STOCHASTIC METHODS IN QUANTUM MECHANICS

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ABSTRACT. This paper discusses different ways of expressing quantum properties as stochastic averages. It is explained how such a formal mathematical connection between quantum mechanics and stochastic processes may be used to compute quantum observables (Monte Carlo simulation). The problems in applying stochastic methods to fermion systems are discussed and a few illustrative results for atoms and molecules are presented.

1. INTRODUCTION

In the present paper we are concerned with the treatment of the nonrelativistic Schrödinger equation using stochastic (or Monte Carlo) methods. The possibility of solving the Schrödinger equation using such techniques may be easily understood when noticing the similarity between the time-dependent Schrödinger equation in imaginary time and a generalized diffusion equation. Most of the Monte Carlo methods developed so far rest on this remark and then make use of a diffusion-like stochastic process in configuration space. However, stochastic methods are more general and, as an example, stochastic processes such as Poisson processes may be used (see below). The main object of this paper is to emphasize on the possibility of expressing quantum properties as stochastic averages. A key point is that the underlying stochastic process from which averages are taken may be chosen in many different ways. To illustrate this idea we present a number of methods based on various stochastic processes. The methods presented here are the so-called variational, diffusion and pure diffusion Monte Carlo methods and a method based on the use of a generalized Poisson process. Other approaches have been developed (1-6) but there will not be discussed here for reasons of space. An important example is the so-called Green's function Monte Carlo method (1-4) which has led to some important results. Once the mathematical connection between quantum and stochastic mean values has been performed, the numerical evaluation of the stochastic averages may be achieved by using standard statistical tools. An important point associated with the practical implementation of a Monte Carlo method is that the efficiency of calculations (i.e. the accuracy obtained from a given

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amount of computer time) is strongly dependent on the stochastic process used and on the property evaluated. To be able to exhibit a large number of different stochastic processes for evaluating a given quantum property is therefore important. In this paper the attention is mainly focused on the theoretical part of stochastic methods; the main features of the practical implementation are only outlined, for a detailed presentation the reader is referred to the original works. A few illustrative results for atoms and molecules are presented. The problems related to the extension of such results to more complex systems are not discussed here (for such a discussion see e.g. Refs. 7,8). Finally, in section 3 the problem of imposing the constraints resulting from the Pauli principle for fermion systems is discussed in the framework of Monte Carlo methods.

2. METHODS

Here we are concerned with quantum systems which can be described by a Hamiltonian written in the form

$$H = -\frac{1}{2}\vec{\nabla}^2. + V(\vec{x}) \qquad (1)$$

where $\vec{x}$ refers to the 3N particle coordinates. Atomic units are used throughout the paper.

2.1. Variational Monte Carlo method

The purpose of the method presented here is to evaluate the total energy associated with a given trial wave function ψ by using a stochastic procedure. This procedure represents an alternative approach to the standard method based on the expansion of ψ in terms of products of simple one-particle functions (gaussian in general) suitable for an easy evaluation of the many-electron integrals. Unfortunately, such an approach prevents using sophisticated forms for ψ . In contrast, in the variational Monte Carlo method no expansion is performed and a rather arbitrary form for ψ may be used without practical difficulties. In particular, it is possible to employ high-quality trial wave functions which explicitly contain the interelectron coordinates r_{ij} to properly describe the electron-electron interaction. The method presented here seems to have been first applied by McMillan (9) for boson systems and by Ceperley et al. (10) for fermion systems.

The variational energy is defined as

$$E(\psi) = \frac{\int \psi H \psi \, d\vec{x}}{\int \psi^2 \, d\vec{x}} \qquad (2)$$

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$$E(\psi) = \int E_L(\vec{x})p(\vec{x})\ d\vec{x} \tag{3}$$

where the so-called local energy E_L (depending on $\vec{x}$) is written

$$E_L(\vec{x}) = \frac{H\psi}{\psi} \tag{4}$$

and $p(\vec{x})$ is a positive function given by

$$p(\vec{x}) = \frac{\psi^2}{\int \psi^2\ d\vec{x}} \tag{5}$$

It should be noted here that only real-valued trial wave functions are used in this paper since H (Eq. (1)) is real.

Now, the method consists in finding a stochastic process admitting $p(\vec{x})$ as stationary density. Such a process is by no means unique, two examples are then presented in the following. Once the process has been determined, the energy mean value may be rewritten as

$$E(\psi) = < E_L > \tag{6}$$

where < ... > stands for the expectation with respect to the stationary density of the process.

This is a first (trivial) example of a quantum property (the energy mean value) expressed as a stochastic average. As concerns the stochastic process, a first possibility is to use the Markov chain in configuration space resulting from the famous algorithm of Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller (11). An essential property of this algorithm based on an acceptation/rejection procedure is that the only quantity needed in the simulation is the ratio $p(\vec{x})/p(\vec{x}')$ (where $\vec{x}$ and $\vec{x}'$ are two arbitrary points in configuration space), a quantity which is independent of the unknown normalization term. For a presentation of this algorithm widely used in many fields of physics, the reader is referred to Refs. (11,12). A second possibility consists in defining a continuous diffusion process in configuration space. Diffusion processes are characterized by the set of their n-time probability densities which obey the following general Fokker-Planck equation: (13)

$$\frac{\partial W}{\partial t} = L\ W \tag{7}$$

where L, the Fokker-Planck operator, is given by

$$L = \sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j} (D_{ij}(\vec{x}).) - \sum_i \frac{\partial}{\partial x_i} (b_i(\vec{x}).) \tag{8}$$

b_i is the so-called drift vector and D_{ij} the so-called diffusion matrix. The stationary density $p(\vec{x})$ of the process is defined by

$$\frac{\partial p}{\partial t} = 0 \tag{9.a}$$

or, equivalently

$$Lp = 0 \tag{9.b}$$

Now, choosing

$$D_{ij} = \frac{1}{2} \delta_{ij} \tag{10}$$

the drift vector corresponding to the stationary density p is easily obtained, we find

$$b_i = \frac{1}{2} \frac{\partial}{\partial x_i} \operatorname{Log} p = \frac{1}{2} \frac{\partial p / \partial x_i}{p} \tag{11}$$

According to Eqs. (9-11), it is then always possible to construct a diffusion process admitting a given arbitrary positive function as stationary density. Now, the problem of evaluating the stochastic average given by Eq. (6) arises. For that, the energy mean value is rewritten as

$$E(\psi) \cong \frac{1}{N} \sum_{i=1}^{N} E_L(\vec{x}^{(i)}) \tag{12}$$

where N is large enough, the equality being valid only as N goes to infinity. $\{\vec{x}^{(i)}\}$ denotes a set of N points distributed according to $p(\vec{x})$. Such a set may be obtained by taking N points on any sample trajectory (random walk) of the diffusion process. Sample trajectories are generated by using the Langevin equation associated with the process. This equation is written (13)

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$$d\vec{X}(t) = \vec{b}(\vec{X}(t))\,dt + d\vec{W}(t) \qquad (13)$$

where $\vec{W}$ is the multidimensional Wiener process and $\vec{b}$ is the drift vector given by Eq. (11). A discretized form suitable for computer simulation is

$$\vec{X}(t+\Delta t) = \vec{X}(t) + \vec{b}(\vec{X}(t))\,\Delta t + \vec{\eta}\,\Delta t^{\frac{1}{2}} \qquad (14)$$

where the $\vec{\eta}$' denote successive samples of a multidimensional Gaussian random vector whose components verify $\langle\eta_i\rangle = 0$ and $\langle\eta_i\eta_j\rangle = \delta_{ij}$. The integration of the Langevin equation (Eq. (13)) using the discretized form (Eq. (14)) leads to the so-called "short-time approximation" resulting from the use of a finite time step Δt instead of an infinitesimal one as required by the continuous form (Eq. (13)). Thus the estimator of the energy is only exact as the time step used in the simulation goes to zero. In contrast, no bias is introduced when using the Metropolis algorithm since it is based on a discrete Markov chain instead of a continuous diffusion process.

We present in Table I some applications of the variational Monte Carlo method for atoms and molecules. The results presented here are issued from a work of Moskowitz and Kalos. (12) The trial wave functions used in these calculations are of the form

$$\psi(\vec{x}) = \det D^{\alpha} \det D^{\beta} \exp\Big(\sum_{i>j} U_{ij} \Big) \qquad (15)$$

where $\det D^{\alpha}$ and $\det D^{\beta}$ denote determinants of one-electron space orbitals for electrons of α and β spin, respectively, and the U_{ij} denote two-particle functions. The product of space-determinants is introduced in order to take account of the antisymmetry required by the Pauli principle. This particular form is presented in section 3.

Table I. Total ground-state energies obtained with the variational Monte Carlo method. (12) Energies are in a.u. Statistical uncertainties are indicated in parentheses. References for the quoted values may be found in Ref. 12.

	He	H_2	Li_2
E(Monte Carlo)	-2.9024(5)	-1.1568(5)	-14.932(3)
E(Hartree-Fock limit)	-2.86168	-1.13363	-14.8719
E(exact)	-2.90372	-1.1746	-14.9967

2.2 Diffusion Monte Carlo method

The so-called Diffusion Monte Carlo (DMC) method has been designed for removing the variational approximation inherent to the method presented above. This is accomplished by defining a generalized diffusion process admitting the following stationary density

$$p(\vec{x}) = \frac{\psi\phi_0}{\int \psi\phi_0 \, d\vec{x}} \tag{16}$$

where ϕ_0 stands for the exact unknown wave function, instead of $p(\vec{x}) = \psi^2 / \int \psi^2 \, d\vec{x}$ as used previously. This latter distribution was obtained as stationary density of the diffusion process corresponding to the following Fokker-Planck operator:

$$L = \frac{1}{2} \vec{\nabla}^2 - \vec{\nabla}(\vec{b}.) \tag{17.a}$$

with

$$\vec{b} = \frac{1}{2} \vec{\nabla} \mathrm{Log}\, \psi^2 \tag{17.b}$$

Now, a "generalized" Fokker-Planck operator is constructed by adding a multiplicative scalar operator to L. We write

$$L^* = L - (E_L(\vec{x}) - E_T) \tag{18}$$

where $E_L(\vec{x})$ is the local energy defined by Eq. (4) and E_T a trial energy. After simple algebra, it is easy to be convinced that the stationary density of this new process, defined by $L^*p = 0$, is $p(\vec{x})$ given by Eq. (16) if E_T is chosen to be the exact unknown energy E_0.

The new term added to the usual Fokker-Planck operator describes a branching process. Indeed, if this term were present alone in L^*, the resulting equation of evolution would be

$$\frac{\partial W}{\partial t} = - (E_L(\vec{x}) - E_T) \, W \tag{19}$$

that is, a rate equation. In practice, the branching process is thus simulated by creating a number of replicas of each point in configuration space according to the magnitude of the local energy. When E_T is adjusted to be the true ground-state energy, E_0, we have

$$< E_L - E_0 > = 0 \qquad (20)$$

and thus the number of points is stabilized.

Finally, the numerical simulation consists in deplacing a finite set of points through configuration space using the Langevin equation(Eq.(14)) for the pure diffusion part of L^* and branching according to Eq. (19) for the scalar part. The stabilization of the total number of points leads to an estimator of the exact energy, E_0, according to Eq. (20). A detailed presentation of the method may be found in the basic paper of Reynolds et al. (14) (See also Anderson (15)). A few illustrative numerical results for atoms and molecules are displayed in Table II. The trial wave functions used in these calculations are of the form (15). The difference between the Monte Carlo results presented in Table II and the exact results is due to the so-called fixed-node approximation resulting from the use of trial wave functions with non-exact nodes. This approximation which is quite good is discussed in section 3 devoted to the many-fermion problem.

Table II. Total ground-state energies obtained with the diffusion Monte Carlo method. (14) Energies are in a.u. Statistical uncertainties are indicated in parentheses. References for the quoted values may be found in Ref. 14.

	H_2	LiH	Li_2	H_2O
E(Monte Carlo)	-1.174(1)	-8.067(2)	-14.990(2)	-76.377(7)
E(Hartree-Fock)	-1.1336	-7.987	-14.872	-76.0675
E(exact)	-1.17447	-8.0699	-14.9967	-76.4376

2.3. Pure diffusion Monte Carlo method

The method presented here is based on the pure diffusion process introduced above (Eqs. (17)). In contrast to the Diffusion Monte Carlo method, no branching is involved.

In the present approach it is convenient to rewrite the Hamiltonian of the system in the form

$$H = H^{(0)} + V_p \tag{21}$$

where $H^{(0)}$ and V_p are called "reference Hamiltonian" and "perturbing potential", respectively. The reference Hamiltonian is constructed from the trial wave function ψ as follows

$$H^{(0)} = -\frac{1}{2}\vec{\nabla}^2 + \frac{1}{2}\frac{\vec{\nabla}^2\psi}{\psi} \tag{22}$$

Stated differently, $H^{(0)}$ is the Hamiltonian of the form (1) verifying

$$H^{(0)}\,\psi = 0 \tag{23}$$

From Eqs. (21) and (22) we derive easily the expression of the perturbing potential in terms of the trial wave function. One obtains

$$V_p = V - \frac{1}{2}\frac{\vec{\nabla}^2\psi}{\psi} \tag{24}$$

or, equivalently

$$V_p = \frac{H\psi}{\psi} \tag{25}$$

Thus V_p coincides with the local energy introduced above (Eq. (4)).

The time-dependent Green's function (in imaginary time) is defined as

$$G(\vec{x},\vec{y};t) = <\vec{x}\,|e^{-tH}|\,\vec{y}> \tag{26}$$

For our purpose, let us define a little more general quantity

$$I^{f,g}(t) = <f\psi\,|e^{-tH}|\,g\psi> \tag{27}$$

where f and g are two arbitrary functions of $\vec{x}$. By choosing f and g respectively as $\delta_{\vec{x}}/\psi$ and $\delta_{\vec{y}}/\psi$ (where δ is the Dirac's δ-function) the usual Green's function (Eq.(26)) is recovered.

Now, it is shown how the generalized Green's function defined by Eq. (27) can be expressed as a stochastic average with respect to the

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reference diffusion process. We only give here the essential steps of the derivation. For the complete derivation the reader is referred to Ref. 16. A first basic ingredient consists in using the Trotter formula:

$$e^{A+B} = \lim_{n\to+\infty} \left(e^{A/n}e^{B/n}\right)^n \tag{28}$$

where A and B denote two arbitrary operators (which do not commute in general). Thus $I^{f,g}(t)$ may be expressed as

$$I^{f,g}(t) = \lim_{n\to+\infty} \langle f\psi \,|\, \left(e^{-\Delta t H^{(0)}} e^{-\Delta t V_p}\right)^n \,|\, g\psi \rangle \tag{29}$$

with $\Delta t = t/n$

Introducing the spectral resolution of operator $\vec{X}$, namely

$$1\!\!1 = \int d\vec{x}\; |\vec{x}\rangle\langle\vec{x}| \tag{30}$$

between each operator involved in the matrix element of the right hand side of Eq. (29), we obtain after some manipulations

$$I^{f,g}(t) = \lim_{n\to+\infty} \int \prod_{i=0}^{n} d\vec{x}_i \; f(\vec{x}_0) g(\vec{x}_n)\; e^{-\Delta t \sum_{i=1}^{n} V_p(\vec{x}_i)} \times \left\{ \psi(\vec{x}_0)\psi(\vec{x}_n) \prod_{i=0}^{n-1} \langle \vec{x}_i | e^{-\Delta t H^{(0)}} | \vec{x}_{i+1} \rangle \right\} \tag{31}$$

The key idea of the present approach is to interpret the quantity in parentheses as the (n+1)-time probability density of the diffusion process, defined by Eqs. (17). For that, we first remark that the reference Hamiltonian $H^{(0)}$ is connected to the Fokker-Planck operator L by the following similarity transformation

$$L = -\,\psi\, H^{(0)} \frac{1}{\psi}\ . \tag{32}$$

From Eq. (32) it follows

$$\langle \vec{x} | e^{-\Delta t H^{(0)}} | \vec{y} \rangle = \frac{\psi(\vec{x})}{\psi(\vec{y})} \langle \vec{y} | e^{\Delta t L} | \vec{x} \rangle \tag{33}$$

In the latter formula $\langle\vec{y}|e^{\Delta tL}|\vec{x}\rangle$ is the time-dependent Green's function of the Fokker-Planck equation associated with L , i.e., the transition probability density of the diffusion process. We thus write

$$p(\vec{x}]\vec{y},\Delta t) = \langle\vec{y}|e^{\Delta t}|\vec{x}\rangle \tag{34}$$

Note that in this notation $\vec{x}$ is the conditioning variable. Using Eqs.(33) and (34) we then obtain

$$\psi(\vec{x}_0)\psi(\vec{x}_n)\prod_{i=0}^{n-1}\langle\vec{x}_i|e^{-\Delta tH^{(0)}}|\vec{x}_{i+1}\rangle = \psi^2(\vec{x}_0)\prod_{i=0}^{n-1}p(\vec{x}_i]\vec{x}_{i+1},\Delta t) \tag{35}$$

Now, by invoking the fundamental property for stationary Markovian processes, namely

$$p_n(\vec{x}_1,t_1;\ldots;\vec{x}_n,t_n) = p_1(\vec{x}_1)\prod_{i=1}^{n-1}p(\vec{x}_i]\vec{x}_{i+1},t_{i+1}-t_i) \tag{36}$$

where p_n is the n-time probability density of the diffusion process, Eq. (35) may be rewritten as

$$\psi(\vec{x}_0)\psi(\vec{x}_n)\prod_{i=0}^{n-1}\langle\vec{x}_i|e^{-\Delta tH^{(0)}}|\vec{x}_{i+1}\rangle = p_{n+1}(\vec{x}_0,0;\ldots;\vec{x}_n,n\Delta t=t) \tag{37}$$

Finally, expression (31) for $I^{f,g}(t)$ is written

$$I^{f,g}(t) = \lim_{n\to+\infty}\int f(\vec{x}_0)g(\vec{x}_n)\ e^{-\Delta t\sum_{i=1}^{n}V_p(\vec{x}_i)} \times p_{n+1}(\vec{x}_0,0;\vec{x}_1,\Delta t;\ldots;\vec{x}_n,t)\prod_{i=0}^{n}d\vec{x}_i \tag{38}$$

The right hand side of Eq. (38) may be interpreted as the expectation value of the functional $f(\vec{x}(0))g(\vec{x}(t))\exp(-\int V_p(\vec{x}(s))ds)$ over the trajectories (or sample paths) of the reference diffusion process. It is of interest to note that, in contrast to other methods, not only the stationary density of the diffusion process is used, but also its dynamics through the transition probability density. In order to illustrate the basic idea of the paper the quantum matrix element is written in the form of the following stochastic average

$$I^{f,g}(t) = \langle\ f(\vec{X}(0))g(\vec{X}(t))\ \exp(-\int_0^t V_p(\vec{X}(s))ds)\ \rangle \tag{39}$$

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where < ... > stands for the expectation value with respect to the diffusion process.

Another point of view is to consider Eq. (38) as defining a functional integral. (17,18) We thus write

$$I^{f,g}(t) = \int_{\Omega(0,t)} f(\vec{X}(0))g(\vec{X}(t)) \exp(-\int_0^t V_p(\vec{X}(s))ds)\, D^{\psi}X \quad (40)$$

where $D^{\psi}X$ denotes the diffusion functional measure associated with the diffusion process and Ω(0,t) the set of continuous trajectories defined in (0,t). In fact, the basic formula above (Eq. (40)) is a generalization of the well-known Feynman-Kac formula (17,18). This latter formula may be recovered by choosing the constant as function ψ and $\delta_{\vec{x}}/\psi$ and $\delta_{\vec{y}}/\psi$ as functions f and g, respectively. Now, it is possible to further extend the generalized Feynman-Kac (GFK) formula (Eq. (40)) into a so-called full generalized Feynman-Kac (FGFK) formula by inserting local operators $A_i(\vec{x})$ at different times into the evolution operator e^{-tH}. Essentially, the derivation is identical (see Ref. 16) and we obtain

$$I^{f,g}_{A_1 \ldots A_q}(t;t_1 \ldots t_q) = \langle f\psi | e^{-t_1 H} A_1 e^{-(t_2-t_1)H} A_2 \ldots A_q e^{-(t-t_q)H} | g\psi \rangle$$

$$= \int_{\Omega(0,t)} f(\vec{X}(0))A_1(\vec{X}(t_1)) \ldots A_q(\vec{X}(t_q))g(\vec{X}(t))\exp(-\int_0^t V_p(\vec{X}(s))ds)\, D^{\psi}X \quad (41)$$

From the general quantum matrix element involved in the latter formula, the desired quantum observables may be extracted. (16) Let us present some examples. In the following formulas the subscript i_0 refers to the lowest eigenstate of H (denoted as ϕ_{i_0}) with non-zero overlap with functions fψ and gψ.

Total energy:

$$E_{i_0} = \lim_{t\to+\infty} -\frac{1}{t} \operatorname{Log} \langle f(\vec{X}(0))g(\vec{X}(t))\exp(-\int_0^t V_p(\vec{X}(s))ds) \rangle \quad (42)$$

First order mean values:

$$\frac{\langle \phi_{i_0}|A|\phi_{i_0}\rangle}{\langle \phi_{i_0}|\phi_{i_0}\rangle} = \lim_{t\to+\infty} \frac{\langle f(\vec{X}(0))A(\vec{X}(t_1))g(\vec{X}(t)) \exp(-\int_0^t V_p(\vec{X}(s))ds) \rangle}{\langle f(\vec{X}(0))g(\vec{X}(t)) \exp(-\int_0^t V_p(\vec{X}(s))ds) \rangle} \quad (43)$$

$$\forall t_1 \in]0,t[$$

Second order mean values:

$$C_{AB}(\tau) = \sum_k \langle\phi_{i_0}|A|\phi_k\rangle\langle\phi_k|B|\phi_{i_0}\rangle \, e^{-\tau(E_k-E_{i_0})}$$

$$= \lim_{t\to+\infty} \frac{\langle f(\vec{X}(0))A(\vec{X}(t_1))B(\vec{X}(t_1+\tau))g(\vec{X}(t))\exp(-\int_0^t V_p(\vec{X}(s))ds)\rangle}{\langle f(\vec{X}(0))g(\vec{X}(t))\exp(-\int_0^t V_p(\vec{X}(s))ds)\rangle} \quad (44)$$

$$\forall t_1 \in \,]0,t[$$

From $C_{AB}(\tau)$ it is possible to show that response properties such as static or dynamic polarizabilities may be derived. (16)

In principle, the numerical evaluation of the stochastic averages would require to sum over the unlimited number of stochastic trajectories in configuration space defined in (0,t). In practice, it is possible to escape from this difficulty by using the ergodic character of the reference diffusion process. This latter property holds only if the stationary density of the process is integrable. (16,19) In the present case it requires that the trial wave function is square-integrable, a condition which is easily fulfilled. Thus, by using the ergodic property the ensemble-averages (over the complete set of trajectories) may be expressed as time-averages along any single sample trajectory (or any finite number of sample trajectories) of the process

$$\langle f(\vec{X}(0))A_1(\vec{X}(t_1))\ldots A_q(\vec{X}(t_q))g(\vec{X}(t)) \exp(-\int_0^t V_p(\vec{X}(s))ds) \rangle$$

$$= \lim_{T\to+\infty} \frac{1}{T}\int_0^T f(\vec{X}^{(0)}(\tau)) \, A_1(\vec{X}^{(0)}(t_1+\tau))\ldots A_q(\vec{X}^{(0)}(t_q+\tau)) \, g(\vec{X}^{(0)}(t+\tau))$$

$$\times \exp(-\int_\tau^{t+\tau} V_p(\vec{X}^{(0)}(s))ds) \, d\tau \quad (45)$$

where $\vec{X}^{(0)}(s)$ denotes an arbitrary trajectory of the diffusion process. Such a trajectory may be obtained by using the Langevin equation (Eqs. (13) and (14)) as explained in subsection 2.1.

Finally, the main ideas of the present quantum Monte Carlo method can be summarized as follows

1. Express the desired quantum observables in terms of stochastic averages by using the FGFK formula.
2. Invoke the ergodic property to convert the ensemble-averages into time-averages along any sample path of the diffusion process.
3. Use the discretized Langevin equation for constructing step by step an arbitrary sample path.

We present in Tables III and IV some results (20) for small systems.

Table III. Total ground-state energies obtained with the pure diffusion Monte Carlo method. (20) Energies are in a.u. Statistical uncertainties are indicated in parentheses. References for the quoted values may be found in Ref. 20.

	He	Be^{++}	H_2
E(Monte Carlo)	-2.9038(10)	-13.655(11)	-1.175(1.7)
E(Hartree-Fock)	-2.8617	-13.6113	-1.1336
E(exact)	-2.90372	-13.6556	-1.1745

Table IV. Ground-state properties for H_2 molecule obtained with the pure diffusion Monte Carlo method. (20) All quantities are in a.u. and statistical uncertainties are indicated in parentheses. References for the quoted values may be found in Ref. 20.

	$R_{H-H} = 1.4$		$R_{H-H} = 4$	
	Monte Carlo	Exact	Monte Carlo	Exact
E_0	-1.175(1.7)	-1.1745	-1.0167(7)	-1.01637
$\langle r_{12}^{-1} \rangle$	0.587(2.6)	0.5874	0.263(1.5)	0.2630
$\langle r_{12} \rangle$	2.169(9)	2.1690	4.33(1.5)	4.327
$\langle r_{12}^2 \rangle$	5.63(4.5)	5.632	20.6(1.3)	20.569
$\langle r_A \rangle$	1.550(6)	1.5499	2.86(1.3)	2.863
$\langle r_A^{-1} \rangle$	0.908(4)	0.9128	0.610(3.5)	0.6136
$\langle r_A^2 \rangle$	3.04(2)	3.036	10.79(8.5)	10.815
$\langle r_A r_B \rangle$	2.71(2)	2.704	6.68(2.3)	6.663
$\langle r_{1A} r_{2A} \rangle$	2.33(1.5)	2.321	6.57(3)	6.551
$\langle r_{1A} r_{2B} \rangle$	2.39(1.5)	2.385	9.82(3)	9.806
$\langle z_1 z_2 \rangle$	-0.156(5.5)	-0.1596	-3.39(6)	-3.392
$\langle x_1 x_2 \rangle$	-0.055(3.5)	-0.0551	-0.039(4.5)	-0.0384
$\langle z^2 \rangle$	1.02(2)	1.023	4.74(4)	4.708
$\langle x^2 \rangle$	0.76(2)	0.762	1.05(1.5)	1.054
$\langle r^2 \rangle$	2.55(4)	2.546	6.85(5.5)	6.815
Q[a]	0.9(1)	0.91	1.3(1.5)	1.38

[a] Q denotes the electric quadrupole moment of the molecule.

2.4. Use of generalized Poisson processes

Following Maslov and Chebotarev (21)(see also Ref. 22) quantum properties may be expressed as stochastic averages by using the time-dependent Schrödinger equation written in real time. This leads to introduce Poisson processes instead of diffusion processes. As an example, we shall derive here the expression of the Fourier transform of the time-dependent wave function in terms of an expectation value with respect to a suitably generalized Poisson process. Additional quantum properties (such as evolution of quantum observables) can be derived (23) but are not considered here. The numerical evaluation of stochastic averages based on Poisson processes seems to have never been considered (to our knowledge). In fact, this is not a straightforward task. The main reasons are i) the oscillatory character of the integrands and ii) the quite restrictive conditions imposed on the potential. Nevertheless, a precise analysis of the methodology motivated by computational purposes remains to be done.

Let us decompose the Hamiltonian H as follows

$$H = H_0 + V \tag{46}$$

where H_0 is the free Hamiltonian and V the potential energy of the system. The Fourier transform of the time-dependent wave function $\psi(\vec{x},t)$ is written

$$\hat{\psi}(\vec{p},t) = \int d\vec{x}\; e^{-i\vec{p}.\vec{x}}\; \psi(\vec{x},t) \tag{47}$$

the converse formula is written

$$\psi(\vec{x},t) = \frac{1}{(2\pi)^d} \int d\vec{p}\; e^{i\vec{p}.\vec{x}}\; \hat{\psi}(\vec{p},t) \tag{48}$$

where d is the dimension of the relevant space (3N for electronic problems). The time evolution of $\psi(\vec{x},t)$ is given by

$$\psi(\vec{x},t) = e^{-i(t-t_0)H}\; \psi(\vec{x},t_0) \tag{49}$$

Let us use the interaction representation. Defining $U(t,t_0)$ as follows

$$U(t,t_0) = e^{iH_0 t}\; e^{-i(t-t_0)H}\; e^{-iH_0 t_0} \tag{50}$$

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we can rewrite Eq. (49) in the following form

$$\psi(\vec{x},t) = e^{-iH_0 t}\, U(t,t_0)\, e^{iH_0 t_0}\, \psi(\vec{x},t_0) \tag{51}$$

Now, from definition (50) it is easy to derive the equation of evolution for $U(t,t_0)$

$$i\,\frac{\partial U(t,t_0)}{\partial t} = V(t)U(t,t_0) \tag{52}$$

where $$V(t) = e^{iH_0 t}\, V(t)\, e^{-iH_0 t} \tag{53}$$

Equation (52) may be rewritten in the equivalent form

$$U(t,t_0) = 1 - i\int_{t_0}^{t} V(\tau)U(\tau,t_0)\, d\tau \tag{54}$$

By iterating Eq. (54) it is found that

$$U(t,t_0) = 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^{t} dt_n \ldots \int_{t_0}^{t_2} dt_1\, V(t_n)\ldots V(t_1) \tag{55}$$

Using Eq. (51) and expressions (55) and (53), the Fourier transform of $\psi(\vec{x},t)$ is written as

$$\hat{\psi}(\vec{p},t) = \int d\vec{x}\, e^{-i\vec{p}.\vec{x}}\, e^{-iH_0 t} \{ 1+\sum_{n=1}^{\infty}(-i)^n \int_{t_0}^{t} dt_n \ldots \int_{t_0}^{t_2} dt_1 \prod_{j=1}^{n} e^{iH_0 t_{n-j+1}}\, V$$
$$\times\, e^{-iH_0 t_{n-j+1}} \} e^{iH_0 t_0} (2\pi)^{-d} \int d\vec{p}\,' e^{i\vec{p}\,'.\vec{x}}\, \hat{\psi}(\vec{p}\,',t_0) \tag{56}$$

Introducing the Fourier transform of V we finally obtain

$$\hat{\psi}(\vec{p},t) = e^{-ih_0(\vec{p})(t-t_0)}\, \hat{\psi}(\vec{p},t_0) + \sum_{n=1}^{\infty}(-i)^n \int_{t_0}^{t} dt_n \ldots \int_{t_0}^{t_2} dt_1 \int \frac{d\vec{p}_n}{(2\pi)^d}\, \hat{V}(\vec{p}_n)\ldots$$
$$\ldots \int \frac{d\vec{p}_1}{(2\pi)^d}\, \hat{V}(\vec{p}_1)\, e^{-ih_0(\vec{p})(t-t_n)} e^{-ih_0(\vec{p}-\vec{p}_1)(t_n-t_{n-1})} \ldots .$$
$$\ldots e^{-ih_0(\vec{p}-\vec{p}_1 \ldots -\vec{p}_n)(t_1-t_0)}\, \hat{\psi}(\vec{p}-\vec{p}_1 \ldots -\vec{p}_n,t_0) \tag{57}$$

where $h_0(\vec{p}) = \vec{p}^2/2$ stands for the free Hamiltonian in momentum-coordinates.

Now, let us define a stochastic process which permits to interpret $\hat{\psi}(\vec{p},t)$ as an expectation value. In the pure diffusion Monte Carlo method (subsection 2.3), the expectation value was defined by

$$<F(\vec{X}(s))> = \lim_{n\to+\infty} < F(\vec{x}_0,0;\vec{x}_1,\Delta t;\dots;\vec{x}_n,t=n\Delta t) >$$

$$= \lim_{n\to+\infty} \int F(\vec{x}_0,0;\vec{x}_1,\Delta t;\dots;\vec{x}_n,t)\ p_{n+1}(\vec{x}_0,0;\vec{x}_1,\Delta t;\dots;\vec{x}_n,t) \prod_{i=0}^{n} d\vec{x}_i \qquad (58)$$

where p_{n+1} denotes the (n+1)-time probability density of the diffusion process and F a rather arbitrary functional of the trajectory. Now, F is a function of $(n,t_1,\dots,t_n,\vec{p}_1,\dots,\vec{p}_n)$ where $n\in\mathbb{N}$, $t_i\in(0,t)$ and $\vec{p}_i\in\mathbb{R}^d$. The average is defined by

$$<F(n,t_i,\vec{p}_i)> = e^{-t\mu}\sum_{n\geq 0}\int_{t_0}^{t} dt_n \dots \int_{t_0}^{t_2} dt_1 \int \frac{d\vec{p}_n}{(2\pi)^d}\,\hat{V}(p_n)\dots \int \frac{d\vec{p}_1}{(2\pi)^d}\,\hat{V}(\vec{p}_1)$$

$$\times\ F(n,t_1,\dots,t_n,\vec{p}_1,\dots,\vec{p}_n) \qquad (59)$$

This definition is valid only if $\dfrac{d\vec{p}}{(2\pi)^d}\,\hat{V}(\vec{p})$ is a positive (bounded) measure; μ stands for the "total mass", that is $\mu = \displaystyle\int \frac{d\vec{p}}{(2\pi)^d}\,\hat{V}(\vec{p})$

We verify that

$$<1> = e^{-t\mu} \sum_{n\geq 0} \frac{t^n}{n!}\,\mu^n = 1 \qquad (60)$$

The probability of having a given value n is obtained as follows

$$P(N=n) = e^{-t\mu}\int_{t_0}^{t} dt_n \dots \int_{t_0}^{t_2} dt_1 \int \frac{d\vec{p}_n}{(2\pi)^d}\,\hat{V}(\vec{p}_n)\dots \int \frac{d\vec{p}_1}{(2\pi)^d}\,\hat{V}(\vec{p}_1)$$

$$= \frac{(t\mu)^n}{n!}\,e^{-t\mu} \qquad (61)$$

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d as follows

$\ldots\int \frac{d\vec{p}_1}{(2\pi)^d} \hat{V}(\vec{p}_1)$

(61)

The average defined above (Eq. (59)) is thus identified to the expectation value with respect to a generalized Poisson process whose trajectories are piecewise constant with a finite number n of jumps. The number of jumps is random and is given by a standard Poisson random variable. In addition, these jumps are uniformly distributed on the time interval (0,t) and their amplitudes are distributed according to the density $\hat{V}(\vec{p})/(2\pi)^d$. Finally, $\hat{\psi}(\vec{p},t)$ is written as the following expectation value

$$\hat{\psi}(\vec{p},t) = e^{t\mu} < e^{-i\int_{t_0}^{t} h(\vec{p}-\vec{P}(\tau))d\tau} (-i)^N \, \hat{\psi}(\vec{p}-\vec{P}(t_0),t_0) > \qquad (62)$$

where N stands for the usual Poisson process (Eq. (61)) and $\vec{P}(\tau)$ is given by

$$\vec{P}(\tau) = \sum_{i=1}^{n} \Theta(t_i-\tau)\, \vec{p}_i \qquad (63)$$

where Θ is the step function

$$\Theta(x)=\begin{cases} 0 & x<0 \\ 1 & x\geq 0 \end{cases}$$

3. THE MANY-FERMION PROBLEM

This section is devoted to the problem of imposing mathematical constraints resulting from the Pauli principle for fermion systems. As a general rule Monte Carlo methods do not involve spin-coordinates. The Pauli principle must be then expressed in a spin-free formalism. In usual space-spin formalism, it is known that the complete wave function (depending on space and spin coordinates) must be antisymmetric. Since only spin-free Hamiltonians are considered here, the wave function can be written as a product of a space function and of a spin function or as a linear combination of such products. On the other hand, the variables of the spin function can take only two values (spin-1/2 particles are treated here), and thus the spin function cannot be antisymmetrized with respect to more than two variables. It results from these constraints that symmetry properties of space functions (i.e. eigenfunctions of H) cannot be arbitrary. On this result is based the partition of eigenfunctions of H between so-called fermionic states (with physical symmetry) and bosonic states (with non-physical symmetry). An illustrative example is the lowest symmetric eigenfunction of H which becomes non-physical as the number of spin-1/2 particles is greater than two. Further explanations concerning the formulation of the Pauli principle in a spin-free formalism may be found in Refs. 24-26. Now, in order to obtain physical solutions to the Schrödinger equation it is necessary to construct space functions ϕ belonging to the different physical symmetry subspaces. The most current form used so far for such space functions is as follows (14,27)

$$\phi(\vec{r}_1,\dots,\vec{r}_N) = \det\left(\prod_{i=1}^{N/2+S} u_i(\vec{r}_i)\right) \det\left(\prod_{i=1}^{N/2-S} u_i(\vec{r}_{i+N/2+S})\right) \qquad (64)$$

where $\{u_i\}$ is a set of $(N/2+S)$ different one-electron space orbitals, N the number of electrons, and S the total spin determining the desired type of symmetry.

Now, it is explained how to introduce such functions in the framework of Monte Carlo methods. For that, let us return to the very basic idea of this paper, namely, the possibility of expressing quantum properties as stochastic averages. From this idea follow two natural ways for introducing the symmetry requirements. First, they may be introduced into the underlying stochastic process. This approach is referred to as the fixed-node approach. Second, symmetry may be introduced into expectation values by using so-called projection functions. We then speak of projection methods. Such an alternative based on the basic idea of stochastic methods is common to all Monte Carlo approaches. However, for concreteness, we illustrate these two procedures in the particular case of the pure diffusion Monte Carlo method presented in subsection 2.3.

Let us consider the problem of evaluating the total energy. According to Eqs. (42) and (39) the quantity to evaluate is

$$I^{f,g}(t) = \langle f\psi | e^{-tH} | g\psi \rangle \qquad (65)$$

Expanding the matrix element by using the resolution of the identity associated with the spectral resolution of H, we obtain

$$I^{f,g}(t) = \sum_i \langle f\psi | \phi_i \rangle \langle \phi_i | g\psi \rangle \, e^{-tE_i} \qquad (66)$$

Now, symmetry is introduced by choosing space functions f,g and ψ so that $f\psi$ and $g\psi$ belong to the desired physical symmetry subspace. Indeed, once this has been done, scalar products $\langle f\psi|\phi_i\rangle$ and $\langle\phi_i|g\psi\rangle$ corresponding to non-physical levels vanish. The two approaches are

i. Fixed-node approach

This approach consists in choosing f=g=1 (no projection functions) and a trial wave function ψ of the form (64). In fact, more sophisticated choice for ψ may be used by multiplying (64) by a symmetric factor which does not change the type of symmetry (essentially for including

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cusp conditions as it is done in form(15)). According to its symmetry properties, such a function must have some nodal hypersurfaces. These nodal hypersurfaces, where the drift is infinite (see Eq. (17.b)), are seen as infinite barriers for any sample trajectory. The diffusion process is then decomposed into a juxtaposition of subprocesses in subdomains delimited by the nodes of ψ. These nodes are not changed in the Monte Carlo simulation. This is the reason why this method is referred to as a fixed-node approach. In addition, if the nodes of the trial wave function are not exact, which is usually the case since symmetry requirements do not determine entirely the nodes of the exact wave function, (28) a bias in the results will appear. This is the origin of the so-called fixed-node approximation. (14) An example of such an approximation may be found in Table II (see also Table V below).

ii. Projection method

In contrast to the fixed-node approach, no approximation occurs. The trial wave function is chosen to be nodeless (bosonic) and symmetry is introduced by choosing space functions f and g with adequate symmetry. A new aspect associated with this choice is that averaged quantities do not have a constant sign. In fact, it is possible to show that the positive and negative contributions nearly cancel. (6,16,29,30) From such a situation result serious numerical difficulties. However, by choosing properly the trial wave function and the projection functions it is possible to attempt to keep under control these difficulties. This is the basic idea of the so-called nodal relaxation method of Ceperley and Alder (30) and of the so-called release-node projection method of Caffarel and Claverie. (16,20) We present in Table V some very good results obtained by Ceperley and Alder in the framework of the Green's function Monte Carlo method using the nodal relaxation algorithm.

Table V. Total ground-state energies obtained with the Green's function Monte Carlo method using the nodal relaxation algorithm. (30) Energies are in a.u. Statistical uncertainties are indicated in parentheses. References for the quoted values may be found in Ref. 30.

	H_3	LiH	Li_2	H_2O
E(fixed-node)	-1.6606(2)	-8.067(1)	-14.990(2)	-76.39(1)
E(release-node)	-1.6617(2)	-8.071(1)	-14.994(2)	-76.43(2)
E(exact)	-1.66194	-8.0705	-14.9967	-76.4376

This work is devoted to the memory of Pierre Claverie who was responsible for its development but not for possible errors contained in the present report.

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