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He and H^- 1^1S and 2^3S States Computed from Feynman Path Integrals in Imaginary Time*

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Feynman path integrals in imaginary time are developed for systems of identical particles exhibiting exchange statistics. The Metropolis–Teller Monte Carlo procedure is applied to the integrals appropriate to H^- and He 1^1S and 2^3S states.

I. INTRODUCTION

The over-all goal of this work is the development of a technique for doing *a priori* quantum and quantum statistical computations on the ground states of many-body systems. We have chosen simple quantum systems as test cases during the course of the development. We assume that extensions to quantum statistics will be directly feasible, when we are satisfied with the basic technique. As we have remarked earlier,[1,2] ancillary goals are associated with elucidating the meaning of the equivalence between the Feynman formulation and the usual one in a somewhat tangible manner. We are also motivated by the apparent simplicity of the path integral approach, from a computational point of view.

In earlier papers[1,2] the authors proposed a numerical method for obtaining the ground state wavefunction and energy of quantum mechanical systems. This procedure involves the evaluation of Feynman path integrals[3] in imaginary time. Applications of the method to simple one-particle problems were considered. In this paper the extension of the procedure to problems of several dimensions involving identical particle exchange symmetry is developed. Two- and three-particle harmonic oscillators are examined as well as the 1^1S and 2^3S states of helium and the hydrogen negative ion. Some of the characteristics of the approach are reviewed in this section, with the development of procedures for handling quantum statistics occurring in subsequent sections.

The basic approach consists of determining the Feynman propagator which is equivalent to the Schrödinger equation

$$\hat{H}\psi(\mathbf{x}, t) = i\hbar[\partial\psi(\mathbf{x}, t)/\partial t]. \tag{1}$$

The quantity "it" is then replaced by the imaginary time coordinate τ with the result that the Schrödinger equation is replaced by

$$\hat{H}\psi(\mathbf{x}, \tau) = -\hbar[\partial\psi(\mathbf{x}, \tau)/\partial\tau]. \tag{2}$$

This is the Bloch equation if $\hbar/\tau = kT$, but, more generally, it is a diffusion-type equation which describes a process that settles down to its ground state as $\tau \to \infty$.

The one-particle propagator in Cartesian coordinates corresponding to Eq. (1) is

$$K(\mathbf{x}_1, \mathbf{x}_2, t_2 - t_1) = A_t \int \exp\left(\frac{i}{\hbar}\int_{t_1}^{t_2} L(\mathbf{x}, \mathbf{x}, t)\,dt\right) D\mathbf{x}(t), \tag{3}$$

where $L(\mathbf{x}, \mathbf{x}, t)$ is the classical Lagrangian, A_t is a normalization factor, and $D\mathbf{x}(t)$ denotes integration over all possible, yet unspecified, paths of the particle. An alternate form of this propagator is

$$K(\mathbf{x}_1, \mathbf{x}_2, t_2 - t_1) = \sum_n \exp[-iE_n(t_2 - t_1)/\hbar] U_n^*(\mathbf{x}_1) U_n(\mathbf{x}_2), \tag{4}$$

where the $U_n(\mathbf{x})$ are a complete set of orthonormal spatial eigenfunctions used to represent $\psi(\mathbf{x}, t)$, i.e.,

$$\psi(\mathbf{x}, t) = \sum_n C_n(t) U_n(\mathbf{x}), \tag{5}$$

where

$$C_n(t) = \int U_n^*(\mathbf{x})\psi(\mathbf{x}, t)\, d^3\mathbf{x} \tag{6}$$

and

$$\psi(\mathbf{x}, t) = \int K(\mathbf{x}', \mathbf{x}, t-t')\psi(\mathbf{x}', t')\, d^3\mathbf{x}'. \tag{7}$$

The equivalent expressions for the propagator of the diffusion-type equation are

$$K(\mathbf{x}_1, \mathbf{x}_2, \tau_2-\tau_1) = A_\tau \int \exp\left(-\frac{1}{\hbar}\int_{\tau_1}^{\tau_2} H(\mathbf{x}, \mathbf{x}, \tau)\, d\tau\right) D\mathbf{x}(\tau) \tag{8}$$

and

$$K(\mathbf{x}_1, \mathbf{x}_2, \tau_2-\tau_1) = \sum_n \exp[-E_n(\tau_2-\tau_1)/\hbar] U_n^*(\mathbf{x}_1)\, U_n(\mathbf{x}_2), \tag{9}$$

where $H(\mathbf{x}, \mathbf{x}, t)$ is the classical Hamiltonian and

$$\psi(\mathbf{x}, \tau) = \sum_n C_n(\tau)\, U_n(\mathbf{x}), \tag{10}$$

where

$$C_n(\tau) = \int U_n^*(\mathbf{x})\psi(\mathbf{x}, \tau)\, d^3\mathbf{x} \tag{11}$$

and

$$\psi(\mathbf{x}, \tau) = \int K(\mathbf{x}', \mathbf{x}, \tau-\tau')\psi(\mathbf{x}', \tau')\, d^3\mathbf{x}'. \tag{12}$$

Thus, the consequences of replacing "it" by τ are the following: First, the Schrödinger equation becomes a diffusion-type equation with a different time dependence, but the same spatial eigenfunctions. The diffusion equation describes a process which settles to its ground state after a sufficiently large time. This can be seen from Eqs. (9), (10), and (12):

$$\psi(\mathbf{x}, \tau) = \int \sum_n \exp[-E_n(\tau-\tau')/\hbar] U_n^*(\mathbf{x}')\, U_n(\mathbf{x}) \times \sum_n C_n(\tau')\, U_n(\mathbf{x}')\, d^3\mathbf{x}' \tag{13}$$

and

$$\lim_{\tau\to\infty}\psi(\mathbf{x}, \tau) = C_0(\tau') \exp[-E_0(\tau-\tau')/\hbar] U_0(\mathbf{x}). \tag{14}$$

Second, the highly oscillatory complex integrand of Eq. (3) has been replaced by a much more slowly varying real integrand in Eq. (8). In particular, for many one-particle problems, the integrand of Eq. (8) is a functional $F[x(\cdot)]$ of the sample functions of a Wiener process. In our previous papers[1,2] we showed that (8) could be numerically evaluated for a large number of sample functions. In this paper we report that numerical evaluation of (8) is possible when the process is a generalization of the Wiener process necessary to take quantum statistics into account.

Two general approaches to determining ψ_0 and E_0 are possible, based on the development outlined above. The most obvious is to evaluate Eq. (12) for a sufficiently large time so the ground state times a function of E_0 and τ is filtered out, as shown in (14). An alternate procedure is to recognize that the limit as $\tau\to\infty$ of the diagonal elements of K reproduces the square of the ground state wavefunction:

$$K(\mathbf{x}, \mathbf{x}, \tau) = \sum_n \exp[-E_n\tau/\hbar] \mid U_n(\mathbf{x}) \mid^2 \tag{15}$$

and

$$\lim_{\tau\to\infty} K(\mathbf{x}, \mathbf{x}, \tau) = \exp(-E_0\tau/\hbar) \mid U_0 \mid^2. \tag{16}$$

This latter approach has the advantage that one is dealing with positive definite quantities so that subtraction errors are avoided. This approach was used by us in Refs. 1 and 2 with the importance sampling Metropolis–Teller Monte Carlo technique, and it has been used by Fosdick[4] and by Fosdick and Jordan,[5,6] who approached the evaluation by way of a Monte Carlo version of Cameron's trapezoidal and Simpson's rules for the determination of Wiener integrals.[7]

The direct evaluation of $\psi(\mathbf{x}, \tau)$, as per Eq. (12), has been used by Grimm and Storer.[8,9] A modified approach, which evaluates a differential equation whose solutions are always positive definite, has been used by Kalos.[10–12] Most of these evaluations (some of the work of Grimm and Storer excepted) have used Monte Carlo techniques. Several previous workers have used various kinds of Monte Carlo techniques, some based on sampling the Wiener process,[13,14] as well as random walks directly on a difference equation approximation to the original differential equation.[15] It is also of interest to mention the work of Goldberg and Schwartz,[16,17] who integrated Eq. (2) directly.

The range of problems explored has been large. Fosdick[4] and Fosdick and Jordan[5] have been interested in the Bloch equation. Kalos has evaluated the Bloch equation[12] and nuclear problems.[10] Grimm and Storer have done atomic and nuclear problems.[8,9] Quantum statistics has been taken into account in various ways. Fosdick[4] has discussed the point of view taken by us and reported below.

For many-body problems the approaches discussed here have several advantages over other techniques. First, they are not demanding of computer storage space. In our approach the only storage requirements are those for one path in the integral and a matrix which reproduces the irreducible symmetry of the total problem (in this case spherical, and thus requiring a one-dimensional matrix). Second, the methods are readily amenable to Monte Carlo techniques. Third, no basis set which must roughly model the system is required—although this characteristic carries with it the drawback that answers are in purely numerical form. Fourth, the result can be expressed in a reduced form. There is no need to carry details beyond those of interest and these extra details of the wavefunction can be almost automatically integrated out. Fifth, and complementary to point four, even though reduced wavefunctions are presented, the interesting information associated with the full wavefunction,

such as multiparticle correlations, can be easily carried along.

An evident drawback of the approach, the fact that it only gives the ground state, is not as severe as it appears. Grimm and Storer regarded the propagator as a matrix to obtain excited states as well.[8] We have shown that the ground state found is that corresponding to a propagator of a particular symmetry.[2] For example, in the hydrogen atom there is a ground state for $l=0, 1, 2, \cdots$, etc. In this paper the 1^1S and 2^3S states are both ground states for particular symmetrys.

II. PATH INTEGRALS IN IMAGINARY TIME

A formulation of the appropriate path integral corresponding to the nonrelativistic Schrödinger equation is described in Ref. 1. We need only outline the essential steps involved in the present case. In units $\hbar=m=1$, the Schrödinger equation for a two-electron problem and in imaginary time may be written as

$$\hat{H}\psi=-\tfrac{1}{2}[\nabla_a^2+\nabla_b^2]\psi(\mathbf{x}_a, \mathbf{x}_b)+V(\mathbf{x}_a, \mathbf{x}_b)\psi(\mathbf{x}_a, \mathbf{x}_b)=-(\partial\psi/\partial\tau)(\mathbf{x}_a, \mathbf{x}_b), \tag{17}$$

where $\mathbf{x}_a$, $\mathbf{x}_b$ denote the position coordinate of the two electrons a, b, respectively, as measured from the nucleus (assumed to be stationary). The potential energy $V(\mathbf{x}_a, \mathbf{x}_b)$ is typically of the form

$$V(\mathbf{x}_a, \mathbf{x}_b)=-z/|\,\mathbf{x}_a\,|-z/|\,\mathbf{x}_b\,|+1/|\,\mathbf{x}_{ab}\,| \qquad (e=1), \tag{18}$$

where z is the nuclear charge and $\mathbf{x}_{ab}=\mathbf{x}_a-\mathbf{x}_b$. For an infinitesimal time $\epsilon=\tau_2-\tau_1$, the Feynman propagator may be formally written as

$$K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a'', \mathbf{x}_b'', \epsilon)=\exp(-\epsilon H'')\delta(\mathbf{x}_a''-\mathbf{x}_a')\delta(\mathbf{x}_b''-\mathbf{x}_b'), \tag{19}$$

where $\hat{H}''$ is the Hamiltonian operator $\hat{H}(\mathbf{x}_a'', \mathbf{x}_b'')$. Using a Fourier representation of the δ function in (19) and following the method of Ref. 1, one can show in a straightforward manner that for an infinitesimally small ϵ, Eq. (19) reduces to

$$K(\mathbf{x}_a', \mathbf{x}_b', \mathbf{x}_c'', \mathbf{x}_b'', \epsilon)=\left(\frac{1}{2\pi\epsilon}\right)^{3/2}\exp\left\{-\epsilon\left[\frac{1}{2}\left(\frac{\mathbf{x}_a''-\mathbf{x}_a'}{\epsilon}\right)^2+\frac{1}{2}\left(\frac{\mathbf{x}_b''-\mathbf{x}_b'}{\epsilon}\right)^2+V(\mathbf{x}_a'', \mathbf{x}_b'')\right]\right\}. \tag{20}$$

The propagator for large time interval $\tau=N\epsilon$ is then obtained, in the usual manner, by successive convolutions of the K's of the type given in Eq. (20). This leads to the following path integral:

$$\begin{aligned}K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \tau)&=\int\cdots\int\prod_{j=2}^{N}d^3\mathbf{x}_a^{(j)}d^3\mathbf{x}_b^{(j)}\prod_{j=1}^{N}K(\mathbf{x}_a^{(j)}, \mathbf{x}_b^{(j)}; \mathbf{x}_a^{(j+1)}, \mathbf{x}_b^{(j+1)})\\&=(1/2\pi\epsilon)^{3N/2}\int\cdots\int\prod_{j=2}^{N}d^3\mathbf{x}_a^{(j)}d^3\mathbf{x}_b^{(j)}\exp\left\{-\epsilon\sum_{j=1}^{N}\left[\frac{1}{2}\left(\frac{\mathbf{x}_a^{(j+1)}-\mathbf{x}_a^{(j)}}{\epsilon}\right)^2+\frac{1}{2}\left(\frac{\mathbf{x}_b^{(j+1)}-\mathbf{x}_b^{(j)}}{\epsilon}\right)^2\right.\right.\\&\qquad\left.\left.+V(\mathbf{x}_a^{(j+1)}, \mathbf{x}_b^{(j+1)})\right]\right\},\end{aligned} \tag{21}$$

with $\mathbf{x}_a^{(N+1)}=\mathbf{x}_a$ and $\mathbf{x}_b^{(N+1)}=\mathbf{x}_b$, where in the second expression on the right, Eq. (20) is used. As shown by (16), for a sufficiently long time τ,

$$K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \tau)_{\mathbf{x}_a'=\mathbf{x}_a,\ \mathbf{x}_b'=\mathbf{x}_b}=\exp(-E_0\tau)\,|\,U_0(\mathbf{x}_a, \mathbf{x}_b)\,|^2, \tag{22}$$

where $U_0(\mathbf{x}_a, \mathbf{x}_b)$ is the ground state wavefunction and E_0 is the corresponding energy. The computer evaluation of the right-hand side of Eq. (22) according to the Monte Carlo scheme of Ref. 1 will then yield $|\,U_0(\mathbf{x}_a, \mathbf{x}_b)\,|^2$. The modification of Eq. (22) required to obtain states of definite symmetry is discussed in Secs. III and IV.

We may add here that a generalization of Eq. (22) to more than two particles is quite straightforward.

III. PATH INTEGRALS FOR PARTICLES OBEYING FERMI OR BOSE STATISTICS

We wish to develop a scheme which introduces Fermi or Bose statistics into the Feynman propagator in imaginary time. Consider first, two identical particles, a and b, whose coordinates may be designated $\mathbf{x}_a$ and $\mathbf{x}_b$, respectively. The symmetrized wavefunctions describing the system will be

$$\Psi(\mathbf{x}_a, \mathbf{x}_b, \tau)=2^{-1/2}(1\pm\hat{P}_{ab})\psi(\mathbf{x}_a, \mathbf{x}_b, \tau), \tag{23}$$

where $\hat{P}_{ab}$ is the permutation operator on the particles a, b, and the $\pm$ corresponds to Bose or Fermi statistics,

respectively. Hence, the propagator (9) becomes

$$\begin{aligned} K_E(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \tau-\tau') &= \sum_n \Psi_n^*(\mathbf{x}_a', \mathbf{x}_b', \tau')\Psi_n(\mathbf{x}_a, \mathbf{x}_b, \tau) \\ &= \tfrac{1}{2}\sum_n (1\pm\hat{P}_{ab})\psi_n^*(\mathbf{x}_a', \mathbf{x}_b', \tau')\,(1\pm\hat{P}_{ab})\psi_n(\mathbf{x}_a, \mathbf{x}_b, \tau) \\ &= \sum_n \{\psi_n^*(\mathbf{x}_a', \mathbf{x}_b', \tau)\psi_n(\mathbf{x}_a, \mathbf{x}_b, \tau)\pm\psi_n^*(\mathbf{x}_a', \mathbf{x}_b', \tau)\psi_n(\mathbf{x}_b, \mathbf{x}_a, \tau)\} \\ &= K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \tau-\tau')\pm K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_b, \mathbf{x}_a, \tau-\tau'), \end{aligned} \tag{24}$$

where K_E is the total propagator, including exchange, and K is the propagator as developed in Sec. II. Note that we have taken advantage of the fact that $K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \tau-\tau')$ is indistinguishable from $K(\mathbf{x}_b', \mathbf{x}_a'; \mathbf{x}_b, \mathbf{x}_a, \tau-\tau')$, and that $K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_b, \mathbf{x}_a, \tau-\tau')$ is indistinguishable from $K(\mathbf{x}_b', \mathbf{x}_a'; \mathbf{x}_a, \mathbf{x}_b, \tau-\tau')$.

If we consider three identical particles with a symmetrical law of interaction between them, we can permute the final coordinates of the particles in six ways. These six permutations fall under three classes, viz., the identity, the three permutations in which two of the coordinates are interchanged, and two more in which all particles are cyclically permuted, the cycle being clockwise and anticlockwise. Thus, we may write,

$$K_E(a', b', c'; a, b, c, \tau-\tau') = [K_I\pm(K_{ab}+K_{bc}+K_{ca})+(K_{abc}+K_{acb})], \tag{25}$$

where we use a simplified notation in which a, b, c are used to denote the coordinates of the particles, K_I represents the original propagator, K_{ab} is the propagator in which $\mathbf{x}_a$ and $\mathbf{x}_b$ have been interchanged, and K_{abc} is one in which the three coordinates are permuted cyclically.

In general, the exchange propagator for any number of particles may be similarly defined by considering all classes of permutations, writing the appropriate propagator corresponding to each permutation in a class, and forming a symmetric or an antisymmetric combination.

Although (24) may be directly evaluated as the sum or difference of two independent propagators, this may not give good results, particularly for Fermi statistics. The difference of two large and nearly equal numbers may have little meaning as a computational result. This point was made in Ref. 1. In Ref. 1 it was also pointed out that $K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \tau-\tau')$ is the equivalent of the propagator of two individual particles for time $\tau-\tau'$, whereas $K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_b, \mathbf{x}_a, \tau-\tau')$ is the equivalent of the propagator of one particle for time $2(\tau-\tau')$.

We can avoid the difficulty associated with subtraction by recognizing that $K_E(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \tau-\tau')$ does not specify when the particle permutation took place. Therefore, many permutations could have occurred in time $\tau-\tau'$, so long as the correct final state is achieved. Hence, instead of regarding K_E as the sum of two independent terms, as in (24), we may regard it as being made up of successive convolutions of a small time step exchange propagator $K_E(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a'', \mathbf{x}_b'', \epsilon)$ as in (21):

$$K_E(\mathbf{x}_a', \mathbf{x}_b', \mathbf{x}_a, \mathbf{x}_b, \tau) = \int\cdots\int \prod_{j=2}^{N} d^3\mathbf{x}_a d^3\mathbf{x}_b \prod_{j=1}^{N} K_E(\mathbf{x}_a^{(j)}, \mathbf{x}_b^{(j)}; \mathbf{x}_a^{(j+1)}, \mathbf{x}_b^{(j+1)}, \epsilon), \tag{26}$$

where

$$K_E(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a'', \mathbf{x}_b'', \epsilon) = K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a'', \mathbf{x}_b'', \epsilon)\pm K(\mathbf{x}_a', \mathbf{x}_b', \mathbf{x}_b'', \mathbf{x}_a'', \epsilon). \tag{27}$$

The results of computations using this form of $K_E(\tau-\tau')$ are given in Sec. V and demonstrate that it is appropriate. The same general idea can be used to avoid all but the two-particle permutation class. That is, K_{abc} may be made up of several two-particle permutations, to a good approximation. We have only verified this idea on a system of three noninteracting identical oscillators so our experience with it to date is limited.

IV. EXCHANGE PROPAGATORS IN THREE-DIMENSIONAL SPACE

The formulas of Sec. III may be directly applied to a number of one-dimensional problems. However, it is necessary to be careful to generate a propagator of the correct symmetry when dealing with three-dimensional space.

In Ref. 2 we showed that a propagator evaluates a system of a certain symmetry, and that its diagonal elements at time $\tau\to\infty$ give the square of the ground state of that symmetry. Propagators for various l quantum numbers were evaluated in Ref. 2 to demonstrate this property.

Consider a two particle quantum system such as the helium atom, where one assumes that the nucleus is fixed. In the absence of spin–spin and spin–orbit coupling, the wavefunctions of this system will be eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ in the two-particle angle space and of $\hat{S}^2$ and $\hat{S}_z$ in the spin space. The eigenfunction of $\hat{L}^2$, $\hat{L}_z$ may be constructed as appropriate linear combinations of products of spherical harmonics, and the possible eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$, will be the singlet state $2^{-1/2}$ $(\uparrow\downarrow-\downarrow\uparrow)$ and the three

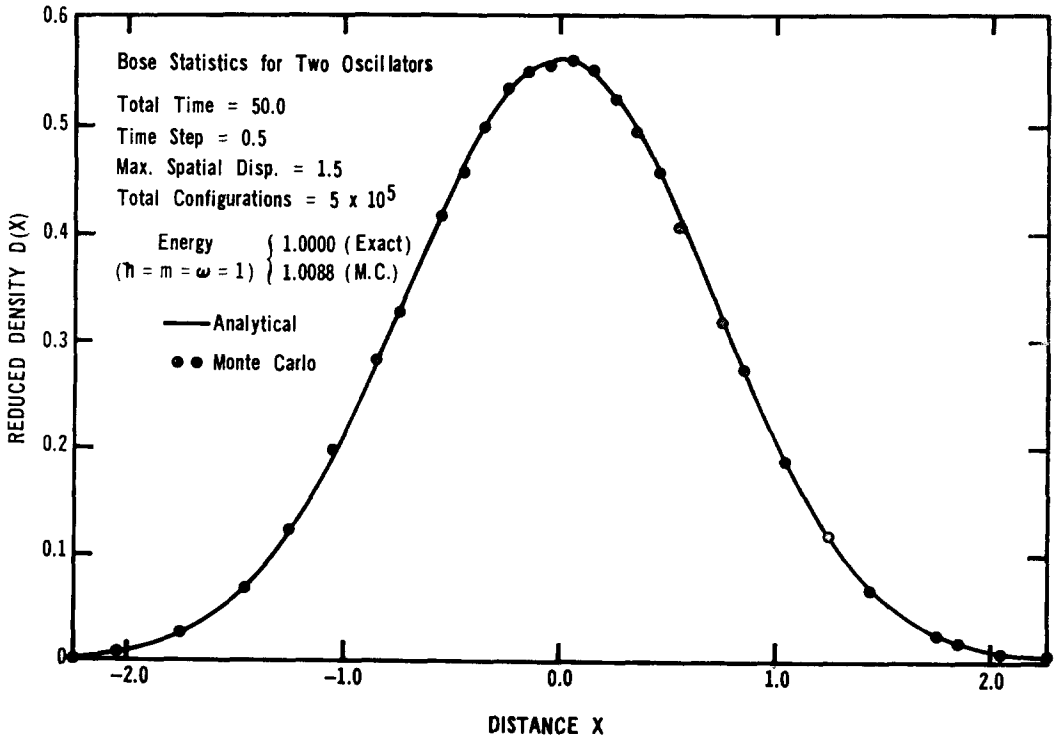

FIG. 1. Comparison of a Monte Carlo calculation with an analytic curve for the case of two oscillators obeying Bose statistics.

triplet states $\uparrow\uparrow$, $\downarrow\downarrow$, $2^{-1/2}(\uparrow\downarrow+\downarrow\uparrow)$. In order to satisfy the Pauli principle the total wavefunction must be antisymmetric under permutation of the space and spin coordinates of the two electrons. For the case of two particles, symmetric and antisymmetric functions are sufficient to span the entire two-particle space.

Thus, the portion of the wavefunction that depends on the radial variables of the two electrons may be either symmetric or antisymmetric. Similarly, the angular functions, which will be eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, will be either symmetric or antisymmetric, and the portion of the wavefunction that is in spin space must be either the antisymmetric singlet or one of the three-symmetric triplet functions.

If we choose the radial portion of the wavefunction to be symmetric, then either the angular portion or the spin portion of the wavefunction must be antisymmetric. The ground state of the system is $(1s)^2$ $^1S_0$ with symmetric radial and angular functions and an antisymmetric spin function in order to satisfy the Pauli principle.

If we require antisymmetry in both the radial and angle spaces, then we must again select the singlet spin function. In order to permit an antisymmetric function in angle space with one electron in a $1s$ state the second electron must be at least in a $2p$ state, and then we expect that the lowest energy state corresponding to both radial and angular antisymmetry will be $(1s2p)^1P_1$.

If we require antisymmetry in the radial variables and symmetry in the angular variables, then the spin function must be the triplet, and under these conditions the lowest energy state should be a $(1s2s)$ state $^3S_1$.

The final possibility is to demand symmetry in the radial variables and antisymmetry in angle space with a triplet spin state. The state of lowest energy in this case will be $(1s2p)$ $^3P_{2,1,0}$.

The above considerations also hold for the Feynman propagator. When time is replaced by imaginary time, then the propagation of an arbitrary initial state to large imaginary time values must yield the state of lowest energy. If we make some symmetry requirement on the propagator, then the result of long imaginary time propagation will be the state of lowest energy that is compatible with the symmetry requirement. If the symmetry in the radial or angular portion of the space is unspecified, then the propagation will select the symmetry that leads to the lowest energy, provided the initial state possessed a portion with this symmetry.

From the discussion above, it is evident that the correct propagator for the 1^1S state of a two electron atom is

$$K_E(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \epsilon) = K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \epsilon) + K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_b, \mathbf{x}_a, \epsilon), \quad (28)$$

where the K's are given as in (20).

For the 2^3S state we want

$$K_E(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \epsilon) = K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a, \mathbf{x}_b, \epsilon) - K(\mathbf{x}_a', \mathbf{x}_b'; \mathbf{x}_a \mid \mathbf{x}_b \mid/\mid \mathbf{x}_a \mid, \mathbf{x}_b \mid \mathbf{x}_a \mid/\mid \mathbf{x}_b \mid, \epsilon). \quad (29)$$

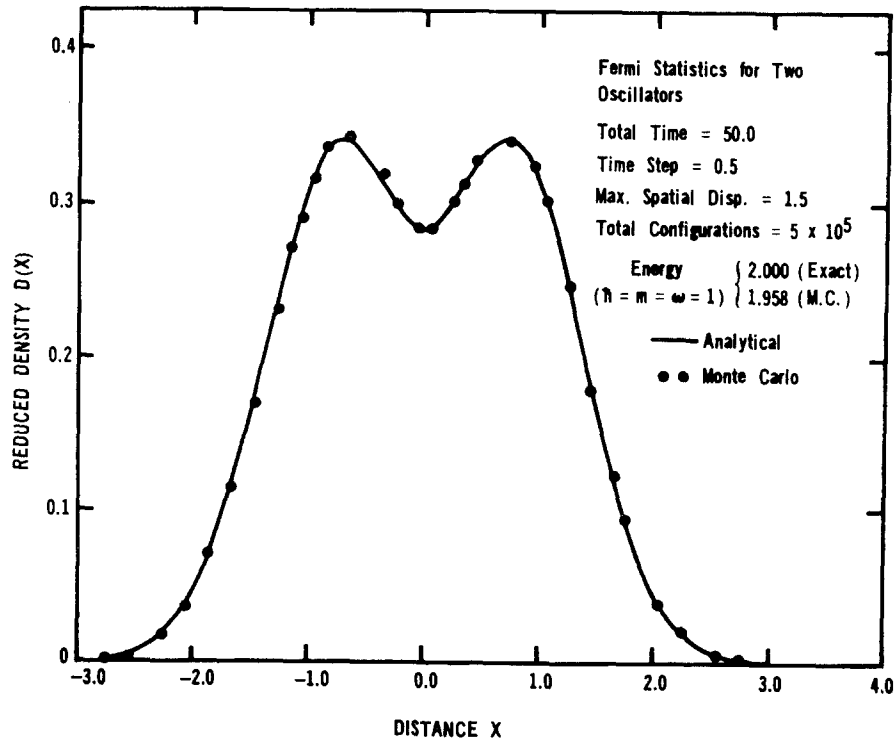

FIG. 2. Comparison of a Monte Carlo calculation with an analytic curve for the case of two oscillators obeying Fermi statistics.

That is, the absolute values, but not the angles, have been interchanged. This corresponds to radial antisymmetry, but angular symmetry.

V. NUMERICAL RESULTS AND DISCUSSION

Figures 1 and 2 show the results of the procedure as applied to a test case made up of a system of two noninteracting identical oscillators. This system has analytic solutions, if no potential interaction occurs between the oscillators. A similar "gedanken" type test problem for the two particle Coulomb central potential can be solved analytically, if the two particles do not have any potential between them. Equivalent results were obtained for both Fermi and Bose statistics on this system. A three-particle harmonic oscillator was also examined, with the approximation (alluded to in Sec. III) of using small time step propagators having two-particle exchange only. This system gave satisfactory results on the computer.

In order to handle the helium atom and the hydrogen negative ion, it is necessary to go to three dimensions, because the electron–electron interaction makes it impossible to simply write the propagator as a sum of various propagators associated with the angular momenta of a single particle, i.e., only L and L_z are good quantum numbers, not l_a, $l_{a,z}$, l_b, and $l_{b,z}$. Given this complication, there appeared to be no reason to use spherical polar coordinates, so the propagator was written in Cartesian coordinates.

For such a problem, display of the results can take several forms. The most obvious display would be to record ψ^2 as a function of all six coordinates. However, this would be unnecessarily demanding of computer storage and probably not too interesting anyway. Instead, one can recognize that the over-all system has spherical symmetry so that a one dimensional matrix can display the minimum meaningful information about the wavefunction; that is, the reduced density $D(r)$, where all other five coordinates have been integrated out.

If it is necessary, one can store other information of interest in other matrices. For example, electron–electron correlation can be stored, as can the average potential interaction between electrons as a function of r.

There are several ways to compute the energy. Because the Metropolis–Teller procedure, as we apply it, does not give the factor $\exp(-E_0\tau/h)$ in the result, we chose to directly compute E_0 by $E_0 = \int \psi \hat{H} \psi d\tau$. The integration can be performed using $D(r)$, if one has also stored information on the average electron–electron interaction in a separate one dimensional

TABLE I. Energies of He and H^- 1^1S and 2^3S states.

	Monte Carlo path integrals	Pekeris[18] variational
H^- 1^1S	0.499 a.u.	0.528 a.u.
H^- 2^3S	0.472 a.u.	0.499 a.u.
He 1^1S	2.997 a.u.	2.904 a.u.
He 2^3S	2.204 a.u.	2.175 a.u.

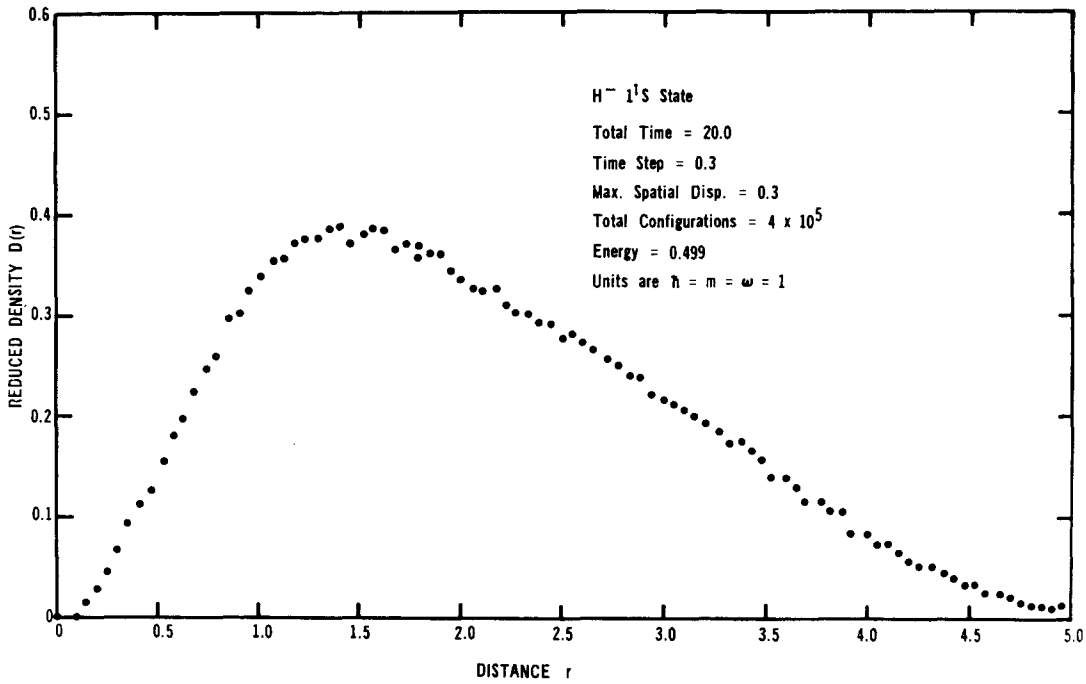

FIG. 3. One dimensional reduced density (including r^2 from volume element) for H^- 1^1S as computed from a path integral evaluation of $K_E(a', b'; a, b, \tau)_{a'=a,b'=b'}$, where K_E is of the form of Eq. (28).

array, this being the only nonspherical interaction in the Hamiltonian $\hat{H}$. Such an approach does not give the best value of E_0, for reasons associated with errors in numerical differentiation, but we regarded this as of secondary importance. We did not expect to be able to compete directly with accurate variational work on a two-particle system at this stage of development of the technique. $D(r)$ for H^- 1^1S, He 1^1S, and He 2^3S is displayed in Figs. 3, 4, and 5, respectively. For reasons mentioned below, it is expected that the peak in $D(r)$ is too low and broadened, particularly for the 1^1S states. This same procedural difficulty has caused us to delay presentation of electron–electron correlation, until it is overcome. The

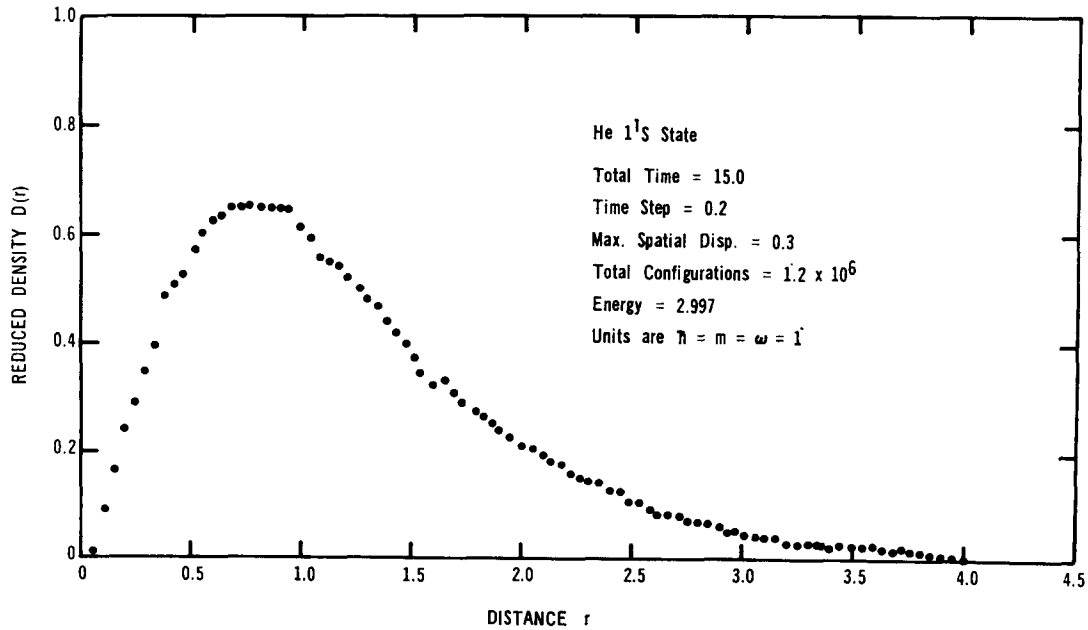

FIG. 4. One dimensional reduced density (including r^2 from volume element) for He 1^1S as computed from a path integral evaluation of $K_E(a', b'; a, b, \tau)_{a'=a,b'=b}$, where K_E is of the form of Eq. (28).

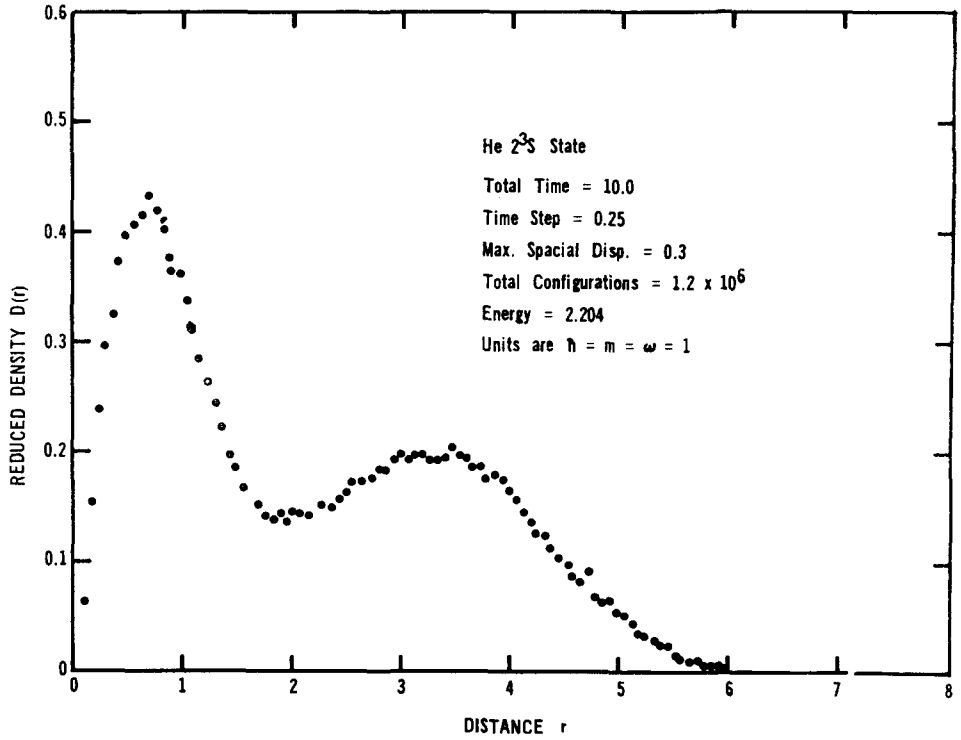

FIG. 5. One dimensional reduced density (including r^2 from volume element) for He 2^3S as computed from $K_E(a', b'; a, b, \tau)_{a'=a,b'=b'}$, where K_E is of the form of Eq. (29).

energies of the four systems, as we obtained them, are given in Table I, where they are compared with Pekeris's[18] variational results. Recall that our computations neglect spin–orbit and spin–spin interactions, as well as any direct relativistic effects.

Some of the error is due to the neglected terms and numerical approximations in computing E_0. However, by far the greatest error is due to the Monte Carlo sampling procedure not correctly sampling the space. This is because the Metropolis–Teller procedure, as described in Ref. 1, does not remember how far away from zero the "energy" of a given path is. For most applications of the procedure that is satisfactory. However, our propagators are developed from an expansion of $\exp[-\epsilon\hat{H}/\hbar]$, which is not accurate, if a given path has too high an "energy." Thus, in computing our results jump steps and values of ϵ were used which minimized this difficulty, but we could not eliminate it.

As is evident from Table I the problem is especially severe for H^-. Further extensions of this approach require the selection of a more appropriate sampling procedure.

VI. SUMMARY AND CONCLUSIONS

We have presented a procedure whereby the evaluation of Feynman path integrals in imaginary time can generate wavefunctions and energies for the ground states of quantum systems of many identical particles. The hydrogen negative ion and the helium atom are treated. At present a procedural difficulty limits the accuracy of the results.

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