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Treatment of the Schrödinger Equation Through a Monte Carlo Method Based upon the Generalized Feynman–Kac Formula

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We present a new Monte Carlo method based upon the theoretical proposal of Claverie and Soto.[1] By contrast with other Quantum Monte Carlo methods used so far,[2–8] the present approach uses a pure diffusion process without any branching. The many-fermion problem (with the specific constraint due to the Pauli principle) receives a natural solution in the framework of this method: in particular, there is neither the fixed-node approximation not the nodal release problem which occur in other approaches (see, e.g., Ref. 8 for a recent account). We give some numerical results concerning simple systems in order to illustrate the numerical feasibility of the proposed algorithm.

OUTLINE OF THE METHOD[1]

Following previous authors,[9] a rather arbitrary Schrödinger Hamiltonian $H^{(0)}$ may be changed through a simple transformation into the infinitesimal generator $L^{(0)}$ of a diffusion process, namely $L^{(0)} = \phi_0^{(0)}(E_0^{(0)} - H^{(0)})(1/\phi^{(0)})$, where $E_0^{(0)}$ and $\phi_0^{(0)}$ denote, respectively, the energy and eigenfunction of the (mathematical) ground state of $H^{(0)}$ (this process was also introduced by Nelson,[10] but in a quite different perspective). The operators $L^{(0)}$ and $E_0^{(0)} - H^{(0)}$ are similar; consequently, the quantum-mechanical Green's function of $H^{(0)}$ is closely related with the Green's function of $L^{(0)}$, namely the transition probability density of the

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diffusion process: hence, the possibility of relating quantum-mechanical quantities of interest with suitable averages (amenable to computer simulation) pertaining to the diffusion process. Through its n-time probability densities, this process defines a measure on the set of sample paths (function space), and this measure defines a functional (path) integral, which generalizes the Wiener functional integral. Then we consider a Hamiltonian $H = H^{(0)} + V$ and using the diffusion process associated with $H^{(0)}$ we have, for a broad class of operators V, a generalized Feynman–Kac formula[1]:

$$I(t) = \langle f\phi_0^{(0)} |\, e^{-t(H-E_0^{(0)})} \,| g\phi_0^{(0)} \rangle = \int_\Omega f^*[\vec{X}(0)]\; g[\vec{X}(t)] \times \exp\left[-\int_0^t V[\vec{X}(s)]\, ds \right] D^{H^{(0)}}\vec{X} \tag{1}$$

where f and g are two arbitrary functions such that $\int f(\phi_0^{(0)})^2\, dx < +\infty$ and $\int g(\phi_0^{(0)})^2\, dx < +\infty$ (it is appropriate to mention here a related work by Pollock and Ceperley,[11] see especially their Appendix A). The diffusion process associated with $H^{(0)}$ is ergodic as soon as the density $(\phi_0^{(0)})^2$ is integrable; choosing $H^{(0)} = H - V$ endowed with this property, averages over paths can be evaluated through time-averaging along any sample path $X^{(0)}(t)$ of the diffusion process

$$\int_\Omega f^*[\vec{X}(0)]\; g[\vec{X}(t)] \exp\left[-\int_0^t V[\vec{X}(s)]\, ds \right] D^{H^{(0)}}\vec{X} = \lim_{T \to +\infty} \frac{1}{T} \int_0^T f^*[\vec{X}^{(0)}(\tau)]\; g[\vec{X}^{(0)}(\tau + t)] \exp\left[-\int_\tau^{t+\tau} V[\vec{X}^{(0)}(s)]\, ds \right] d\tau \tag{2}$$

The right-hand side of this equation can be evaluated numerically from the computer-simulated trajectory $X^{(0)}(t)$ and, according to the generalized Feynman–Kac formula we get a *numerical* evaluation of the function $I(t)$, whose analytical expression in terms of the spectral expansion of H writes

$$I(t) = \langle f\phi_0^{(0)} |\, e^{-t(H-E_0^{(0)})} \,| g\phi_0^{(0)} \rangle = \sum_i \langle f\phi_0^{(0)} | \phi_i \rangle \langle \phi_i | g\phi_0^{(0)} \rangle \times \exp[-(E_i - E_0^{(0)})\, t] \tag{3}$$

E_i and ϕ_i denote the eigenvalues and eigenfunctions of H, respectively. The spectrum of H can thus be obtained by analyzing $I(t)$ into a sum of real

exponentials. Extracting the leading exponential $\exp[-(E_0 - E_0^{(0)})\,t]$ can be done by considering the behavior of $I(t)$ for $t \to \infty$. We also performed a more complete analysis by resorting to an original procedure,[12] namely the Padé–Laplace (or Padé z transform) method. The essential idea is to apply to the function $I(t)$ a suitable integral transform (namely Laplace or z transform for the case of analysis into exponentials), and to get an analytical (rational) representation of this transform in terms of Padé approximants, which are in turn decomposed into partial fractions, which give the desired decomposition.

According to the Pauli principle, the physical states belong to any one of the representations of the symmetric group whose Young diagrams have at most two columns. If we denote by P the projection operator corresponding to the subspace of eigenfunctions to be selected, we just have to choose f and/or g such that $P|f\phi_0^{(0)}\rangle = |f\phi_0^{(0)}\rangle$ and/or $P|g\phi_0^{(0)}\rangle = |g\phi_0^{(0)}\rangle$, then the amplitudes of the exponentials corresponding to levels excluded by the Pauli principle vanish. We present an example (see (c) below) of this symmetry-adapted procedure (lowest state of *odd* parity for the anharmonic oscillator), which illustrates the possibility of dealing with the physical ground state of systems with more than two fermions.

EXAMPLES PRESENTED

(a) Some low excitation energies of the harmonic oscillator, using only the knowledge of the ground state wave function (check that $L^{(0)}$ and $E_0^{(0)} - H^{(0)}$ have the same spectrum)

(b) Energy of the mathematical (or "bosonic") ground state (which is physical for systems involving at most two fermions) for the quartic anharmonic oscillator and for the helium atom (preliminary results)

(c) Energy of states belonging to some prescribed symmetry type (as mentioned above, this is needed if we want to get states fulfilling the Pauli principle for more than two fermions): states of *odd* parity with respect to the change $x/-x$ (essentially the lowest one), for the quartic anharmonic oscillator

DISCUSSION OF SOME COMPUTATIONAL ASPECTS OF THE METHOD

(a) Since the method is fully of Monte Carlo type (no preliminary computation of a trial wave function as is required in the methods using the fixed-node approximation), exact results may in principle be expected,

within the statistical error due to the finite simulation time; noticeably, memory requirements remain perfectly bounded.

(b) The Monte Carlo simulation program is *very short* (about 400 Fortran statements presently) and it may be readily adapted to any kind of system, since the only requirement is the explicit knowledge of the additional potential $V = H - H^{(0)}$. Noticeably, it should be possible to deal with a *full* molecular Hamiltonian (including "nuclear motion").

(c) The amount of computation is expected to increase slowly with the number n of particles (roughly like n^2 when two-body interaction potentials are involved).

(d) Besides the problem of using a large enough simulation time T (in order to reach convergence of the time average), we put into evidence three possible sources of error in the method:

(1) insufficient quality of the pseudo-random number generator—thus, the standard congruential generator using 31-bit integers was actually not sufficient (too-short period) and we had to implement a generator using larger integers (up to 56 bits), accordingly having a larger period.

(2) Systematic error in generating the sample trajectory of the diffusion process—due to the use of a finite step Δt in the numerical solution of the stochastic differential equation (this defect is analogous to the so-called "short-time approximation" discussed by previous authors, Refs. 2–8, in connection with other Monte Carlo methods based upon branching diffusion processes). This error can be suppressed completely by using the exact transition probability (corresponding to the used time-step Δt), whenever it is available.

(3) The error pertaining to the numerical evaluation of the integral over the potential V in (1) or (2)—due to the use of a finite step $\Delta t'$ in the numerical integration procedure (in actual practice $\Delta t'$ has to be some multiple of the time-step Δt considered above).

Due to the possibility of eliminating the error (2) and of reducing the errors (1) and (3) to a negligible amount, it is possible to keep under control each one of these sources of error separately, and this opens the way to the designing of numerical procedures with optimal efficiency.

(e) Not surprisingly, there is a price to pay for all these advantages; namely, the amount of computation appears rather large for the small systems considered so far. But here it must be emphasized that the method is very well-suited for vector computing and more specifically for *multi-tasking* proper: indeed, instead of generating a single sample trajectory over

a total time T, it is possible to generate *simultaneously* N trajectories over a time T/N, and to take the mean value of the N results thus obtained. We feel that this feature provides one of the most promising lines of development for Monte Carlo methods such as the one considered here.

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