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

Korzeniowski et al. [1] have presented a method for solving the many electron problem based on Feynman-Kac path integrals. But the efficiency of the proposed method is low because no importance sampling is used, a spatial grid has been used unnecessarily, antisymmetry has not been correctly taken into account, and the results have converged to the wrong energy levels in violation of a variational bound.

The basis of the quantum Monte Carlo method (QMC) is that $\exp(-tH)$ can be interpreted as a diffusion process and can project out the ground state of H. To generate free Brownian trajectories and to take the average of the potential is a particularly easy task on a computer. However, such a scheme is highly inefficient: evaluating the time integral along a Brownian trajectory with a strongly fluctuating potential converges slowly both in the number of trajectories and in the discretization of "time."

Improved methods have been introduced [2]. With importance sampling one biases the walk using a drift given by $\nabla \ln \Psi_T$, and Ψ_T an assumed trial function [2–4]. Aside from the complications of computing the trial function, the computer program is almost as trivial. But the fluctuations due to the bare potential are replaced by the much smaller fluctuations of the local energy, $H\Psi_T/\Psi_T$. There are many applications directly based on the importance sampled Feynman-Kac formula [2].

In the diffusion Monte Carlo method [4, 5] the Feynman-Kac exponential weight is replaced by an equivalent branching process which further increases the efficiency allowing calculations of liquid and solid helium [3], the electron gas [6], and numerous molecular systems [7]. In the most advanced related method, Green's function Monte Carlo, there are no time step errors [3]. All these methods are mathematically equivalent.

To deal with fermions, Korzeniowski et al. have chosen the standard approach in QMC, the fixed-node approximation [5]. The Schrödinger equation with the boundary condition that the wave function vanish on an assumed hypersurface is solved by only taking walks that never cross it. The energy so obtained is an upper bound to the ground state having the same symmetry as the nodal surface and obtaining the exact energy only for the exact surface. Since the exact nodal surfaces of general electronic systems are not known, this method is only approximate.

For nodal surfaces, the authors projected the coordinates of each electron onto the $\{1, 1, 1\}$ direction and discarded random walks whenever two electrons with the same spin had the same projection. The nodes and resulting wave functions are too simple for real atoms or molecules, and in two of the examples (the He and Li atoms) their assumed nodal surface has the parity of an excited state. The lowest triplet ($S = 1$) state ($1s2s$) of the He atom has even parity and energy -2.1752 a.u. The odd parity triplet state ($1s2p$) has energy -2.1333 a.u. Since inversion maps a point from one nodal region to the other nodal region, their state has odd parity and by the variational principle its energy must be greater than the lowest triplet odd parity state, i.e., above -2.1333 a.u. To obtain the energy of the even parity state one must use the nodal condition $r_1 = r_2$. Similarly, their Li energy must be higher than -7.410 a.u. Hence there must be a perfectly compensating systematic error (greater than 0.042 a.u. for He and 0.068 a.u. for Li) to bring their results in precise agreement with the even parity energy levels.

It is possible to incorporate the exact fermion symmetry in QMC by using any antisymmetric function as an initial state and to project against at the end [2, 8], but the error of the energy becomes much larger than its mean value at large time or as the number of electrons increases. It is to this sign problem that much research has been addressed.

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