Comparison of different propagators in diffusion Monte Carlo simulations of noble gas clusters

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Several short-time approximations of the imaginary-time propagator of the Schrödinger equation are compared working on small helium and neon clusters. A recently discussed fourth order short time approximation of the propagator [Phys. Rev. E **61**, 2050 (2000)] allows us to compute several properties practically unaffected by the time step bias. The comparison among simulations of the same length shows that this algorithm permits the use of larger time steps, leading to more accurate statistics than the ones obtained by employing commonly used schemes. Results of the mixed estimator of the potential energy, of the first two momenta of the interparticle distribution, and of the particle-center-of-mass distribution seem to indicate that the new propagator is able to perform unbiased sampling even when very large time steps are used. Also, the relative population of the four Ne_7 isomers sampled using the fourth order propagator does not show any time step bias in the 200–1000 hartree^{-1} time step range. This fact indicates that using the fourth order propagator with large time steps is a viable approach to tackle ergodicity problems in semirigid clusters. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1598957]

I. INTRODUCTION

As the interest in atomic and molecular clusters widespreads due to the increasing number of experimental applications,[1–3] flexible and reliable theoretical methods are needed to support and guide the interpretation of these experiments. Among the most popular techniques, the diffusion Monte Carlo (DMC) method appears to be one of the most flexible tools to study the ground state of quantum clusters at 0 K.[4,5] For pure and doped He clusters, due to a vibrational excitation gap of roughly 1.7 K,[5] simulating pure and doped He clusters at 0 K often represents an accurate first approximation of their quantum behavior at the experimental temperature (0.3 K).

The DMC method is based on two main assumptions. First, the possibility of interpreting a function, whose form depends on the specific formulation of the method, as a probability density. Second, the existence of an operator, called propagator or projector, able to generate the exact ground state eigenfunction for a given Hamiltonian. These two aspects are represented by the fundamental equation of the method,

$$\Psi(\mathbf{R}',t+\tau)=\int G(\mathbf{R}\rightarrow\mathbf{R}',\tau)\Psi(\mathbf{R},t)d\mathbf{R}, \tag{1}$$

where, in order to make the integral operator matching our requests, G has to be the Green's function for the imaginary time Schrödinger equation. Here, $\Psi(\mathbf{R},t)$ and $\Psi(\mathbf{R}',t+\tau)$ are, respectively, the wave function describing the system at $\mathbf{R}$ and time t, and the projected (or propagated) wave function at $\mathbf{R}'$ after the elapsed time step τ. DMC simulates the action of the operator on the function as a sequence of diffusive and branching steps on a given population of walkers.[6] This way of proceeding can be mathematically justified through the so-called short time approximation (STA). This, roughly speaking, consists of substituting the exact G with a new function, G_{STA}, whose action is exact up to a certain order in τ. The introduced error is usually referred to as time step bias. The simplest form of G_{STA}, apart an uninfluent normalization factor, is obtained using Trotter (T) formula,[7] and reads

$$G^{T}_{\mathrm{STA}}(\mathbf{R}\rightarrow\mathbf{R}',\tau)=\exp\left[-\frac{m(\mathbf{R}'-\mathbf{R})^2}{2\tau}\right]\exp\left[-\tau\frac{V(\mathbf{R})+V(\mathbf{R}')}{2}\right]. \tag{2}$$

More recently Suzuki[8] proposed a fourth order (FO) approximation, whose form is

$$G^{\mathrm{FO}}_{\mathrm{STA}}(\mathbf{R}\rightarrow\mathbf{R}',\tau)=\int d\mathbf{R}''\exp\left[-\frac{m(\mathbf{R}'-\mathbf{R}'')^2}{\tau}\right]\times\exp[-\tau\tilde{V}(\mathbf{R}'')]\exp\left[-\frac{m(\mathbf{R}''-\mathbf{R})^2}{\tau}\right]\times\exp\left[-\tau\frac{V(\mathbf{R})+V(\mathbf{R}')}{6}\right], \tag{3}$$

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where $\tilde{V}=(2V/3)+(\tau^2/72)(\nabla V)^2/m$. This has been independently implemented by Chin,[9] Drozdov,[10] Jang, Jang, and Voth,[11] and Mella, Morosi, and Bressanini[12] in different contexts. For both T and FO, importance sampling (IS) can be easily introduced by multiplying the just defined G_{STA} functions by the ratio $\Phi_T(\mathbf{R}')/\Phi_T(\mathbf{R})$.[13] This allows the sampling of the distribution $\Phi_T\Psi_0$. Algorithms associated to these modified Green's functions will be called T-IS and FO-IS. It is known that IS can also be implemented using the equation,

$$G_{\mathrm{STA}}^{\mathrm{DRIFT}}(\mathbf{R}\rightarrow\mathbf{R}',\tau) = \exp\left[-\frac{m[\mathbf{R}'-\mathbf{R}-\tau\mathbf{F}/m]^2}{2\tau}\right] \times\exp\left[-\tau\frac{(E_{\mathrm{loc}}(\mathbf{R}')+E_{\mathrm{loc}}(\mathbf{R}))}{2}\right], \tag{4}$$

where $E_{\mathrm{loc}}(\mathbf{R})=H\Phi_T(\mathbf{R})/\Phi_T(\mathbf{R})$, $\mathbf{F}=\nabla\ln|\Phi_T(\mathbf{R})|$ is the quantum force, and the algorithm is hereafter referred as DRIFT.[14] In the actual implementation of the DRIFT algorithm, an accept/reject Metropolis step is used to satisfy detailed balance. Also, the branching process is carried out at every step instead of having walkers with fluctuating weight. No time-dependent cutoff is used to reduce the effect of the singular behavior of $E_{\mathrm{loc}}(\mathbf{R})$. We stress the fact that one is forced to use the DRIFT approach when dealing with potentials not bounded from below (i.e., the electron–nucleus Coulomb interaction). If Φ_T is cleverly chosen, $E_{\mathrm{loc}}(\mathbf{R})$ is much better behaved than the bare $V(\mathbf{R})$, often effectively eliminating its divergence toward $-\infty$. In this respect, it is worth mentioning that Forbert and Chin[15] have recently developed a fourth order algorithm based on a previously proposed factorization of the evolution operator and on a fourth order Runge–Kutta algorithm for the computation of the drift displacement. However, this last part of the algorithm requires four evaluations of $\nabla\ln|\Phi_T|$, so that this method is expected to be four times more expensive that the common DMC scheme.

In Ref. 12, the approximations to the exact G given by Eqs. (2)–(4) were already compared studying simple model Hamiltonians whose potentials were bounded from below. Notwithstanding the common belief that the DRIFT algorithm is the most efficient DMC implementation, the results presented in Ref. 12 pointed out that both $G_{\mathrm{STA}}^{\mathrm{FO}}$ and G_{STA}^{T} can achieve a largely better efficiency than $G_{\mathrm{STA}}^{\mathrm{DRIFT}}$. This is due to the possibility of employing a larger time step τ in $G_{\mathrm{STA}}^{\mathrm{FO}}$ and G_{STA}^{T} than in $G_{\mathrm{STA}}^{\mathrm{DRIFT}}$ for a chosen total accuracy of the results. However, the model Hamiltonians employed in Ref. 12 might not be considered as an exhaustive test of the relative performance of the different algorithms, lacking some of the ''unpleasant'' features (e.g., the strong repulsive wall of the short range van der Waals interaction) of a realistic potential. Therefore, the aim of the present work is to test the algorithms more thoroughly comparing several aspects of their numerical performances when employed to simulate noble gas clusters. The systems we chose are helium clusters, the most investigated ones, and the more strongly bound neon clusters. These last ones are known to possess various closely lying local minima of the potential and hence to be semirigid. This last fact would introduce a bias in the simulation results unless the sampling is ergodic. So, Ne_n clusters allow us to test the propagators without importance sampling and to see if the use of large time steps allows to sample ergodically the configurational space.

II. RESULTS

As a general strategy, for all systems we employed potentials and trial functions, respectively, of the form

$$V(\mathbf{R})=\sum_{i<j} v(r_{ij}) \tag{5}$$

and

$$\Phi_T(\mathbf{R})=\prod_{i<j} \phi_T(r_{ij}). \tag{6}$$

The details of the implementation of the FO and FO-IS schemes are similar to those presented in Ref. 12.

A. Time step bias

As a first test case DRIFT, T-IS, and FO-IS were applied to compute the total energy E_0 of He_6 and He_{13} as a function of τ using the LM2M2 potential.[16] The analytical form of the pair function used in the simulations was taken to be

$$\phi_T(r)=\exp[-p_5/r^5-p_2/r^2-p_0\ln(r)-p_1 r - c_0\exp(c_1-r)], \tag{7}$$

whose parameters had been previously optimised minimizing the variational energy.[17] The curves obtained by plotting the energy as a function of the time step show a similar behavior for both systems and we therefore comment only the He_{13} case in order to illustrate the main features. Figure 1 shows that the three propagators substantially differ in their energy trends. In the explored τ range, the FO-IS algorithm gives statistically equal energy values for each time step, T-IS shows a quadratic energy trend, and DRIFT does not possess a monotonic behavior. Besides, DRIFT shows instability for the simulations with τ larger than a threshold value. This is evidenced by the sudden increase of the standard deviation for $\tau=600$ and 800 hartree^{-1}, and by the fact that we were unable to perform simulations for $\tau>800$ hartree^{-1}. This outcome, previously noticed on some analytical model systems,[12] seems to depend on the form of the employed trial function, whose local kinetic energy [i.e., $\nabla^2\Phi_T(\mathbf{R})/\Phi_T(\mathbf{R})$] diverges toward $-\infty$ faster than the potential energy for small values of the He–He distance. Finally, we stress that, according to Fig. 1, for the DRIFT algorithm one should use a time step smaller or equal to 50 hartree^{-1} to have an estimated energy value statistically equal to the extrapolated FO-IS and T-IS ones.

Another interesting test case is represented by neon clusters. These are largely studied by means of infrared spectroscopy[18] of their doping impurities. Compared with the He clusters, they exhibit a less quantum, but nevertheless quite anharmonic, behavior. Because of the deeper potential and the heavier mass of this element, Ne clusters are less

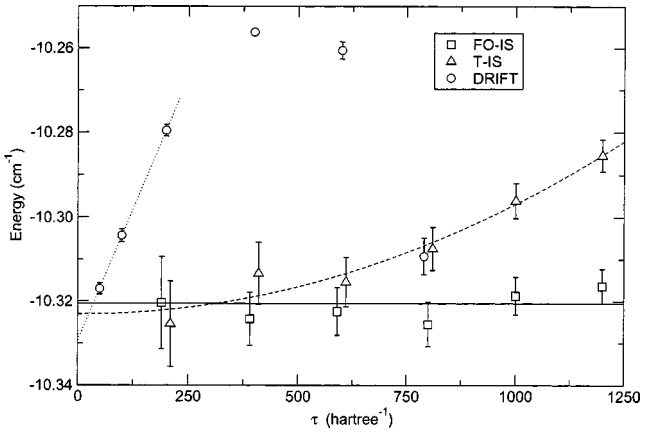

FIG. 1. Total energy for the He_{13} cluster. The lines represent the fitting of the FO-IS data with a constant, of the T-IS data with $a+b\tau^2$, and of the DRIFT data up to 200 hartree^{-1} with $a+b\tau$. The DRIFT data set was obtained by running much longer simulations than for T-IS and FO-IS data sets. Efficiency comparisons in the text are made by using equal simulation lengths.

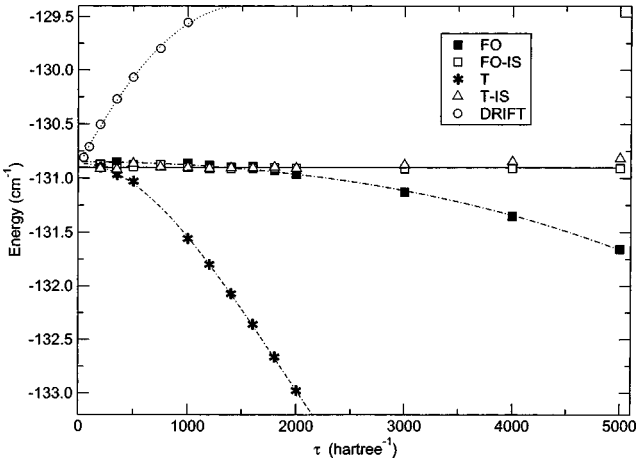

FIG. 2. Total energy for the Ne_5 cluster. The lines are a visual guide for the eye for the DRIFT and T data sets. The FO and FO-IS data sets are fitted using $a+b\tau^4$ and a constant, respectively.

likely to dissociate during a DMC simulation without importance sampling. This fact might allow us to perform, besides the usual importance sampling calculations, simulations using the simpler T and FO schemes. In these cases the mean potential estimator proposed by Anderson[6] must be employed to compute E_0 in spite of its larger variance than the mixed estimator. The use of the T and FO schemes might allow a quick estimate of the energy without the problem of defining and optimizing a Φ_T as in IS algorithms. However, the sampling of Ψ_0 instead of $\Psi_0\Phi_T$ does not allow to extract information on the properties beyond the energy, unless a future walking approach is used to compute bilinear estimators.[19] This algorithm should be adopted also when using a simulation with IS to compute unbiased estimates.

First of all, we investigated the behavior of all propagators simulating Ne_2 and Ne_5. Particle interactions are described by a Lennard-Jones potential and the trial function for the IS simulations is taken of the form,

$$\phi_T(r)=\exp[-p_5/r^5-p_2/r^2-p_0\ln(r)-p_1 r]. \tag{8}$$

The parameters for both V and $\phi_T(r)$ were taken from the work by Rick, Lynch, and Doll.[20]

Again, because of the high similarity between the results of the two systems, we shall comment only the ones obtained for Ne_5. With regard to the IS simulations, the results plotted in Fig. 2 show the same, although more marked, features already observed on helium systems. These are a steep increase of the time step error $E(\tau)-E(0)$ for DRIFT, a weak quadratic behavior of $E(\tau)$ for T-IS, and a practically constant energy value for FO-IS. Besides, despite an expected larger standard deviation than the IS counterpart for equal time step, the FO values plotted in Fig. 2 show a flatter time-dependency than the DRIFT ones and can be used to give a more precise estimate of $E(0)$. Also, T shows an evident second order dependency on τ for the smallest time steps. As a final comment on the time step error of the computed energy, it must be stressed that the employed analytical form for the trial function was found to be somehow inadequate to describe Ne_5. This is due to a lack of flexibility in accounting for the bipyramidal structure of the cluster, as suggested by the calculations presented in Ref. 20. Surprisingly, our results by FO-IS do not appear to be influenced by this rough choice of Φ_T.

We should mention that we observed a strong population bias when using the FO and T propagators at short time steps. We addressed this problem using a large number of walkers (up to 20 000). The importance of this issue is usually reduced by employing the DRIFT propagator where a smoother quantity (E_{eloc}) is used to branch the population. Also, it is possible that a different implementation of the branching part using weighted walkers may reduce the population bias issue for all algorithms.

As far as larger systems are concerned, avoiding importance sampling can be useful when accurate wave functions are not available for them, or when the risk of importance sampling with an unphysical distribution is fairly high. This may happen, for instance, in the case of large clusters of heavy noble gas atoms, or when the cluster possesses two or more minima of the potential energy with similar energies. This is exactly the case for Ne_7 which possesses four closely lying minima.[21] In these cases, IS might so heavily bias the second order estimate (Refs. 22, 23) of the observables different from the energy to make preferable to perform a simulation without it using the future walking algorithm. IS might also bias the future walking algorithm forcing it to use long projection times in order to get rid of the wave function inaccuracy. This would introduce large fluctuations in the walker weights, and hence less precise estimates of the observables.

The previous results on the smaller Ne_2 and Ne_5 clusters encouraged us to extend the application of FO and T to larger systems, namely Ne_7 and Ne_{13}. As to the time step bias, for both systems T shows a quadratic dependence on τ, so it requires an extrapolation to the limiting value $E(0)$. The FO results in the τ range from 200 to 500 hartree^{-1} for Ne_7 and from 250 to 1000 hartree^{-1} for Ne_{13} appear to be statistically equal, therefore indicating that an extrapolation procedure is indeed not necessary, allowing a more reliable and precise

evaluation of $E(0)$. This makes FO once again the best propagator for such a kind of studies as far as the energy time step bias is concerned. However the population bias, already observed on Ne_5, is much larger in these systems and it shows up also at larger time steps than in Ne_5 clusters. In order to give a clearer picture of this difficulty it is worth mentioning that, while we were able to obtain accurate energy values for Ne_7 using 30 000 walkers [$E_0 = -242.193(6)\ cm^{-1}$], even using a population composed by 50 000 configurations the energy results for Ne_{13} still show a significant population bias. In conclusion it is not possible to solve the problem for large clusters simply by using larger numbers of walkers, and a neater solution would be to use one of the algorithms that have been proposed to cure the population bias. This problem was discussed by Hetherington,[24] and solutions were proposed by Umrigar, Nightingale, and Runge,[25] Sorella and co-workers,[26] and Assaraf, Caffarel, and Khelif.[27] However, whereas the dependency on the number of configurations used in the simulation is a well known problem,[24,27] much less is known about the dependency of the population bias on the time step. Calculations on model systems[28] and on Ne_5 show that the differences between the slopes of the straight lines fitting the energy values calculated for each time step as a function of 1/M are small. It must be pointed out that Eq. (27) of Ref. 24 already indicated the root of this τ dependency to be primarily the branching factor, but also that it was not recognized at that time. It is also worth pointing out that the inclusion of importance sampling significantly reduces the population bias, even if it cannot eliminate it completely.

At this point it is important to stress that the clusters simulated to test the different projectors were chosen because they accurately represent their family features, while at the same time allow to obtain, in a reasonable amount of time, mean values with a statistical error small enough to thoroughly infer trends. The computational effort needed to simulate larger clusters, notwithstanding their importance, to accurately compare the different STA's will soon become unaffordable even using a smaller number of time steps.

Because energy is a rather special property (for example, the zero variance principle holds for it[29]), one might ask if the observed features of the different propagators are nothing but peculiarities of this observable. Therefore, we believe that comparing other physical properties besides the energy is a necessary test to perform. In this regard, we studied the mean values of the potential energy and the first two momenta of the interparticle distribution and of the particle-center-of-mass distribution, employing the mixed estimator

$$\langle O \rangle = \frac{\int \Psi_0 O \Phi_T d\mathbf{R}}{\int \Psi_0 \Phi_T d\mathbf{R}} \tag{9}$$

in an IS simulation.

All the computed properties show similar trends and, as an example, the Ne_5 average particle-center-of-mass distance R is plotted in Fig. 3. For all the computed quantities, DRIFT manifests the strongest time step dependence and its trend resembles the one observed for the energy. The behavior of T-IS is somehow surprising: if, on the one hand, the energy showed only a weak quadratic dependency on τ, on the other hand the trend of R is characterized by a much stronger quadratic time step behavior. Finally, the FO-IS results appear to be independent of the time step for all the performed estimates, showing that this last propagator is reliable for several other observables besides the energy. Therefore, one can argue that the entire sampled distribution is practically unbiased, that is, every observable is estimated correctly regardless of the time step. This idea is also supported by the results for the walker populations contained in the basin of attraction of each of the four Ne_7 potential energy minima. These were obtained by saving periodically the walkers and minimizing their potential energy to discover which basin they belong to. From the results shown in Fig. 4, it is possible to note that the ratio between different isomers remains constant over all the explored range of time steps. In turn, this fact indicates that the FO projector introduces no bias in the structural properties of these clusters, and suggests that large time steps could be used to speed up the ergodic exploration of the configurational space for these semirigid systems. Also, our results show an inversion of the expected population between the two highest potential minima, respectively, $-385.8\ cm^{-1}$ and $-384.3\ cm^{-1}$, that may be due to a wider basin of attraction of the second minimum.

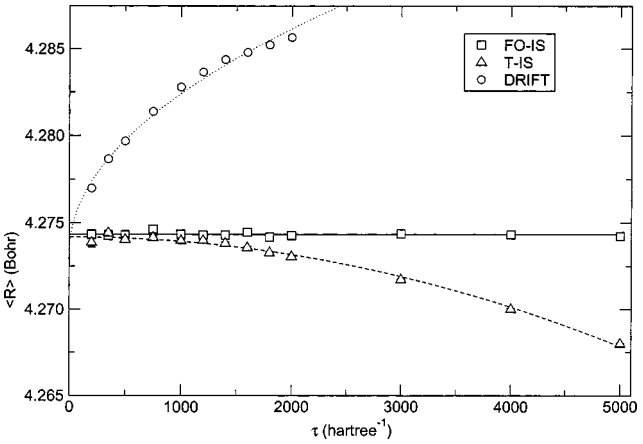

FIG. 3. Average particle-center-of-mass distance for the Ne_5 cluster. The lines are a visual guide for the eye.

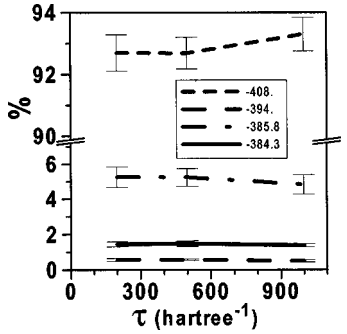

FIG. 4. Percentage of the walker population found in the basin of attraction of the four energy minima of Ne_7 at different time steps. The value of the potential energy (cm^{-1}) for each minimum is also shown in the picture.

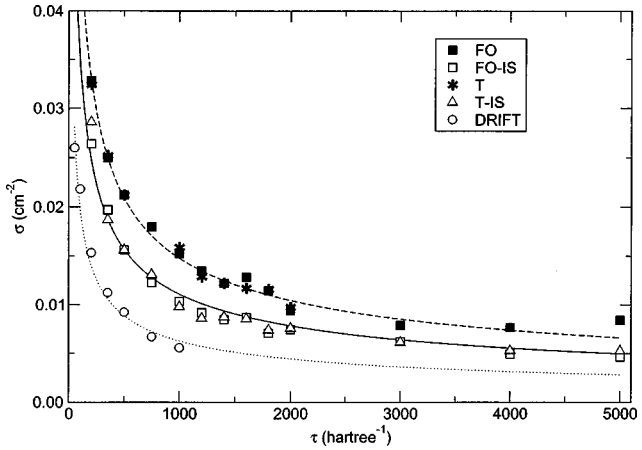

FIG. 5. Standard deviations for the Ne_5 cluster. The lines represent the fitting of three subsets of data, namely DRIFT, FO-IS plus T-IS, and FO plus T, using $f(\tau)=k\tau^{-1/2}$. The k values are 0.1987, 0.3594, and 0.4718, respectively.

B. Efficiency comparison

As already done in Ref. 12, the computed energy values presented above can also be used to discuss the relative efficiency of the various schemes. The standard deviation of simulations performed with the same number of blocks and steps per block decreases upon increasing the time step because of the greater decorrelation among the steps constituting a block. It is of course assumed that the length of the block for the shortest time step assures decorrelation between blocks. A typical trend ''standard deviation vs time step'' is reported in Fig. 5 for Ne_5. As evident from the figure, for a chosen τ the standard deviation increases following the order: $\sigma_{\mathrm{DRIFT}}<\sigma_{\mathrm{FO\text{-}IS}}\simeq\sigma_{T\text{-}\mathrm{IS}}<\sigma_{\mathrm{FO}}\simeq\sigma_T$. This ordering is different from the ones obtained from the simulations on model Hamiltonians, and seems to indicate the DRIFT method as the most efficient one. However, this conclusion is changed if the time step bias, and so the total accuracy of the results, is taken into account. To show this, let us begin by noticing that, in the range of time steps displayed in Figs. 2 and 5, both energies and variances of FO-IS and T-IS may be regarded as practically coincident. Also, all the FO-IS and T-IS energies shown are statistically identical and equal to the extrapolated one, so that one is allowed to use anyone of them as the exact one. On the contrary, the only point of DRIFT whose total accuracy is comparable to that of FO-IS or T-IS is the one computed using the time step of 50 hartree^{-1}, whose standard deviation is roughly 0.024 cm^{-1}. As to FO-IS or T-IS, we can choose the energy at 2000 hartree^{-1}, which has a standard deviation of about 0.0076 cm^{-1}. Thus, in order to have computed points with the same total accuracy and statistical precision, DRIFT needs a calculation 10 times longer than FO-IS and T-IS. Similar results are found comparing FO with DRIFT, while the situation is different for T, owing to its quadratic time step dependence of the energy. The superiority of the FO algorithm is evidenced also by the helium systems, where we found a ratio between the simulation lengths of DRIFT and FO-IS of about 9 to get the same accuracy and statistical precision.

From a different point of view, one could also exploit the results shown in Figs. 2 and 5 to discuss the effect of the trial wave function quality on the simulation efficiency for the FO projector. With respect to this, one may consider the simulation without importance sampling as the worst scenario for this algorithm, i.e., a constant trial wave function. Conversely, the IS results indicates what is the gain in efficiency and in reduction of the time step bias obtained using a function, although not exceedingly accurate, to guide the simulations. These are due to the use of a renormalized estimator for the energy, and to the fact that IS reduces the volume of the sampled configuration space.

As it is apparent from comparing FO and FO-IS in Figs. 2 and 5, the net effect amounts only to reduce the standard deviation of the energy, which is easily estimated by computing the variance of the local energy of the wave function, the time step bias being largely unaffected up to 2000 hartree^{-1}. This finding clearly indicates that, whereas one should expect only a reduction of the statistical error upon increasing the quality of the trial wave function employed in the simulations, worsening it may also introduce a small time step bias, but only for large τ. This weak dependency on the trial wave function quality for the FO projector is an useful property not possessed by the DRIFT one, whose stability is also dependent on the overall accuracy of the Φ_T.

A remark is important at this point if one needs to extrapolate to $\tau=0$. Since in every case FO-IS gave a largely flat trend for the energy, a least squares fitting could be performed using a constant function on a fairly wide τ range. In this case the standard deviation associated to the extrapolated value $E(0)$ is $\sigma^2_{E(0)}=(\Sigma_\tau 1/\sigma^2_{E(\tau)})^{-1}$, and $\sigma_{E(0)}$ is lower than every $\sigma_{E(\tau)}$. Differently, for DRIFT a straight line with nonzero slope must be employed to fit and extrapolate the energies. If simulations of the same length are performed, $\sigma_{E(\tau)}$ increases diminishing τ and a large $\sigma_{E(0)}$ is expected. Indeed, this is exactly what we found for Ne_5. Thus, not only is one forced to use small time steps because of the limited range of linearity, but also only a poorly precise estimate of $E(0)$ is achieved.

III. CONCLUSIONS

In conclusion, our results indicate that the fourth order propagator should be preferred to compute the energy, therefore confirming theoretical predictions and numerical results on model systems. Although the behavior of the standard deviations vs τ is different from the one observed for the model Hamiltonians, a combined examination of accuracy and precision demonstrates that FO-IS is by far the best algorithm. Moreover, our calculations show that not only the energy is unbiased, but that the entire sampled distribution has this useful property and can thus be reliably employed for the computation of other observables. Nevertheless, as FO requires the calculation of the gradient of the potential and an intermediate evaluation of the potential energy, a greater computational effort per time step is needed. Although the calculation of the intermediate potential is completely extra, a properly coded gradient computation is not time consuming, because most of the quantities already com-

puted for the potential can be reorganized to give the gradient, as we already pointed out in our previous work.[12] When the rate determining step of the simulation is the potential calculation, the straightforward consequence is a doubling of the required computing time. However, to have values of comparable precision and accuracy by means of the DRIFT algorithm, much longer simulations are required making the FO algorithm overall advantageous.

With respect to the last issue, a rule of thumb estimating what time step bias should be expected for larger systems would be rather useful. In order to address this issue, it appears interesting to compare the time step bias for similar systems containing different numbers of atoms. To do so, we arbitrarily consider $E(\tau)$ to be unbiased if it differs by less than 0.1% from the extrapolated energy value ($\tau=0$), and list the time step at which $E(\tau)$ shows this absolute error. The choice of this value is dictated by the magnitude of the statistical error of the mean energy at small time step.

As to the neon clusters, we found that the FO results for Ne_2, Ne_5, Ne_7, and Ne_{13} are unbiased up to, respectively, 2000, 2000, 2000, and 1500 hartree^{-1}. If IS is introduced in the simulations, the two smallest clusters showed no sign of bias up to 5000 hartree^{-1}. These findings lead us to think that even a rough choice of Ψ_T (e.g., a simple description in the repulsive potential region) for Ne_{13} would reduce the bias at large τ.

As far as helium clusters are concerned, we found for FO-IS that both He_6 and He_{13} show no signature of the time step bias for all the explored range of τ, i.e., 0–1200 hartree^{-1}. Conversely, the T-IS simulations shows the onset of the bias in the 750–800 hartree^{-1} range for both clusters, whereas DRIFT results differs by more than a standard deviation from the extrapolated one already at 150 hartree^{-1}.

As to the problem of the population bias, in the future we are planning to investigate the algorithms proposed by Assaraf, Caffarel, and Khelif[27] to deal with this problem coupled with the fourth order propagator. In this way we hope to be able to cope with both population and time step biases.

As a final comment, we mention that our results bear some importance also for the path integral Monte Carlo (PIMC) method and the solution of the time-dependent Schrödinger equation for large systems. For instance, in Ref. 11 it was shown that the FO factorization employed by us in simulating noble gas clusters is also advantageous in studying the quantum-thermal behavior of water and an excess electron in He. While such a conclusion could be inferred from our previous work[12] basing on the formal similarity between PIMC and DMC, we did not deal with the issue of efficiency as carefully done in Ref. 11.

Given the overall advantages described in this work, we hope to see in the near future a wide spreading in DMC simulations of this FO factorization.

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