Unbiased estimators in quantum Monte Carlo methods: Application to liquid ^{4}He

J. Casulleras and J. Boronat
Departament de Física i Enginyeria Nuclear, Campus Nord B4-B5,
Universitat Politècnica de Catalunya, E-08028 Barcelona, Spain
(Received 13 January 1995; revised manuscript received 25 April 1995)

A Monte Carlo algorithm for computing quantum-mechanical expectation values of coordinate operators in many-body problems is presented. The algorithm, which relies on the forward walking method, fits naturally in a Green's function Monte Carlo calculation, i.e., it does not require side walks or a bilinear sampling method. Our method evidences stability regions large enough to accurately sample unbiased pure expectation values. The proposed algorithm yields accurate results when it is applied to test problems such as the hydrogen atom and the hydrogen molecule. An excellent description of several properties of a fully many-body problem such as liquid ^{4}He at zero temperature is achieved.

I. INTRODUCTION

Quantum Monte Carlo (QMC) methods have become an invaluable tool in the study of many-body systems over recent decades. Among them, the Green's function Monte Carlo (GFMC) method[1–3] has been extensively applied to the calculation of ground-state properties of small molecules and quantum liquids and solids at zero temperature. Within the GFMC techniques one can distinguish between the domain GFMC,[1] which stochastically constructs the Green's function, and the diffusion Monte Carlo (DMC) method[4] based on a short-time approximation for the Green's function. We will focus our discussion on the DMC method but the algorithm we present here for the evaluation of pure estimators can also easily be incorporated in a domain GFMC program.

The DMC method solves the Schrödinger equation in imaginary time for the function $f(\mathbf{R},t)=\psi(\mathbf{R})\Psi(\mathbf{R},t)$,

$$-\frac{\partial f(\mathbf{R},t)}{\partial t}=-\frac{1}{2}\nabla^2_{\mathbf{R}}f(\mathbf{R},t)+\frac{1}{2}\nabla_{\mathbf{R}}[\mathbf{F}(\mathbf{R})f(\mathbf{R},t)] +[E_L(\mathbf{R})-E]\,f(\mathbf{R},t)\ , \tag{1}$$

$\Psi(\mathbf{R},t)$ being the wave function of the system and $\psi(\mathbf{R})$ a trial function used for importance sampling. In Eq. (1), which is written in atomic units, $E_L=\psi(\mathbf{R})^{-1}H\psi(\mathbf{R})$ is the local energy and $\mathbf{F}(\mathbf{R})=2\psi(\mathbf{R})^{-1}\nabla_{\mathbf{R}}\psi(\mathbf{R})$ is the so-called quantum force; $\mathbf{R}$ stands for a $3N$-coordinate vector and E is an arbitrary energy shift. The Schrödinger equation for $f(\mathbf{R},t)$ (1) presents in the right-hand side three terms that are associated, by analogy to classical equations, with diffusion, drift, and branching processes, respectively. The asymptotic solution of Eq. (1), for any value E close to the energy of the ground state and for long times ($t\to\infty$), gives the ground-state wave function $\Phi_0(\mathbf{R})$ provided that there is a nonzero overlap between $\Psi(\mathbf{R},t=0)$ and $\Phi_0(\mathbf{R})$. The formal solution of Eq. (1) is

$$f(\mathbf{R}',t+\Delta t)=\int d\mathbf{R}\ G(\mathbf{R}',\mathbf{R},\Delta t)f(\mathbf{R},t)\ , \tag{2}$$

where the Green's function $G(\mathbf{R}',\mathbf{R},\Delta t)$ gives the probability of transition from $\mathbf{R}$ to $\mathbf{R}'$ in a time interval Δt. The DMC method solves Eq. (2) stochastically assuming reasonable approximations for the Green's function when $\Delta t\to 0$.[4,5] After an iterative process, the asymptotic solution $f(\mathbf{R},t\to\infty)=\psi(\mathbf{R})\Phi_0(\mathbf{R})$ is finally obtained.

The direct calculation of the expectation value of an operator $A(\mathbf{R})$ from the asymptotic function $f(\mathbf{R},t\to\infty)$ corresponds to the mixed estimator

$$\langle A(\mathbf{R})\rangle_m=\frac{\langle\psi(\mathbf{R})\,|\,A(\mathbf{R})\,|\,\Phi_0(\mathbf{R})\rangle}{\langle\psi(\mathbf{R})\,|\,\Phi_0(\mathbf{R})\rangle}\ . \tag{3}$$

It gives an exact result only when A is the Hamiltonian H or commutes with H. Among the different methods to calculate expectation values for operators that do not commute with H, the extrapolation method[1,6] is the most widely used. Following this method, which has been extensively applied in QMC calculations, one has an approximation to the "pure" (exact) value,

$$\langle A(\mathbf{R})\rangle_p=\frac{\langle\Phi_0(\mathbf{R})\,|\,A(\mathbf{R})\,|\,\Phi_0(\mathbf{R})\rangle}{\langle\Phi_0(\mathbf{R})\,|\,\Phi_0(\mathbf{R})\rangle}\ , \tag{4}$$

by means of a linear extrapolation

$$\langle A(\mathbf{R})\rangle_e=2\,\langle A(\mathbf{R})\rangle_m-\langle A(\mathbf{R})\rangle_v\ , \tag{5}$$

where

$$\langle A(\mathbf{R})\rangle_v=\frac{\langle\psi(\mathbf{R})\,|\,A(\mathbf{R})\,|\,\psi(\mathbf{R})\rangle}{\langle\psi(\mathbf{R})\,|\,\psi(\mathbf{R})\rangle} \tag{6}$$

is the variational estimator of $A(\mathbf{R})$.

The accuracy of the extrapolation method is closely related to the trial wave function used for importance sampling. Furthermore, in spite of using accurate trial wave functions, the extrapolated estimator is always biased by a quantity difficult to assess. In order to overcome these important restrictions, several algorithms have been proposed in recent years. In the approach of Zhang and

0163-1829/95/52(5)/3654(8)/$06.00

Kalos[7] a bilinear sampling method is used. In this scheme, the system is doubled and the random walks take place in an enlarged configuration space. Other approaches are based on the estimation of the quotient (Φ_0/ψ) from the asymptotic offspring coming from the branching term.[8] In this line, Barnett *et al.*[9,10] and Runge and Runge[11] have constructed tagging algorithms to properly account for the asymptotic number of descendants. Although the latter scheme has provided satisfactory results in some specific cases, the large fluctuations observed in the asymptotic offspring, and therefore in the corresponding weights (Φ_0/ψ), have precluded the consideration of forward walking as a stable and reliable method. In contrast with these considerations, we find that these statistical fluctuations (of unphysical origin) show a highly depressed effect over integrated quantities, and that in order to accurately sample pure estimators stable regions can be reached. The method we present is related to the one of Ref. 9 but with the advantage of not requiring a tagging algorithm. As we shall show in Sec. II, the averages are basically taken as mixed expectation values, and therefore the pure estimators can be readily incorporated in the original Monte Carlo algorithms.

The layout of this paper is as follows. In Sec. II the algorithm for the evaluation of pure estimators of coordinate operators is described. In order to check the correctness of our implementation in a diffusion Monte Carlo code, as well as the capability and resolution of the method, results for several moments of H and H_2, where exact results are available, are presented in Sec. III. Pure results for the partial energies and structure properties of liquid ^{4}He are reported in Sec. IV. The application of the method to a real many-body problem is a compelling test for its reliability and stability. Finally, the main conclusions are discussed in Sec. V.

II. PURE EXPECTATION VALUES

The pure estimator of an operator $A(\mathbf{R})$ (4) may be written as

$$\langle A(\mathbf{R})\rangle_p = \left\langle \Phi_0(\mathbf{R}) \left| A(\mathbf{R}) \frac{\Phi_0(\mathbf{R})}{\psi(\mathbf{R})} \right| \psi(\mathbf{R}) \right\rangle \Big/ \left\langle \Phi_0(\mathbf{R}) \left| \frac{\Phi_0(\mathbf{R})}{\psi(\mathbf{R})} \right| \psi(\mathbf{R}) \right\rangle \ . \tag{7}$$

Following Liu *et al.*,[8] $\Phi_0(\mathbf{R})/\psi(\mathbf{R})$ can be obtained from the asymptotic offspring of the $\mathbf{R}$ walker. In fact, assigning to each walker $\mathbf{R}_i$ a weight $W(\mathbf{R}_i)$ proportional to its number of descendants

$$W(\mathbf{R}) = n(\mathbf{R}, t \to \infty) \ , \tag{8}$$

Eq. (7) becomes

$$\langle A(\mathbf{R})\rangle_p = \frac{\sum_i A(\mathbf{R}_i)\, W(\mathbf{R}_i)}{\sum_i W(\mathbf{R}_i)} \ , \tag{9}$$

where the summation $\sum_i$ runs over all walkers and all times in the asymptotic regime. As is clear from its proper definition, the weight of a walker existing at time t, given by Eq. (8), is not known until a future time $t' \geq t + T$, T being a time interval long enough so that Eq. (8) could be replaced by $W(\mathbf{R}(t)) = n(\mathbf{R}(t'))$.

In order to proceed to the evaluation of Eq. (9) two different approaches are possible. In the first one, a tagging algorithm capable of identifying, at any time, which walker of any preceding configuration originated an actual walker could be used. Then, one could determine the number of descendants of the former $\mathbf{R}_i$, and accumulate its contribution to Eq. (9) "from the distance." Such a tagging algorithm has been devised in Refs. 9–11. On the other hand, one can work out an algorithm that operates with only the actual values of $A(\mathbf{R}_i)$, in such a way that a weight proportional to its future progeny is automatically introduced. This second approach is the one we have followed in the present work.

The schedule of the algorithm is the following. The set of walkers at a given time $\{\mathbf{R}_i\}$ and the values that the operator A takes on them $\{A_i\}$ evolve, after a time step, to

$$\{\mathbf{R}_i\} \to \{\mathbf{R}'_i\} \ , \tag{10}$$

$$\{A_i\} \to \{A'_i\} \ . \tag{11}$$

In the same time interval, the number of walkers N changes to N'. In order to sample the pure estimator of A, we introduce an auxiliary variable $\{P_i\}$, associated with each walker, with an evolution law given by

$$\{P_i\} \to \{P'_i\} = \{A'_i\} + \{P^t_i\} \ , \tag{12}$$

where $\{P^t_i\}$ is the old set $\{P_i\}$ "transported" to the new one, in the sense that each element P_i is replicated as many times as the $\mathbf{R}_i$ walker, without any other changes. $\{P_i\}$ is initialized to zero when the run starts.

With this procedure, after M addition steps (12) we end up with a set of N_f values $\{P_i\}$. A pure estimator of A is given by

$$\langle A(\mathbf{R})\rangle_p = \sum_{i=1}^{N_f} \{P_i\} / (M \times N_f) \ . \tag{13}$$

The contributions to the $\{P_i\}$ entering in Eq. (13) coming from the set of walkers at a past time t, $\{\mathbf{R}_i(t)\}$, can be determined by following the evolution of the series. The population as a whole has been evolving with branching from a starting time $t = 0$, giving as a result at time t a population of walkers $\{\mathbf{R}_i(t)\}$ with a distribution probability given by the trial function times the

exact one. Now, the values $A(\mathbf{R}_i)$ existing at time t enter in the pure estimator with weight 1 (although they contribute together with other values corresponding to previous times which have already been weighted). From now on, if any of the descendants of $\mathbf{R}(t)$ disappears or replicates, the former contribution does so. As a result, $A(\mathbf{R}(t))$ appears in as many rows of $\{P\}$ as descendants of $\mathbf{R}(t)$ exist, and therefore its contribution to Eq. (13) is proportional to the weight $W(\mathbf{R}(t))$ (8). Notice that no overlap exists between the time interval where the branching was used to obtain the trial function times the exact one and the interval where the branching has provided the additional weight to sample the exact ground state.

A final regard concerning the implementation of the algorithm has to be made. In Eq. (12), the "transport" operation accounts for the replication of the $A(\mathbf{R})$ contribution. In order to ensure the asymptotic condition (8), the series are continued for a while only with the reweighting law

$$\{P_i\} \rightarrow \{P_i'\} = \{P_i^t\} \ . \tag{14}$$

Since a calculation is usually divided into several blocks, one can collect data during a block and allow for a further reweighting in the following one. In this second block, new information can be accumulated to be reweighted in the next block. This mechanism can be incorporated in the algorithm in a rather simple way. The final result is that, after a first initialization block, each new block gives a value for the pure expectation value of A.

An alternative to the simple branching algorithm, implicitly assumed in the above method, is the use of weights $p(\mathbf{R}_i)$ related to the branching factor. In fact, it has been proved[9,11] that the branching algorithms with weighting allow for some reduction in the variance of the expectation values. Our method for computing pure estimators is easily extended to these algorithms. In particular, the evolution laws (12) and (14) become

$$\{P_i\} \rightarrow \{P_i'\} = \{p(\mathbf{R}_i') \times A_i'\} + \left\{ \frac{p(\mathbf{R}_i')}{p(\mathbf{R}_i)} \times P_i^t \right\} \ , \tag{15}$$

$$\{P_i\} \rightarrow \{P_i'\} = \left\{ \frac{p(\mathbf{R}_i')}{p(\mathbf{R}_i)} \times P_i^t \right\} \ , \tag{16}$$

whereas the expression of the pure expectation value (13) is only modified by a normalization factor.

III. APPLICATION TO SIMPLE SYSTEMS: H AND H_2

As a test of the algorithm developed in the preceding section, we present results for the lowest coordinate moments of the hydrogen atom H and the hydrogen molecule H_2. In both systems the nuclei are kept fixed and relativistic corrections are neglected. Atomic units have been used throughout the section.

The DMC program used in the calculations is exact up to order $(\Delta t)^2$ in the short-time approximation for the Green's function. More specific details of the algorithm are given in Ref. 12. Chin[5] has extensively discussed the relation between a quadratic time-step dependence of the eigenvalue and the violation of the cusp condition in electronic systems. However, the achievement of a quadratic dependence in Δt, which has also been discussed by Umrigar *et al.*,[13] is not the main objective of the present work. Our aim is to check the efficiency of the algorithm for the extraction of pure expectation values in simple systems, such as H and H_2, where exact results are available.

We have tested the reliability of our method by including it in two versions of the original code, corresponding to the use or not of the weights $p(\mathbf{R}_i)$ (15) and (16). In both cases, satisfactory results are obtained, the variance of the mixed and pure estimators being slightly reduced when the weights $p(\mathbf{R}_i)$ are considered in the branching process.

A. Hydrogen atom

Two different guiding functions are used for importance sampling in the H calculation. The first one corresponds to a $1s$ Slater orbital

$$\psi_{\mathrm{I}} = \exp(-\alpha r) \tag{17}$$

with a slightly modified exponent ($\alpha = 0.9$). The second one is taken as the product of the $1s$ Slater orbital with a Gaussian

$$\psi_{\mathrm{II}} = \exp(-\alpha r - \beta r^2) \tag{18}$$

with $\alpha = 1.0$ and $\beta = 0.06$. The analytic variational energies are $E_v = -0.495$ for ψ_{I} and $E_v = -0.4853$ for ψ_{II}, to be compared with the exact result $E = -0.5$. A difference between ψ_{I} and ψ_{II}, which could be relevant in the time-step dependence of the energy, is that whereas ψ_{II} satisfies the cusp condition ψ_{I} does not. As far as the DMC calculation is concerned, we have used $\Delta t = 0.05$ in both cases with no significant differences when Δt is reduced by a factor of 2. The number of walkers was maintained at a value of 700 with an unnoticeable bias with respect to larger populations. The samplings were performed over approximately 4×10^5 configurations.

In Table I variational (6), mixed (3), and extrapolated (5) estimators of the potential energy V, the radial distance r, the squared radial distance r^2, and z^2 are reported in comparison with the exact results. The extrapolated expectation values improve the mixed results, lying near the exact ones. However, some differences which depend on the trial function used for importance sampling remain, showing that the extrapolation method suffers from a systematic bias related to ψ.

The pure expectation values of the same coordinate moments are reported in Table II. Neither the ψ_{I} nor the ψ_{II} results are biased with respect to the exact values. In fact, as happens in the exact mixed estimator for the Hamiltonian, the quality of the trial function is only reflected in the magnitude of the variance. This influence

TABLE I. Variational, mixed, and extrapolated expectation values for H using $\psi_{\rm I}$ and $\psi_{\rm II}$. All the results are analytic.

	$\langle V\rangle$	$\langle r\rangle$	$\langle r^2\rangle$	$\langle z^2\rangle$
$\psi_{\rm I}$				
Variational	-0.9000	1.6667	3.7037	1.2346
Mixed	-0.9500	1.5789	3.3241	1.1080
Extrapolated	-1.0000	1.4912	2.9445	0.9815
$\psi_{\rm II}$				
Variational	-1.1507	1.2560	2.0333	0.6778
Mixed	-1.0818	1.3623	2.3072	0.7690
Extrapolated	-1.0129	1.4686	2.5811	0.8602
Exact	-1.0	1.5	3.0	1.0

TABLE II. Pure expectation values for H, using $\psi_{\rm I}$ and $\psi_{\rm II}$, in comparison with the exact results. The statistical errors are indicated in parentheses.

	$\langle V\rangle$	$\langle r\rangle$	$\langle r^2\rangle$	$\langle z^2\rangle$
$\psi_{\rm I}$	-0.9987(10)	1.4999(10)	3.0002(36)	1.0004(17)
$\psi_{\rm II}$	-0.9975(14)	1.4993(28)	2.995(14)	0.9964(61)
Exact	-1.0	1.5	3.0	1.0

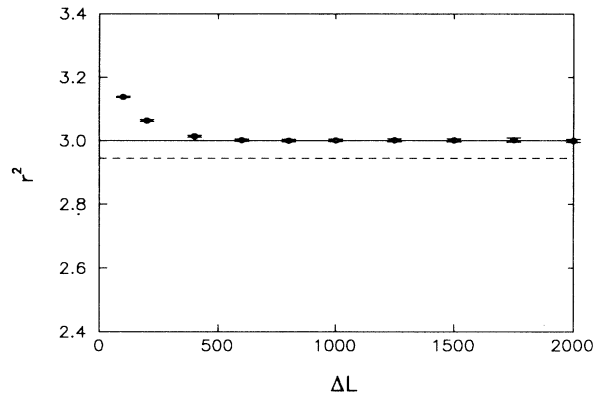

FIG. 1. Pure expectation value of r^2 for H as a function of the block length ΔL using $\psi_{\rm I}$. The solid and dashed lines correspond to the exact and extrapolated results, respectively.

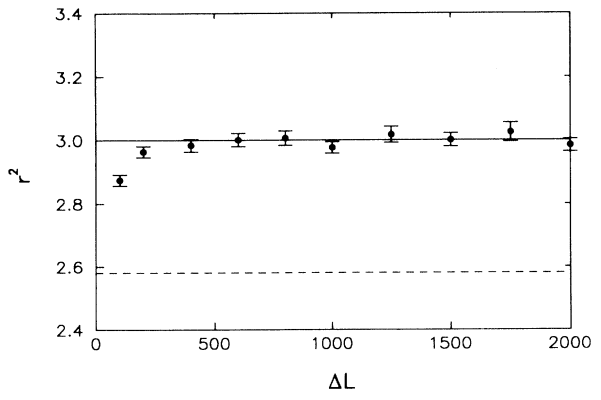

FIG. 2. Same as in Fig. 1 but for $\psi_{\rm II}$.

may be observed in the larger errors of the pure estimators for $\psi_{\rm II}$ with respect to the ones for $\psi_{\rm I}$.

The DMC calculation is divided into blocks of a number of iterations ΔL. According to the algorithm developed in Sec. II the block length has to be long enough to ensure the pure estimation in the asymptotic regime. In Figs. 1 and 2, the ΔL dependence of the pure expectation value for r^2 is plotted for $\psi_{\rm I}$ and $\psi_{\rm II}$, respectively. Also shown are the exact result (solid line) and the extrapolated estimator (dashed line) corresponding to the trial function used in the calculation. The bias coming from the wave function components other than the ground state is rapidly suppressed, as expected from the evolution law $\exp(-Ht)$. The asymptotic condition is satisfied in both cases for values $\Delta L \geq 500$. Beyond a transient regime, the prediction of the pure estimator is stable for a wide range of ΔL values with a negligible systematic bias. The statistical error in the $\psi_{\rm II}$ case is larger than in the $\psi_{\rm I}$ one but, in both cases, the central value reproduces accurately the exact results. On the other hand, the extrapolated predictions are biased with respect to the exact and pure values, significantly for $\psi_{\rm II}$ as expected from its poorer variational quality.

B. Hydrogen molecule

The trial wave function we have used in the study of the hydrogen molecule is of the form[4]

$$\Phi = \phi(r_{1A}, r_{1B})\,\phi(r_{2A}, r_{2B})\,\exp[a r_{12}/(1 + b r_{12})] \quad (19)$$

with the molecular orbital

$$\phi(r_{iA}, r_{iB}) = \exp(-\zeta\, r_{iA}) + \exp(-\zeta\, r_{iB})\ . \quad (20)$$

The distances r_{iA} and r_{iB} correspond to the electron-nucleus separation, and r_{12} stands for the electron-electron distance. The internuclear separation is kept fixed at the equilibrium distance $r_{AB} = 1.401$. In order to test the accuracy of the pure algorithm, we have used the trial function (19)–(20) with two different sets of parameters,[5]

$$\psi_{\rm I} = \Phi(\zeta = 1.189,\ a = 0.50,\ b = 0.40) \quad (21)$$

and

$$\psi_{\rm II} = \Phi(\zeta = 1.189,\ a = 0.0,\ b = 0.0)\ . \quad (22)$$

The value of ζ is obtained from the cusp condition between an electron and a nucleus ($\zeta = 1 + \exp[-\zeta\, r_{AB}]$). The Jastrow factor between the electrons appearing in the general form (20) is suppressed in $\psi_{\rm II}$ whereas it is considered in $\psi_{\rm I}$ with a value for the parameter a which guarantees the electronic cusp condition. The variational energies are $E_v = -1.1471(9)$ for $\psi_{\rm I}$ and $E_v = -1.1288(8)$ for $\psi_{\rm II}$, to be compared with the exact result $E = -1.174\,47\ldots$.[14]

The DMC calculations have been carried out with $\Delta t = 0.05$ and an average population of 500 walkers. The sampling has been made over 2×10^5 configurations.

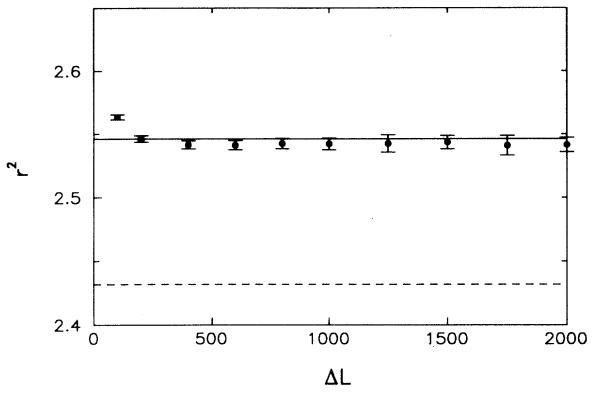

FIG. 3. Pure expectation value of r^2 for H_2 as a function of the block length ΔL using ψ_I. The solid and dashed lines correspond to the exact and extrapolated results, respectively.

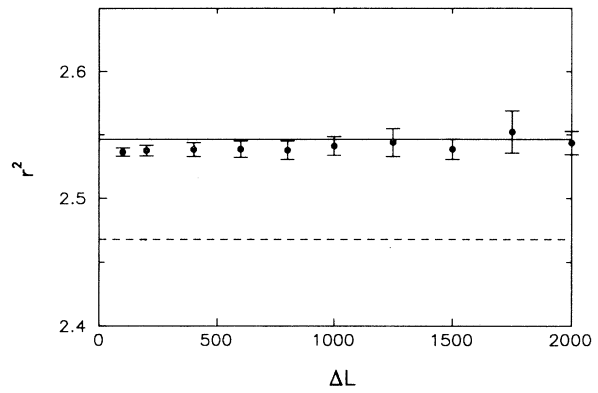

FIG. 4. Same as in Fig. 3 but for ψ_{II}.

TABLE III. Variational, mixed, and extrapolated expectation values for H_2 using ψ_I and ψ_{II}.

	$\langle V \rangle$	$\langle r^2 \rangle$	$\langle z^2 \rangle$
ψ_I			
Variational	-2.1034(9)	3.0740(1)	1.2813(38)
Mixed	-2.2415(7)	2.7530(14)	1.1281(12)
Extrapolated	-2.3796(17)	2.4320(28)	0.9749(45)
ψ_{II}			
Variational	-2.2254(19)	2.6155(23)	1.0942(22)
Mixed	-2.3012(13)	2.5416(42)	1.0409(19)
Extrapolated	-2.3770(32)	2.4677(87)	0.9876(44)
Exact	-2.3489	2.5464	1.0230

TABLE IV. Pure expectation values for H_2, using ψ_I and ψ_{II}, in comparison with the exact results.

	$\langle V \rangle$	$\langle r^2 \rangle$	$\langle z^2 \rangle$
ψ_I	-2.3448(24)	2.5424(46)	1.0244(23)
ψ_{II}	-2.3454(39)	2.5412(74)	1.0210(44)
Exact	-2.3489	2.5464	1.0230

We have checked that the biases due to the time step and the finite population are smaller than the statistical error.

The H_2 results closely follow the trends observed in the H calculation. The ΔL dependence in the pure estimator of r^2 is shown in Fig. 3 for ψ_I and in Fig. 4 for ψ_{II}. Similar behaviors have been obtained for the other operators. One can see that the asymptotic region is already reached at relatively small values of ΔL. In the asymptotic regime, the pure values fluctuate around the exact value[15] (solid line) with a statistical noise related to the quality of the trial function used for importance sampling. The growth of the error bars due to the death of walkers in the forward walking process is only significant for the largest ΔL values. The extrapolated prediction (dashed line) is manifestly biased.

In Table III, we report results for variational, mixed, and extrapolated estimators of V, r^2, and z^2 using ψ_I (21) and ψ_{II} (22) as trial functions. As one can see, the variational results of the coordinate moments for ψ_{II} are closer to the exact values than for ψ_I, although ψ_I is energetically preferred to ψ_{II}. Nevertheless, the simple extrapolated expectation values are in neither case statistically compatible with the exact values.[15] In Table IV the pure expectation values for the same moments are reported in comparison with the exact results. In spite of the shortcomings of these trial functions in reproducing the properties of H_2, the pure estimator does reproduce the exact values independently of the trial wave function.

IV. LIQUID ^{4}He

Domain GFMC and DMC methods have been extensively applied to the study of the ground-state properties of liquid ^{4}He for the last 15 years.[12,16] The exactness of these methods joined with the accuracy in the knowledge of the He interatomic potential has made feasible an excellent agreement between theoretical results and experimental data. In order to sample expectation values other than the Hamiltonian, e.g., partial energies or the radial distribution function $g(r)$, the extrapolation method has been commonly used. In spite of the success in describing properties such as $g(r)$ a small bias is present in integrated quantities such as the potential energy. Furthermore, the extrapolated estimator has evidenced its shortcomings in the calculation of density profiles of ^{4}He clusters by producing unphysical negative values for $\rho(r)$ in the cluster surface.[17] We have applied the algorithm developed in Sec. II to bulk liquid ^{4}He in order to show both its applicability to a fully many-body problem and its capacity of removing the uncertainties introduced by the extrapolation method.

The Schrödinger equation is solved by means of a quadratic diffusion Monte Carlo method considering the N-particle Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2_{\mathbf{R}} + V(\mathbf{R}) , \tag{23}$$

where $\mathbf{R} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and $V(\mathbf{R})$ is the interatomic po-

tential. The results presented below have been obtained considering the HFD-B(HE) potential proposed by Aziz *et al.*[18] In a previous paper[12,19] we have shown that this renewed version of the well-known Aziz potential[20] appreciably improves the equation of state of liquid ^{4}He with respect to the Aziz results.

In order to establish the influence of the trial wave function used for importance sampling several options have been considered. The first one is the simple McMillan two-body function[21]

$$\psi_{J1} = \prod_{i<j} \exp\left[-\frac{1}{2}\left(\frac{b}{r_{ij}}\right)^5\right] \tag{24}$$

with $b = 1.20\sigma$ ($\sigma = 2.556$ Å). The second one is an improved version of (24) proposed by Reatto[22]

$$\psi_{J2} = \prod_{i<j} \exp\left\{-\frac{1}{2}\left(\frac{b}{r_{ij}}\right)^5 - \frac{L}{2}\exp\left[-\left(\frac{r_{ij}-\lambda}{\Lambda}\right)^2\right]\right\} \tag{25}$$

with $b = 1.20\sigma$, $L = 0.2$, $\lambda = 2.0\sigma$, and $\Lambda = 0.6\sigma$. Finally, we have also used a trial wave function which contains three-body correlations,[23]

$$\psi_{JT} = \psi_{J1} \exp\left[-\frac{1}{4}\lambda\sum_k \mathbf{G}_k\cdot\mathbf{G}_k + \frac{1}{2}\lambda\sum_{i<j}\xi^2(r_{ij})\,r_{ij}^2\right], \tag{26}$$

where

$$\mathbf{G}_k = \sum_{l\neq k}\xi(r_{kl})\mathbf{r}_{kl} \tag{27}$$

and

$$\xi(r) = \exp\left[-\left(\frac{r-r_t}{r_\omega}\right)^2\right]. \tag{28}$$

The values for the triplet parameters are $\lambda = -1.08\sigma^{-2}$, $r_t = 0.80\sigma$, and $r_\omega = 0.41\sigma$. In the three trial functions, the values of the parameters are those which optimize the variational energy at the experimental equilibrium density $\rho_0^{\rm expt} = 0.365\sigma^{-3}$. All the results presented below correspond to the density $\rho_0^{\rm expt}$ that coincides with the theoretical equilibrium density.[12]

Results for the potential energy per particle using ψ_{J1}, ψ_{J2}, and ψ_{JT} as importance sampling are reported in Table V. A small but significant difference between the extrapolated results $\langle V/N\rangle_e$ appears, pointing to a bias related to the quality of the trial wave function. The bias is completely removed when the pure estimator is calculated, as one can see in the last row of Table V. The three values for $\langle V/N\rangle_p$ are indistinguishable and, what is more important, they evidence a systematic error of the extrapolation approximation. In fact, none of the extrapolated values is statistically compatible with the common pure value, the closest estimation being the one obtained with ψ_{JT}, which actually is the best variational choice. Considering the result for the energy per particle $E/N = -7.267 \pm 0.013$ K,[12] the pure result for the kinetic energy is $T/N = 14.32 \pm 0.05$ K. Experimental determinations from analysis of deep inelastic scattering data predict a slightly lower value $(T/N)^{\rm expt} = 13.3 \pm 1.3$ K,[24] the difference being mainly due to the significant errors in the experimental measurement of the tail of the response function.

As far as the stability of the method is concerned, the dependence of the pure expectation value of V/N on the length of the forward walking is plotted in Fig. 5. The results obtained (points with error bars) follow the trends observed in Sec. III (Figs. 1–4). After a transition regime, and already for relatively small ΔL values ($\Delta L \geq 250$), an asymptotic limit is reached where the systematic error is practically negligible. Notice that in the simple algorithm we have presented in Sec. II a forward walking of length ΔL is constructed from data ranging from ΔL to $2\Delta L$, and hence the length of the forward walking is not the same for all the walkers. This effect is not relevant provided that a region of stability exists. On the other hand, one can determine the asymptotic value within a single run by collecting data for different block lengths. The statistical errors associated with each individual ΔL value can be lowered in the same way as mixed estimators, i.e., by continuing the evolution of the series. The biases associated with the extrapolated expectation values are also shown in Fig. 5, where $\langle V/N\rangle_e$ using ψ_{J2} and ψ_{JT} are represented by a long-dashed and a short-dashed line, respectively.

TABLE V. Variational, mixed, extrapolated, and pure expectation values of V/N (in K) for liquid ^{4}He at $\rho_0^{\rm expt}$ using different trial wave functions ψ.

	ψ_{J1}	ψ_{J2}	ψ_{JT}
$\langle V/N\rangle_v$	-21.054(26)	-21.311(18)	-21.348(20)
$\langle V/N\rangle_m$	-21.459(8)	-21.600(8)	-21.541(8)
$\langle V/N\rangle_e$	-21.864(30)	-21.889(24)	-21.734(25)
$\langle V/N\rangle_p$	-21.56(5)	-21.59(5)	-21.58(5)

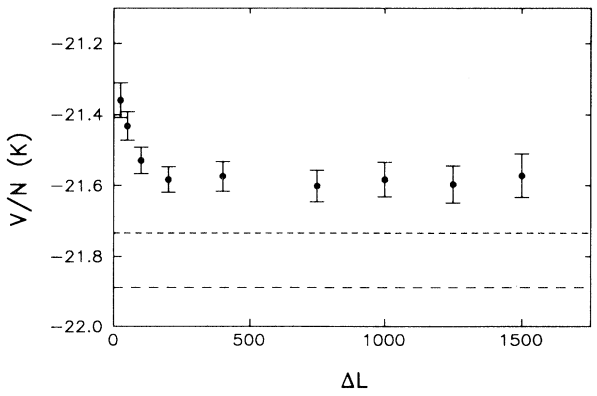

FIG. 5. Pure expectation value of V/N for liquid ^{4}He at $\rho_0^{\rm expt}$ as a function of the block length ΔL. The long-dashed and short-dashed lines stand for the extrapolated estimations using ψ_{J2} and ψ_{JT}, respectively.

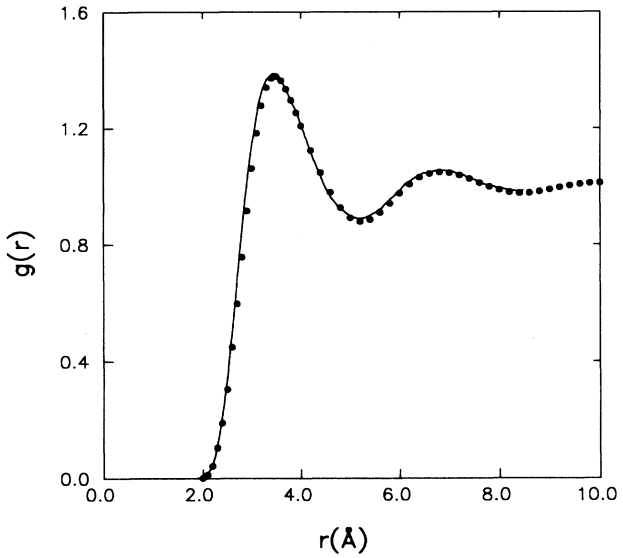

FIG. 6. Pure expectation result of the two-body radial distribution function (solid line) for liquid ^{4}He at ρ_0^{expt} in comparison with the experimental data (points) of Ref. 25.

Other important quantities in the study of quantum liquids can also be calculated with the pure algorithm. In particular, the two-body radial distribution function

$$g(r_{12}) = \frac{N(N-1)}{\rho^2} \frac{\int |\Phi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)|^2 \, d\mathbf{r}_3 \ldots d\mathbf{r}_N}{\int |\Phi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)|^2 \, d\mathbf{r}_1 \ldots d\mathbf{r}_N} \tag{29}$$

and the static structure function

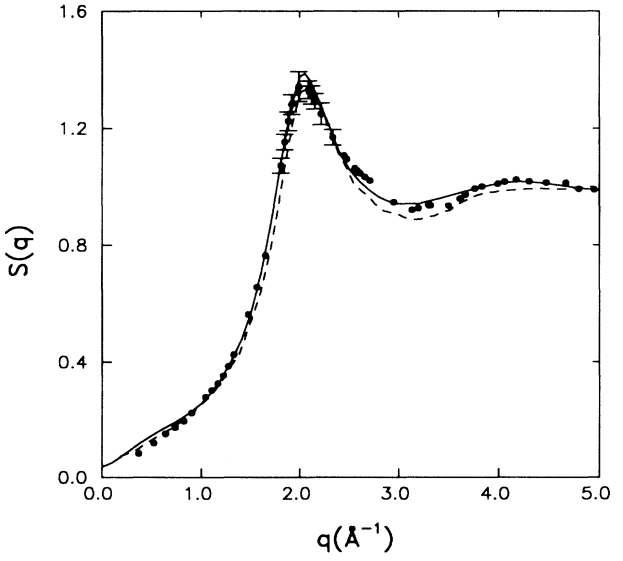

FIG. 7. Pure estimation of the static structure function (points) for liquid ^{4}He at ρ_0^{expt} in comparison with the experimental determinations of Refs. 25 (solid line) and 26 (dashed line). The error bars of the theoretical points are only depicted where larger than the size of the symbols.

$$S(q) = \frac{1}{N} \frac{\langle \Phi_0 | \rho_{\mathbf{q}} \, \rho_{-\mathbf{q}} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} \tag{30}$$

with

$$\rho_{\mathbf{q}} = \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i} \, . \tag{31}$$

The result obtained for $g(r)$ is shown in Fig. 6 in comparison with the experimental data of Ref. 25. As one can see, the pure expectation value of $g(r)$ is in good agreement with the experimental $g(r)$ for all the calculated r values. In Fig. 7 the pure structure function $S(q)$ is plotted together with the experimental measures of Refs. 25 and 26. An overall agreement between the theoretical and experimental $S(q)$ is obtained, our result lying well between the two experimental determinations. The extrapolated estimations[12,16] of $g(r)$ and $S(q)$ are not significantly different from the pure result. It is clear that the difference between the results provided by the extrapolated and pure estimators is larger for integrated quantities such as, for instance, the partial energies.

V. CONCLUDING REMARKS

We have presented a simplified version of the forward walking method to obtain unbiased expectation values for operators that do not commute with the Hamiltonian. One of the advantages of this algorithm, compared with others based on side walks or bilinear sampling, is that it enters "naturally" in any domain or short-time Green's function Monte Carlo program. The sampling of the pure estimator closely follows the standard procedure to sample mixed expectation values. Nevertheless, the main point is the stability of the method. The exponential decrease of the bias with the forward walking length and the evidence of a slow increase of the statistical uncertainties for *physical* quantities result in stability regions large enough to sample pure expectation values with negligible biases. In contrast, we do find also the common result that the weight associated with the offspring of an individual walker fluctuates all along the stability region. However, looking for stability in the values of the weights is more than should be asked for. What is mainly required from a Monte Carlo method is stability in the expectation value of an operator A, $\langle A \rangle_p$. The computation of this average has clearly a much better chance of success.

The accuracy of the method has been first verified in the H atom and the H_2 molecule. In both systems, the pure expectation values reproduce the exact results with statistical errors which are not appreciably larger than the ones associated with the extrapolated predictions. In all cases, the extrapolated expectation values appear significantly biased with respect to the pure/exact values by a quantity which is related to the trial function but difficult to assess *a priori*.

Finally, the pure algorithm has been applied to study some properties of liquid ^{4}He at zero temperature. The implementation of this algorithm in a many-body prob-

lem is also quite straightforward and the results obtained follow the same trends analyzed in the simple systems (H and H_2). The method is stable and generates results which are not biased by the importance sampling as happens with the extrapolated estimations. In order to reduce the error bars of the pure values to the level of those associated with the total energy, the series have to be a bit longer. However, one does not have to perform the auxiliary variational Monte Carlo calculation required by the extrapolation method and, more importantly, the guarantee of an exact result is fulfilled.

ACKNOWLEDGMENTS

This work has been supported in part by DGICYT (Spain) Grant Nos. PB92-0761 and PB90-06131.

[1] D.M. Ceperley and M.H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer-Verlag, Berlin, 1979).
[2] K.E. Schmidt and M.H. Kalos, in *Applications of the Monte Carlo Method in Statistical Physics*, edited by K. Binder (Springer-Verlag, Berlin, 1984).
[3] R. Guardiola, in *First International Course on Condensed Matter*, edited by D. Prosperi, S. Rosati, and G. Violini (World Scientific, Singapore, 1988).
[4] P.J. Reynolds, D.M. Ceperley, B.J. Alder, and W.A. Lester, Jr., J. Chem. Phys. **77**, 5593 (1982).
[5] S.A. Chin, Phys. Rev. B **42**, 6991 (1990).
[6] P.A. Whitlock, D.M. Ceperley, G.V. Chester, and M.H. Kalos, Phys. Rev. B **19**, 5598 (1979).
[7] S. Zhang and M.H. Kalos, J. Stat. Phys. **70**, 515 (1993).
[8] K.S. Liu, M.H. Kalos, and G.V. Chester, Phys. Rev. A **10**, 303 (1974).
[9] R.N. Barnett, P.J. Reynolds, and W.A. Lester, Jr., J. Comput. Phys. **96**, 258 (1991).
[10] P.J. Reynolds, R.N. Barnett, B.L. Hammond, and W.A. Lester, Jr., J. Stat. Phys. **43**, 1017 (1986).
[11] K.J. Runge and R.J. Runge, in *Quantum Simulations of Condensed Matter Phenomena*, edited by J.D. Doll and J.E. Gubernatis (World Scientific, Singapore, 1990); Phys. Rev. B **45**, 7229 (1992).
[12] J. Boronat and J. Casulleras, Phys. Rev. B **49**, 8920 (1994).
[13] C.J. Umrigar, M.P. Nightingale, and K.J. Runge, J. Chem. Phys. **99**, 2865 (1993).
[14] W. Kolos and L. Wolniewicz, J. Chem. Phys. **49**, 404 (1968).
[15] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).
[16] M.H. Kalos, M.A. Lee, P.A. Whitlock, and G.V. Chester, Phys. Rev. B **24**, 115 (1981).
[17] S.A. Chin and E. Krotscheck, Phys. Rev. B **45**, 852 (1992).
[18] R.A. Aziz, F.R.W. McCourt, and C.C.K. Wong, Mol. Phys. **61**, 1487 (1987).
[19] J. Boronat, J. Casulleras, and J. Navarro, Phys. Rev. B **50**, 3427 (1994).
[20] R.A. Aziz, V.P.S. Nain, J.S. Carley, W.L. Taylor, and G.T. McConville, J. Chem. Phys. **70**, 4330 (1979).
[21] W.L. McMillan, Phys. Rev. **138**, 442 (1965).
[22] L. Reatto, Nucl. Phys. **A328**, 253 (1979).
[23] K. Schmidt, M.H. Kalos, M.A. Lee, and G.V. Chester, Phys. Rev. Lett. **45**, 573 (1980).
[24] T.R. Sosnick, W.H. Snow, and P.E. Sokol, Phys. Rev. B **41**, 11 185 (1990).
[25] E.C. Svensson, V.F. Sears, A.D.B. Woods, and P. Martel, Phys. Rev. B **21**, 3638 (1980).
[26] F.H. Wirth and R.B. Hallock, Phys. Rev. B **35**, 89 (1987).