

Combination of the pair density approximation and the Takahashi-Imada approximation for path integral Monte Carlo simulations

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Abstract

We construct an accurate imaginary time propagator for path integral Monte Carlo simulations for heterogeneous systems consisting of a mixture of atoms and molecules. We combine the pair density approximation, which is highly accurate but feasible only for the isotropic interactions between atoms, with the Takahashi-Imada approximation for general interactions. We present finite temperature simulation results for energy and structure of molecules-helium clusters $X^4\text{He}_{20}$ ($X = \text{HCCH}$ and LiH) which show a marked improvement over the Trotter approximation which has a 2nd-order time step bias. We show that the 4th-order corrections of the Takahashi-Imada approximation can also be applied perturbatively to a 2nd-order simulation.

Keywords: Path integral Monte Carlo, superfluid helium-4, helium matrix isolation spectroscopy

1. Introduction

Path integral Monte Carlo simulations at finite temperature (PIMC) or path integral ground state Monte Carlo simulations ($T = 0$) require the numerical evaluation of the imaginary-time evolution operator or *propagator*, $e^{-\beta H}$, where $H = T + V$ is the N -body Hamiltonian operator consisting of the (non-commuting) kinetic and potential operators, T and V . For ground state simulations, β is the imaginary time interval over which a trial wave function decays to the ground state [1]. For finite temperature simulations $\beta = 1/(k_B T)$ is the inverse of the temperature, and $e^{-\beta H}$ is proportional to the N -body density matrix, $\rho(\beta) = e^{-\beta H} / \text{Tr}[e^{-\beta H}]$ [2]. The evolution operator is usually evaluated by splitting β in small steps $\tau = \beta/M$ (small imaginary time steps or high temperature steps) and employing an approximation for $e^{-\tau H}$. The goal is a high-order approximation that allows to use large τ , but is easy to implement and fast to evaluate during the simulation.

In this work we present a combination of established approximations, the pair density approximation (PDA) and the Takahashi-Imada approximation (TIA), for simulations of heterogeneous many-body systems, i.e. systems where the highly accurate PDA is feasible for only a part of the system. Our specific interest are simulations of dopant solvation in ^4He nanodroplets, where one or more molecules are surrounded by He atoms. The PDA is well-established for point-like particles with spherical interactions like He atoms and is explained in Ref. [3]. Although, the PDA can of course be generalized to interactions like those between He atoms and molecules, which depend on the molecule orientation, numerical evaluations during the simulations would be rather time-consuming, thus providing little gain in efficiency. To our knowledge the PDA has never been implemented for anything else than point-particles. Therefore, for simulations of molecule-helium systems, the PDA has often been combined with the second-order Trotter approximation, also called primitive approximation (PA)[4]. This combination fulfills the goals of easy implementation and fast evaluation, but requires to use very small τ , particularly for strong molecule-He interactions. Our combination of PDA and TIA is still easy to implement and fast to evaluate, but the TIA is a 4th-order method and thus constitutes a significant improvement over the PA. In this paper, we use finite- T PIMC simulations to assess our method, but it would work equally well of course for path integral ground state Monte Carlo (PIGSMC) simulations.

2. Method

In the following, we assume a system of N point-like particles that can therefore be described by N coordinates (below we will generalize this to molecules, which are characterized not just by their center of mass

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position but also by their orientation). As mentioned in the introduction, in the canonical ensemble the equilibrium state at a temperature T is described by the density matrix $\rho(\beta) = e^{-\beta H}/Z$ where $Z = \text{Tr}[e^{-\beta H}]$ is the partition function. In PIMC, averages of quantities like the energy, the pair distribution function etc. are obtained from a Monte Carlo evaluation of $\langle A \rangle = \text{Tr}[A\rho(\beta)]$ where A is the operator associated with the quantity. Following the Metropolis procedure [5], we have to be able to evaluate the propagator $G(\beta) \equiv e^{-\beta H}$ in order to perform the random walk in configuration space; note, that the normalization given by the partition function Z is not needed for Metropolis sampling. In our case, the sampling is done in the continuous space of all particle coordinates, $R \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$ (below we also add molecule orientations). Exact evaluation of $e^{-\beta H}$ is generally impossible, but many approximate schemes are available for small β , i.e. high temperature. Therefore we split β into small time steps (high temperature steps) $\tau = \beta/M$ and factorize

$$G(\beta) = \prod_{i=1}^M G(\tau)$$

In the basis of particle coordinates R , the propagator is a function of $2dN$ variables, where d is the dimensionality. The above equation becomes a high-dimensional integral

$$G(R, R'; \beta) = \int dR_2 \dots dR_M G(R, R_2; \tau) \dots G(R_M, R'; \tau)$$

The simplest approximation for $G(\tau)$ is the primitive approximation

$$G(\tau) = e^{-\tau V/2} e^{-\tau T} e^{-\tau V/2} + \mathcal{O}(\tau^3)$$

Since M time steps τ are needed to complete the full path of length β , statistical averages such as energy, density etc. have one order less accuracy than G . In case of the primitive approximation, this means they have an error of order τ^2 . Hence, the primitive approximation is a second-order approximation.

For strongly interacting, dense systems like ^4He , the primitive approximation would require very small time steps and thus a very large M . The resulting long chains would render calculations of the superfluid fraction very slow, and in fact impossible at the time of the first PIMC calculations of the superfluid fraction of bulk ^4He [6]. A great improvement beyond the PA is the pair density approximation (PDA) where the high-temperature N -body density matrix $\rho(R, R'; \tau)$ is approximated by a product of the exact two-body density matrices $\rho_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2; \tau)$. ρ_2 can be calculated by a squaring technique [3]. However storage and evaluation of ρ_2 becomes computationally demanding for anything else than the isotropic interaction between two point-particles, such as ^4He atoms. In the isotropic case, ρ_2 can be expressed as a function of three coordinates. The PDA propagator leads to a time step error proportional to τ^3 , one order better than the PA. Additionally the prefactor of τ^3 is very small because the residual energy is less singular than for other approximations, see Ref. [3] for more details. The PDA has been applied successfully to the simulations of superfluid ^4He and time steps as large as 1/40K can be used with negligible bias on the results.

More recently, new families of 4th-order propagators [7], effective 6th-order propagators [8], and even any-order propagators [9] have been developed for path integral Monte Carlo simulations. All these schemes have in common that one or more *intermediate* time steps are inserted within the time step τ . Fortunately, the added numerical overhead is more than compensated by the high-order accuracy that allows to use larger time steps.

The aim of this work is to combine the well-tested PDA for point-particle interactions with a simple 4th-order scheme for more complicated interactions. As an application we show the improved accuracy achieved for simulations of a molecule in ^4He , which is relevant for helium matrix isolation spectroscopy [10]. The He-molecule interaction depends not just on the distance between He and molecular center of mass but also on the molecule orientation. We want to avoid inserting intermediate time steps, because they are superfluous for major part of the system, which is described by point-particle interactions, namely the ^4He cluster. Therefore we choose the Takahashi-Imada approximation (TIA) [11, 12] which does not require intermediate time steps and uses the following approximation for the propagator

$$G^{(\text{TIA})}(\tau) = e^{-\frac{\tau}{2}T} e^{-\tau V - \frac{\tau^3}{24}[V, [T, V]]} e^{-\frac{\tau}{2}T}$$

$G^{(\text{TIA})}(\tau)$ is *not* a 4th-order propagator itself, but it is related to a fourth-order approximation by a similarity transformation. Therefore, the partition function Z is accurate up to 4th order, $Z = \text{Tr}[\prod G^{(\text{TIA})}(\tau)] + \mathcal{O}(\tau^4)$. Since the TIA does not require intermediate time steps and since the double commutator is diagonal in coordinate representation (i.e. is a function of coordinates like the potential itself) a PIMC code employing the primitive

approximation can be trivially modified to incorporate the TIA by replacing the bare potential V with the corrected potential $V + \frac{\tau^2}{24}[V, [T, V]]$. However, only Z , but not $G^{(\text{TIA})}$ is accurate up to 4th order, therefore averages have to be obtained from appropriate derivatives of Z . The energy is obtained from the β -derivative,

$$E = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (1)$$

while averages of operators A depending only on coordinates but not momenta can be obtained from

$$\langle A \rangle = -\frac{1}{\beta Z} \left. \frac{\partial Z(V + \lambda A)}{\partial \lambda} \right|_{\lambda=0} \quad (2)$$

The β derivative leads to additional contributions coming from the double commutator in $\rho^{(\text{TIA})}(\tau)$, as discussed in the next section. As an example for A , we calculated the ^4He density in the molecule frame, i.e. the molecule-He pair density.

In the present case, the Hamiltonian of N ^4He atoms and one molecule is given by

$$H = H_{\text{He}} + H_{\text{mol}} + V$$

$H_{\text{He}} = T_{\text{He}} + U = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i < j} u(|\mathbf{r}_i - \mathbf{r}_j|)$ is the pure helium Hamiltonian consisting of kinetic energy and the pair interaction between He atoms. $H_{\text{mol}} = T_{\text{mol}} + BL^2$ is the Hamiltonian for a free linear molecule (mass M and rotational constant B), where $T_{\text{mol}} = -\frac{\hbar^2}{2M} \nabla_0^2$ is the translational kinetic energy and \mathbf{L} is the angular momentum operator. Let \mathbf{x}_i be the coordinates of the ^4He atoms in the molecule frame of reference defined by a z axis along the axis of the linear molecule and the origin coinciding with the molecule center of mass. Then the interaction between the He atoms and the linear molecule can be written as $V = \sum_i v(x_i, \theta_i)$, where θ_i is the polar angle of \mathbf{x}_i , i.e. the angle between the molecule axis specified by a unit vector Ω and the direction from the molecule center of mass to a He atom. The LiH-He interaction $v(x, \theta)$ is taken from Refs.[13, 14], and the HCCH-He interaction from Ref. [15], although alternative models for the HCCH-He complex are available, such as most recently Ref. [16]. The He-He interaction $u(r)$ is taken from Ref. [17].

Since we want to use the PDA for the pure helium part H_0 , we do not split H into kinetic contributions and potential contributions, but instead we split H into $H_{\text{He}} + H_{\text{mol}}$ and the molecule-He interaction V :

$$G^{(\text{TIA})}(\tau) = e^{-\frac{\tau}{2}(H_{\text{He}} + H_{\text{mol}})} e^{-\tau V - \frac{\tau^3}{24}[V, [H_0 + H_{\text{mol}}, V]]} e^{-\frac{\tau}{2}(H_{\text{He}} + H_{\text{mol}})} \quad (3)$$

$$= e^{-\frac{\tau}{2}H_{\text{He}}} e^{-\frac{\tau}{2}H_{\text{mol}}} e^{-\tau V - \frac{\tau^3}{24}[V, [H_0 + H_{\text{mol}}, V]]} e^{-\frac{\tau}{2}H_{\text{mol}}} e^{-\frac{\tau}{2}H_{\text{He}}} \quad (4)$$

where we used that H_{He} and H_{mol} commute. Thus all we have to do to improve upon the primitive approximation for the molecule-helium interaction is to apply a correction to V ,

$$V \longrightarrow V + \frac{\tau^2}{24}[V, [T, V]]$$

where $T = T_{\text{He}} + T_{\text{mol}} + BL^2$ in the present case of a linear molecule in helium. The double commutator yields a local function of x_i and θ_i , hence it constitutes a local correction potential to the bare molecule-He interaction V that can be calculated and possibly tabulated for use in the simulation,

$$\frac{1}{2}[V, [T, V]] = \sum_i \left[\frac{\hbar^2}{2\mu} (v_x(x_i, \theta_i))^2 + \frac{v_\theta(x_i, \theta_i)^2}{x_i^2} + Bv_\theta(x_i, \theta_i)^2 \right]$$

where $v_x = \frac{\partial v}{\partial x}$, $v_\theta = \frac{\partial v}{\partial \theta}$, and μ is the reduced mass. $e^{-\frac{\tau}{2}H_{\text{He}}}$ is approximated by the PDA, and $e^{-\frac{\tau}{2}H_{\text{mol}}} = e^{-\frac{\tau}{2}T_{\text{mol}}} e^{-\frac{\tau}{2}BL^2}$ can be calculated exactly [18]. In the following section we demonstrate for two very different molecule- ^4He clusters that the combination of PDA and TIA indeed leads to much more accurate energies and structural quantities like the molecule-He pair densities.

3. Results

We tested our combination of the PDA and the TIA with PIMC simulations of HCCH- $^4\text{He}_{20}$ and LiH- $^4\text{He}_{20}$ clusters. Both systems have been studied with quantum Monte Carlo simulations in the past [19, 20], we merely use them as a benchmark for simulations of dopant molecules in helium clusters. The HCCH-He interaction is not very anisotropic [15], while the LiH-He interaction has a very narrow and deep minimum on the Li side of the molecule[13, 14]. The large gradients associated with this potential well are expected to lead to a large time-step bias, as has been observed in Ref. [20], where the primitive approximation was employed.

Energy. We calculate the energy from the partition function $Z^{(\text{TIA})}$ obtained with the TIA using eq.(1)

$$E^{(\text{TIA})} = \langle H_{\text{He}} \rangle^{\text{TIA}} + \langle H_{\text{mol}} \rangle^{\text{TIA}} + \langle V + \frac{\tau^2}{8} [V, [T, V]] \rangle^{\text{TIA}} \quad (5)$$

where $\langle \dots \rangle^{\text{TIA}}$ denotes averages from PIMC simulations employing the TIA propagator in combination with the PDA for the helium part, eq. (4) (we do not include PDA in the superscript because the PDA is common to this and the following two estimators). Note that the β -derivative also acts on the $\tau^3 = (\beta/M)^3$ factor of the correction potential, resulting in the factor $\tau^2/8$. We compare the TIA energy estimator $E^{(\text{TIA})}$ with the energy obtained in the primitive approximation

$$E^{(\text{PA})} = \langle H_{\text{He}} \rangle^{\text{PA}} + \langle H_{\text{mol}} \rangle^{\text{PA}} + \langle V \rangle^{\text{PA}} \quad (6)$$

where $\langle \dots \rangle^{\text{PA}}$ denotes averages from PIMC simulations employing the PA propagator in combination with the PDA for the helium part.

Comparing eqns.(5) and (6) suggest an intermediate approximation, where the correction potential is included only *perturbatively*,

$$E_{\text{pert}}^{(\text{TIA})} = \langle H_{\text{He}} \rangle^{\text{PA}} + \langle H_{\text{mol}} \rangle^{\text{PA}} + \langle V + \frac{\tau^2}{8} [V, [T, V]] \rangle^{\text{PA}} \quad (7)$$

Note that we are sampling from a random walk using the PA propagator. This allows to apply the corrections even retroactively, provided that the path trajectories have been stored. We refer to this approximation as perturbative TIA.

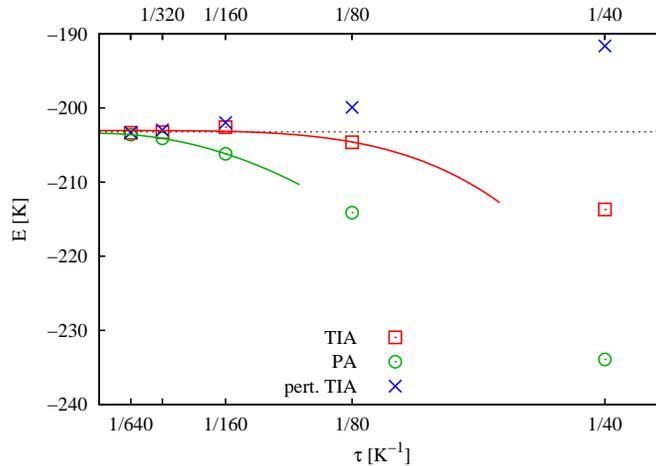


Figure 1: (color online) Equilibrium energy E of $\text{HCCH-}^4\text{He}_{20}$ at $T = 0.625\text{K}$, using the primitive approximation (PA, circles), the Takahashi-Imada approximation (TIA, squares), and perturbative TIA (crosses). Statistical errors are smaller than the symbol size. Also shown are quadratic fits to the PA energy for the three smallest time steps and quartic fits to the TIA energies for the four smallest time steps.

We compare these three approximations to the energy E for time steps $\tau = 1/40; 1/80; 1/160; 1/320; 1/640\text{K}$. for $\text{HCCH-}^4\text{He}_{20}$ (Fig. 1) and $\text{LiH-}^4\text{He}_{20}$ (Fig. 2). The strong LiH-He interaction indeed leads to a much larger error for the $\text{LiH-}^4\text{He}_{20}$ cluster. Apart from this different relative scale of the time step bias, the two figures qualitatively show the same behavior of the bias of $E^{(\text{PA})}$, $E^{(\text{TIA})}$, and $E_{\text{pert}}^{(\text{TIA})}$. The error of $E^{(\text{PA})}$ increases very quickly. In fact, the quadratic τ -dependence of the error is fulfilled only for $\tau \lesssim 1/160$ ($\text{HCCH-}^4\text{He}_{20}$) or $\tau \lesssim 1/320$ ($\text{LiH-}^4\text{He}_{20}$), while for larger τ , the τ -dependence of the error appears to contain also a linear contribution. The quadratic fits shown in the two figures only use the $E^{(\text{PA})}$ values for the lowest three and two time steps for $\text{HCCH-}^4\text{He}_{20}$ and $\text{LiH-}^4\text{He}_{20}$, respectively. The TIA estimator $E^{(\text{TIA})}$ allows to use significantly larger time steps with very small bias. For example for the $\text{HCCH-}^4\text{He}_{20}$ cluster, the error is negligible even for $\tau = 1/80\text{K}$. Note, that all simulation results are still afflicted with errors that are much harder to control or estimate than the well-controlled time step bias: errors in the interaction potentials, both between molecule and He and between two He atoms, but also errors stemming from three-body forces that are usually neglected

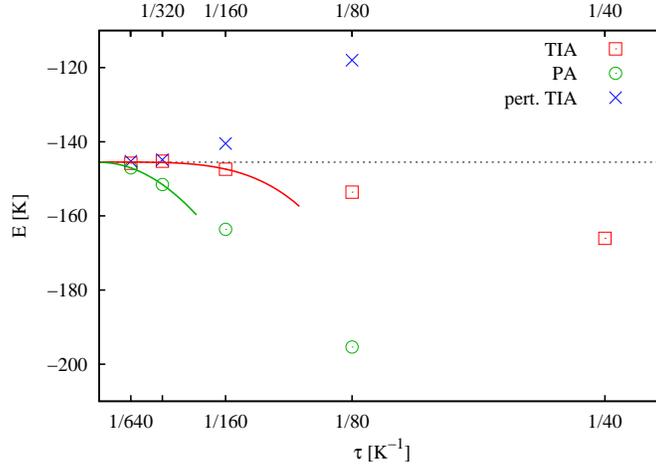


Figure 2: (color online) Same as Fig. 1 for $\text{LiH-}^4\text{He}_{20}$. The quadratic and quartic fits use only the lowest two and three data points, respectively.

altogether. We fitted a quartic function $f_4(x) = E_0 + c_4\tau^4$ to the $E^{(\text{TIA})}$ values for the four ($\text{HCCH-}^4\text{He}_{20}$) and three ($\text{LiH-}^4\text{He}_{20}$) lowest time steps. The extrapolated values are almost identical to those obtained from the quadratic fit to the $E^{(\text{PA})}$ values. Similar to the PA energy estimator, the TIA energy estimator has an approximately linear error for very large τ . Figs. 1 and 2 also show the perturbative TIA energy estimator $E_{\text{pert}}^{(\text{TIA})}$, obtained from sampling PIMC paths stored during a PA simulation. The time step bias has a positive sign now, but for the $\text{HCCH-}^4\text{He}_{20}$ cluster the absolute value of the error of $E_{\text{pert}}^{(\text{TIA})}$ is only slightly larger than the error of $E^{(\text{TIA})}$. The comparison for the $\text{LiH-}^4\text{He}_{20}$ cluster shows that this is not generally true; in this case of an extremely large He-molecule force around the global potential minimum, the TIA estimator fares better than the perturbative TIA estimator. Particularly, for $\tau = 1/40\text{K}$, $E^{(\text{TIA})}$ looks still reasonable, while we obtain a meaningless value of $E_{\text{pert}}^{(\text{TIA})} = +31.9\text{K}$ with perturbative TIA. Nonetheless, both figures demonstrate that with the perturbative TIA estimator a stored PA simulation can be improved retroactively, as long as τ was not too large in the first place.

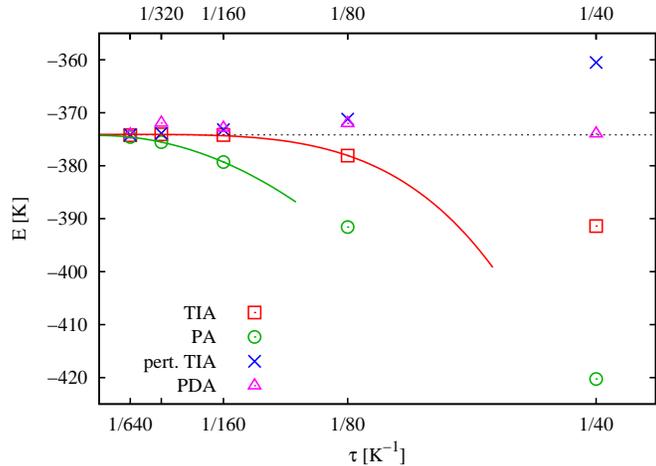


Figure 3: (color online) Same as Fig. 1 for a $^4\text{He}_{20}$ cluster doped with a spherical particle, see text. In addition we compare also with the full PDA which has negligible error over the whole τ range.

We note that the deviation of E from the $\tau \rightarrow 0$ limit consists of the time step bias of the PA or TIA, respectively, but also the bias of the PDA. The latter is very small up to $\tau = 1/40\text{K}$ at least for bulk ^4He , as mentioned above, but strictly speaking a quartic fit is not correct for the TIA+PDA combination due to the τ^3

bias of the PDA. The quartic fits are meant to guide the eye and to extrapolate to zero time step. Regardless of the fits, Figs. 1 and 2 show very clearly the superiority of the TIA-PDA combination over the PA-PDA combination.

In order to assess the τ^3 bias of the PDA, we studied, in addition to the realistic doped clusters above, an artificial spherical molecule (three times heavier than a ^4He atom) in a $^4\text{He}_{20}$ cluster. The molecule interaction is modeled by an isotropic Lennard-Jones potential $v(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)$ with parameters $\epsilon = 40\text{K}$ and $\sigma = 3.75\text{\AA}$. Hence the molecule-He interaction is significantly stronger than the He-He interaction as is the case for most real molecules. For the isotropic molecule-He interaction we can easily apply the PDA. This allows us to compare the three approximations above with the full PDA, where the pair density approximation is used for both the He-He and the molecule-He interaction. In Fig. 3), we show the energies obtained with PA, TIA, perturbative TIA, and full PDA. The latter has a negligible error over the whole τ range studied in this paper. Hence the τ^3 bias of the PDA is indeed negligible, at least for the application to molecule-doped ^4He clusters, and we effectively have the τ^4 error of the TIA.

Structure. We want to calculate the pair density between ^4He and the molecule, usually referred to simply as ^4He density. The corresponding operator $A = \rho$ in coordinate representation is a function of all ^4He coordinates, the molecule center of mass position and the molecule orientation Ω . In the molecule frame the ^4He density is the average of the operator

$$\rho(\mathbf{x}) = \sum_i \delta(\mathbf{x} - \mathbf{x}_i)$$

where again \mathbf{x}_i are the coordinates of the ^4He atoms in the molecule frame. For a linear molecule, $\langle \rho(\mathbf{x}) \rangle$ only depends on x and θ (θ is defined above), and we only need to take averages of

$$\rho(x, u) = \sum_i \delta(u - u_i) \frac{\delta(x - x_i)}{2\pi(x - x_i)^2} = \sum_i \Delta(x - x_i, u - u_i) \quad (8)$$

where we abbreviate $u = \cos\theta$. The first expression for density operator contains δ -functions, but for Monte Carlo sampling, ρ has to be sampled with finite resolution, for example on a regular grid of resolution $(\Delta x, \Delta u)$. Thus the δ -function is replaced by a function Δ of finite width centered at a grid point, as indicated in the rightmost expression.

We use eq.(2) to obtain the average $\langle \rho \rangle$ from the partition function, from which we obtain (using that ρ and V commute)

$$\rho^{(\text{TIA})} = \langle \rho \rangle^{\text{TIA}} + \frac{\tau^2}{12} \langle [\rho, [T, V]] \rangle^{\text{TIA}} \quad (9)$$

The double commutator term is again local function consisting of products of derivatives of ρ and of V

$$\frac{1}{2} [\rho, [T, V]] = \sum_i \left[\frac{\hbar^2}{2\mu} (\Delta_x v_x + \frac{\Delta_\theta v_\theta}{x_i^2}) + B \Delta_\theta v_\theta \right] \quad (10)$$

where in analogy to v_x and v_θ , Δ_x and Δ_θ are the x - and θ -derivative of $\Delta(x, \theta)$, respectively. As for the energy, the TIA density estimator involves a correction term, which depends on the molecule-He potential. And as for the energy, we will compare the TIA density estimator with the PA estimator and the perturbative TIA estimator,

$$\rho^{(\text{PA})} = \langle \rho \rangle^{\text{PA}} \quad (11)$$

and

$$\rho_{\text{pert}}^{(\text{TIA})} = \langle \rho \rangle^{\text{PA}} + \frac{\tau^2}{12} \langle [\rho, [T, V]] \rangle^{\text{PA}} \quad (12)$$

Regarding the choice of Δ in eq.(8), one typically uses simply a top hat function, i.e. a function that is constant around a grid point and zero elsewhere, which leads to a histogram for $\rho(x, u)$ (“binning”). However, we see from eq.(10) that first derivatives of Δ need to be calculated, so the simple binning procedure to get a density histogram does not work. We choose a piecewise bilinear function $\Delta(x, u)$ which from a finite value at the origin linearly goes to zero at the neighboring grid points $x = \pm\Delta x$ and $u = \pm\Delta u$ and is zero elsewhere. $\Delta(x, u)$ is piecewise continuously differentiable, which is sufficient for our purpose.

Figs. 4 and 5 compare the three approximations to the ^4He density $\rho(x, u)$ for $\text{HCCH-}^4\text{He}_{20}$ (time steps $\tau = 1/40; 1/80; 1/160; 1/320\text{K}$) and $\text{LiH-}^4\text{He}_{20}$ ($\tau = 1/80; 1/160; 1/320; 1/640\text{K}$), respectively. We show $\rho(x, u)$ for $u = -1$, i.e. along the axis of the HCCH and LiH. For HCCH, $u = 1$ and $u = -1$ are equivalent of course,

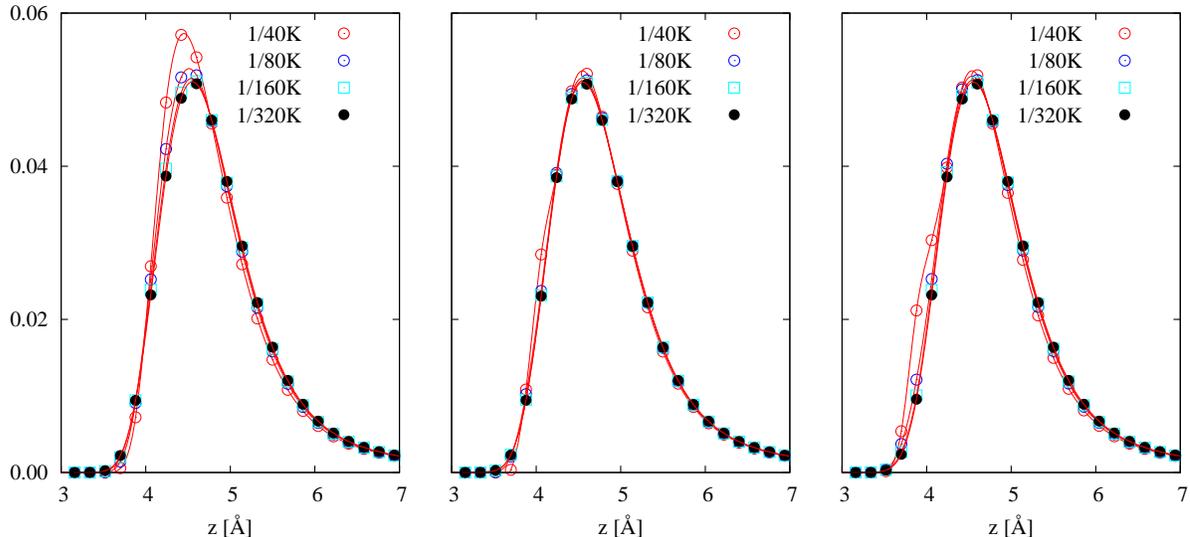


Figure 4: (Color online) Density of ${}^4\text{He}$ in the $\text{HCCH-}{}^4\text{He}_{20}$ cluster at $T = 0.625\text{K}$ for time steps $\tau = 1/40; 1/80; 1/160; 1/320\text{K}$. The left panel shows the primitive approximation (PA), the middle panel the Takahashi-Imada approximation (TIA), and the right panel the perturbative TIA. Statistical errors are smaller than the symbol size. The lines are guides to the eye.

but for LiH, $u = -1$ is the direction intersecting the deep global minimum, where we expect the largest time step bias. In addition, the τ bias for the peak of the ${}^4\text{He}$ density around HCCH and LiH is shown in Fig.6, where we plot $\rho(z_0)$ as function of τ ($z_0 = 4.42\text{\AA}$ in the case of HCCH and $z_0 = 2.26\text{\AA}$ in the case of LiH). The PA estimator for the ${}^4\text{He}$ density around HCCH, Fig. 4, yields a peak too high at $\tau = 1/40\text{K}$, while both the TIA and the perturbative TIA estimators yield a peak density at $\tau = 1/40\text{K}$ that is almost indistinguishable from results for smaller τ . Note however, there are artifacts on the steep slope for $\tau = 1/40\text{K}$, especially for the perturbative TIA estimator. This is where the potential gradients and thus the corrections proportional to τ^2 are largest, see eqns.(9) and (12). These over-corrections become very pronounced for the ${}^4\text{He}$ density in the LiH- ${}^4\text{He}_{20}$ cluster, Fig. 5. The PA estimator yields a peak density almost 50% too high at $\tau = 1/80\text{K}$. Both the TIA and the perturbative TIA estimators are affected by large artifacts at this time step, but reducing τ to $1/160\text{K}$ yields a peak ${}^4\text{He}$ density almost indistinguishable from the $\tau \rightarrow 0$ limit, while the PA estimate at $\tau = 1/160\text{K}$ is still almost 20% too high. Thus we conclude that, as for the energy, both the full and the perturbative TIA leads to a marked improvement of the density average, but unlike for the energy, one has to be more careful with choosing an appropriate time step in order to avoid artifacts in regions where the TIA corrections are largest.

4. Conclusions

We propose a simple, but accurate propagator approximation for path integral Monte Carlo simulations that combines the pair density approximation (PDA) for point-like particles with the 4th-order Takahashi-Imada approximation (TIA) for general interactions. As a test, we calculated the time step bias of the energy and of the ${}^4\text{He}$ density for small ${}^4\text{He}$ clusters doped with a HCCH or a LiH molecule. As expected, the PDA+TIA combination exhibits a much smaller time step bias, and thus constitutes a marked improvement over the combination of PDA with the 2nd-order primitive approximation (Trotter expansion), that has been widely used for simulations of doped ${}^4\text{He}$ clusters. Additionally, we showed that even if the corrections due to TIA are applied only perturbatively to a simulation done with the primitive approximation, the time step bias can be reduced significantly. There are of course many other schemes to achieve high-order accuracy in path integral simulations, which have a smaller time step bias than the TIA. However, they usually require intermediate time steps between full time steps. Since the TIA propagator does not require intermediate time steps, it is easy to implement it in an existing code based on the PDA, is fast to evaluate, and furthermore allows to apply the TIA corrections retroactively to 2nd-order simulations.

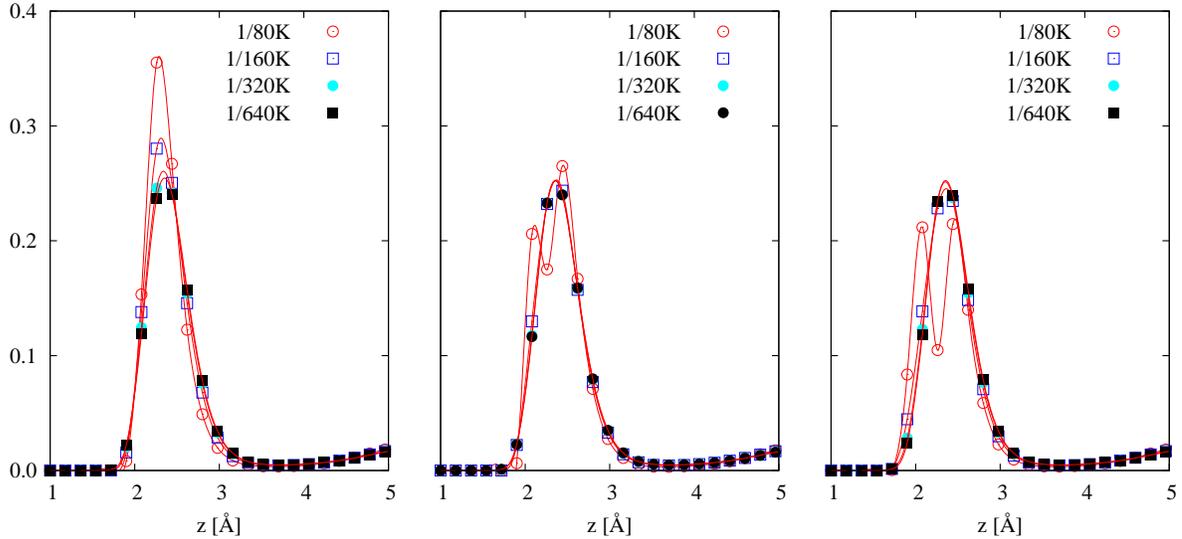


Figure 5: (Color online) Same as Fig. 4 for the $\text{LiH-}^4\text{He}_{20}$ cluster for time steps $\tau = 1/80; 1/160; 1/320; 1/640\text{K}$.

Acknowledgments

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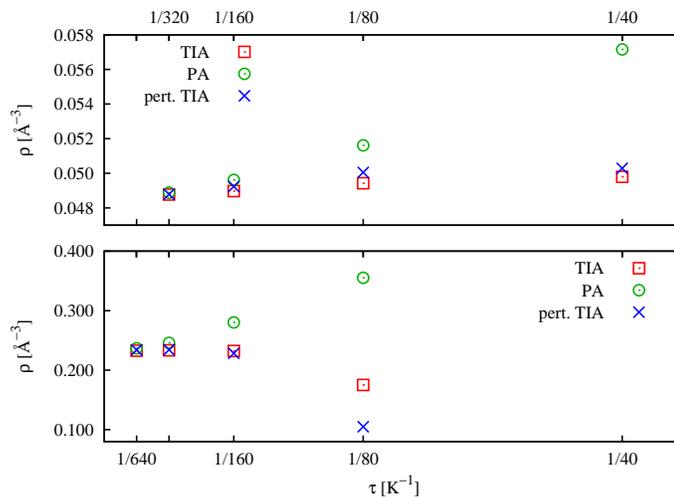


Figure 6: (Color online) The ${}^4\text{He}$ density $\rho(z_0)$ (see Figs.4 for HCCH and 5 for LiH) near the peak is shown as function of τ for the primitive approximation (PA), the Takahashi-Imada approximation (TIA) and the perturbative TIA. The top panel shows $\rho(z_0)$ for HCCH ($z_0 = 4.42\text{\AA}$) and the bottom panel shows $\rho(z_0)$ for LiH ($z_0 = 2.26\text{\AA}$).

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