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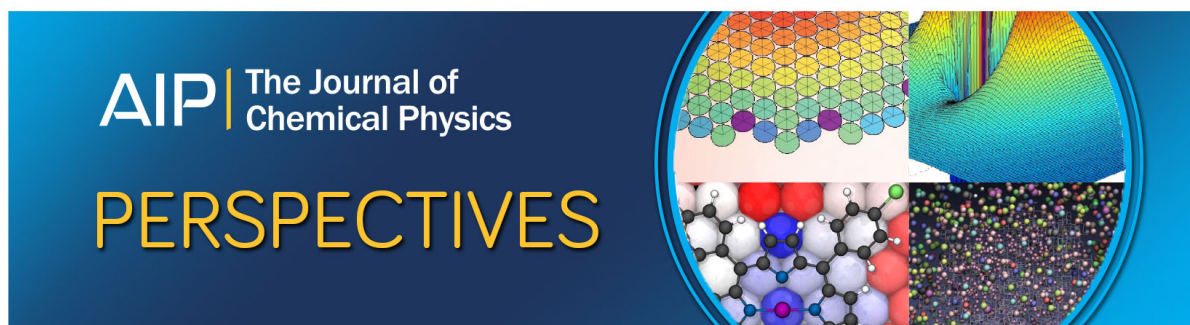
Development of a pure diffusion quantum Monte Carlo method using a full generalized Feynman–Kac formula. I. Formalism

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This paper presents systematic developments in the previously initiated line of research concerning a quantum Monte Carlo (QMC) method based on the use of a pure diffusion process corresponding to some reference function and a generalized Feynman–Kac path integral formalism. Not only mean values of quantum observables, but also response properties are expressed using suitable path integrals involving the diffusion measure of the reference diffusion process. Moreover, by relying on the ergodic character of this process, path integrals may be evaluated as time-averages along any sample trajectory of the process. This property is of crucial importance for the computer implementation of the method. As concerns the treatment of many-fermion systems, where the Pauli principle must be taken into account, we can use the fixed-node approximation, but we also discuss the potentially exact release-node procedure, whereby some adequate symmetry is imposed on the integrand (of the generalized Feynman–Kac formula), associated with a possibly refined choice of the reference function.

I. INTRODUCTION

This paper deals with the treatment of the time-independent Schrödinger equation using a Monte Carlo method. Essentially, the purpose of this method is to obtain values of observables pertaining to the lowest eigenstate(s) of any given symmetry type. The "observables" are the usual quantum averages associated with the eigenstate under consideration (e.g., energy, dipole moment,...) or response properties which are usually written as second-order perturbation expressions (e.g., static and dynamic polarizabilities).

Monte Carlo methods have been used with success in treating many-body boson systems.[1–6] Unfortunately, due to the Pauli principle requirements for fermion systems, atoms and molecules are much less easy to manage. A basic reason for this is the nonconstant sign of Fermi wave functions, a property which implies unavoidable numerical difficulties. Nevertheless, for about 15 years specific Monte Carlo schemes for dealing with molecular systems have been developed. A few approaches have resulted[7–14] and very accurate results for total energies on systems involving a number of 2–10 electrons have been obtained.[9,14–17] Further methodological developments are presently under investigation, particularly to calculate excited state energies and ground state properties other than energy.[18]

The basic common idea of these different approaches, called quantum Monte Carlo (QMC) methods, rests on the similarity between the time-dependent Schrödinger equation in imaginary time and a generalized diffusion equation. These methods have important advantages:

(i) The exact resolution of the Schrödinger equation within the statistical errors due to the finite simulation time (no "truncation error" as occurs unavoidably in the framework of variational methods due to the use of finite basis sets).

(ii) The computational complexity of the code increases slowly with the number of particles. An increase proportional to n^3 at most is expected for fermionic problems with two-body potentials as explained in Ref. 9 (see note 20) for systems of given density. However, if we consider systems with a density increasing with n such as atoms with higher and higher Z, then a more rapid increase of the computation time as a function of n could happen.[19]

(iii) Memory requirements remain perfectly bounded (as opposed to the very fast increase of memory required in variational approaches).

(iv) The short and simple codes are very well suited for vector computing and more specifically for multitasking proper.

A new quantum Monte Carlo method is presented here. We have developed the line of investigation initiated by Soto and Claverie[20] aiming at the design of a Monte Carlo method based on the use of a generalized Feynman–Kac formula applied to a pure diffusion process. More precisely, we have further extended here the previous generalized Feynman–Kac (GFK) formula[20,21] into a so-called full generalized Feynman–Kac (FGFK) formula. The former (GFK) formula expresses as a functional integral the matrix elements of the (imaginary-time) evolution operator $\exp(-tH)$ and thus gives access essentially to energy eigenvalues of H. Now, the latter (FGFK) formula expresses matrix elements of operator products such as

$$\exp(-\tau_1 H)A_1 \exp(-\tau_2 H)A_2 \cdots A_q \exp(-\tau_{q+1} H),$$

where $\Sigma_{i=1}^{q+1}\tau_i = t$ and the A_i's are q scalar multiplicative operators. This enables us to evaluate not only *mean values* of such operators A_i (so-called "first-order" properties in perturbation-theoretic language), but also n-time "quantum correlation functions" (in terms of the Heisenberg picture, cf. e.g., Ref. 22), which are related to *response properties*: e.g., for $n = 2$ we get second-order response properties such as polarizabilities (static and dynamic as well). These various matrix elements involve the evolution operator $\exp(-tH)$ with t arbitrary but fixed. They will be ultimately evaluated as suitable time-averages over sample trajector-

ies for a long enough simulation time T (theoretically we should take the limit $T \to + \infty$ for fixed t). The clear distinction between t and T is of overwhelming importance and will be emphasized at appropriate places below.

The underlying stochastic process (with respect to which our functional integrals are defined) is a *pure diffusion* process, associated with some reference function $\varphi_0^{(0)}$: no branching is involved, in contrast with most proposals of quantum Monte Carlo schemes presented so far.[7,9,14] Some connection with these methods can be established by noticing that their branching term plays a role which is analogous with the role played in our own approach by the "Feynman–Kac integrand" $\exp\{ - \int V_p[X(s)]ds\}$ which appears in the FGFK formula (cf. Sec. III). This point has been noticed by Ceperley and Alder[14] [see their Eq. (11)] and Pollock and Ceperley[23] [see Eq. (A5) in their Appendix A]. Details about the correspondence with our present formalism are provided in the Appendix. Another point which deserves to be mentioned is the fact that in previous Monte Carlo methods the simulation time T is also the imaginary time appearing in the evolution operator. In our notation this amounts to putting $t = T$. We shall see below how the possibility of distinguishing t and T may be advantageous, especially in order to keep variance under control.

As recalled above, a serious challenge for all Monte Carlo methods is the treatment of many-fermion systems due to the specific constraints imposed by the Pauli principle. We therefore paid due attention to this problem, and we discuss several ways of solving it.

The full mathematical details are reported elsewhere in previous papers.[20] However, in order to make the present paper self-contained, all that is necessary to understand the theory is briefly recalled at each appropriate place.

The contents of this paper are as follows. In Sec. II we present the basic similarity transformation which permits mathematically connecting the quantum formalism with the stochastic processes. The essential idea is to associate a diffusion process with some given reference function $\varphi_0^{(0)}$ (to which a "reference Hamiltonian" $H^{(0)}$ is also associated). Section III is devoted to the presentation and derivation of the full generalized Feynman–Kac formula alluded to above. In Sec. IV we describe how this FGFK formula can be used for expressing quantum observables (mean values and response properties). In Sec. V we give an outline of the theoretical algorithm (further details concerning its computer implementation are deferred to a companion paper). Section VI deals with the Pauli principle requirements and with some directions for treating this problem. Finally, Sec. VII presents some conclusions and perspectives.

II. DIFFUSION PROCESS ASSOCIATED WITH AN ARBITRARY REFERENCE FUNCTION

We are interested in the nonrelativistic quantum problem of N particles interacting via a potential $V(x)$ (x denotes the $3N$ space-coordinates $r_1, r_2, ..., r_N$). For the sake of simplicity atomic units will be used throughout the paper and the same electronic mass $m_e = 1$ is chosen for the N particles. The Hamiltonian operator is written

$$H = -\tfrac{1}{2}\nabla^2 + V. \qquad (2.1)$$

Following previous authors[24] this Hamiltonian operator H may be changed through a similarity transformation into the Fokker–Planck operator L of a diffusion process. With φ_i denoting an arbitrary eigenstate of H and E_i the associated energy, it can be proven after simple algebra that[20]

$$\varphi_i(E_i - H)1/\varphi_i = L, \qquad (2.2)$$

where L is a Fokker–Planck operator:

$$L = \tfrac{1}{2}\, \mathscr{D}\, \nabla^2 - \nabla(\mathbf{b}.) \qquad (2.3)$$

The "drift" vector $\mathbf{b}$ and the diffusion coefficient $\mathscr{D}$ are given by

$$\mathbf{b} = \nabla\varphi_i/\varphi_i, \qquad (2.4a)$$

$$\mathscr{D} = 1. \qquad (2.4b)$$

From equality (2.2) it follows the expression of the eigenfunctions and eigenvalues of the Fokker–Planck operator L:

$$L\varphi_i\varphi_k = (E_i - E_k)\varphi_i\varphi_k. \qquad (2.5)$$

In this last expression (E_k, φ_k) are the eigensolutions of the usual eigenproblem, namely

$$H\varphi_k = E_k\varphi_k \qquad (2.6a)$$

but with the *unusual boundary conditions*

$$\varphi_k = 0 \quad \text{at any point where} \quad \varphi_i = 0. \qquad (2.6b)$$

Because of these possibly unusual boundary conditions, it is clear that the previous eigensolutions may differ from the usual ones. As a particular case, if φ_i is chosen to be the nodeless bosonic ground state, φ_0, no extra boundary conditions are introduced (since φ_0 does not vanish at finite distances) and the previous eigenvalues E_k are the usual eigenvalues of H obtained from the usual boundary conditions. This possible modification of the spectrum due to the nodal hypersurfaces of φ_i is responsible for the so-called "fixed-node" approximation (for more details see Sec. VI dealing with the Pauli principle). In addition, note that the wavefunction φ_i is now a ground state in the new eigenvalue problem (2.6). From equality (2.5) we deduce that the stationary probability density $p(x)$ of the diffusion process (which is defined as the eigenfunction of L corresponding to the zero eigenvalue) is nothing but the probability density associated with the wave function, namely

$$p(x) = \varphi_i^2(x). \qquad (2.7)$$

Now, it is possible to generalize this construction, that is, to associate a diffusion process with any arbitrary function. The generalization rests on the fact that any given function can always be considered as an eigenstate of a Hamiltonian built from it. We decided to note as $\varphi_0^{(0)}$ this arbitrary function and $H^{(0)}$ the associated Hamiltonian. The expression of $H^{(0)}$ in terms of the function $\varphi_0^{(0)}$ is given by

$$H^{(0)} = -\tfrac{1}{2}\nabla^2 + V^{(0)}, \qquad (2.8a)$$

where

$$V^{(0)} = E_0^{(0)} + \tfrac{1}{2}\nabla^2\varphi_0^{(0)}/\varphi_0^{(0)}. \qquad (2.8b)$$

Throughout the paper, the function $\varphi_0^{(0)}$ will be called "reference function" and $H^{(0)}$ "reference Hamiltonian." In order to avoid any risk of confusion, the superscript (0) will

always be used to label quantities related to $H^{(0)}$. Note that only derivations have to be performed to determine $H^{(0)}$ and that the constant $E_0^{(0)}$ in Eq. (2.8b) may be chosen arbitrarily. Now, we can apply to this Hamiltonian $H^{(0)}$ the similarity transformation exactly in the same way as done in Eq. (2.2). We get the following basic relations:

$$\varphi_0^{(0)}(E_0^{(0)} - H_0^{(0)})1/\varphi_0^{(0)} = L^{(0)}, \qquad (2.9)$$

where $L^{(0)}$ is the "reference" Fokker–Planck operator

$$L^{(0)} = \tfrac{1}{2}\mathscr{D}\,\nabla^2 - \nabla(\mathbf{b}.) \qquad (2.10)$$

with

$$\mathbf{b} = \nabla\varphi_0^{(0)}/\varphi_0^{(0)}, \qquad (2.11a)$$

$$\mathscr{D} = 1. \qquad (2.11b)$$

Of course, if the reference function $\varphi_0^{(0)}$ is chosen to be one of the eigenstates of H and $E_0^{(0)}$ the corresponding energy, we are led to the previous particular case where $H^{(0)} = H$.

Finally, let us now present a fundamental relation derived from the basic similarity transformation (2.9). A stationary diffusion process is entirely determined by its transition probability density defined as

$$p^{(0)}(x|y,t) = \langle y|e^{tL^{(0)}}|x\rangle, \qquad (2.12)$$

where $L^{(0)}$ is the Fokker–Planck operator of the diffusion process. Note that we use a bracket enclosing the conditioning variable x instead of a simple bar as usual. Now, from Eq. (2.9) we get

$$p^{(0)}(x|y,t) = \varphi_0^{(0)}(y)/\varphi_0^{(0)}(x)e^{tE_0^{(0)}}G^{(0)}(x,y;t), \qquad (2.13)$$

where $G^{(0)}(x,y;t)$ is the quantum time-dependent Green's function (in imaginary time) defined as

$$G^{(0)}(x,y;t) = \langle x|e^{-tH^{(0)}}|y\rangle. \qquad (2.14)$$

The fundamental relation (2.13) between the quantum Green's function of $H^{(0)}$ and the Green's function of $L^{(0)}$, i.e., the transition probability density of the process, will permit us to express quantum quantities related to $H^{(0)}$ in terms of suitable averages pertaining to the diffusion process and conversely. However, we are interested in quantum properties related to H and not to $H^{(0)}$ and, except for a few very simple systems for which eigenstates of H are known, these two Hamiltonians will be different. The aim of the next Section is to present a possible way of escaping from this difficulty using a so-called "full generalized Feynman–Kac formula."

III. THE FULL GENERALIZED FEYNMAN–KAC FORMULA

Let us decompose the Hamiltonian into two parts:

$$H = H^{(0)} + V_p, \qquad (3.1)$$

where $H^{(0)}$ is the reference Hamiltonian built from the reference function $\varphi_0^{(0)}$ and V_p the "perturbing" potential defined as the difference $H - H^{(0)}$. From Eqs. (2.1) and (2.8) we get the expression of the perturbing potential in terms of the reference function:

$$V_p = V - V^{(0)} = V - E_0^{(0)} - \tfrac{1}{2}\nabla^2\varphi_0^{(0)}/\varphi_0^{(0)}. \qquad (3.2)$$

The usual Feynman–Kac formula expresses the quantum time-dependent Green's function (in imaginary time) in terms of a functional integral[25,26]:

$$G(x,y;t) = \int_{\Omega(x,\,-\,t/2;y,t/2)}$$
$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^WX, \qquad (3.3)$$

where $\Omega(x, - t/2;y,t/2)$ denotes the set of continuous trajectories starting from x at time $- t/2$ and ending at y at time $t/2$. In this formula V_p is defined by $H = -\tfrac{1}{2}\nabla^2 + V_p$, which is of the form (3.1) with $H^{(0)} = -\tfrac{1}{2}\nabla^2$ (free-particle Hamiltonian). The functional measure D^WX is the usual Wiener measure. It is well known that it can be reinterpreted as a diffusion measure, namely the diffusion measure associated with the free Brownian process (see e.g., Sec. I.3.1 in Ref. 27, see also Ref. 28). Note that this later process is the diffusion process obtained from the similarity transformation (2.9) with $H^{(0)} = -\tfrac{1}{2}\nabla^2$, $\varphi_0^{(0)} = 1$ and $E_0^{(0)} = 0$.

Glimm and Jaffe (Sec. I.3 in Ref. 27) have given a first generalization of this formula. Using the decomposition

$$H = -\tfrac{1}{2}\nabla^2 + \tfrac{1}{2}x^2 - \tfrac{1}{2} + V_p(x), \qquad (3.4)$$

they derived a generalized Feynman–Kac formula written in the form:

$$G(x,y;t) = \int_{\Omega(x,\,-\,t/2;y,t/2)}$$
$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{GJ}X. \qquad (3.5)$$

In their derivation they introduced explicitly a diffusion process associated with the harmonic oscillator (the Ornstein–Ulhlenbeck process) which corresponds in our language to the diffusion process obtained from the similarity transformation (2.9) with $H^{(0)} = -\tfrac{1}{2}\nabla^2 + \tfrac{1}{2}x^2 - \tfrac{1}{2}$, $\varphi_0^{(0)} = e^{-x^2/2}$ and $E_0^{(0)} = 0$. In formula (3.5) above, we denote as $D^{GJ}X$ the diffusion measure associated with the diffusion process built from the Gaussian reference function[27] (the superscript GJ in $D^{GJ}X$ stands for Glimm and Jaffe).

A generalization of this approach has been made by Soto and Claverie[20] to the more general case of an arbitrary nonperturbed Hamiltonian $H^{(0)}$, thus encompassing the two previous trivial cases of the free particle (Feynman–Kac formula with $H^{(0)} = -\tfrac{1}{2}\nabla^2$) and of the harmonic oscillator (Glimm and Jaffe with $H^{(0)} = -\tfrac{1}{2}\nabla^2 + \tfrac{1}{2}x^2 - \tfrac{1}{2}$). This generalized Feynman–Kac formula corresponding to $H = H^{(0)} + V_p$ is written

$$G(x,y;t) = \int_{\Omega(x,\,-\,t/2;y,t/2)}$$
$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{\varphi_0^{(0)}}X, \qquad (3.6)$$

where the measure $D^{\varphi_0^{(0)}}X$ is the diffusion measure[29] associated with the diffusion process built from the reference function $\varphi_0^{(0)}$.

We shall now derive a very general formula including all the previous ones and allowing to evaluate all quantum mean values we are interested in. This formula is written

$I_{A_1 \ldots A_q}(t;t_1,\ldots,t_q)$

$$\equiv \langle f\varphi_0^{(0)}|e^{-(t_1+t/2)(H-E_0^{(0)})}A_1 e^{-(t_2-t_1)(H-E_0^{(0)})}$$

$$\times A_2 \ldots A_q e^{-(t/2-t_q)(H-E_0^{(0)})}|g\varphi_0^{(0)}\rangle$$

$$= \int_{\Omega(-t/2;t/2)} f[X(-t/2)]$$

$$\times A_1[X(t_1)]\ldots A_q[X(t_q)]g[X(t/2)]$$

$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right]D^{\varphi_0^{(0)}}X \qquad (3.7)$$

with $-t/2 < t_1 \leqslant t_2 \ldots \leqslant t_q < t/2$. The A_i's are q scalar multiplicative operators and f, g two arbitrary functions verifying

$$\int f\varphi_0^{(0)2}dx < \infty \quad \text{and} \quad \int g\varphi_0^{(0)2}dx < \infty.$$

$\Omega(-t/2;t/2)$ is the set of continuous trajectories defined in the time interval $(-t/2,t/2)$.

Proof

Let us note $\tau_1 = t_1 + t/2$, $\tau_2 = t_2 - t_1,\ldots,\tau_{i+1} = t_{i+1} - t_i,\ldots,\tau_{q+1} = t/2 - t_q$:

$$R^{(0)} = E_0^{(0)} - H^{(0)} \qquad (3.8)$$

and $I = I_{A_1 \ldots A_q}(t;t_1,\ldots,t_q)$.
We then have

$$I = \langle f\varphi_0^{(0)}|e^{\tau_1 R^{(0)} - \tau_1 V_p}A_1 \ldots A_i e^{\tau_{i+1}R^{(0)} - \tau_{i+1}V_p}A_{i+1}$$

$$\times \ldots A_q e^{\tau_{q+1}R^{(0)} - \tau_{q+1}V_p}|g\varphi_0^{(0)}\rangle.$$

Using the usual following Trotter formula

$$e^{A+B} = \lim_{n \to +\infty} [e^{A/n}e^{B/n}]^n \qquad (3.9)$$

we obtain

$$I = \lim_{n \to +\infty} \langle f\varphi_0^{(0)}|[e^{\epsilon_1 R^{(0)}}e^{-\epsilon_1 V_p}]^n A_1$$

$$\times \ldots A_i [e^{\epsilon_{i+1}R^{(0)}}e^{-\epsilon_{i+1}V_p}]^n A_{i+1}$$

$$\times \ldots A_q [e^{\epsilon_{q+1}R^{(0)}}e^{-\epsilon_{q+1}V_p}]^n|g\varphi_0^{(0)}\rangle,$$

where $\epsilon_i = \tau_i/n$.

Introducing the spectral resolution of operator X, namely

$$1 = \int dX|X\rangle\langle X| \qquad (3.10)$$

between each operator involved in the above matrix element we get

$$I = \lim_{n \to +\infty} \int \prod_{j=1}^{q+1} \prod_{i=0}^{2n} dX_i^{(j)} \langle f\varphi_0^{(0)}|X_0^{(1)}\rangle$$

$$\times \prod_{j=1}^{q+1} \prod_{i=0}^{2n-2,2} \langle X_i^{(j)}|e^{\epsilon_j R^{(0)}}|X_{i+1}^{(j)}\rangle \langle X_{i+1}^{(j)}|e^{-\epsilon_j V_p}|X_{i+2}^{(j)}\rangle$$

$$\times \prod_{j=1}^{q} \langle X_{2n}^{(j)}|A_j|X_0^{(j+1)}\rangle \langle X_{2n}^{(q+1)}|g\varphi_0^{(0)}\rangle,$$

where $\Pi_{i=0}^{n,m}$ means $\Pi_{i=0}^{n}$ with steps of size m.
Using relations

$$\langle X_{i+1}^{(j)}|e^{-\epsilon_j V_p}|X_{i+2}^{(j)}\rangle$$

$$= \delta(X_{i+1}^{(j)} - X_{i+2}^{(j)})e^{-\epsilon_j V_p(X_{i+2}^{(j)})}, \qquad (3.11a)$$

$$\langle X_i^{(j)}|e^{\epsilon_j R^{(0)}}|X_{i+1}^{(j)}\rangle$$

$$= \varphi_0^{(0)}(X_i^{(j)})/\varphi_0^{(0)}(X_{i+1}^{(j)})p^{(0)}(X_i^{(j)}]X_{i+1}^{(j)},\epsilon_j), \qquad (3.11b)$$

where relation (3.11b) results from Eqs. (2.13), (2.14), and (3.8), and after integrating over variables $X_{2i+1}^{(j)}$ (for $i = 0$ to $n-1$ and $j = 1$ to $q+1$), we obtain

$$I = \lim_{n \to +\infty} \int \prod_{j=1}^{q+1} \prod_{i=0}^{n} dX_{2i}^{(j)} \langle f\varphi_0^{(0)}|X_0^{(1)}\rangle \varphi_0^{(0)}(X_0^{(1)}) \prod_{j=1}^{q} \frac{\varphi_0^{(0)}(X_0^{(j+1)})}{\varphi_0^{(0)}(X_{2n}^{(j)})} \prod_{i=0}^{2n-2,2} p^{(0)}(X_i^{(j)}]X_{i+2}^{(j)},\epsilon_j) e^{-\epsilon_j V_p(X_{i+2}^{(j)})}$$

$$\times \prod_{j=1}^{q} \langle X_{2n}^{(j)}|A_j|X_0^{(j+1)}\rangle \prod_{i=0}^{2n-2,2} p^{(0)}(X_i^{(q+1)}]X_{i+2}^{(q+1)},\epsilon_{q+1})e^{-\epsilon_{q+1}V_p(X_{i+2}^{(q+1)})} \frac{1}{\varphi_0^{(0)}(X_{2n}^{(q+1)})} \langle X_{2n}^{(q+1)}|g\varphi_0^{(0)}\rangle.$$

The A_i's are scalar multiplicative operators, we then have

$$\langle X_{2n}^{(j)}|A_j|X_0^{(j+1)}\rangle = \delta(X_{2n}^{(j)} - X_0^{(j+1)})A_j(X_0^{(j+1)}). \qquad (3.12)$$

Inserting Eq. (3.12) into the expression of I and integrating over $X_{2n}^{(j)}$ (for $j = 1$ to q), we get, after the change of notation $X_{2i}^{(j)} \to X_i^{(j)}$:

$$I = \lim_{n \to +\infty} \int \prod_{j=1}^{q+1} \prod_{i=0}^{n-1} dX_i^{(j)} dX_n^{(q+1)} f(X_0^{(1)})$$

$$\times \prod_{j=1}^{q} A_j(X_0^{(j+1)})g(X_n^{(q+1)}) \prod_{j=1}^{q+1} \prod_{i=0}^{n-1} e^{-\epsilon_j V_p(X_{i+1}^{(j)})}$$

$$\times \varphi_0^{(0)2}(X_0^{(1)}) \prod_{j=1}^{q+1} \prod_{i=0}^{n-1} p^{(0)}(X_i^{(j)}]X_{i+1}^{(j)},\epsilon_j).$$

In the last formula and below, we use the convenient identity:

$$X_n^{(j)} \equiv X_0^{(j+1)} \quad (\text{for } j = 1 \text{ to } q).$$

Using the fundamental property for stationary Markovian processes, namely

$$p_n^{(0)}(X_1,t_1;\ldots;X_n,t_n)$$

$$= p^{(0)}(X_1)\prod_{i=1}^{n-1} p^{(0)}(X_i]X_{i+1},t_{i+1} - t_i), \qquad (3.13)$$

where $p_n^{(0)}$ is the n-time probability density of the diffusion process, we get

$$I = \lim_{n \to +\infty} \int f(X_0^{(1)}) \prod_{j=1}^{q} A_j(X_0^{(j+1)}) g(X_n^{(q+1)})$$

$$\times \prod_{j=1}^{q+1} \prod_{i=0}^{n-1} e^{-\epsilon_j V_p(X_{i+1}^{(j)})}$$

$$\times p_{n(q+1)+1}^{(0)}(X_0^{(1)}, -t/2;...;X_n^{(q+1)}, t/2)$$

$$\times \prod_{j=1}^{q+1} \prod_{i=0}^{n-1} dX_i^{(j)} dX_n^{(q+1)}. \qquad (3.14)$$

This expression is symbolically written as:

$$\int_{\Omega(-t/2;t/2)} f[X(-t/2)] A_1[X(t_1)]...A_q[X(t_q)]$$

$$\times g[X(t/2)] \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{\varphi_0^{(0)}} X$$

Q.E.D.

We give to this equality the name of "full generalized Feynman–Kac (FGFK) formula."

At this point, it is interesting to notice that the full generalized Feynman–Kac formula (3.7) is essentially based on the possibility of expressing the diffusion measure $D^{\varphi_0} X$ (associated with the exact eigenstate φ_0 of H) in terms of the diffusion measure $D^{\varphi_0^{(0)}} X$ (associated with the reference function $\varphi_0^{(0)}$) through a suitable "relative density" (the so-called Radon–Nikodym derivative: see Chap. III, Sec. 12 in Ref. 29), which can be noted $D^{\varphi_0} X / D^{\varphi_0^{(0)}} X$. This relative density (pertaining to function space!) is actually given (except for a normalization constant) by the "Feynman–Kac integrand" in the long time limit $\lim_{t \to +\infty} \exp\{-\int_{-t/2}^{t/2} V_p[X(s)]ds\}$. The normalization factor actually appears explicitly in the expressions for operator mean values derived in the next section.

Now, it is of crucial importance to remark that the diffusion measure, $D^{\varphi_0^{(0)}} X$, involved in the path integrals may be chosen ergodic. A diffusion measure is said to be ergodic when any sample trajectory is recurrent in space. A theorem due to Has'minskii[30] shows that integrability of the stationary density $p^{(0)}(x)$, i.e., $\int p^{(0)}(x)dx < \infty$, is a sufficient condition for ergodicity. Accordingly, if the reference function $\varphi_0^{(0)}$ has been chosen such that $p^{(0)}(x) = \varphi_0^{(0)2}$ is integrable (and from now on it will be always the case), the following ergodic property may be invoked to evaluate functional integrals:

$$\int_{\Omega(-t/2;t/2)} f[X(-t/2)] \prod_{i=1}^{q} A_i[X(t_i)] g[X(t/2)]$$

$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{\varphi_0^{(0)}} X$$

$$= \lim_{T \to +\infty} \frac{1}{T} \int_0^T f[X^{(0)}(-t/2+\tau)]$$

$$\times \prod_{i=1}^{q} A_i[X^{(0)}(t_i+\tau)] g[X^{(0)}(t/2+\tau)]$$

$$\times \exp\left[-\int_{-t/2+\tau}^{t/2+\tau} V_p[X^{(0)}(s)]ds\right] d\tau, \qquad (3.15)$$

where $X^{(0)}(s)$ denotes an arbitrary sample trajectory of the diffusion process.

It must be emphasized that in the basic formula (3.7) (and in the formulas derived from it) we only have the time parameter t and functional integrals, the simulation time T appears only when these functional integrals are expressed as time-averages over sample trajectories according to the previous formula (3.15). Once this is done these formulas would exhibit $T \to +\infty$, while t remains fixed, and, therefore, the distinction between T and t remains perfectly clear.

We can now discuss with more detail the connection with other Monte Carlo methods based on the use of a branching term. The "trial wave function" ψ_T introduced in these methods corresponds exactly to our reference function $\varphi_0^{(0)}$,[31] and accordingly the pure "drifting-diffusion" part of their process would be identical with our own diffusion process. Our Fokker–Planck equation (with drift term $\nabla \varphi_0^{(0)} / \varphi_0^{(0)}$) is actually identical with the evolution equation of the branching-diffusion process [see, e.g., Eq. (6) in Ref. 9] when the branching term is removed. Adding the branching term modifies the process and thus generates a new measure in function space (space of trajectories). Instead of directly sampling this new functional measure, as has been done in most previous work, it would be conceivable to use a Feynman–Kac type formula applied to the reference (pure drifting-diffusion) process. This second alternative has precisely been noticed by Ceperley and Alder [see their Eq. (11) in Ref. 14] and by Pollock and Ceperley [see their Appendix A, notably Eq. (A5) in Ref. 23]. It must be emphasized, however, that the branching-diffusion process is not identical with the pure diffusion process corresponding to the exact state φ_0, if only because the former has the stationary density $\varphi_0 \psi_T$, while the latter has the stationary density φ_0^2. In the Appendix, we present further discussion concerning the connection between the various approaches and, more specifically, between the possibly associated Feynman–Kac type formulas.

IV. EXPRESSIONS OF QUANTUM MEAN VALUES AND RESPONSE PROPERTIES USING THE FGFK FORMULA

A. Energy

Taking $A_i = 1$, for $i = 1$ to q in the FGFK formula, we obtain

$$I(t) = \langle f\varphi_0^{(0)} | e^{-t(H-E_0^{(0)})} | g\varphi_0^{(0)} \rangle$$

$$= \int_{\Omega(-t/2;t/2)} f[X(-t/2)] g[X(t/2)]$$

$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{\varphi_0^{(0)}} X. \qquad (4.1)$$

We now introduce on the left- and right-hand sides of operator $e^{-t(H-E_0^{(0)})}$ the resolution of the identity associated with the spectral resolution of H, namely

$$1 = \sum_i |\varphi_i\rangle\langle\varphi_i|. \tag{4.2}$$

The summation sign $\sum_i$ here is a shorthand notation which may represent either a discrete summation or a continuous integration. This notation will be used throughout the paper. Using the orthogonality relation

$$\langle\varphi_i|\varphi_k\rangle = \delta_{ik} \tag{4.3}$$

we obtain

$$I(t) = \sum_i \langle f\varphi_0^{(0)}|\varphi_i\rangle\langle\varphi_i|g\varphi_0^{(0)}\rangle e^{-t(E_i - E_0^{(0)})}. \tag{4.4}$$

From Eq. (4.4) it is then easy to derive that

$$E_{i_0} = E_0^{(0)} - \lim_{t \to +\infty} 1/t$$

$$\times \log \int_{\Omega(-t/2;t/2)} f[X(-t/2)]g[X(t/2)]$$

$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{\varphi_0^{(0)}}X, \tag{4.5}$$

where E_{i_0} is the energy associated with the lowest state φ_{i_0} having nonzero overlap with the functions $f\varphi_0^{(0)}$ and $g\varphi_0^{(0)}$.

In actual fact more sophisticated schemes to extract the exponent of the leading real exponential will be considered in numerical calculations (see companion paper).

B. Expression of quantum averages

Taking $A_1 = A$ and $A_2 = \ldots = A_q = 1$ in the FGFK formula, we obtain

$$I_A(t;t_1) = \langle f\varphi_0^{(0)}|e^{-(t_1 + t/2)(H - E_0^{(0)})}Ae^{-(t/2 - t_1)(H - E_0^{(0)})}|g\varphi_0^{(0)}\rangle$$

$$= \int_{\Omega(-t/2;t/2)} f[X(-t/2)]A[X(t_1)]g[X(t/2)]\exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right]D^{\varphi_0^{(0)}}X. \tag{4.6}$$

By inserting the spectral expansion by Eq. (4.2) at each side of the three operators into the quantum matrix element we get

$$I_A(t;t_1) = \sum_{i,j,k,l} \langle f\varphi_0^{(0)}|\varphi_i\rangle\langle\varphi_i|e^{-(t_1 + t/2)(H - E_0^{(0)})}|\varphi_j\rangle\langle\varphi_j|A|\varphi_k\rangle\langle\varphi_k|e^{-(t/2 - t_1)(H - E_0^{(0)})}|\varphi_l\rangle\langle\varphi_l|g\varphi_0^{(0)}\rangle$$

$$= e^{-t(E_{i_0} - E_0^{(0)})}\langle f\varphi_0^{(0)}|\varphi_{i_0}\rangle\langle\varphi_{i_0}|g\varphi_0^{(0)}\rangle$$

$$\times \left[\langle\varphi_{i_0}|A|\varphi_{i_0}\rangle + \sum_{\substack{i,k \\ i>i_0;k>i_0}} \frac{\langle f\varphi_0^{(0)}|\varphi_i\rangle\langle\varphi_i|A|\varphi_k\rangle\langle\varphi_k|g\varphi_0^{(0)}\rangle}{\langle f\varphi_0^{(0)}|\varphi_{i_0}\rangle\langle\varphi_{i_0}|g\varphi_0^{(0)}\rangle} e^{-t_1(E_i - E_k) - \frac{t}{2}[(E_i - E_{i_0}) + (E_k - E_{i_0})]}\right]$$

taking $A = 1$ in the last equality we obtain

$$I(t) = e^{-t(E_{i_0} - E_0^{(0)})}\langle f\varphi_0^{(0)}|\varphi_{i_0}\rangle\langle\varphi_{i_0}|g\varphi_0^{(0)}\rangle\left[1 + \sum_{i>i_0} \frac{\langle f\varphi_0^{(0)}|\varphi_i\rangle\langle\varphi_i|g\varphi_0^{(0)}\rangle}{\langle f\varphi_0^{(0)}|\varphi_{i_0}\rangle\langle\varphi_{i_0}|g\varphi_0^{(0)}\rangle} e^{-t(E_i - E_{i_0})}\right]$$

finally we find

$$\lim_{t \to +\infty} \frac{I_A(t;t_1)}{I(t)} = \langle\varphi_{i_0}|A|\varphi_{i_0}\rangle \quad \forall t_1 \epsilon] - t/2, t/2[$$

or

$$\langle\varphi_{i_0}|A|\varphi_{i_0}\rangle = \lim_{t \to +\infty} \frac{\int_{\Omega(-t/2;t/2)} f[X(-t/2)]A[X(t_1)]g[X(t/2)]\exp\{-\int_{-t/2}^{t/2} V_p[X(s)]ds\}D^{\varphi_0^{(0)}}X}{\int_{\Omega(-t/2;t/2)} f[X(-t/2)]g[X(t/2)]\exp\{-\int_{-t/2}^{t/2} V_p[X(s)]ds\}D^{\varphi_0^{(0)}}X}. \tag{4.7}$$

C. Second-order mean values

We apply the FGFK formula to the case $A_1 = A, A_2 = B$. Using the same kind of arguments as in the both previous cases it is easy to be convinced that the following matrix element:

$$I_{AB}(t;t_1,t_2) = \langle f\varphi_0^{(0)}|e^{-(t_1 + t/2)(H - E_0^{(0)})}Ae^{-(t_2 - t_1)(H - E_0^{(0)})}Be^{-(t/2 - t_2)(H - E_0^{(0)})}|g\varphi_0^{(0)}\rangle$$

may be written in the form

$$e^{-t(E_{i_0} - E_0^{(0)})}\langle f\varphi_0^{(0)}|\varphi_{i_0}\rangle\langle\varphi_{i_0}|g\varphi_0^{(0)}\rangle\left\{\sum_k \langle\varphi_{i_0}|A|\varphi_k\rangle\langle\varphi_k|B|\varphi_{i_0}\rangle e^{-(t_1 - t_2)(E_{i_0} - E_k)}\right.$$

$$\left. + \sum_{\substack{i>i_0 \\ m>i_0}} e^{-t/2[(E_i - E_{i_0}) + (E_m - E_{i_0})]} \frac{\langle f\varphi_0^{(0)}|\varphi_i\rangle\langle\varphi_m|g\varphi_0^{(0)}\rangle}{\langle f\varphi_0^{(0)}|\varphi_{i_0}\rangle\langle\varphi_{i_0}|g\varphi_0^{(0)}\rangle}\left[\sum_k \langle\varphi_i|A|\varphi_k\rangle\langle\varphi_k|B|\varphi_m\rangle e^{-t_1(E_i - E_k) - t_2(E_k - E_m)}\right]\right\}.$$

We now extract the following quantity:

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

where $\tau = t_2 - t_1$, in a way similar to that used for obtaining $\langle \varphi_{i_0} | A | \varphi_{i_0} \rangle$ in the previous derivation [Eq. (4.7)]. We thus obtain

$$C_{AB}(\tau) = \lim_{t \to +\infty} \frac{\int_{\Omega(-t/2;t/2)} f[X(-t/2)]A[X(t_1)]B[X(t_1+\tau)]g[X(t/2)]\exp\left\{-\int_{-t/2}^{t/2} V_p[X(s)]ds\right\} D^{\varphi_0^{(0)}}X}{\int_{\Omega(-t/2;t/2)} f[X(-t/2)]g[X(t/2)]\exp\{-\int_{-t/2}^{t/2} V_p[X(s)]ds\} D^{\varphi_0^{(0)}}X}$$

$$\forall t_1, t_2 \in] - t/2, t/2[. \qquad (4.8)$$

From the Laplace-transform of $C_{AB}(\tau)$ one obtains

$$\mathscr{L}[C_{AB}(\tau)] = \int_0^{+\infty} e^{-\omega\tau} C_{AB}(\tau) d\tau$$

$$= \sum_k \frac{\langle \varphi_{i_0} | A | \varphi_k \rangle \langle \varphi_k | B | \varphi_{i_0} \rangle}{\omega + (E_k - E_{i_0})}. \qquad (4.9)$$

Now, we can consider for example the dynamic dipole polarizability tensor $A(\omega)$ at frequency ω for an atomic or molecular system, which is given by the second-order perturbation formula[32]:

$$A(\omega) = 2 \sum_{k \neq 0} \frac{\mu_{k0} \otimes \mu_{k0} E_{k0}}{E_{k0}^2 - \omega^2}, \qquad (4.10)$$

where $E_{k0} = E_k - E_0$ and $\mu_{k0} = \langle \varphi_k | \mu | \varphi_0 \rangle$ denotes the matrix elements of the dipole operator $\mu = \Sigma_{j=1}^N q_j r_j$ and $\otimes$ denotes the tensor product. Now, as remarked, e.g., by Tang and Karplus,[33] Eq. (4.10) may be written as

$$A(\omega) = A^+(\omega) + A^+(-\omega), \qquad (4.11)$$

where

$$A^+(\omega) = \sum_{k \neq 0} \frac{\mu_{k0} \otimes \mu_{k0}}{\omega + E_{k0}}. \qquad (4.12)$$

This last quantity may be evaluated with

$$\mathscr{L}[C_{AB}(\tau) - \langle A \rangle \langle B \rangle]$$

$$= \sum_{k \neq i_0} \frac{\langle \varphi_{i_0} | A | \varphi_k \rangle \langle \varphi_k | B | \varphi_{i_0} \rangle}{\omega + E_k - E_{i_0}}, \qquad (4.13)$$

where $A = B = \mu$. Of course, the subscript i_0 used in Eq. (4.13) for labeling the fermionic quantities corresponds to the subscript 0 appearing in the standard Eqs. (4.10)–(4.12).

It must be emphasized here that all the formulas just derived (for energy, mean values, and second-order properties) are expressed in terms of one and same diffusion measure (corresponding to the reference function $\varphi_0^{(0)}$). Only the integrand changes from one functional integral to the other. Moreover, according to the ergodic property (3.15), these functional integrals may be reformulated as time-averages of the corresponding integrands over any given sample trajectory of the diffusion process (associated with $\varphi_0^{(0)}$). This use of one and the same trajectory for evaluating all quantities of interest is a very appealing feature, and deserves to be contrasted with the situation encountered in previous QMC methods.[7-18] As a general rule, these methods introduce a branching process designed for generating a cloud of points asymptotically distributed according to the density $\varphi\psi_T$ (where φ denotes the exact eigenfunction of H and ψ_T

the so-called trial function). Now, such a density enables one to evaluate exactly the mean value of the energy, or more generally of any observable A commuting with H, but gives only an approximate mean value for other observables.[18] If an exact mean value is wanted, a modified procedure has to be used in order to generate the exact density φ^2. In the same way that in the previous Sec. III, we emphasize that our formulas (4.5), (4.7), and (4.8) involve only the time parameter t and functional integrals; only when expressing the latter integrals as time-averages [Eq. (3.15)] we would get a simulation time T systematically involved in a limit $T \to +\infty$ to be performed for each value of t. Then formulas (4.5), (4.7), and (4.8) would give rise to a double limit $t \to +\infty$ $[T \to +\infty]$. It is *a priori* allowed neither to interchange these two limits nor to collapse them into a single limit by putting $(t = T) \to +\infty$. Any such changes should be carefully justified. An illustrative and important case where even the collapse of the two limits is *not* justified will be encountered in the release-node treatment of the fermion problem (see Sec. VI).

Finally, as far as we know, no procedure aiming at evaluating *second-order* properties seems to have been proposed in the framework of these previous QMC methods, and our procedure offers in this respect an important potential advantage.

V. THEORETICAL ALGORITHM

We present here the basic ideas of the algorithm. The main steps are:

(i) Choose some suitable reference function $\varphi_0^{(0)}$ from which the reference diffusion is built [see Eqs. (2.9)–(2.11)].

(ii) Using the stochastic differential equation (SDE) associated with the reference diffusion process[34] generate through a step-wise procedure (with a time step Δt) a stochastic trajectory $X^{(0)}(t)$. The SDE is written

$$dX(t) = b[X(t)]dt + \mathscr{D}^{1/2}dW, \qquad (5.1)$$

where W is the multidimensional Wiener process and b, $\mathscr{D}$ are given by Eqs. (2.11).

(iii) According to formula (3.15), evaluate the desired functional integrals as time-averages over the stochastic trajectory $X^{(0)}(t)$.

In actual fact, it is appropriate to introduce, instead of a single very long trajectory, a set of shorter trajectories because the corresponding set of mean values enable us to evaluate the variance using standard statistical methods.[35]

VI. THE PAULI PRINCIPLE AND ITS CONSTRAINTS

A. General framework

The quantum mechanics of fermionic systems with a spin-free Hamiltonian can be formulated independently of spin functions or spin operators. The requirements of the Pauli principle are then expressed as follows: among eigenfunctions of H only those belonging to irreducible representation (IR) of the symmetric group $S(N)$ (where N is the number of particles) with a Young diagram containing at most two columns are allowed. These states are referred to as the fermionic states. Moreover, for each of these allowed representation there corresponds a well-defined total spin S for the system. Further explanations concerning the formulation of the Pauli principle in a spin-free formalism may be found elsewhere (a convenient reference is the textbook by Landau and Lifshitz,[36] see also Hamermesh[37] and Matsen[38]).

In Sec. IV above, the expressions of quantum mean values and response properties have been given for the lowest state (which was denoted as φ_{i_0}) having nonzero overlap with $f\varphi_0^{(0)}$ and $g\varphi_0^{(0)}$. Now, by choosing the functions f, g, and $\varphi_0^{(0)}$ such that the space-functions $\phi_f = f\varphi_0^{(0)}$ and $\phi_g = g\varphi_0^{(0)}$ belong to the desired IR, it is possible to determine quantum observables for the lowest fermionic state corresponding to a given total spin. The construction of such space-functions ϕ corresponding to a given type of symmetry is easily done (see, e.g., Chap. 7 in Ref. 37). Let us give here the most common choice for ϕ[9,39]:

$$\phi(\mathbf{r}_1,...,\mathbf{r}_N) = \det\left(\prod_{i=1}^{N/2+S} u_i(\mathbf{r}_i)\right)$$

$$\times \det\left(\prod_{i=1}^{N/2-S} u_i(\mathbf{r}_{i+N/2+S})\right), \quad (6.1)$$

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

B. Some practical procedures

1. Fixed-node approximation (FNA)

In this approach, we take

$$f = g = 1 \quad (6.2)$$

and we introduce the symmetry into the diffusion process through the reference function $\varphi_0^{(0)}$:

$$\varphi_0^{(0)} = \phi_f = \phi_g = \phi. \quad (6.3)$$

According to its symmetry properties, such a reference function $\varphi_0^{(0)}$ must have some nodal hypersurfaces. These nodal hypersurfaces, where the drift $\mathbf{b} = \nabla\varphi_0^{(0)}/\varphi_0^{(0)}$ is infinite, 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 nodal hypersurfaces of the reference function $\varphi_0^{(0)}$. Now, as rightfully pointed out by Klein and Pickett,[40] the full nodal hypersurface of any space-function ϕ obeying the Pauli principle requirement cannot be completely determined by these symmetry requirements. In actual fact, the full nodal

hypersurface of any *continuous* function $\phi(\mathbf{r}_1,...,\mathbf{r}_N)$ of $3N$ variables is obviously of dimension $(3N - 1)$ and bifurcates the $3N$-dimensional space. In contrast, the symmetry requirements determine only *subhypersurfaces* of *lower* dimension $(3N - 3)$ embedded in the full nodal hypersurface of ϕ.[40] We shall denote these subhypersurfaces as *exchange* or *symmetry* nodal hypersurfaces. The subset (also of dimension $3N - 1$) of the full nodal hypersurface, which complements the symmetry nodal hypersurface, will be referred to for definiteness as *peculiar nodal hypersurface*. For example, in the case of the lowest triplet state of helium-like systems,[40] the *full nodal hypersurface* (of dimension $6 - 1 = 5$) is defined by $|\mathbf{r}_1| = |\mathbf{r}_2|$, while the *symmetry nodal subhypersurface* (of dimension $6 - 3 = 3$) is defined by $\mathbf{r}_1 = \mathbf{r}_2$. Now, the exchange (symmetry) nodes are exact by their very definition (i.e., they may be taken identical for the exact solution φ_{i_0} of the Schrödinger equation and for the reference function $\varphi_0^{(0)} = \phi$): thus, they correspond to correct (but unfortunately incomplete) boundary conditions. In contrast, since the peculiar nodal hypersurface of ϕ has no reason to coincide with the exact peculiar nodal hypersurface (of the exact function φ_{i_0}) it will impose to the eigenfunctions of the Schrödinger Hamiltonian some *wrong* boundary conditions (i.e., boundary conditions different from those pertaining to the original problem of solving the genuine Schrödinger equation, where the only condition imposed to the eigenfunctions is in general vanishing at infinity). Consequently, the eigenvalues of the Schrödinger operator modified in this way will be somewhat different from those of the genuine Hamiltonian H, and some bias will be accordingly introduced. This is the well-known fixed-node approximation (see, e.g., Ref. 9).

2. Projection methods

In this case the reference function $\varphi_0^{(0)}$ is chosen nodeless and the symmetry is introduced via the functions f and g:

$$f = \phi_f/\varphi_0^{(0)}, \quad (6.4a)$$

$$g = \phi_g/\varphi_0^{(0)}. \quad (6.4b)$$

Since no extra boundary conditions are imposed to the eigenfunctions of the Schrödinger operator, the requirements concerning the Pauli principle are fulfilled here without any approximation.

We have distinguished two versions of the projection method:

(*i*) *Simple projection (SP) method.* In order to reduce the perturbing potential V_p, the reference function $\varphi_0^{(0)}$ is chosen as close as possible to the bosonic ground state φ_0 of H. In particular, no built-in structure akin to the exact wave function φ_{i_0} is introduced into $\varphi_0^{(0)}$.

(*ii*) *Release-node projection (RNP) method.* In this approach we use a more refined choice of the reference function. Choosing a symmetry-adapted ϕ close to the wave function φ_{i_0} and introducing a nonvanishing "connecting piece" function, noted cpf(x), we construct the reference function in the following way:

$$\varphi_0^{(0)} = |\phi| \quad \text{when } |\phi| > \epsilon, \quad (6.5a)$$

$$\varphi_0^{(0)} = \text{cpf}(x) \quad \text{otherwise,} \quad (6.5b)$$

where ϵ is a threshold value. Continuity of $\varphi_0^{(0)}$ and its first derivative is imposed at the points where $\varphi_0^{(0)} = \epsilon$. This construction is illustrated in Fig. 1.

In these projection methods, and in contrast to the fixed-node approach, the product

$$f[X(-t/2+\tau)]\, g[X(t/2+\tau)]$$

may change sign. This change occurs when the trajectory goes through nodal surfaces of ϕ an odd number of times in the time interval $(-t/2+\tau, t/2+\tau)$. Note that our release-node projection method is essentially similar to the so-called nodal relaxation method of Ceperley and Alder (see Secs. III B and IV in Ref. 14).

C. Further remarks concerning the exact projection methods

1. Choice of $\varphi_0^{(0)}$, f, and g

Let us consider for definiteness the problem of evaluating $I(t)$ given by Eq. (4.1):

$$I(t) = \int_{\Omega(-t/2;t/2)} f[X(-t/2)]g[X(t/2)]$$

$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{\varphi_0^{(0)}} X. \quad (6.6)$$

Numerical difficulties are essentially due to the non constant sign of $f[X(-t/2)]\, g[X(t/2)]$. We shall therefore write

$$I(t) = I_+(t) - I_-(t), \quad (6.7)$$

where $I_+(t)$ and $I_-(t)$ are the contributions coming respectively from the positive and negative values of the product $f[X(-t/2)]\, g[X(t/2)]$, namely

$$I_\pm(t) = \int_{\Omega(-t/2;t/2)} \frac{1}{2}\{|f[X(-t/2)]$$

$$\times g[X(t/2)]| \pm f[X(-t/2)]g[X(t/2)]\}$$

$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right] D^{\varphi_0^{(0)}} X. \quad (6.8)$$

Using $|fg| = |f\|g|$, we can also [according to Eq. (4.1)] express $I_\pm(t)$ as follows:

$$I_\pm(t) = \frac{1}{2}\left[\langle|f|\varphi_0^{(0)}|e^{-t(H-E_0^{(0)})}\|g|\varphi_0^{(0)}\rangle\right.$$

$$\left. \pm \langle f\varphi_0^{(0)}|e^{-t(H-E_0^{(0)})}|g\varphi_0^{(0)}\rangle\right]. \quad (6.9)$$

We can now apply to each matrix element the same procedure as used in obtaining Eq. (4.4):

$$\langle|f|\varphi_0^{(0)}|e^{-t(H-E_0^{(0)})}\|g|\varphi_0^{(0)}\rangle$$

$$= \langle|f|\varphi_0^{(0)}|\varphi_0\rangle\langle\varphi_0\|g|\varphi_0^{(0)}\rangle e^{-t(E_0-E_0^{(0)})} + \cdots, \quad (6.10a)$$

$$\langle f\varphi_0^{(0)}|e^{-t(H-E_0^{(0)})}|g\varphi_0^{(0)}\rangle$$

$$= \langle f\varphi_0^{(0)}|\varphi_{i_0}\rangle\langle\varphi_{i_0}|g\varphi_0^{(0)}\rangle e^{-t(E_{i_0}-E_0^{(0)})} + \cdots, \quad (6.10b)$$

where φ_{i_0} is the lowest state belonging to the symmetry type imposed by f and g. Note that in the previous matrix element (6.10a) the expansion actually begins with the bosonic ground state φ_0 of H, since $|f|\varphi_0^{(0)}$ and $|g|\varphi_0^{(0)}$ are nonnegative everywhere, as is φ_0. Let us denote for brevity:

$$[f\varphi_0^{(0)}, g\varphi_0^{(0)}](t) = \langle f\varphi_0^{(0)}|e^{-t(H-E_0^{(0)})}|g\varphi_0^{(0)}\rangle. \quad (6.11)$$

We can rewrite Eq. (6.9) as

$$I_\pm(t) = \frac{1}{2}\{[|f\varphi_0^{(0)}|, |g\varphi_0^{(0)}|](t)$$

$$\pm [f\varphi_0^{(0)}, g\varphi_0^{(0)}](t)\}. \quad (6.12)$$

We now notice the remarkable fact that $I_+(t)$ and $I_-(t)$, like $I(t)$ itself, depend only on $\phi_f = f\varphi_0^{(0)}$ and $\phi_g = g\varphi_0^{(0)}$, and *not* on f, g, and $\varphi_0^{(0)}$ separately. Consequently, the choice of $\varphi_0^{(0)}$ is not directly crucial at this stage, since it is always possible to compensate it through a suitable choice of f and g in such a way as to get prescribed functions
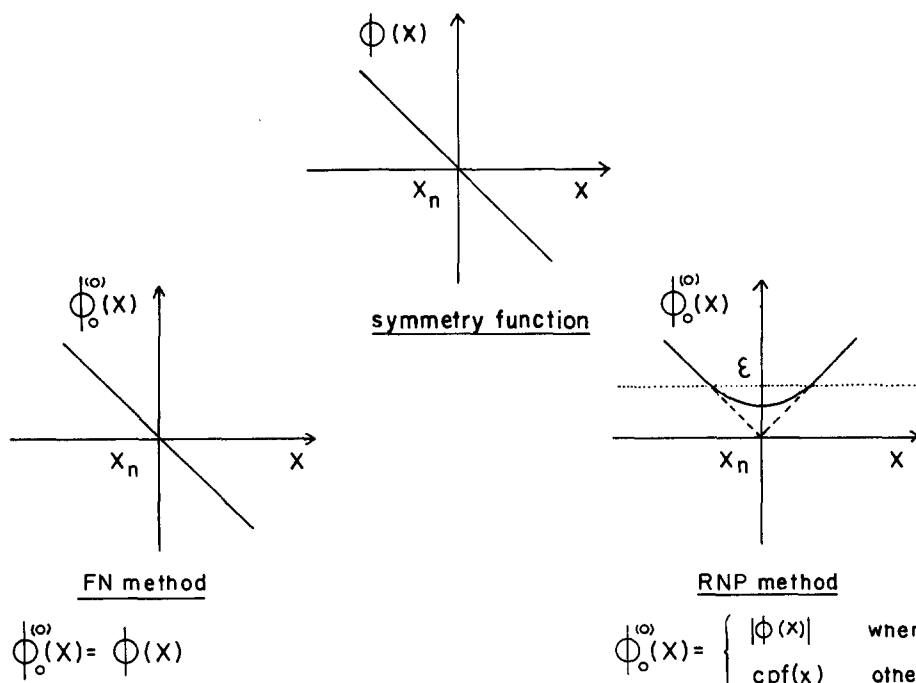

FIG. 1. Comparison between the fixed-node (FN) method and the release-node projection (RNP) method. In both cases, the behavior of the reference function $\varphi_0^{(0)}$ in the neighborhood of the node X_n is pictured. The continuous line — represents $\varphi_0^{(0)}(X)$. In the RNP case, the dashed line - - - represents $|\phi|(X)$.

$\phi_f = f\varphi_0^{(0)}$ and $\phi_g = g\varphi_0^{(0)}$. At this stage, it therefore appears convenient to proceed in two steps for our discussion:

(i) Choice of ϕ_f and ϕ_g (in actual practice, we generally take $\phi_f = \phi_g = \phi$).

(ii) Once ϕ_f and ϕ_g have been chosen, what role is left for the choice of $\varphi_0^{(0)}$?

As concerns the choice of ϕ_f and ϕ_g, it must first be emphasized that $I_+(t)$ and $I_-(t)$ contain unavoidably nonzero contributions from the unwanted bosonic states. These contributions are actually identical, since they are provided by the matrix element $[|\phi_f|, |\phi_g|](t)$, common to both $I_+(t)$ and $I_-(t)$. The other matrix element $[\phi_f, \phi_g](t)$ $= I(t)$ contains no such bosonic contribution, according precisely to the *ad hoc* choice of ϕ_f and ϕ_g. According to Eqs. (6.10), it now appears that ϕ_f and ϕ_g should be chosen so as to maximize the overlap integrals $\langle \phi_f | \varphi_{i_0} \rangle$ and $\langle \varphi_{i_0} | \phi_g \rangle$, while also minimizing the overlap integrals $\langle |\phi_f| \varphi_{i<i_0} \rangle$ and $\langle \varphi_{i<i_0} \| \phi_g | \rangle$. From these requirements, taking $\phi_f = \phi_g = \phi$ close to the desired (fermionic) state φ_{i_0} looks like a reasonable choice.

Once ϕ_f and ϕ_g have been so chosen, $I_+(t)$ and $I_-(t)$ are determined, and the choice of $\varphi_0^{(0)}$ now concerns the variance (for any given simulation time) in the Monte Carlo estimation of $I_+(t)$ and $I_-(t)$. Thus, the release-node projection method consists in choosing $\varphi_0^{(0)}$ close to $|\varphi_{i_0}|$, and $f = g$ close to sign (φ_{i_0}), while the simple projection method chooses $\varphi_0^{(0)}$ close to the bosonic ground state φ_0. Numerical experiment (see Ref. 14 and part II of the present work) so far indicates that the RNP method indeed exhibits lower variance.

2. On the role played by the distinction between the evolution time parameter t and the simulation time T

We are now in a position to discuss in a precise manner the difficulties associated with the Pauli principle requirements alluded to in the Introduction. As emphasized by other authors (see, e.g., Refs. 8, 14, and 41), the fermionic quantity of interest is obtained as the difference of two (bosonic type) larger quantities which have the same order of magnitude. This is a typically unfavorable situation from the numerical point of view. More precisely, in our formalism, the desired fermionic quantity is $I(t)$, and the two bosonic quantities are $I_+(t)$ and $I_-(t)$ [see Eq. (6.7)]. Then, according to Eqs. (6.9) and (6.10) we have, for large t:

$$I_+(t) \sim I_-(t) \sim [|f\varphi_0^{(0)}|, |g\varphi_0^{(0)}|](t) \sim e^{-t(E_0 - E_0^{(0)})},$$
(6.13a)

$$I(t) = [f\varphi_0^{(0)}, g\varphi_0^{(0)}](t) \sim e^{-t(E_{i_0} - E_0^{(0)})},$$
(6.13b)

hence

$$I(t)/I_\pm(t) \underset{t \to +\infty}{\sim} e^{-t(E_{i_0} - E_0)}.$$
(6.14)

Now the Monte Carlo simulation will provide the values of $I_+(t)$ and $I_-(t)$ with some statistical uncertainty (standard deviation) leading to a relative error of the form (for large T)

$$\delta I_\pm(t)/I_\pm(t) \sim C_\pm(t)T^{-1/2},$$
(6.15)

where T denotes the simulation time, while $C_+(t)$ and $C_-(t)$ are independent of T (and in general increase with t). Since we have no reason to assume that the errors δI_+ and δI_- are correlated, the error δI should be of the same order of magnitude, and consequently the relative error pertaining to $I(t)$ would be of the form

$$\delta I/I \sim C(t)T^{-1/2}e^{t(E_{i_0} - E_0)}.$$
(6.16)

According to this formula, in order to keep $\delta I/I$ under control, it appears essential to vary t and T independently. Noticeably, when t increases, it will become necessary, sooner or later, to have T increasing *much faster*. Any method in which t and T are (possibly in an implicit way) taken of the same order of magnitude will fail to meet this requirement and will therefore become useless for large enough values of $t \approx T$. Such a method will be able to work for not too large values of $t \approx T$, and under the condition that $C(t)$ is small enough. Since $C(t)$ gives the (relative) variance for $T = 1$, we may expect to reduce it by improving the choice of the reference function $\varphi_0^{(0)}$. Apparently, the situation just described corresponds to the previous Monte Carlo procedures,[8,14] where the simulation time T is also the evolution "imaginary" time t. In actual fact, a discussion similar to the above one has been given by Kalos[42] in the framework of the Green's function Monte Carlo method. This can be seen by comparing his Eq. (14) with our Eqs. (6.7) and (6.13). Kalos's Eq. (14) involves only *one parameter n*, proportional to the total simulation time (that we denote T), a situation which reflects the implicit relationship $t = T$. By contrast, in our procedure, t and T remain perfectly distinct, which in principle offers the possibility of correctly evaluating $I(t)$ *for fixed t* by making T large enough. Now, in order to obtain the energy E_{i_0}, the straightforward procedure corresponding to formula (4.5) requires large values of t. This could result in a demand for unrealistically large values of the simulation time T. However, we could then still resort to more sophisticated procedures using only values of $I(t)$ for a set of values of t restricted to some reasonable interval (see the Padé-integral procedure in the companion paper).

VII. CONCLUSION

A basic feature of the Monte Carlo method developed in the present work is the definition of a reference diffusion process associated with some reference function $\varphi_0^{(0)}$, with the crucial property that the Fokker–Planck operator $L^{(0)}$ of this process is connected through a similarity transformation with some reference Hamiltonian $H^{(0)}$ itself easily defined from $\varphi_0^{(0)}$. By relying on this connection between $L^{(0)}$ and $H^{(0)}$, we showed that it is possible to express in an easy and systematic way quantum properties pertaining to any Hamiltonian $H = H^{(0)} + V_p$, in terms of functional integrals (involving the "perturbing" potential V_p) making use of the diffusion measure associated with the reference diffusion process. Its simple and systematic character makes this approach quite attractive. Thus, to our knowledge, the possibility of easily obtaining expressions for response properties (beyond usual mean values) is a specific advantage of our approach over the other Monte Carlo methods. Needless to say, this possibility is also a very attractive feature with re-

spect to standard methods based on the use of basis sets, since the evaluation of response properties then implies the introduction of basis sets augmented with suitable "polarization" functions (with little assurance concerning the quality of the results, beyond the simplest systems).

Similarly, it has been possible to discuss in a natural way some "hierarchy" of solutions concerning the problems posed by the Pauli principle requirements for many-fermion problems. First, as is the case in other Monte Carlo schemes, we could define a so-called *fixed-node* approximation, whereby approximate eigenfunctions of the Hamiltonian H are obtained, subject to the constraint that they vanish along the nodes of the reference function $\varphi_0^{(0)}$. But in order to give to the Monte Carlo approach its full power, it is of course essential to go beyond this approximation, and we therefore examined a theoretically rigorous procedure for getting access to eigenspaces belonging to some *prescribed symmetry type*. As done in previous work (see, e.g., Refs. 8 and 14) we further considered two variants for this procedure, based on different choices for the reference function $\varphi_0^{(0)}$. The first choice is a mere "bosonic" ground state, with no built-in structure akin to the desired symmetry type. The second choice, although being everywhere strictly positive (as it must), is required to remain close to $|\phi|$, where ϕ is some function belonging to the desired symmetry type, and, as far as possible, close to the desired exact function (in order to reduce the perturbing potential V_p). The latter choice, of course, looks more attractive than the former one, but adequate checking of both variants remains to be done.

In a companion paper, the computer implementation of the method will be considered in more detail. We shall describe a few illustrative examples, namely one-dimensional systems first, and then some simple systems of chemical interest (atoms and the H_2 molecule).

ACKNOWLEDGMENT

APPENDIX

In this Appendix, we present the rigorous relationship existing between our generalized Feynman–Kac formula and quite similar formulas written down without explicit derivation by Pollock and Ceperley [formula (A5) in Ref. 23] and Ceperley and Alder [formula (11) in Ref. 14].

For that purpose we start from our basic FGFK formula (3.7) with $A_i = 1$, $i = 1$ to q:

$$\langle f\varphi_0^{(0)}|e^{-t(H-E_0^{(0)})}|g\varphi_0^{(0)}\rangle$$

$$= \int_{\Omega(-t/2;t/2)} f[X(-t/2)]g[X(t/2)]$$

$$\times \exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right]D^{\varphi_0^{(0)}}X. \qquad (A1)$$

Choosing $f = \delta_r/\varphi_0^{(0)}$ and $g = \delta_{r'}/\varphi_0^{(0)}$ we get

$$\langle r|e^{-tH}|r'\rangle$$

$$= \frac{e^{-tE_0^{(0)}}}{\varphi_0^{(0)}(r)\varphi_0^{(0)}(r')}\int_{\Omega(-t/2;t/2)} \delta_r[X(-t/2)]\delta_{r'}$$

$$\times [X(t/2)]\exp\left[-\int_{-t/2}^{t/2} V_p[X(s)]ds\right]D^{\varphi_0^{(0)}}X. \qquad (A2)$$

Note that $\langle r|e^{-tH}|r'\rangle$ is the usual time-dependent Green function (or density matrix). Using notations from Refs. 14 and 23 and the time-shifting invariance of the functional integral, equality (A2) may be rewritten in the form

$$\rho(r,r',\beta) = \frac{e^{-\beta E_0^{(0)}}}{\varphi_0^{(0)}(r)\varphi_0^{(0)}(r')}$$

$$\times \int_{\Omega(0,\beta)} \delta_r[X(0)]\delta_{r'}[X(\beta)]$$

$$\times \exp\left[-\int_0^\beta V_p[X(s)]ds\right]D^{\varphi_0^{(0)}}X. \qquad (A3)$$

Now, we express the previous functional integral under its constructive form, namely

$$\lim_{n\to+\infty}\int dX_0\cdots dX_n\, \delta_r(X_0)\delta_{r'}(X_n)$$

$$\times p_{n+1}^{(0)}(X_0,0;X_1,\Delta\beta;\cdots;X_n,n\Delta\beta)$$

$$\times \exp\left[-\Delta\beta\sum_{i=1}^n V_p(X_i)\right] \qquad (A4)$$

with $\Delta\beta = \beta/n$. Integrating over X_0 and X_n, using Eq. (3.13) and the property $p^{(0)} = \varphi_0^{(0)2}$, lead to the following expression for $\rho(r,r',\beta)$:

$$\rho(r,r',\beta) = e^{-\beta E_0^{(0)}}\frac{\varphi_0^{(0)}(r)}{\varphi_0^{(0)}(r')}\lim_{n\to+\infty}\int dX_1\cdots dX_{n-1}$$

$$\times p^{(0)}(r]X_1,\Delta\beta)\cdots p^{(0)}(X_{n-1}]r',\Delta\beta)$$

$$\times \exp\left[-\Delta\beta\sum_{i=1}^n V_p(X_i)\right]. \qquad (A5)$$

Equality (2.13) gives

$$p^{(0)}(r]r',\beta) = \frac{\varphi_0^{(0)}(r')}{\varphi_0^{(0)}(r)}e^{\beta E_0^{(0)}}\rho^{(0)}(r,r',\beta),$$

where $\rho^{(0)}$ is the time-dependent Green function (or density matrix) associated with $H^{(0)} = H - V_p$. Equality (A5) becomes

$$\rho(r,r',\beta) = \rho^{(0)}(r,r',\beta)\lim_{n\to+\infty}\int dX_1\cdots dX_{n-1}$$

$$\times \frac{p^{(0)}(r]X_1,\Delta\beta)\cdots p^{(0)}(X_{n-1}]r',\beta)}{p^{(0)}(r]r',\beta)}$$

$$\times \exp\left[-\Delta\beta\sum_{i=1}^n V_p(X_i)\right]. \qquad (A6)$$

Now, using Eq. (3.13) and the definition of the conditional probability densities, namely

$$p_{p|n+p}(X_1,t_1;\cdots;X_p,t_p]X_{p+1},t_{p+1};\cdots;X_{p+n},t_{p+n})$$

$$= p_{p+n}(X_1,t_1;\cdots X_{p+n},t_{p+n})/p_p(X_1,t_1;\cdots;X_p,t_p);$$

(A7)

the infinitesimal probability

$$\frac{p^{(0)}(\mathbf{r}]X_1,\Delta\beta)\cdots p^{(0)}(X_{n-1}]\mathbf{r}',\Delta\beta)}{p^{(0)}(\mathbf{r}]\mathbf{r}',\beta)} d X_1\cdots d X_{n-1}$$

may be rewritten as

$$p\left(\mathbf{r},0;\mathbf{r}',\beta]X_1,\Delta\beta;\cdots;X_{n-1},\Delta\beta\frac{n-1}{n}\right)d X_1\cdots d X_{n-1},$$

(A8)

which leads to a conditioned measure over the space of trajectories, namely the measure associated with the drifting random walks satisfying the boundary conditions $X(0) = \mathbf{r}$ and $X(\beta) = \mathbf{r}'$. The corresponding functional integral has been denoted $\langle\cdots\rangle_{DRW}$ by Pollock and Ceperley. Finally, using this notation we have

$$\rho(\mathbf{r},\mathbf{r}',\beta) = \rho^{(0)}(\mathbf{r},\mathbf{r}',\beta)$$

$$\times\left\langle\exp\left[-\int_0^\beta V_p[X(s)]ds\right]\right\rangle_{DRW}.$$

(A9)

This formula coincides with formulas (11) in Ref. 14 and (A5) in Ref. 23. In conclusion, expression (A5) of Ref. 23 appears to be a particular case of our more general FGFK formula.

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