psi_T$  which is that for a harmonic oscillator in two dimensions twisted about the origin by an angle  $\theta$ ,

$$\begin{aligned} \Psi_T &= \exp(-au^2) \exp(-bv^2)u, \\ u &= x \cos \theta + y \sin \theta, \\ v &= -x \sin \theta + y \cos \theta. \end{aligned} \quad (23)$$

The constants are  $a = 1.2$ ,  $b = 4.0$ , and  $\theta = \pi/6$ . In testing the method we purposely chose poor representations of the exact solutions for  $\Psi_G$  and  $\Psi_T$ .

The zero of potential energy was shifted by 50 a.u. so that the bottom of the box was at  $-50$  a.u. and the maximum of potential energy was  $-10$  a.u. The input energy  $E$  required for the scaling parameter  $k$  and the multiplication factor  $(V/E)$  of Eqs. (2) and (5) was specified as the shifted exact value,  $-43.5394$  a.u. If the energy were not known an iteration would be required to determine  $E$  for adjusting the

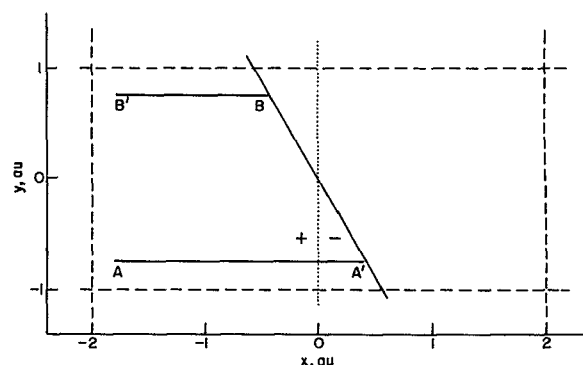


FIG. 4. Two-dimensional box produced by intersecting channels. Dotted line: exact node line for first excited state, wave function positive on left. Solid line: dividing line twisted  $30^\circ$  from node line. The wave function along lines  $AA'$  and  $BB'$  is shown in Fig. 5.

zero of potential energy. We have found previously<sup>12</sup> that the calculated value for  $E$  is insensitive to small errors in the input value for  $E$ .

A calculation was begun with 5000 psips of equal weight distributed evenly in the region  $-0.8 < x < -0.2$  and  $-0.4 < y < +0.4$ . The dividing line was selected as a straight line like that of Fig. 3, matching the node of the trial wave function but not the node of the true wave function, and having symmetry of inversion through the origin. This allowed the possibilities of a node at  $x = 0$  corresponding to a reflection symmetry, a node at  $y = 0$  similarly, or any node of inversion symmetry such as a "yin-yang" node. The space was divided into cells of relatively large size, 0.2 by 0.2, to facilitate choosing groups of psips for multiple cancellations.

An iteration was carried out by first multiplying the weight of each psip by  $V(X')/E$  and dividing each into psips of unit weight with any fractional unit remaining retained at unit weight with a probability equal to the fraction. Any psips on the right side of the dividing line were moved to the left by inversion of their coordinates and reversal of their signs.

Cancellations were carried out as described above with values of  $G_0(X, X')$  calculated with the aid of look-up tables of coefficients for polynomials fit for small intervals of the argument of the required Bessel function. The selection of psip moves, sampling the Green's function  $G_0(X, X')$ , was carried out as described by Kalos<sup>10</sup> for a system without cancellations.

The distribution of psips evolved in less than 50 iterations to a distribution resembling the true wave function on the left side of the dividing line. The calculation was continued for 10 000 iterations to accumulate data. The net distribution of psips matched the exact wave function as illustrated in Fig. 5. The node of the calculated distribution appeared at  $x = 0$  to duplicate that of the exact wave function. The energy determined using the trial wave function for importance sampling was  $6.4603 \pm 0.0005$  a.u., almost exactly equal to the true energy.

Repeated calculations for several different dividing lines gave similar results. When the dividing line matched the ex-

act node, the ratio of positive to negative psips at steady state was approximately 100 to 1. More important in energy determination is the ratio of the sum of the positive products of  $\Psi\Psi_T$  to the sum of the negative products  $\Psi\Psi_T$ . For the same conditions this ratio was approximately 150 to 1.

### EXAMPLE: $H_2 \ ^3\Sigma_u^+$

For a second example we describe calculations for the two-electron system  $H_2 \ ^3\Sigma_u^+$  at an internuclear distance of 1.4 a.u. The wave function for this system is symmetric to rotation about the internuclear axis ( $z$  axis), antisymmetric to reflection in a plane perpendicular to and bisecting the axis, and antisymmetric to inversion through the midpoint of the axis. In addition, an "unexpected" symmetry of the nodal hypersurface which has been described by Anderson<sup>13</sup> for  $1s2p \ ^3P$  He is likely. However, these symmetries are not sufficient for the specification of the nodal hypersurface. The "exact" value of the energy is known from highly accurate analytic variation calculations for the system to be  $-0.7830$  a.u.<sup>14</sup>

We used a dividing surface specified as the node of an approximate wave function of the type

$$\Psi_D = f(1)f(2)(z_1 - z_2), \quad (24)$$

giving a "planar" node structure consisting of a hypersurface given by  $z_1 = z_2$ .

The trial wave function used was

$$\begin{aligned} \Psi_T = \{ & \exp[-a(r_{1A} + r_{2B})] \\ & - \exp[-a(r_{2A} + r_{1B})] \} \\ & \times \exp[br_{12}/(1 + cr_{12})] \end{aligned} \quad (25)$$

with the coefficients  $a = 1.0$  a.u.<sup>-1</sup>,  $b = 0.25$  a.u.<sup>-1</sup>, and  $c = 0.25$  a.u.<sup>-1</sup>. This wave function has a nodal hypersurface which is substantially different from that of the exact wave function. The trial wave function was not optimized.

A guide function was used in this calculation and it was found to lead to reduced energy variance as expected. The function used was

$$\Psi_G = |\Psi_T| + c, \quad (26)$$

with the constant  $c = 0.1$ . Calculations were carried out for 20 000 psips started with positive signs in the region of positive  $\Psi_D$ . Multiple cancellations were carried out for 3126 cells in the five-dimensional configuration space remaining after full use of symmetry as described above. At steady state the ratio of positive to negative psips was approximately 10 to 1 and the ratio of positive  $\Psi\Psi_T$  to negative  $\Psi\Psi_T$  was also about 10 to 1.

The energy determined was  $-0.7838 \pm 0.0007$  a.u., in good agreement with the results of prior analytic variational calculations. The nodal hypersurface obtained by sampling is shown in Fig. 6. To obtain the plot we assumed the nodal hypersurface is symmetric to rotation about the axis of the molecule in the same way that the hypersurface for  $1s2p \ ^3P$  helium is symmetric to rotation about the  $z$  axis.<sup>13</sup> For any position of the first electron the positions of the second electron which produce a value of zero for the wave function are on a surface which is symmetric to rotation about the axis

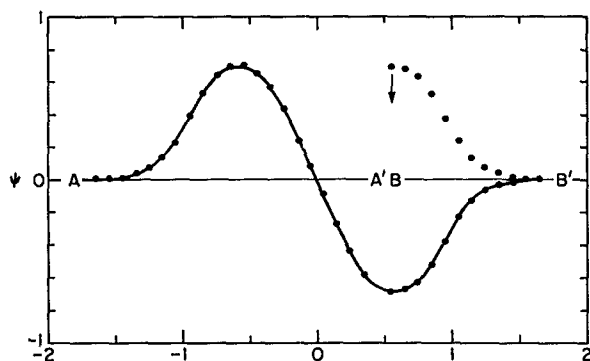


FIG. 5. Comparison of the calculated wave function with the exact analytic wave function for the first excited state of a particle in a two-dimensional box. Calculated: points. Analytic: solid curve. The wave function is shown along lines  $AA'$  and  $BB'$  (also inverted) of Fig. 4.

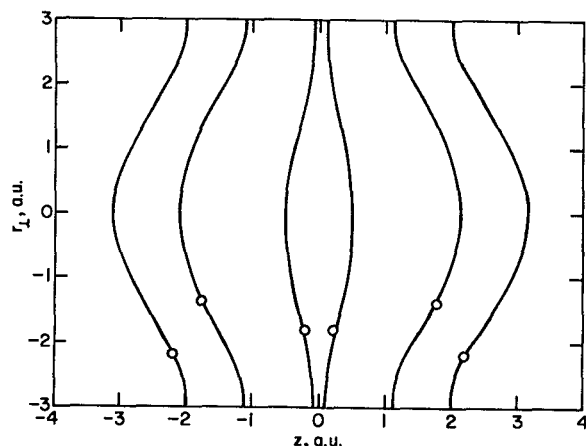


FIG. 6. Nodal hypersurface determined in Monte Carlo Calculations for  $\text{H}_2 \ ^3\Sigma_u^+$ . For the first electron at each of the open circles the positions of the second electron which give a value of zero for the wave function are given by the line passing through the circle. The resolution is about 0.3 a.u.

and passes through the first electron. The five-dimensional hypersurface in six-dimensional space may thus be represented by a series of lines in two-dimensional space like that of Fig. 6.

### EXAMPLE: LINEAR SYMMETRIC H-H-H

The three-electron system H-H-H is an intermediate in that most elementary of reactions, the hydrogen exchange reaction  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ . For this reason the system has been the subject of a number of quantum calculations beginning in the 1930s. The saddle point in the potential-energy barrier to reaction occurs for the collinear configuration with internuclear separations of approximately 1.757 a.u. between adjacent hydrogen nuclei. The barrier height is approximately 9.65 kcal/mol relative to exact  $\text{H} + \text{H}_2$  with  $\text{H}_2$  at its equilibrium separations.

There have been several prior calculations of high accuracy for this system. These include the following: analytic variational calculations by Liu,<sup>15(a)</sup> Siegbahn and Liu,<sup>15(b)</sup> and Liu;<sup>15(c)</sup> fixed-node Monte Carlo calculations by Mentch and Anderson<sup>2(f)</sup> and Barnett, Reynolds, and Lester;<sup>2(g)</sup> and transient estimate calculations by Ceperley and Alder.<sup>16</sup>

For our Monte Carlo calculations we used the same trial function for both  $\Psi_D$  and  $\Psi_T$ ,

$$\begin{aligned} \Psi_D = \Psi_T = & (g_{A1}g_{B2} - g_{A2}g_{B1} + g_{A1}g_{C2} - g_{A2}g_{C1} \\ & + g_{B1}g_{C2} - g_{B2}g_{C1}) \\ & \times (g_{A3} + g_{B3} + g_{C3})J_{12}J_{13}J_{23}, \end{aligned} \quad (27)$$

where, for example,

$$g_{A1} = \exp(-ar_{1A})$$

and the Jastrow terms are, for example,

$$J_{12} = \exp[br_{12}/(1 + cr_{12})].$$

The coefficients are  $a = 1 \text{ a.u.}^{-1}$ ,  $b = c = 0.25 \text{ a.u.}^{-1}$  for electrons of like spin (1 and 2) and  $0.50 \text{ a.u.}^{-1}$  for electrons

of unlike spin (1 and 3, 2 and 3). The wave function was not optimized.

The configuration space was divided into 6562 cells of width 1.0–2.0 a.u. in each of eight dimensions. The ninth dimension was eliminated by rotating the electrons about the nuclear axis to place one electron in the  $x = 0$  plane as for the  $\text{H}_2$  calculations.

Calculations were carried out for 20 000 psips. At steady state the ratio of positive to negative psips was approximately 6 to 1 and the ratio of positive  $\Psi\Psi_T$  to negative  $\Psi\Psi_T$  was about 8 to 1.

The energy from a calculation of several hours on an IBM-3090 was  $-1.6591 \pm 0.0003 \text{ a.u.}$  corresponding to a barrier height of  $9.6 \pm 0.2 \text{ kcal/mol}$ . This is in good agreement with the estimated true value of 9.65 kcal/mol,<sup>16,2(g),15(c)</sup> and provides confirmation of the validity of the procedure. Additional calculations for a variety of nuclear configurations with optimized trial wave functions can now be carried out to obtain a potential-energy surface of very high accuracy.

### DISCUSSION

The improved cancellation method was found to be computationally stable for each of the example problems and to yield energies exact within sampling error in each case. The steady-state ratio of positive to negative psips changed from 150/1 to 10/1 to 6/1 as the number of dimensions changed from 2 to 6 to 9. One key to effective cancellation is a high density of psips in a restricted region of configuration space. Since it is relatively easy to increase the number of psips by a factor of 10–100, we expect to reach one or two dimensions higher without difficulty. Another key to effective cancellation in higher dimensions is the scaling of self-cancellations which is nearly independent of dimensionality.

It was pointed out by Zhang and Kalos<sup>7</sup> that since the use of cancellation allows the possibility of negative psips, the potential energy  $V$  need not be maintained negative by an offset in the energy  $E$ .<sup>12</sup> The value of  $E$  may be set slightly negative and very large step sizes ( $X - X'$ ) may be used. The effect is a significant reduction in serial correlation of local energies and a corresponding reduction in computation effort as well as an increase in the range of cancellation. While we have not taken advantage of these gains in the present work we expect they are easily realized.

Extension to systems of as many as five electrons appears to be readily possible. Beyond that, except in the most favorable cases, it seems likely that additional aids to cancellation will be required for stable calculations. A number of possibilities remain for such aids and we anticipate that at least one of them will be successful in extending the improved method to systems of ten or more electrons.

The advantages of cancellation in producing a stable net positive population of psips relative to a transient net positive population given by the transient-estimate method are several. Since the cancellation of psips requires very little additional calculational effort, the computation time and memory requirements are significantly reduced, although the extent of reduction is highly dependent on the positive-to-negative psip ratio. Even in cases for which a stable popu-



lation is not obtained, cancellation is likely to be useful in extending the length of the useful part of a transient calculation from which data may be gathered.

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