Time step bias improvement in diffusion Monte Carlo simulations

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A Makri-Miller approximation to the exact propagator and the improved split-operator propagator proposed by Drozdov are implemented within the diffusion Monte Carlo method for the simulation of boson systems, and confronted with the Trotter formula and with the importance sampling technique. As a preliminary approach, we compute analytically the time step bias of the mean energy for the different propagators in the simple case of the harmonic oscillator. These results indicate the improved split-operator propagator as the most accurate. Simulations on one- and three-dimensional model systems confirm the analytical results showing that this propagator is very efficient in reducing the time step bias, therefore improving the efficiency of the algorithm.

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I. INTRODUCTION

The diffusion Monte Carlo (DMC) method is a useful tool to study both ground and excited states of many body systems. At first, it was employed to solve the Schrödinger equation for electronic systems, i.e., to compute the electronic energy and structure of atoms and molecules [1], and later to study the nuclear wave function of large atomic and molecular aggregates [2]. Among the main advantages this method offers are the ability to easily cope, at least in principle, with any kind of interaction potential without the necessity to tailor the computer code, and the possibility to avoid the basis set expansion. Moreover, the computational effort grows slowly with the increase of the dimensionality of the problem unlike methods based on linear combination of basis functions [1].

Although these features make the DMC method appear as the method of choice for all problems where correlation between motions plays a fundamental role in describing correctly the physics of a system, its use has been hindered by its statistical nature and by the necessity to reduce the statistical error to compute accurate energy differences. The most frequently employed approach to reduce the statistical error of the DMC results is the importance sampling (IS) method [3], where an approximate trial wave function is used to guide the Monte Carlo sampling by means of a generalized Metropolis scheme based on Langevin dynamics [4]. Although this method has been found to reduce dramatically the statistical error for equal number of sampled configurations when employed in simulating the electronic structure of molecules, it requires more computational time for each simulation step and the selection and optimization of the trial function. This last step might become computationally more expensive than the DMC itself, therefore reducing the overall advantage of the IS procedure. Nevertheless, once one has an optimized trial function, IS-DMC can be efficiently used to compute the mean energies and properties using different time steps in order to eliminate the time step bias. Moreover, when the IS method is coupled with an accept-reject step based on the approximate trial wave function, the time step bias is usually reduced. Since this and related methods are well described in the literature, we refer the reader to those publications for further details [4].

Another indirect and less walked path to the reduction of the statistical error is given by the time step bias improvement that a more accurate propagator can produce [5]. This reduction of the time step bias has many advantages with respect to the simple IS: it allows us to use larger time steps, therefore improving the statistical accuracy of the results or, alternatively, reducing the computational cost for the extrapolation. This is usually obtained because the improved propagator has a leading term in the error whose order in the time step is higher than the less accurate one, and a smaller prefactor in this leading term. Furthermore, it does not require a trial wave function as IS does, freeing ourselves from the burden to define complex and highly optimized trial wave functions to guide the simulation and to compute the mean energy by the mixed estimator, since different estimators can be used. This can be advantageous when observables different from the energy are required. In this way one would not introduce any prior information in the simulation, therefore avoiding to bias the sampled distributions [6].

In this work we follow this alternative to the IS technique to reduce the time step bias, examining different propagators that have been proposed and implementing them in DMC simulations of model systems. The outline of this paper follows. Section II presents the analytical form of the propagators we compared in this work, and a summary of the analytical results for their time step bias of the mean energy in the harmonic oscillator case. In Sec. III we show the numerical energy results for three model systems and report a discussion of the relative efficiency of the propagators. Finally,

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Sec. IV contains our conclusions and proposal for future work in this direction.

II. METHOD

A. Theory of propagators in diffusion Monte Carlo

An imaginary-time version of the Schrödinger equation serves as starting point to develop the theory of the DMC methods. Specifically, this reads

$$\frac{\partial \Psi(\mathbf{R},t)}{\partial t} = \sum_i \frac{\nabla_i^2}{2m_i}\Psi(\mathbf{R},t) - V(\mathbf{R})\Psi(\mathbf{R},t), \qquad (1)$$

where $V(\mathbf{R})$ is the interaction potential, and $\mathbf{R}$ is a point in three-dimensional (3D) space.

Although we leave the analytical form of the interaction potential undefined as a way to stress the ability of Monte Carlo to cope with any local potential, we point out that the quality, accuracy, and stability of the method strongly depend on the specific potential. For instance, although all the propagators we tested can be employed to simulate Coulomb systems, their simulations might become unstable due to population blow up since this potential in atomic and molecular systems is not bound from below. Therefore, we suggest to intend our work as aimed to improve the efficiency of the DMC simulations for systems whose potential is bound from below (e.g., atomic clusters).

For the nodeless function case we consider in this work (i.e., we restrict ourselves to particles obeying Bose's statistics), the previous equation is formally equivalent to a classic diffusion process with sink and source terms dependent on the position in space. Equation (1) can be recast in the integral form

$$\Psi(\mathbf{R}',t+\tau) = \int d\mathbf{R}\, G(\mathbf{R}\to\mathbf{R}',t)\Psi(\mathbf{R},\tau), \qquad (2)$$

where $G(\mathbf{R}\to\mathbf{R}',t) = \langle \mathbf{R}'|e^{-tH}|\mathbf{R}\rangle$ is the imaginary time Green's function. If this function were known, Monte Carlo methods could be used to estimate the above integral, projecting out all the excited state components from the starting wave function $\Psi(\mathbf{R},0)$ [4].

Unfortunately, the exact Green's function is known only for very simple model Hamiltonians. For systems whose ground state wave function has no nodes, the theory of DMC relies completely on the ability to find an accurate approximation to the imaginary time Green's function of the Schrödinger equation. The usual short time approximation (STA) to this function is given by the Trotter (T) formula [7]

$$G_{\mathrm{STA}}^{T}(\mathbf{R}\to\mathbf{R}',t) = \prod_i \left(\frac{m_i}{2\pi t}\right)^{3/2} \exp\left[\frac{m_i(\mathbf{r}_i'-\mathbf{r}_i)^2}{2t}\right] \times \exp\left[-t\,\frac{V(\mathbf{R})+V(\mathbf{R}')}{2}\right] \qquad (3)$$

that is supposed to be accurate to a second order in t, i.e., for short time steps the error is proportional to t^2. This is true for the harmonic oscillator, as we will show analytically below, but it does not appear to be correct for a general potential.

During the last few years, attention has been paid to the issue of finding more accurate and more efficient STA's than this function, in order to reduce the computational effort needed for a given statistical accuracy. To tackle this problem two different approaches have been used: the first by Makri and Miller [8] and the second by Suzuki [9], Chin [10], and Drozdov [11].

In the first approach, Makri and Miller (MM) [8] expanded the logarithm of the coordinate representation of the exact Green's function as a power series in t of the form

$$G(\mathbf{R}\to\mathbf{R}',t) = t^{-3N/2}\exp\left[-t^{-1}\sum_{n=0} t^n W_n(\mathbf{R}')\right], \qquad (4)$$

where N is the total number of particles, and the $W_n(\mathbf{R}')$ were obtained exploiting the fact that the propagator is a solution of the imaginary-time Schrödinger equation. If the power series is truncated to $n=2$, one obtains the short-time approximation

$$G_{\mathrm{STA}}^{\mathrm{MM}}(\mathbf{R}\to\mathbf{R}',t) = \prod_i \left(\frac{m_i}{2\pi t}\right)^{3/2} \exp\left[\frac{m_i(\mathbf{r}_i'-\mathbf{r}_i)^2}{2t}\right] \times \exp\left[-t\int_0^1 d\xi\, V[\mathbf{R}+\xi(\mathbf{R}'-\mathbf{R})]\right], \qquad (5)$$

where $\mathbf{R}=(\mathbf{r}_1,\ldots,\mathbf{r}_N)$. This approximation has been shown to be more accurate than the T one [Eq. (3)], but the presence of the integrals over the straight motion path of a configuration limits the possibility to use it to those forms of potentials whose integrals are analytically solvable. One possible solution to this problem might be to fit the interaction potential by means of spline functions: since these are piece-wise polynomial functions, all the requested integrals can be computed analytically allowing the use of this approximation in the simulations.

Comparing the MM form and T formula, it appears that the second can be derived from the first by means of a two point approximation to the integral in $d\xi$, specifically $\int_0^1 d\xi\, V[\mathbf{R}+\xi(\mathbf{R}'-\mathbf{R})] \simeq [V(\mathbf{R})+V(\mathbf{R}')]/2$. This fact suggests the idea that one might improve the T propagator employing more points in the integral in Eq. (5) or, alternatively, a piecewise approximation of the potential by straight lines. The accuracy of these approximations to Eq. (5) could be improved also by choosing better integration rules than the one used above, e.g., Gaussian quadrature. Nevertheless, it is important to keep in mind that the efficiency of the simulation is an important issue: so the use of a larger number of integration points can reduce the computational speed of the code.

A different approach from the MM one has been pursued by Suzuki [9], Chin [10], and Drozdov [11], employing the split-operator techniques. They proposed various approximations of the exponential operator e^{-tH}, factorizing the kinetic energy and potential components of the Hamiltonian in different ways than Trotter. Among the proposed formulas, the one suggested by Drozdov (D) [11] seems to be the easiest to implement in a DMC simulation. This formula reads

$$G^{D}_{\mathrm{STA}}(\mathbf{R}\rightarrow\mathbf{R}',t)=\exp\left[-t\frac{V(\mathbf{R})+V(\mathbf{R}')}{6}\right]\times\int d\mathbf{R}''\prod_i\left(\frac{m_i}{\pi t}\right)^{3/2}\times\exp\left[\frac{m_i(\mathbf{r}_i'-\mathbf{r}_i'')^2}{t}\right]\exp[-t\tilde{V}(\mathbf{R}'')]\times\left(\frac{m_i}{\pi t}\right)^{3/2}\exp\left[\frac{m_i(\mathbf{r}_i''-\mathbf{r}_i)^2}{t}\right],\tag{6}$$

where

$$\tilde{V}(\mathbf{R})=\frac{2V(\mathbf{R})}{3}+\frac{t^2}{72}\sum_i\frac{[\nabla_i V(\mathbf{R})]^2}{m_i}.\tag{7}$$

This factorization of the evolution operator was already shown to be an improvement with respect to the standard T formula at least in path-integral simulations [11], where it allowed one to use longer time steps still giving an accurate representation of the propagated wave function. However, it has never been tested directly in a DMC calculation, so we decided to implement this propagator to compute mean energies and other observables in order to test its performance.

As pointed out by Drozdov [11], differently from T and MM formulas, the D approximation requires the computation of an integral over the intermediate point $\mathbf{R}''$. In the DMC simulation, this can be easily carried out by a Gaussian sampling of the displacement from $\mathbf{R}$ to $\mathbf{R}''$, therefore it requires a double number of normal Gaussian variates. Since the most expensive step in the DMC calculation, when no trial wave function is used, is the evaluation of the potential energy, this additional request does not spoil the efficiency of the algorithm. Instead, care must be used in programming the calculation of the gradient of the potential, since this step could become quite expensive. In Appendix A we show that for a two-body potential $V(r_{ij})$ this additional step does not introduce any significant cost in the simulation.

As the last propagator formula, we report the one employed in the standard IS-DMC algorithm that reads [3]

$$G^{\mathrm{IS}}_{\mathrm{STA}}(\mathbf{R}\rightarrow\mathbf{R}',t)=\prod_i\left(\frac{m_i}{2\pi t}\right)^{3/2}\exp\left[\frac{m_i[\mathbf{r}_i'-\mathbf{r}_i-tF_i(\mathbf{R})/(2m_i)]^2}{2t}\right]\times\exp\left[-t\frac{E_{\mathrm{loc}}(\mathbf{R})+E_{\mathrm{loc}}(\mathbf{R}')}{2}\right],\tag{8}$$

where $E_{\mathrm{loc}}=H\Psi_t/\Psi_t$, and $F_i=\nabla\Psi_t/\Psi_t$. Differently from the previous formulas, that in the long time regime sample a distribution proportional to the ground state wave function Ψ_0, the IS propagator samples the distribution $f=\Psi_t\Psi_0$. As already pointed out in the Introduction, this formula is usually coupled to an accept or reject step based on the generalized Metropolis acceptance matrix. Before we show the results obtained by the above propagators in real DMC simulations, in the next paragraph we present some analytical results for a simple model system: the harmonic oscillator.

B. Theoretical results for the harmonic oscillator

The harmonic oscillator system is one of the favorite playgrounds of chemists and physicists to test approximate methods before applying them to more complex models, or even real systems. In this work we analytically studied the accuracy of the proposed propagators employing the harmonic oscillator as a test case. This choice is based on the observation made by Lee and Lee [12] that the propagation of a Gaussian $\Psi(\mathbf{R},0)=e^{-\alpha x^2}$ by means of Eq. (2) leaves its analytical form unchanged, and only modifies the width α in a way that depends on the time step t used. This fact allows us to get a better understanding of the features of every propagator, especially of the one used by Drozdov [11] that represents the most promising one. Exploiting the mentioned result, one can solve the eigenvalue equation

$$\Psi(\mathbf{R}',t)=e^{\lambda}\int d\mathbf{R}\,G_{\mathrm{STA}}(\mathbf{R}\rightarrow\mathbf{R}',t)\Psi(\mathbf{R},0),\tag{9}$$

where the parameter t is the time step used, λ the eigenvalue, and the exact Green's function has been substituted by one of its short time approximations. The ground state solution of Eq. (9) of the form $\Psi(x)=e^{-\alpha(t)x^2}$ can be used to compute various quantities (e.g., the mean energy and potential estimator) whose values will also depend on t. Therefore, from these results one is able to judge the accuracy of the different approximations, i.e., the time step bias, varying the time step in the simulation.

Before presenting our analytical results for the harmonic oscillator with unitary mass and force constant, it is relevant to point out that the energy mean values were calculated employing both the mixed estimator [13]

$$\langle E_H(t)\rangle=\frac{\int\Psi_0(\mathbf{R})He^{-cx^2}d\mathbf{R}}{\int\Psi_0(\mathbf{R})e^{-cx^2}d\mathbf{R}}\tag{10}$$

and the mean potential estimator [1]

$$\langle E_V(t)\rangle=\frac{\int\Psi_0(\mathbf{R})V(\mathbf{R})d\mathbf{R}}{\int\Psi_0(\mathbf{R})d\mathbf{R}}\tag{11}$$

and that these quantities converge to the ground state energy for $t\rightarrow 0$. In Eq. (10) e^{-cx^2} is the trial function, whose width parameter is c. Although the mean potential estimator was the first estimator of the energy used in DMC calculations, it is no longer employed in simulating Coulomb systems due to its larger variance with respect to the mixed estimator. This is due to the fact that the mixed estimator has the nice property that it gives the exact energy, independently of the time step used, when the trial wave function is the exact one. This property is reflected in the well-known reduction of the statistical error of the simulation when the difference between the trial wave function and the exact one decreases. Nevertheless, the potential estimator is widely employed to compute mean energies for atomic and molecular clusters when a trial wave function is not at hand [14], so we feel it is worth

studying its time step bias as well as the one of the mixed estimator. Another interesting quantity that we were able to compute is the variance of these estimators, i.e., $\langle E(t)^2\rangle - \langle E(t)\rangle^2$, that is directly related to the algorithm efficiency. To avoid to burden this theoretical presentation we report the variance for the different propagators in Appendix B.

Using T [Eq. (3)], one obtains

$$\langle E_H(t)\rangle = \frac{1+c(4+t^2)^{1/2}}{4c+(4+t^2)^{1/2}} \simeq 1/2 + \frac{2c-1}{16(1+2c)}t^2, \quad (12)$$

$$\langle E_V(t)\rangle = \frac{1}{(4+t^2)^{1/2}} \simeq 1/2 - \frac{t^2}{16}, \quad (13)$$

where, for $t \to 0$, both quantities converge towards the exact value 1/2. It is interesting to note that for small time steps these two mean values are accurate to second order in t, i.e., the error is proportional to t^2. This fact contradicts the findings of Makri and Miller [8], at least for this model system.

As far as the MM [8] approximation [Eq. (5)] is concerned, our analytical results are

$$\langle E_H(t)\rangle = \frac{3+c(36+3t^2)^{1/2}}{12c+(36+3t^2)^{1/2}} \simeq 1/2 + \frac{2c-1}{48(1+2c)}t^2, \quad (14)$$

$$\langle E_V(t)\rangle = \frac{(3)^{1/2}}{(12+t^2)^{1/2}} \simeq 1/2 - \frac{t^2}{48}. \quad (15)$$

Both T and MM formulas are correct to second order in t, but with better prefactor for MM. Since the MM approach does not appear to be easy to implement for a general class of potentials and does not introduce a large improvement in the time step bias, we decided to avoid to carry out more tests on it.

With regard to the D formula, we obtained

$$\langle E_H(t)\rangle = \frac{3(12+t^2)^{1/2}+c(432+36t^2+t^4)^{1/2}}{12c(12+t^2)^{1/2}+(432+36t^2+t^4)^{1/2}} \simeq 1/2 + \frac{2c-1}{1728(1+2c)}t^4, \quad (16)$$

$$\langle E_V(t)\rangle = \frac{3(12+t^2)^{1/2}}{(432+36t^2+t^4)^{1/2}} \simeq 1/2 - \frac{t^4}{1728}, \quad (17)$$

where both the energy estimators are dependent on the fourth power of the time step. Moreover, the coefficients of t^4 are two orders of magnitude smaller than the t^2 coefficients for the other approximations: this formula could give more accurate results, using the same time step, than the previous approximations.

Since the IS-DMC method samples the distribution $f = \Psi_t \Psi_0$ instead of Ψ_0, the mean potential estimator is no longer valid to compute the mean energy during the simulation. For the IS propagator, where no accept or reject step is employed, the mixed estimator gives the result

$$\langle E_H(t)\rangle = \frac{-1+4c^3t-c(4-8ct+t^2)^{1/2}}{-4c+4c^2t-(4-8ct+t^2)^{1/2}} \simeq 1/2 + \left(\frac{c}{2}-c^2\right)t, \quad (18)$$

where c is the width of the Gaussian used to guide the simulation and to compute the mean energy. The error of the mixed estimator for IS-DMC has a linear dependence on the time step, a much worse result than the previous propagators. Unfortunately, we were not able to obtain the same quantity for the IS algorithm coupled to the accept or reject step.

A different method to introduce the importance sampling in the DMC simulations was developed by Kalos [13], and it is based on a simple reweighting scheme of the branching factor. Specifically, the branching factor of the propagator is multiplied by $\Psi_t(\mathbf{R}')/\Psi_t(\mathbf{R})$, where $\mathbf{R}'$ and $\mathbf{R}$ are, respectively, the final and initial positions of a walker in a Monte Carlo step. This approach can be easily employed for any analytical propagator once one has a suitable trial wave function to guide the simulation. Using an analytical approach similar to the one explained above, we were able to obtain the time step dependence of the mixed estimator $E_H(t)$ for the T, MM, and D formulas when employed with this IS procedure. It was surprising to see that these results do not differ from the ones obtained without the IS procedures for all the propagators: this way to carry out the IS procedure does not modify either the order of the algorithm or its prefactor.

III. MONTE CARLO RESULTS AND DISCUSSION

The aim of this section is to report and discuss the time step bias and the efficiency of the propagators presented above when applied to the simulation of low dimensional model systems. As the first test model we chose a harmonic oscillator with the same mass and force constant as the one we employed in our analytical calculations. This choice allows us to compare our simulations with the analytical results directly, in order to test the correctness of the implementation of all the algorithms. In all the numerical simulations we employed a target population of 500 walkers, and a Gaussian trial wave function with width parameter $c = 0.801$ to compute the mean energy. Instead of reporting long tables with the numerical results of our calculations, in Fig. 1 we show the DMC mean potential estimator [Eq. (11)] for the T and D formulas, together with the corresponding analytical solutions. Since for the IS algorithm with the accept or reject step the potential estimator is no longer a valid energy estimator, we do not compare its results with the D and T ones.

From Fig. 1 one can note that the D approximation to the exact propagator gives much better results, in terms of the time step bias, than the standard Trotter formula as expected from the analytical results. Moreover, the numerical values appear in complete agreement with the equations presented in the previous section. More specifically, the potential results obtained using the D formula are in statistical agreement with the exact value of 0.5 Hartree already at $t = 0.95$ Hartree^{-1}. A similar behavior was found for the mixed estimator as shown in Fig. 2. This estimator allows a more fair comparison of the time step bias of the algorithms, as also IS results can be confronted with T and D values.

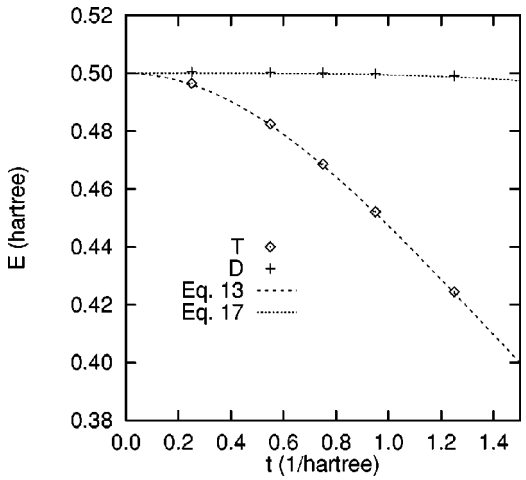

FIG. 1. Time step dependence of the mean potential estimator of the energy $E_V(t)$ for the harmonic oscillator. The symbols represent the results of DMC simulations, while the lines are the analytical results shown in the text.

From Fig. 2 it can be seen that the IS algorithm is less accurate than the Trotter formula even if accept or reject is employed in the simulation. The results of the D formula for the mixed estimator show a large improvement in the time step bias with respect to the standard T formula.

As a second example, we tested the three propagators on a unitary mass particle confined in the one-dimensional double-well potential

$$V(x)=\frac{x^4}{4}-2x^2, \tag{19}$$

a prototypical system widely employed to model the tunnel effect. This model system, whose exact ground state energy is -2.6614 Hartree [15], was used by Drozdov to test the D formula in path integral calculations [11]. All the simulations on this model system were carried out using the same target population as for the harmonic oscillator case, i.e., 500 walkers. As a trial wave function to compute the mean energy we

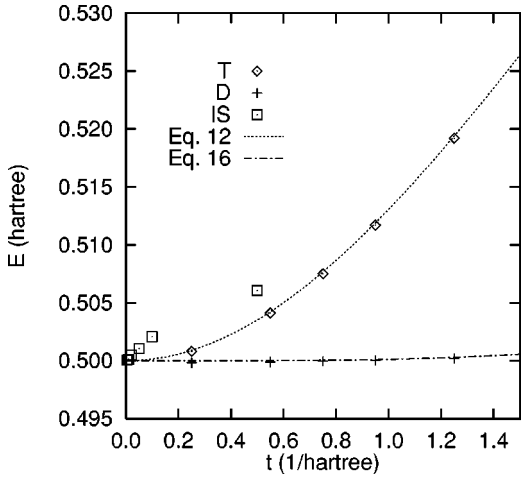

FIG. 2. Time step dependence of the mixed estimator of the energy $E_H(t)$ for the harmonic oscillator. The symbols represent the results of DMC simulations, while the lines are the analytical results shown in the text.

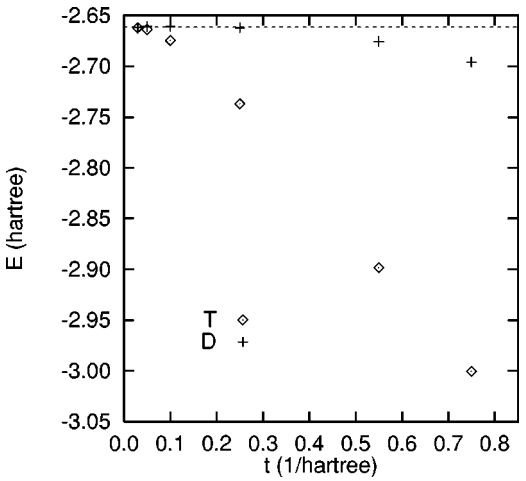

FIG. 3. Time step dependence of the mean potential estimator of the energy $E_V(t)$ for the double well potential. The symbols represent the results of DMC simulations, while the line is the exact energy.

used the sum of two Gaussians centered on the potential minima $x_m=\pm 2$ and whose width parameter was $c=1.41$. The mean potential results for this system are shown in Fig. 3, together with the exact energy. From the plot, it appears clearly that the D propagator is quite more accurate than the T one, showing practically no time step bias up to 0.25 Hartree^{-1}. As far as the mixed estimator is concerned, we show in Fig. 4 the numerical results of our simulations. Again, as noted previously for the harmonic oscillator, both T and D formulas appear much more accurate than the IS algorithm, whose simulations become unstable for time steps larger than 0.04 Hartree^{-1}.

As a last test on time step bias of the mixed energy estimator for the three propagators, we simulated the ground state of a unitary mass particle in a 3D potential

$$V(x,y,z)=\frac{\nabla^2 f(x,y,z)}{2f(x,y,z)}-\frac{b^2}{2B}+\alpha+\beta, \tag{20}$$

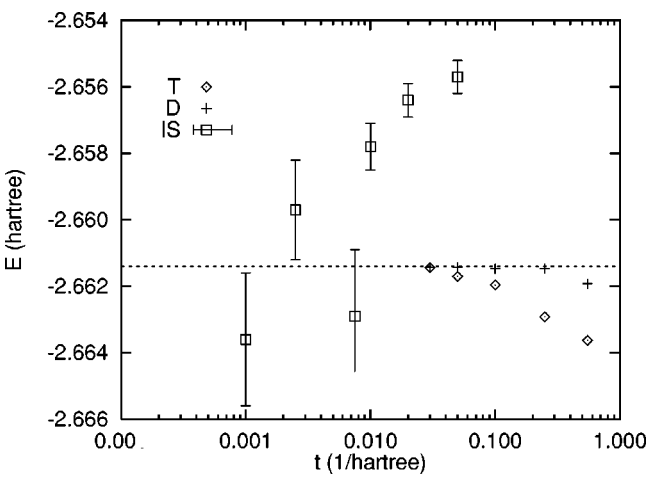

FIG. 4. Time step dependence of the mixed estimator of the energy $E_H(t)$ for the double well potential. The symbols represent the results of DMC simulations, while the line is the exact energy. Note the logarithmic scale on the time step axis.

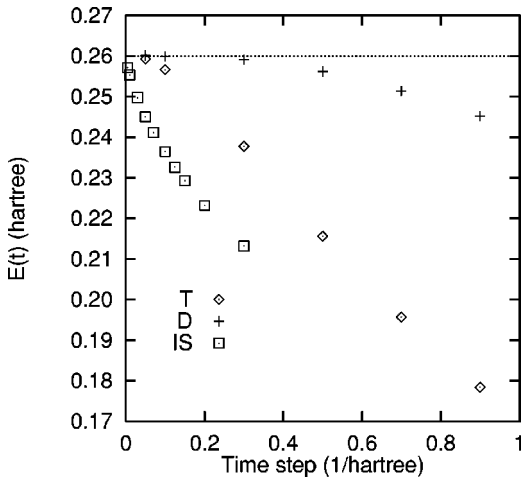

FIG. 5. Time step dependence of the mixed estimator of the energy $E_H(t)$ for the 3D model potential. The symbols represent the results of DMC simulations, while the line is the exact energy.

$$f(z,y,z)=\frac{e^{-\alpha x^2-\beta y^2}}{e^{-az^3}+Be^{bz}}, \tag{21}$$

where $f(x,y,z)$ is the ground state wave function, and $E_0=-b^2/2B+\alpha+\beta$ is its energy. In our simulations we assumed $\alpha=0.3$, $\beta=0.2$, $a=0.7$, $b=1.2$, and $B=3.0$: the exact energy of this system is $E_0=0.26$ Hartree.

As pointed out in the Introduction, to carry out the simulations for systems of physical interest and more complex than the monodimensional models we have presented so far, the IS-DMC method is frequently used. For this reason, and for having a fair comparison between the efficiency of the T and D propagators with the IS-DMC algorithm, we decided to run all the simulations on our 3D model using the reweighting scheme proposed by Kalos [13] to introduce the importance sampling. As trial wave function to guide the simulations we used $f(z,y,z)$ employing slightly different parameter values than the exact ones. The mean local energy results of these simulations, where we employed 3000 walkers, are shown in Fig. 5 together with the E_0 energy.

As far as the D and T propagators are concerned, once again the results show the D formula to give more accurate results than the T one. Comparing the mean energy results of these two propagators with the values obtained employing the standard IS-DMC method, one can notice that for this system the last method gives even less accurate results than the simple T propagator. Moreover, we were not able to carry out simulations using a time step larger than 0.4 Hartree^{-1} for the IS-DMC method due to systematic explosions of the walker population. We attribute this to an instability of the branching factor based on the local energy of the trial wave function. This shows a strong divergency to large negative values for $z\rightarrow\pm\infty$ for all the parameter values we tried. The D and T propagators are not affected by this feature since their branching factor is dependent only on the potential energy and its gradient. Since these quantities are bound from below they cannot produce a population explosion as in the local energy case.

As already pointed out in the Introduction, more accurate propagators give the possibility to use larger time steps during the simulation. This fact leads to a dramatic decrease of the statistical error of the results, due to a faster decorrelation of the configurations between two successive steps. This, in turn, allows one to reduce the length of the simulations or to obtain more accurate results for the constant simulation length.

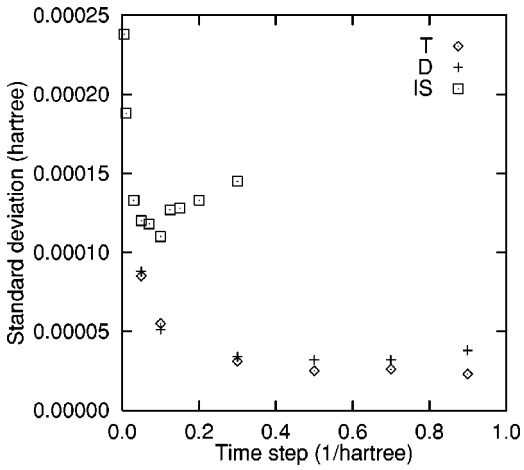

FIG. 6. Time step dependence of the standard deviation of the mixed estimator of the energy $E_H(t)$ for the 3D model potential. The symbols represent the results of DMC simulations.

To discuss the relative efficiency of the propagators, we show in Fig. 6 the standard deviation of the mixed estimator of the energy, obtained from the simulations on the 3D model potential presented above, versus the time step used. All the simulations were carried out employing 3000 walkers, 200 blocks of 500 steps each, so that the statistical error is a direct mesure of the efficiency. The statistical error of the D propagator is similar to the one of T in the time step range $0-0.5$ Hartree^{-1}; for larger time steps it increases slightly with respect to T. We attribute this feature to the presence in the branching factor of a term depending on t^3 that starts to play an increasing role for $t\geqslant 0.5$ Hartree^{-1}.

The T and D propagators appears to be much more efficient than the IS-DMC algorithm for all the studied time steps, showing a statistical error smaller by a factor of 2–4. We feel this trait is due to the different branching factor in the propagators, since, using the same time step, the diffusion factor of the IS-DMC algorithm generates larger accepted displacements than the other propagators. The gain in the overall efficiency of the simulations can be easily understood recalling that the standard deviation of the results is proportional to $(N_{\mathrm{ind}})^{-1/2}$, where N_{ind} is the number of statistically decorrelated samples obtained during a simulation. This means that a decrease of a factor of 2 in the standard deviation represents an increase of a factor of 4 in N_{ind}, or a decrease of a factor of 4 in the computational time for the same statistical accuracy.

In comparing more accurately the efficiency of the T and D propagators, one should keep in mind that a step of the D propagator is slightly more expensive than a step of the T propagator. This is due to the necessity of a double number of random variates to produce the diffusion displacement, and of three calculations of the potential energy and one of its gradient instead of only two potential evaluations. Therefore, the single D propagator step is roughly one and one-half times more expensive, since the generation of the ran-

dom variates is usually two orders of magnitude faster than the calculation of the potential energy. Nevertheless, the possibility of using time steps in the D propagator larger by a factor of 2–3 than in the T propagator obtaining the same time step bias more than supersedes the additional computational cost request by this algorithm, and makes attractive its use for more complex systems. For instance, the same time step error, namely, 0.001 Hartree, is obtained using a time step of 0.05 Hartree^{-1} with T and of 0.30 Hartree^{-1} with D (see Fig. 5). This fact reflects itself in a standard deviation for the D result that is 2.5 times smaller than the same quantity for T, therefore allowing to reduce the simulation length by a factor of 6. These conclusions remain similar even for the harmonic oscillator and for the double well potential.

IV. CONCLUSIONS

The main goal of this work was to compare the accuracy and the efficiency of two proposed propagators with respect to the Trotter formula commonly used in DMC simulation of atomic and molecular aggregates. From the results we obtained, it appears that the propagator based on the fourth order symmetric splitting proposed by Chin [10], and exploited by Drozdov [11] in path integral calculations, allows one to use a larger time step than the Trotter propagator. This fact reflects itself in a shorter correlation length between the sampled data, hence in statistically more accurate mean values. We propose to employ this propagator in simulating weakly bound atomic and molecular clusters whose interaction potential is bound from below, since this case does not suffer for the possible population blow up that plagues the simulations on atomic and molecular electronic structures.

As far as total simulation time is concerned, we found the gain in statistical efficiency obtained using longer time steps with this propagator much larger than the additional computation time needed to calculate its more complex branching factor. This feature should make the D propagator a compelling alternative to the T for the Monte Carlo practitioners. Moreover, the increased efficiency of the propagator can be exploited in the finite field method proposed by Sandler, Buck, and Clary [14], to compute more accurate mean values of structural and energetic interest.

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APPENDIX A: THE CALCULATION OF $[\nabla_i V(\mathbf{R})]^2$

Given a two-body approximation of the potential $V(\mathbf{R}) \simeq \Sigma_{ij} v(r_{ij})$, where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$, differentiating with respect to $\mathbf{r}_i$ one obtains

$$\nabla_i v(r_{ij}) = \frac{\mathbf{r}_i-\mathbf{r}_j}{r_{ij}} \frac{\partial v(r_{ij})}{\partial r_{ij}}. \tag{A1}$$

Its square is

$$[\nabla_i v(r_{ij})]^2 = \left[\frac{\partial v(r_{ij})}{\partial r_{ij}}\right]^2. \tag{A2}$$

Since the two-body potentials are usually written as a sum of terms containing exponential functions and negative powers of r_{ij}, the calculation of these derivatives only requires that we reassemble quantities that were already computed, therefore reducing the additional cost almost to zero.

APPENDIX B: STATISTICAL ERROR OF THE MONTE CARLO SIMULATION AND VARIANCE OF THE ESTIMATOR

The statistical error of a MC simulation can be computed by means of

$$\sigma = \left[\frac{\text{var}[O(t)]}{N_{\text{ind}}-1}\right]^{1/2}, \tag{B1}$$

where N_{ind} is the number of independent samples in the simulation and $\text{var}[O(t)]$ is the variance of the estimator over the sampled distribution.

While N_{ind} depends on the ability of the particular algorithm in decorrelating the walker population, $\text{var}[O(t)]$ is dependent only on the accuracy of the sampled distribution, i.e., the accuracy of the propagator, and of the trial wave function. The time step dependency of this last quantity can be computed for the harmonic oscillator similar to the way used for the two energy estimators.

These variances are, for the T formula,

$$\text{var}[E_H(t)] = \frac{2(4c^2-1)^2}{[4c+(4+t^2)]^2}, \tag{B2}$$

$$\text{var}[E_V(t)] = \frac{2}{4+t^2}. \tag{B3}$$

For the MM formula

$$\text{var}[E_H(t)] = \frac{18(4c^2-1)^2}{[12c+(36+3t^2)]^2}, \tag{B4}$$

$$\text{var}[E_V(t)] = \frac{6}{4+t^2}. \tag{B5}$$

For the D formula

$$\text{var}[E_H(t)] = \frac{18(12+t^2)(4c^2-1)^2}{12c(12+t^2)^{1/2}+(432+36t^2+t^4)^{1/2}}, \tag{B6}$$

$$\text{var}[E_V(t)] = \frac{18(12+t^2)}{432+36t^2+t^4}. \tag{B7}$$

For the IS algorithm

$$\text{var}[E_H(t)] = \frac{2(4c^2-1)^2}{[4c-4c^2t+(4-8ct+t^2)^{1/2}]^2}. \tag{B8}$$

It is interesting to note that, while for the *T*, MM, and *D* formulas the variance is defined for all *t*, the IS estimator for var$[E_H(t)]$ requests $c \leqslant t/8+1/(2t)$ for the square root in its denominator to be defined for all the time steps. This fact means that for $c>0.5$, i.e., the value of the minimum of $t/8+1/(2t)$, there is always a time step beyond which this estimator has no sense, and the simulation may show instability with respect to population blow up. The root cause of this effect has not yet been clearly identified, but a possibility that we feel is worth investigating is represented by the different effect the local energy can have on the branching factor when c is varied. Specifically, when $c>0.5$ the local energy diverges toward $-\infty$ for $x \rightarrow \pm\infty$, while if $c<0.5$ it diverges toward $+\infty$. Moreover, comparing numerically the var$[E_H(t)]$ estimator for the different propagators it strikes us that the one of the IS algorithm assumes the highest value, therefore showing a minor efficiency with respect to other formulas.

Recently, a modified IS propagator, where the branching factor was built to control the divergency of the local energy, has been proposed [16]. Unfortunately, we were not able to solve the integral equation for this propagator, so a direct comparison is not yet possible.

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