

Feynman-Kac Path-Integral Calculation of the Ground-State Energies of Atoms

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Since its introduction in 1950, the Feynman-Kac path-integral approach has received limited use in spite of its simplicity in solving the quantum many-body problem. This paper provides a procedure to include permutation symmetries for identical particles in the Feynman-Kac method. It demonstrates that this formulation is ideally suited for massively parallel computers. This new method is used for the first time to calculate energies of the ground state of H, He, Li, Be, and B, and also the first excited state of He.

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In spite of its many successes, the original Feynman path-integral formalism [1] suffers from lack of mathematical rigor in the definition of the path integral itself. In fact, Cameron's theorem states that a finite (real or complex) Lebesgue measure for the path integral defined by Feynman does not exist [2], so other measures are required. The difficulty in implementing Feynman's method is evidenced by the fact that the path-integral solution for the hydrogen atom was achieved only recently [3]. One justification of the Feynman approach may be given in terms of the Wiener measure of a path integral [4]. This was first recognized by Kac, and reported in a famous but rarely cited paper [5] which provided a mathematically rigorous path-integral approach to quantum mechanics. The Wiener measure is a well-defined probability measure on the space of continuous functions and may be used to justify Feynman's path integral as an analytic continuation to imaginary time of a Wiener path integral. The Feynman-Kac (FK) method is well known among mathematicians and mathematical physicists [2,4,6], and is mathematically rigorous and relatively simple to implement. Surprisingly, it has been ignored almost completely for the last forty years as a computational technique. Numerical work with the procedure employing modern computers has not been reported for even the simplest systems during the forty years since the original work.

The purpose of this paper is to provide a simple method of treating permutation symmetries of systems of identical particles within the Kac method and to demonstrate that the FK formalism provides the basis for very simple and accurate calculations of ground-state properties of many-particle systems. Although a generalized FK method has been developed [7], it introduces considerable complexity through importance sampling distributions, and requires the fixed-node approximation. The first calculations using the original Feynman-Kac path-integral formulation are reported here for the atoms H, He, Li, Be, and B.

Kac's theory is developed as follows. For a given Hamiltonian, $H = -\Delta/2 + V(x)$, consider the following ini-

tial-value problem:

$$\frac{\partial U(t,x)}{\partial t} = [\frac{1}{2}\Delta - V(x)]U(t,x), \quad (1)$$

with $x \in R^d$ and $U(0,x) = 1$.

This may be viewed as the time-dependent Schrödinger equation for purely imaginary time, or simply as an equation defining the function $U(t,x)$ with a convenient auxiliary variable, t , which will be used in a limiting procedure to determine the eigenvalues of the time-independent Schrödinger equation for H . Here $-\Delta/2$ is the kinetic energy operator for the quantum system including all particles (e.g., nuclei and electrons). In the Born-Oppenheimer approximation (infinitely massive nuclei) it is replaced by the kinetic energy for N electrons, in which case the dimension of the space is $d = 3N$ in Eq. (1). The celebrated Kac formula [5], derived with restrictions upon allowed potentials, gives the solution of Eq. (1) in terms of a Wiener path integral and may be written

$$U(t,x) = E \exp \left[- \int_0^t V(x+B(s)) ds \right], \quad (2)$$

where $B(s)$ is the d -dimensional Brownian motion such that $B(0) = 0$, and E is the expected (average) value of the exponential term (see Ref. [4]). With restrictions on $V(x)$ and considering one-dimensional motion, Kac obtained a mathematically rigorous result for the lowest eigenvalue of the Hamiltonian which may be written as a limit of a functional of Brownian motion as follows:

$$\lambda_1 = \lim_{t \rightarrow \infty} -\frac{1}{t} \ln \left[E \exp \left[- \int_0^t V(x+B(s)) ds \right] \right]. \quad (3)$$

Many years after this equation was obtained Donsker and Varadhan [8] used large-deviation results to prove that it is equivalent to

$$\lambda_1 = - \inf \left\{ \int_{R^d} V(x) \varphi^2(x) dx + \frac{1}{2} \int_{R^d} \langle \nabla \varphi(x), \nabla \varphi(x) \rangle dx \right\}, \quad (4)$$

where φ is Lebesgue square integrable, $\varphi \in L^2(R^d)$ and $\|\varphi\|_{L^2} = 1$. Here "inf" indicates the minimum value for

any function φ in this class and \langle, \rangle is the dot product in R^d . Generalizations of the class of potential functions for which Eqs. (2)–(4) hold were given by Simon [6] and include most physically interesting potentials (positive or negative, with $1/x$ singularities allowed). Equation (4) is a statement that the Raleigh-Ritz variational formula is recovered by averaging the contributions of the potential $V(x)$ on the Brownian-motion path up to the time t , for large t . Restrictions on allowed trajectories of Brownian motion must be imposed, as discussed below, to get an energy for a state of the desired symmetry.

Extension of Eq. (3) to an arbitrary number of dimensions was implied by Kac [5], and has been given rigorous mathematical justification by Korzeniowski [9], who also used it to solve the classical heat equation and the Schrödinger equation for the hydrogen molecule [10]. In numerical implementation of Eq. (3) the $3N$ -dimensional Brownian motion is replaced by $3N$ independent, properly scaled one-dimensional random walks on a discrete grid. Generating N_{rep} independent replications $Z_1, Z_2, \dots, Z_{N_{\text{rep}}}$ of

$$Z_m = \exp \left[-\frac{1}{n} \sum_{l=1}^m V(x + W^m(l)) \right] \quad (5)$$

and using the law of large numbers, $(Z_1 + Z_2 + \dots + Z_{N_{\text{rep}}})/N_{\text{rep}} = Z(t)$, gives an approximation to $U(t, x)$ in Eq. (2) which combined with (3) gives

$$\lambda_1 \approx -\frac{1}{t} \ln Z(t). \quad (6)$$

Here $W^m(l)$, $m=1, 2, \dots, N_{\text{rep}}$, denotes the m th realization of $W(l)$, out of N_{rep} independently run simulations, where $W(l)$ is the l th step in a discrete random-walk approximation to $B(s)$ in $3N$ dimensions. For large t and N_{rep} this approximation approaches the energy given by (3), and forms the basis of a computational scheme for the lowest energy of a system of many particles with a prescribed symmetry. In actual practice a modified version is employed to improve convergence [5]:

$$\lambda_1 \approx -\frac{1}{t_2 - t_1} \ln \left[\frac{Z(t_2)}{Z(t_1)} \right], \quad (7)$$

where t_1 and t_2 are sufficiently large and different times.

The symmetries required for a purely spatial representation of the many-body wave function for a Hamiltonian which is independent of spin are best described by the Young's diagram of the desired number of fermions and total spin [11]. The procedure employed here is based upon the following considerations.

(i) To generalize Eqs. (2), (3), and (4) to states of a particular permutation symmetry the Brownian motion must be confined to an appropriate region of R^{3N} . In this case an indicator function, $1_{\{t^D > t\}}$, should multiply the exponential functions in (2) and (3), where $D \subset R^{3N}$, and τ^D is the first (random) time when the motion hits the

surface containing D . Before such time the function is 1 and after, if the event occurs, it is zero. In Eq. (4) the corresponding integration is then taken over the region D .

(ii) According to a result due to Ray [12] a solution to Eq. (3) which satisfies the condition $\varphi=0$ on the boundary of D will be found by eliminating all paths which hit the boundary of D by time t according to the procedure of (i).

(iii) For two particles ($N=2$) the subset D of R^6 is defined by

$$D = \{(x_1, y_1, z_1, x_2, y_2, z_2) | x_1 + y_1 + z_1 - x_2 - y_2 - z_2 > 0\}.$$

In this case the boundary is defined by the hyperplane equation $x_1 + y_1 + z_1 - x_2 - y_2 - z_2 = 0$. Note that this is a five-dimensional surface as it must be [7], but it is different from the one discussed in [13].

(iv) Permutation antisymmetric functions may be obtained by discarding paths crossing the permutation hyperplane for any pair of permutation antisymmetric variables in the Young's diagram. Restrictions are not required for variables in the Young's diagram which are permutation symmetric.

(v) Steps (i)–(iv) guarantee that the lowest-energy solution will be found with a given Young's diagram. To find other states with the same diagram requires a projection method or knowledge of the additional zeros of the excited state [7].

The present method is ideally suited for massively parallel computers since sampling over many paths may be done in parallel. The approximation to Brownian motion employs an integer grid which allows control of statistically insignificant trajectories and reduces the numerical error associated with the commonly used Gaussian distribution approximations [10]. The FK method was coded in FORTRAN 90 and executed on the Connection Machine model CM-2. A parallel trial consisted of 8192 Wiener path integrals running simultaneously, with the average over paths done at the end. Within each segment $3N$ processors were used for each trial, one processor for each coordinate of each of the N electrons in the system. The $3N \times 8192$ processors were all assigned separate random-number generators, which were used to create independent paths for all coordinates. A lagged-Fibonacci pseudo-random-number generator [14] with a period of 5.3×10^{15} values provided the approximate Brownian-motion distribution $W(l)$ of Eq. (5). The step size $\Delta x = 1/\text{scale} = 1/\sqrt{n}$ in atomic units was made uniform in space for each atom. Here the integer n is the total number of time steps. The parameter scale was chosen to give comparable accuracy for the first five atoms of the periodic table (from 30 for H to 75 for B), but the resulting ground-state energies have not been extrapolated to $\Delta x = 0$ at this time. The Brownian motion times ranged from 4 to 20 atomic units of time in Eq. (7), and the number of paths sampled was increased with the number of electrons per atom (from 64K for H to 256K

TABLE I. Atomic energies (minus signs omitted) for H, He, Li, Be, and B. Energies are reported in hartrees. Numbers in parentheses are estimated statistical errors. Exact values are estimates for the nonrelativistic Hamiltonian in the Born-Oppenheimer approximation. Experimental values are the sum of the ionization energies. VQMC and QMC are the results of elaborate variational Monte Carlo and quantum Monte Carlo calculations, respectively.

	H	He	Li	Be	B
HF ^a	0.5000	2.8617	7.4327	14.5730	24.5291
Kac	0.496(6)	2.906(5)	7.472(9)	14.659(9)	24.640(9)
Exact ^b	0.5000	2.9037	7.4781	14.6673	24.6539
Expt. ^c	0.4996	2.8990	7.4760	14.6644	24.6485
VQMC ^d	...	2.9036(1)	7.4768(3)	14.6370(6)	24.6156(6)
QMC ^e	...	2.9038(1)	7.4781(2)	14.6655(7)	...

^aReference [15].

^bReference [16].

^cReference [17].

^dReference [18].

^eReference [19].

for B). CPU times on the CM-2 ranged from 0.5 min for H to 23 min for B.

Ground-state energies for the first five atoms of the periodic table computed with the FK path-integral approach within the Born-Oppenheimer approximation are shown in Table I. Included in the table are Hartree-Fock (HF) [15], Kac, "exact," and experimental values for the ground-state energies of the atoms H, He, Li, Be, and B. The exact values are estimates made by Clementi and Veillard [16] for the nonrelativistic Hamiltonian neglecting nuclear motion. Estimated statistical errors for the last digit are shown in parentheses in Table I. Experimental values were obtained by adding up the ionization energies of each atom [17]. Also shown in Table I are large-basis-set variational and variational quantum Monte Carlo (VQMC) calculations [18] and other quantum Monte Carlo (QMC) results [19]. Since the original Kac method had not been applied to atoms, the main purpose of this paper was to test the Kac procedure. This was done for atoms in Table I using short computer runs. These rather brief runs already provide an accuracy of several millihartrees or a fraction of an eV/atom. By increasing the number of paths to 10^6 , the ground-state energy of He was found to be $-2.90382(17)$ hartrees, in close agreement with the exact value and QMC results [19]. Using 400000 paths the first excited state of He was found to be $-2.1771(28)$, which compares well with the recent calculation of Zhang and Kalos, $-2.1752(13)$ hartrees, and the exact result of -2.175229 hartrees [20]. More complete results for atoms, including excited states will be presented in another paper.

Evidence obtained in this study convinces the authors that the Feynman-Kac method can provide accurate ground-state energies for atoms. Contrary to other methods, no trial functions were needed at this point. The method is also easy to implement, even when including the permutation symmetries for fermion systems. The "sign problem" addressed in several recent Letters [20,21] is trivially solved here [a one line statement in the

computer code verifying the condition described in (ii) above]. The present method is free of the usual complexities of quantum chemistry such as multideterminantal wave functions (and their associated integrals and gradients) and requires, in effect, only the ability to toss a coin and add or subtract. The FORTRAN 90 parallel computer code consists of about 125 statements and can be employed also for molecules, with or without the Born-Oppenheimer approximation. The path integrals all consist of identical sets of operations which can be performed in parallel for different paths in almost identical times. This makes the parallel algorithms very efficient. As massively parallel computers become more massive and more available, this path-integral approach will become not only more accurate than other many-body methods, but also more efficient, especially when accurate results are needed for larger systems.

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