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Comparison of two non-primitive methods for path integral simulations: Higher-order corrections versus an effective propagator approach

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Two methods are compared that are used in path integral simulations. Both methods aim to achieve faster convergence to the quantum limit than the so-called primitive algorithm (PA). One method, proposed by Takahashi and Imada, is based on a higher-order approximation (HOA) of the quantum-mechanical density operator. The other method is based upon an effective propagator (EPr). This propagator is constructed such that the correct quantum properties are obtained even at finite Trotter numbers P in the limit of small densities. We discuss the conceptual differences between both methods and compare their convergence rate. While the HOA method converges faster than the EPr approach, EPr gives good estimates of thermal quantities already for $P=1$. Despite a significant improvement with respect to PA, neither HOA nor EPr overcome the need to increase P linearly with inverse temperature. We also derive the proper estimator for radial distribution functions for HOA based path integral simulations and show that the $1/P^4$ convergence in the HOA approach also applies if the interatom repulsion is treated realistically. The case studies include an HOA based virial expansion of ^{4}He and a Lennard-Jones model of solid argon.

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I. INTRODUCTION

Path integral Monte Carlo (PIMC) (Ref. 1) and path integral molecular dynamics (PIMD) (Ref. 2) have proven useful in the atomistic simulation of quantum effects occurring in condensed matter at low temperatures. The broad range of applications includes among other things superfluid ^{4}He,[3] isotope effects in crystalline rare gas solids,[4,5] as well as phase transitions with strong quantum-mechanical effects in Josephson junctions[6,7] and molecular solids.[8,9] Recently, path integral methods have also been applied to calculate low-temperature material properties of systems that are computationally less easily tractable than Lennard-Jones type systems: solid germanium,[10] crystalline polyethylene,[11] diamond,[12] silica,[13] and even Wigner crystals,[14] to name a few.

A disadvantage of PIMC and PIMD is the increase of necessary computing time t_{CPU} with decreasing temperature T at a given required accuracy. Using the so-called primitive approximation together with the most efficient sampling algorithms that completely eliminate critical slowing down (see Refs. 2 and 15 for a thorough discussion), it is not possible to overcome $t_{\mathrm{CPU}}\propto 1/T$. Different improvements on the primitive algorithms have been suggested that render path integral simulations more efficient. One may subdivide the bulk of such attempts into three categories: (i) methods that are based on higher-order approximants (HOA) of the high-temperature density matrix,[16] (ii) methods that use effective propagators (EPr) that automatically yield the proper two-particle behavior,[3,17] and (iii) methods that decompose the Hamiltonian into a harmonic and an anharmonic contribution before applying the Trotter formula.[18,19] The latter category, also referred to as the effective potential (EP) method, will not be discussed any further in this study, mainly due to its unfavorable scaling of t_{CPU} with particle number N. Additionally, harmonic approximations are problematic for many systems of interest, in particular those involving ^{3}He and ^{4}He. Yet, another advantage of HOA and EPr methods over the EP method is that the pathological behavior of the attractive Coulomb potential is overcome automatically.[17,20–22]

In this study, we want to compare the convergence of the HOA method, the EPr method, and the primitive algorithm (PA) for a simple model system. As long as the interaction potentials are well behaved, the convergence generally does not depend on the specific form of the potential.[23] The test model system should of course be chosen such that it does not favor intrinsically one approach over the other, e.g., we may not choose a two-particle system, because then the EPr model would be exact per definition. As we are not interested in the EP approach, we can choose a simple monoatomic chain with harmonic next-neighbor coupling. This choice of system enables us to do the bulk of the calculations analytically so that statistical error bars are eliminated completely. We also want to investigate how the Trotter number P necessary to keep the systematic errors below a well-defined percentage scales with inverse temperature for the different approaches investigated in this study.

The HOA approach may become problematic if the interaction potentials are not well behaved. For example, the Lennard-Jones (LJ) potential has a $1/r^{12}$ singularity at small interatomic distances r. In such a situation the prefactor of the $1/P^4$ correction term may be ill defined, resulting in a convergence that is less favorable than that of well-behaved potentials. We therefore extend our study by also analyzing the HOA convergence of expectation values of observables in realistic systems.

It should be emphasized that the HOA method and the EPr method are conceptually different. In an EPr path integral simulation, one tries to generate radial distribution functions that are in the quantum limit (at least in a low-density approximation). Evaluating observables such as the thermal expectation value of the potential energy $\langle V\rangle$ is done by simply evaluating the operator of the potential energy at the given distance. In an HOA path integral simulation, generalized estimators have to be defined even for those observables that are orthogonal in real space. We will comment on this in more depth in the following section. In particular we will derive an expression for the HOA estimator of the radial distribution function, which has not been given hitherto, which might explain the sparse use of the method in the literature. The new estimator will be used to calculate the argon argon radial distribution function in a simple three-dimensional Lennard-Jones crystal. The different methods employed in this study will be outlined in Sec. II. In this section we will also present a simplified approach to the EPr approach, which we call reduced effective propagator (r-EPr) approach. The results are presented in Sec. III, and a short summary is given in Sec. IV.

II. METHODS

A. Primitive algorithm

The primitive algorithm for path integrals is based on Feynman's idea to represent the partition function of a quantum-mechanical point particle $Z(\beta)$ as a partition function of a classical ring polymer.[24,25] The potential $V_{\mathrm{rp}}(\{r\})$ of the classical ring polymer has the form

$$V_{\mathrm{rp}}(\{r\})=\sum_{t=1}^{P}\left[\frac{1}{2}\,\frac{mP^2}{\beta^2\hbar^2}(r_t-r_{t+1})^2+V(r_t)\right], \tag{1}$$

with $\beta=1/k_BT$. r_t represents the position of monomer t in the ring polymer ($r_t=r_{t+P}$), and V is the real (physical) potential. t is sometimes interpreted as an imaginary time and P is commonly called the Trotter number. The PIMC or PIMD program is then assumed to generate distributions such that the probability of configuration $\{r\}$ to occur is proportional to $\exp[-\beta V_{\mathrm{rp}}(\{r\})/P]$. All thermal expectation values of observables diagonal in real space can be determined directly from the configurations, e.g.,

$$\langle V\rangle=\lim_{P\to\infty}\lim_{M\to\infty}\frac{1}{MP}\sum_{i=1}^{M}\sum_{t=1}^{P}V(r_{t,i}), \tag{2}$$

where $r_{t,i}$ is the position of the tth monomer in the ith Monte Carlo step and M is the number of observations in the Monte Carlo simulation. We refer to Refs. 1–3 for further details on the primitive algorithm.

B. Higher-order approximant method

The HOA method is based on a fourth-order Hermitian Trotter decomposition of the high-temperature density matrix.[26] The decomposition was first applied to continuous degrees of freedom by Takahashi and Imada[16] as well as by Li and Broughton.[20] The basic idea of the decomposition is to approximate the high-temperature density matrix $\hat{\rho}=\exp(-\beta\hat{H}/P)$ with

$$\hat{\rho}\approx e^{-\beta\hat{V}/2P}e^{-\beta\hat{T}/2P}e^{-\beta\hat{V}_{\mathrm{cor}}/P}e^{-\beta\hat{T}/2P}e^{-\beta\hat{V}/2P}, \tag{3}$$

where $\hat{H}=\hat{T}+\hat{V}$ corresponds to the Hamiltonian and $V_{\mathrm{cor}}=\beta^2[[\hat{V},\hat{T}],\hat{V}]/24P^2$ is a correction term. $\hat{T}$ and $\hat{V}$ are usually chosen to be kinetic and potential energy, respectively. For this decomposition, the correction energy V_{cor} can be written as

$$V_{\mathrm{cor}}=\frac{\beta^2\hbar^2}{24P^2}\sum_{n=1}^{N}\frac{1}{m_n}(\nabla_n V)^2, \tag{4}$$

where m_n corresponds to the mass of particle n. Owing to the temperature dependence of V_{cor}, thermal expectation values of observables O have to be reevaluated with respect to the primitive algorithm, e.g., averages of functions diagonal in real space read

$$\langle\hat{O}\rangle=\frac{1}{MP}\lim_{P\to\infty}\lim_{M\to\infty}\left[\sum_{i=1}^{M}\sum_{t=1}^{P}\left\{O(\{r\})+\sum_{n=1}^{N}\frac{\beta^2\hbar^2}{12m_nP^2}(\nabla_n V)(\nabla_n O)\right\}\right], \tag{5}$$

where V on the right-hand side of Eq. (5) only includes the original potential and not the correction term V_{cor}. The accuracy of the HOA method outlined above allows one to determine thermal expectation values with a leading correction of $1/P^4$, while the primitive algorithm has leading corrections in the order of $1/P^2$.[16,20,23]

Equation (5) allows one easily to find the estimator for the potential energy to be $V+2V_{\mathrm{cor}}$, see Refs. 16 and 20 for further details on the calculation of thermal expectation values. To our knowledge, however, it is has not yet been discussed that even the estimator for radial distribution functions $g(r)$ needs to be altered with respect to the primitive approach, for which the estimator can be written as

$$g_{\mathrm{prim}}^{\mathrm{estim}}(r)\propto\delta(r-|\mathbf{r}_{t,i,n}-\mathbf{r}_{t,i,n'}|)/r^2, \tag{6}$$

$\mathbf{r}_{t,i,n}$ denoting the position of particle n of the t's monomer in ring polymer (particle) n. Applying Eq. (5) to Eq. (6) leads to a shift of the estimator for the distance between particle n and n'. Simply applying Eq. (5) to the operator for the square of the distance between particle n and n' yields the estimator $r_{n,n'}^{\mathrm{estim}}$ for the distance between particle n and n', which is found to be

$$r_{n,n'}^{\mathrm{estim}}=\{(\mathbf{r}_{t,i,n}-\mathbf{r}_{t,i,n'})^2+\Delta_{n,n'}\}^{1/2} \tag{7}$$

with

$$\Delta_{n,n'}=\frac{\beta^2\hbar^2}{6P^2}\left(\frac{\nabla_n V}{m_n}-\frac{\nabla_{n'}V}{m_{n'}}\right)(\mathbf{r}_{t,i,n}-\mathbf{r}_{t,i,n'}). \tag{8}$$

Thus $r_{n,n'}^{\mathrm{estim}}$ should replace r in the argument of the δ function on the right-hand side of Eq. (6) in order to calculate $g(r)$. Based on this relation, one may say that the HOA method does not correspond strictly to an importance sampling algorithm in the sense that the probability for a configuration to occur in the simulation is proportional to the diagonal elements of $\hat{\rho}$ in a real-space representation.

Note that the choice of the distance estimator in Eq. (7) is by no means unique, because one can add correction terms in higher orders of $\beta^2\hbar^2/mP^2$ without affecting the convergence rate for well-behaved potentials. Such generalizations may prove important if V has strongly repulsive parts at small distances. Equation (7) can then result in imaginary values of $r^{\mathrm{estim}}_{n,n'}$ if the distance between two interacting particles is sufficiently small, even though the probability of the configuration to occur is nonzero. We did not observe such a situation in any of our simulations, because such small separations are extremely unlikely. However, the issue becomes relevant if one does a quantum virial expansion in terms of numerical matrix multiplication (NMM).[27–30] See Sec. III C for some more details on NMM. One possibility to remedy this situation is to replace Eq. (7) with

$$r^{\mathrm{estim}}_{n,n'}=r_{n,n'}\exp(\Delta_{n,n'}/2r^2_{n,n'}). \tag{9}$$

C. Effective propagator approach

An alternative nonprimitive method to the HOA method is to construct effective potentials such that the two-particle propagators are reflected accurately, e.g., it is correct in all orders of $\hbar$. This effective potential is then used in a multiparticle simulation and hence produces the proper thermal behavior in the low-density limit. No effective estimators have to be defined for observables diagonal in real space and in this sense, the approach is an importance sampling algorithm. The effective propagator (EPr) method is particularly useful for ill-behaved potentials such as the attractive Coulomb potential.[17] One may write the high-temperature two-particle density operator in the following way:

$$\langle \mathbf{r}_1\mathbf{r}_2|e^{-\beta\hat{H}/P}|\mathbf{r}_1'\mathbf{r}_2'\rangle\propto\exp\left[-\frac{\beta}{P}V_{\mathrm{eff}}\right]\exp\left[-\frac{\beta}{P}\,\frac{mP^2}{2\beta^2\hbar^2}\times\{(\mathbf{r}_1-\mathbf{r}_1')^2+(\mathbf{r}_2-\mathbf{r}_2')^2\}\right]. \tag{10}$$

V_{eff} is a function that depends on $\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2$, and $\mathbf{r}_2'$. Therefore the interaction can be said to be nonlocal in imaginary time, e.g., in the primitive decomposition $\mathbf{r}_1$ does not couple directly to $\mathbf{r}_2'$. The calculation of both the diagonal and the nondiagonal elements in more than one dimension is not trivial for nonharmonic potentials and we refer to Ref. 3 for an in-depth discussion of that problem. For our one-dimensional model system, however, the approach can be simplified significantly, i.e., it can be solved analytically up to a summation over a finite number of terms. This will be done in Sec. III.

1. *r-EPr method*

In general the implementation of the full two-particle pair propagator with correct diagonal and nondiagonal elements is difficult, because one has to use the two-particle high-temperature density matrix (HTDM) $\langle \mathbf{r}_1\mathbf{r}_2|e^{-\beta\hat{H}/P}|\mathbf{r}_1'\mathbf{r}_2'\rangle$. In principle one can evaluate this expression prior to the simulation. However, this is tedious due to the dimensionality of the matrix, in particular for anharmonic $d=3$-dimensional systems. Even if one expresses the HTDM in the center-of-mass system of the coordinates $\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_1',\mathbf{r}_2'$ and even if one uses an appropriate orientation of the axes within a molecular-fixed frame, one is a left with a three-dimensional table and transformations between molecular-fixed frames and laboratory system. It is also difficult to find good fit functions for the effective potential V_{eff}.

The main idea of a reduced effective potential approach (r-EPr) is to only incorporate those corrections to the primitive decomposition that are local or in other words only the corrections on the diagonal of the density matrix. The terms in the high-temperature density matrix that involve coordinates at different Trotter indices are neglected. This means, if one carries out a simulation at inverse temperature β with Trotter number P, one uses an effective classical potential that reproduces the correct two-particle distribution function in the low-density limit at inverse temperature β/P. For well-behaved potentials, the method must converge to the proper quantum limit, because the leading differences between the r-EPr effective potential and the true potential vanish with $1/P^2$.

The r-EPr approach is similar to an idea suggested by Thirumalai *et al.*,[31] who constructed effective interaction potentials from the diagonal elements of the high-temperature density matrix, see also a related paper by Pollock and Ceperley.[29]

III. RESULTS

A. Linear, harmonic chain

In order to analyze the convergence of primitive algorithm, HOA and EPr method respectively, we choose a one-dimensional linear chain with harmonic next-neighbor coupling,

$$V=\frac{1}{2}\sum_{n=1}^{N}k(r_n-r_{n+1})^2. \tag{11}$$

Periodic boundary conditions, $r_{N+1}=r_1$, are applied and the masses m are identical for all atoms.

HOA and EPr invoke correction terms in the potential energy of the ring polymers with respect to the original expression of the primitive approach that is given in Eq. (1) for a one-particle problem. All three approaches can be represented as the limiting case of a $(1+1)$-dimensional solid with harmonic coupling between nearest neighbors, next-nearest, and next-next-nearest neighbors. A graphical illustration is given in Fig. 1.

The new effective energy $\tilde{V}_{\mathrm{rp}}$ that enters the Boltzmann factor reads

$$\tilde{V}_{\mathrm{rp}}=\frac{1}{2}\sum_{n=1}^{N}\sum_{t=1}^{P}\sum_{\pm}\,[(\kappa+\tilde{\kappa}_1)(r_{t,n}-r_{t+1,n})^2+(k+\tilde{k}_1)(r_{t,n}-r_{t,n+1})^2+\tilde{\kappa}_2(r_{t,n}-r_{t\pm1,n+1})^2+\tilde{k}_2(r_{t,n}-r_{t,n+2})^2]. \tag{12}$$

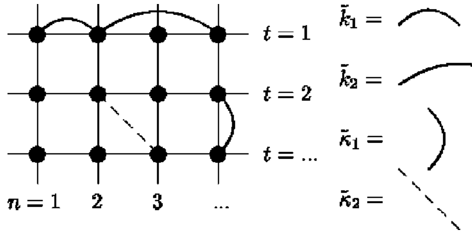

FIG. 1. Illustration of coupling between atoms. Atoms can only oscillate in the horizontal direction. Vertical springs also act in the horizontal direction. The straight horizontal lines represent springs between nearest neighbors of stiffness k, the solid vertical lines springs of stiffness $mk_b^2T^2P^2/\hbar^2$.

The expression $\tilde{V}_{\rm rp}$ can be diagonalized in terms of Fourier modes,

$$\tilde{r}_{q,\omega}=\sqrt{\frac{1}{PN}}\sum_{t=1}^{P}\sum_{n=1}^{N} r_{t,n}e^{2\pi iqn/N}e^{2\pi i\omega t/P}. \qquad (13)$$

It is convenient to introduce $k'=k+\tilde{k}_1$ and $\kappa'=\kappa+\tilde{\kappa}_1$ with $\kappa=mP^2/(\beta^2\hbar^2)$ in order to reexpress $\tilde{V}_{\rm rp}$ as

$$\tilde{V}_{\rm rp}=\frac{1}{2}\sum_{\omega=1}^{P}\sum_{q=1}^{N} k_{q,\omega}|\tilde{r}_{q,\omega}|^2 \qquad (14)$$

with

$$\begin{aligned}\tilde{k}_{q,\omega}=&\,\kappa' 4\sin^2\left(\frac{\pi}{P}\omega\right)+k' 4\sin^2\left(\frac{\pi}{N}q\right)\\&+\tilde{\kappa}_2 4\{\sin^2[\pi(q/N+\omega/P)]+\sin^2[\pi(q/N-\omega/P)]\}\\&+\tilde{k}_2 4\sin^2\left(\frac{\pi}{N}2q\right).\end{aligned} \qquad (15)$$

The partition function Z_c for the classical system illustrated in Fig. 1 can then be reduced to NP Gaussian integrals. Z_c is proportional to

$$Z_c=\prod_{q=1}^{N}\prod_{\omega=1}^{P}\sqrt{\frac{2\hbar^2\beta^2}{mP^2}\tilde{k}_{q,\omega}}^{\,-1}. \qquad (16)$$

For the different algorithms we find different functions for $\tilde{k}_1,\tilde{k}_2,\tilde{\kappa}_1$, and $\tilde{\kappa}_2$. The expressions for these effective coupling coefficients are summarized in Table I. The expressions A and C used in Table I for the EPr treatment will be given and derived below.

TABLE I. Expressions for the effective coupling coefficients that are represented in Fig. 1.

	PA	HOA	EPr	r-EPr
$\tilde{k}_1$	0	$(\hbar\beta k)^2/(3mP^2)$	$k(A-C-1)$	$k(A-1)$
$\tilde{k}_2$	0	$-(\hbar\beta k)^2/(12mP^2)$	0	0
$\tilde{\kappa}_1$	0	0	$-kC$	0
$\tilde{\kappa}_2$	0	0	$\frac{1}{2}kC$	0

We will now calculate the thermal expectation value of the potential energy $\langle V_P\rangle$ for a given Trotter number P. One can expect that the errors in different observables vanish with the same power of P, which is why it is sufficient to only investigate $\langle V_P\rangle$. The prefactor of the corrections can certainly depend on the observable, for example if the system has many different energy scales. The calculations for the three approaches will be separated into three subchapters.

1. Solution for the primitive method

In the primitive method, the usual thermodynamic relationships can be used in a straightforward way without modification, albeit their use can be impractical for technical reasons. In order to calculate the thermal expectation value of $\langle V_P\rangle$, one can use the relation

$$\langle V_P\rangle=-\frac{k}{\beta}\frac{d}{dk}\ln(Z_c), \qquad (17)$$

where all effective coupling coefficients vanish. This relationship simply follows from the formal expression for the quantum-mechanical partition function of a linear, monoatomic harmonic chain. The final expression for $\langle V_P\rangle$ then is

$$\langle V_P\rangle=\frac{k}{2\beta}\sum_{q=1}^{N}\sum_{\omega=1}^{P}\frac{4\sin^2(\pi q/N)}{\tilde{k}_{q,\omega}}. \qquad (18)$$

This equation can be interpreted as follows: Equipartition requires that $\tilde{k}_{q,\omega}\langle|x_{q,\omega}|^2\rangle = k_BT$. Hence $\tilde{k}_{q,\omega}$ appears in the denominator. The amount of *real* potential energy in these modes, however, is only $\tilde{k}_q|x_{q,\omega}|^2/2$, where $\tilde{k}_q$ is the stiffnes that can be associated with the mode q in a classical linear chain.

2. Solution for the HOA method

Equation (17) also holds for the HOA method, because the only modification with respect to the primitive approximation (PA) is that a better approximant for the high-temperature density matrix is employed. However, the correct coupling coefficients $\tilde{k}_1$ and $\tilde{k}_2$ have to be used. The expressions for $\tilde{k}_1$ and $\tilde{k}_2$ stated in Table I are obtained in a straightforward way by inserting Eq. (11) into Eq. (4). This leads to the expression

$$\begin{aligned}\langle V_P\rangle=\frac{k}{2\beta}\sum_{q=1}^{N}\sum_{\omega=1}^{P}&\left\{\left[1+\frac{2}{3}\frac{\hbar^2}{m}\left(\frac{\beta}{P}\right)^2k\right]4\sin^2\left(\frac{\pi}{N}q\right)\right.\\&\left.-\frac{2}{3}\frac{\hbar^2}{m}\left(\frac{\beta}{P}\right)^2k\sin^2\left(\frac{\pi}{N}2q\right)\right\}\Big/\tilde{k}_{q,\omega}^{\rm HOA},\end{aligned} \qquad (19)$$

where $\tilde{k}_{q,\omega}^{\rm HOA}$ refers to that expression for $\tilde{k}_{q,\omega}$ in Eq. (15) which is obtained by inserting the HOA values for $\tilde{k}_1$ and $\tilde{k}_2$. The same result for $\langle V_P\rangle$ could have been obtained by calculating the second moments of the eigenmodes $\langle|\tilde{x}_{q,\omega}|^2\rangle$ from equipartition. The resulting $\langle|\tilde{x}_{q,\omega}|^2\rangle$ could then have been used to calculate the proper HOA potential energy estimator $V+2V_{\rm cor}$.

3. Solution for the EPr method

In the EPr approach, Z_c does not follow from a Hermitian decomposition of the high-temperature density matrix. Therefore Eq. (17) cannot be employed for the calculation of $\langle V_P \rangle$. However, we can use the fact that EPr is an importance sampling method. Since we can obtain $\langle |\tilde{x}_{q,\omega}|^2 \rangle$ from equipartition and since the real potential energy of mode q in a (classical) linear chain is proportional to $k \sin^2(\pi q/N)$, it is possible to use Eq. (18) where the denominator $\tilde{k}_{q,\omega}$ is taken from the EPr column in Table I. Hence,

$$\langle V_P \rangle = \frac{k}{2\beta} \sum_{q=1}^{N} \sum_{\omega=1}^{P} \frac{4 \sin^2(\pi q/N)}{\tilde{k}^{\mathrm{EPr}}_{q,\omega}}. \tag{20}$$

We are now concerned with the derivation of the expressions for A and C in Table I. To do this, one has to consider a dimer in which the two atoms are coupled by a harmonic spring of stiffness k. One then transforms the dimer Hamiltonian into the center-of-mass system with $R=(r_1+r_2)/2$ the center-of-mass coordinate and $\Delta R=(r_1-r_2)$ the reduced distance between the two atoms. These two coordinates can be associated with two modes, the center-of-mass mode with mass $M=2m$ and the internal oscillator mode with stiffnes k and reduced mass $\mu=m/2$. Both the free particle density matrix and the high-temperature density matrix (HTDM) of an oscillator with spring constant k and mass μ are known exactly. The free particle HTDM is simply proportional to $\exp[-MP(R-R')^2/2\hbar^2\beta]$ [see Eq. (1)] while the oscillator's HTDM is given by[25]

$$\rho(\Delta R, \Delta R', \beta/P) = \sqrt{\frac{\sqrt{\mu k}}{2\pi\hbar \sinh(2f)}} \exp\left\{ -\frac{\beta}{P} \frac{k}{f \sinh(f)} \times [(\Delta R^2 + \Delta R'^2)\cosh(f) - 2\Delta R\, \Delta R'] \right\}. \tag{21}$$

The prefactor on the right-hand side of Eq. (21) provides an irrelevant offset in V_{eff}, which will be neglected in the following treatment. One then needs to transform the product of the free HTDM and the internal oscillator HTDM back into the laboratory system and express the effective potential according to Eq. (10). With the definition of

$$f = \frac{\beta}{P} \hbar \sqrt{\frac{2k}{m}} \tag{22}$$

we obtain the parameters A and C

$$A = \frac{2}{f} \tanh\left(\frac{f}{2}\right), \tag{23}$$

$$C = \frac{2}{f^2} \left\{ 1 - \frac{f}{\sinh(f)} \right\} \tag{24}$$

that were introduced in Table I.

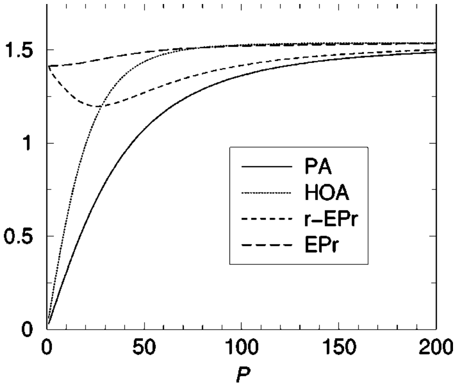

FIG. 2. Thermal expectation value of the potential energy $\langle V_P \rangle$ as a function of Trotter number P; $\beta\hbar\sqrt{k/m}=64$.

4. Solution for the r-EPr approach

According to Sec. II C 1, we need to know the quantum-mechanical radial distribution function $g(r)$ at inverse temperature β/P for the reduced harmonic oscillator in order to construct the r-EPr effective potential V_{eff}. For this purpose, it is sufficient to know the internal energy of the reduced harmonic oscillator, since $g(r)$ is a simple Gaussian at all temperatures. Hence we need to find the effective coupling constant k' which generates a second moment $\langle x^2 \rangle$ in a classical treatment at temperature PT such that the the real potential energy $k\langle x^2 \rangle/2$ corresponds to the quantum limit at temperature PT. This condition, which defines k', can be written as

$$\langle V(\beta/P) \rangle_{\mathrm{exact}} = \frac{1}{2} \frac{k}{k'} k_B T P, \tag{25}$$

where $\langle V(\beta/P) \rangle_{\mathrm{exact}}$ is the correct thermal potential energy for an oscillator at temperature PT. For a harmonmic oscillator, $\langle V(\beta/P) \rangle_{\mathrm{exact}}$ is half the internal energy U, given by $U=0.5\hbar\omega \coth(\beta\hbar\omega/2)$ with frequency $\omega=\sqrt{k/\mu}=\sqrt{2k/m}$. We solve for k' and find $k'=A\,k$. The parameter A is given in Eq. (23) and $\tilde{k}_1 = k(A-1)$ as stated in Table I follows.

5. Comparison of the methods

The main issue of this study is the analysis of the convergence of thermal expectation values such as the potential energy $\langle V_P \rangle$ to the proper quantum limit as a function of Trotter number P. We consider a linear chain consisting of $N=5$ atoms and periodic boundary conditions. The convergence does not depend on N in a qualitative way. It is examined at a fixed thermal energy well below the Debye frequency of the chain, namely at inverse temperature $\beta = 64/(\hbar\sqrt{k/m})$. A linear plot of $\langle V_P \rangle$ is shown in Fig. 2.

It can be seen that at $P=1$ the EPr and the r-EPr methods start off with estimates that are very close to the quantum limit while PA and HOA start off with an estimate near the classical value. Upon increasing P the EPr approaches the proper value from below, while for the r-EPr method the deviation between estimate and proper result first increases before it decreases again. At a Trotter number $P \approx 64$, the

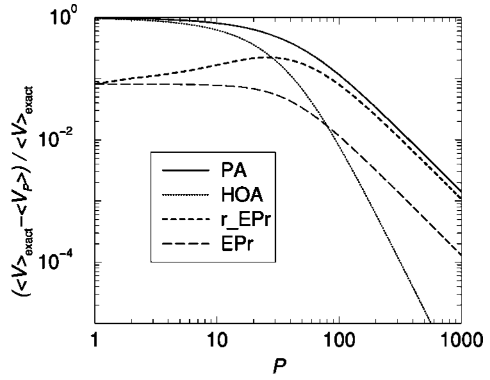

FIG. 3. Relative error of the potential energy for an $N=5$ chain at $\beta\hbar\omega=64$ as a function of Trotter number P.

HOA method becomes similarly good as the EPr approach. In order to address the convergence in a more quantitative way, it is convenient to analyze the relative deviation of $\langle V_P\rangle$ from the exact value $\langle V_E\rangle$ as a function of P in a double logarithmic plot, which is done in Fig. 3.

It can be seen that at large Trotter numbers the HOA method converges with P^{-4} to the quantum limit, while all other methods only converge with P^{-2}. The prefactor for the EPr, however, is much smaller than for r-EPr and PA. The value of P at which convergence starts is similar in all approaches, e.g., $k_B TP$ is larger than but in the order of $\hbar\sqrt{k/m}$. The accuracy where HOA becomes better than EPr is 1.7%. For this particular model system, this value of 1.7% was found to be independent of temperature. We expect it to be similar for all systems that are dominated by harmonic interactions. We will now address the question of how we have to increase P for the various approaches if we lower T and require the relative accuracy to be constant, e.g., 1%. The results are shown in Fig. 4.

In order for the relative error to be constant, all methods require that P increases linearly with inverse temperature β. The r-EPr approach, which is a little more difficult to implement than the PA method, requires slightly reduced Trotter numbers with respect to PA. We want to emphasize that the behavior shown in Fig. 4 is qualitatively similar if the accuracy criterion for P is changed, however, the stricter the criterion the larger the gap between EPr and HOA. This trend can be seen in Fig. 4(b), where we require one time 0.1% accuracy instead of 1% as shown in Fig. 4(a). Only if one is confined to the use of very small P might EPr be the better choice. One may conclude that the optimal method depends on the desired accuracy.

B. Quartic oscillator

The HOA $1/P^4$ corrections are not only valid for the harmonic oscillator. They also apply to other well-behaved potentials such as the quartic oscillator. Its potential energy has the form

$$V(x)=\frac{1}{4}k_4x^4. \tag{26}$$

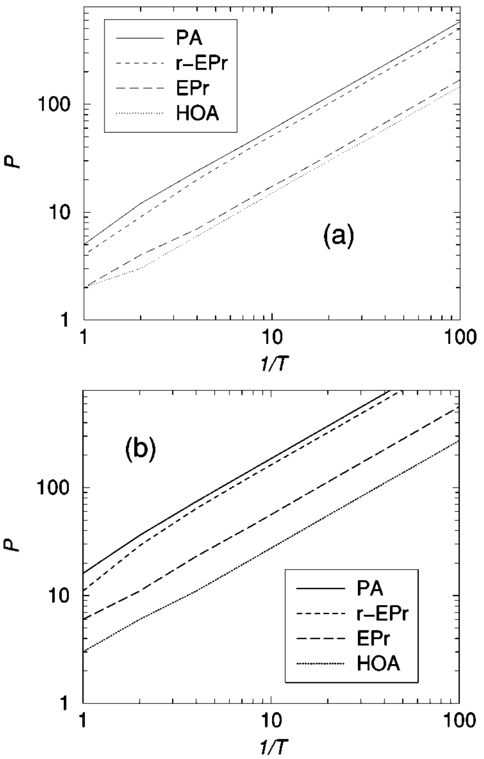

FIG. 4. Necessary Trotter number P to reach a relative accuracy of (a) 10^{-2} and (b) 10^{-3} in the potential energy $\langle V_P\rangle$ at different inverse temperatures $1/T$ for the linear chain consisting of $N=5$ atoms. All parameters other than temperature ($\hbar$, k, m) are set to unity.

We have confirmed the HOA $1/P^4$ convergence for the one-dimensional quartic oscillator and the double well potential by means of numerical matrix multiplication (NMM).[27–30] (See Sec. III C for some more details on NMM.) Both potential energy and kinetic energy show the same convergence rate. One may conjecture that similar behavior is found for more general Φ^4 potentials, i.e., double well or multiwell potentials. Indeed, the HOA treatment of a linear rotor impurity in a three-dimensional multiwell potential showed similar behavior as that found for our simple one-dimensional quartic oscillator.[32] In that HOA study, the Debye anomaly in the specific heat (due to tunneling between equivalent minima in the potential energy) could be observed at much smaller Trotter numbers than if the primitive approach had been used.

C. Gaseous helium

The proof for the $1/P^4$ convergence of the HOA approach relies on the assumption that the thermal expectation value of the commutator $[\hat{T},\hat{V}]$ and higher-order commutators such as $[\hat{V},[\hat{T},\hat{V}]]$ are well-defined.[16,23,26] More realistic potentials like the Lennard-Jones potential $V=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$ may not satisfy this assumption. Hence it is important to test how higher-order approximants perform for this class of potentials in particular in a situation where the system is far from being harmonic. The study of gaseous helium can therefore elucidate the convergence of HOA methods, because quantum effects are strong even in the dilute gas phase as discussed recently, for example, by Müser and Luijten.[30] Moreover, gaseous helium satisfies the condition of being strongly anharmonic.

In the low-density limit, noble gases are approximated rather well in terms of the second-order virial coefficient B_2. The calculation of B_2 for quantum systems can be done in terms of numerical matrix multiplication (NMM). NMM exploits the idea that squaring of the thermal density matrix $\rho(T)$ at temperature T results in $\rho(T/2)$.[27–30] This procedure can be repeated n times so that one can easily calculate the low-temperature density matrix $\rho(T/2^n)$ from a high-temperature $\rho(T)$, for which the actions are reasonably approximated either by the decomposition underlying the primitive approach or that leading to the higher-order approximants. The squaring procedure allows one to estimate the systematic error due to the finiteness of P without conducting explicit simulations. NMM can also be used to initialize the proper effective interactions underlying the EPr simulations.

NMM becomes increasingly more complex with increasing dimensionality of the Hilbert space, i.e., exponentially more complex with the number of particles. As described previously in Refs. 27–29, the calculations can be simplified for systems whose description can be reduced to the case of one particle moving in a central potential. We do not want to repeat the details of method, but we would like to comment on an issue that is relevant to our case. To analyze the convergence with P in dimensions larger than 1, it is necessary to use the proper modified Bessel functions for the free-particle kernel at given angular momentum l; see Eq. (4.43) in Ref. 3. Otherwise the leading corrections cannot vanish faster than with $1/P^2$. Moreover, it is necessary to chose the discretization of the real space sufficiently small.

We have analyzed the convergence rate of B_2 for argon gas (Lennard-Jones potential) and gaseous ^{4}He (Aziz potential[33]). We found that the convergence of the higher-order approximants remain $1/P^4$ like for well-behaved potentials, however, the crossover to the regime in which the leading correction is in the order of $1/P^4$ happens at values of P that are larger than those values of P where the crossover takes place for the primitive approach. The reason why the singularity does not affect the convergence rate at large P lies in the fact that there is no wave function in the singularity and its statistical weight near the singularity vanishes sufficiently fast. We note in passing that the situation is less clear cut for the repulsive Coulomb potential.

In Fig. 5 we show exemplarily the relative error of the second virial coefficient of one-dimensional Lennard-Jonesium at two different temperatures. The choice of $d=1$ is motivated in part by the argument that the effect of a singularity is particularly large for a small-dimensional system. Moreover the numerical stability and the range of Trotter numbers that can be investigated are larger in $d=1$ than in $d=3$. In Fig. 5, results are shown for Lennard-Jonesium characterized by a de Boer parameter $\lambda = h/\sqrt{M\sigma^2\epsilon}$ of $\lambda = 2.7$, which reflects approximately ^{4}He. The two thermal energies emploied in Fig. 5 correspond to $T=2$ K and $T=20$ K if we interpret $\lambda=2.7$ Lennard-Jonesium as ^{4}He. The convergence of the virial coefficient in $d=1$ is similar to that described above in the previous paragraph for $d=3$: Despite the singularity the HOA approach converges with $1/P^4$ to the proper quantum limit. The convergence starts at values of P that are slightly larger than those of the primitive approach.

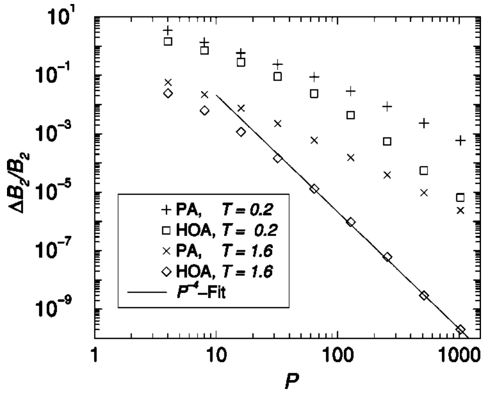

FIG. 5. Relative error of the virial coefficient B_2 of Lennard-Jonesium with de Boer parameter $\lambda=2.7$, an approximate description of ^{4}He. The PA method and the HOA method are compared at two different temperatures, where the dimensionless temperatures $T=0.2$ and $T=1.6$ correspond to 2 and 16 K, respectively, in the case of ^{4}He.

We have also analyzed the kinetic and potential energy in the dilute gas phase as a function of Trotter number P. Both observables converge in a similar way as B_2, that is to say, the leading corrections are in the order of $1/P^4$ for HOA and of order $1/P^2$ for PA. Note that the EPr approach is exact by construction for dilute gases.

D. Crystalline argon

It has been pointed out in Sec. II B that in order to calculate radial correlation functions, it is necessary to correct the estimator for $g(r)$. An important question to address is how well the HOA approach allows one to calculate $g(r)$. In order to examine this issue we apply the HOA method [making use of the proper estimator, see Eq. (7)] to crystalline argon. We model the system with the same Lennard-Jones potential as one of us[5] previously, namely $\epsilon = 120\ k_B$K and $\sigma = 3.405$ Å. The number of atoms used in the simulation cell was $N=500$. The geometry and the size of the simulation cell was allowed to fluctuate. The initial state was chosen such that the average geometry was cubic. Since our intention is to study the convergence with respect to P, we do not discuss finite-size effects in $g(r)$. The results are presented in Fig. 6.

It is interesting to note that $g(r)$ is too broadened for the HOA approach while it is too narrow using the PA algorithm. Obviously, the agreement of the $P=12$ HOA calculation is already very close to the quantum limit. This is a little surprising as the product of k_BTP is still far below the thermal energy of the Debye temperature, which is about $T_D \approx 85$ K. We want to note that if the $g(r)$ are obtained without corrections, the agreement is distinctly reduced. This might be the reason why the convergence of $g(r)$ reported

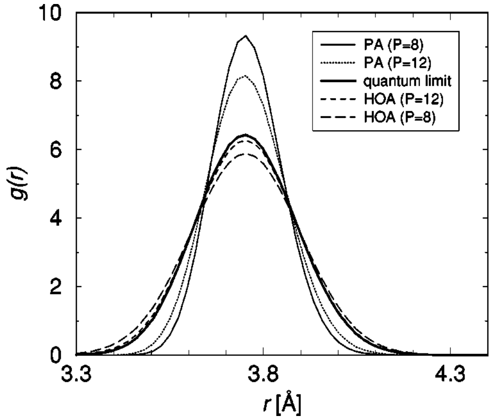

FIG. 6. Pair correlation function $g(r)$ of crystalline argon at $T=2$ K calculated with the PA and HOA algorithm for Trotter numbers $P=8$ and $P=12$. As a reference a quasiexact correlation function (HOA, $P=256$) is included.

by Li and Broughton for the attractive Coulomb potential was so slow.[20] In our case, omitting the corrections to the $g(r)$ estimator leads to peaks in $g(r)$ that are even sharper than those obtained with PA using identical Trotter numbers.

Similar to the second virial coefficient, kinetic and potential energy both cross over (individually) to the $1/P^4$ convergence if the HOA is employed. The crossover to the values of P, where the leading corrections $1/P^n$ dominate the finite P error, is larger for HOA than for PA. Hence this behavior ressembles that of the B_2 expansion (discussed in Sec. III C), despite the fact that the argon crystal is relatively harmonic, that is to say, the harmonic approximation is stable and accounts for most of the ground-state energy.

Although it is necessary to alter the distance estimator, there is no need to alter the volume estimator, see Eq. (5). This is because the volume per atom is entirely determined by the periodic boundary conditions and thus independent of the atomic positions. Similar comments apply to second (and higher)-order distribution functions of the strain tensor from which the elastic constants follow.

It is well-known that deviations of the (average) atomic volume $\langle v \rangle$ from its value in the harmonic approximation are due to anharmonicity. Quantum fluctuations often enhance anharmonicity. For solid argon at $T=2$ K, the anharmonicity is even dominated by quantum fluctuations. Hence the convergence of $\langle v \rangle$ with P to the quantum-mechanical reference value is an important test for the HOA method. Results are shown in Fig. 7 for crystalline argon at $T=2$ K. As in all other cases discussed above, HOA leads to distinctly reduced systematic errors with respect to PA. It is possible to confirm the $1/P^4$ convergence for the HOA algorithm within the statistical error bars.

IV. SUMMARY

In this study we have compared the convergence to the quantum limit for different path integral approaches. As the convergence rate does not depend on the specific model system (as long as the potentials are well behaved), we have focused our attention to a linear chain of harmonically coupled atoms. We disregarded methods making explicit use of a decomposition into a harmonic and an anharmonic part of the Hamiltonian among other reasons due to the unfavorable scaling of the numerical effort with system size.

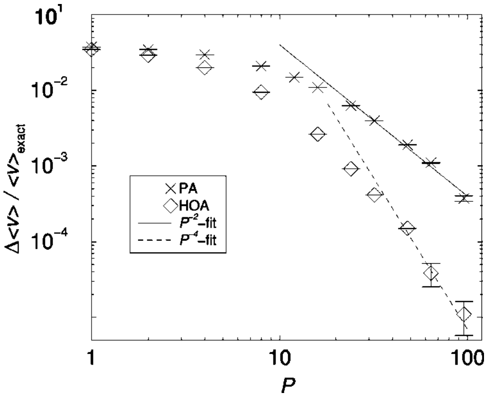

FIG. 7. Relative error of the atomic volume for crystalline argon at $T=2$ K as a function of Trotter number P calculated with the PA (crosses) and HOA (diamond) algorithm.

The three main approaches investigated were the so-called primitive algorithm (PA), a method based on a higher-order approximant (HOA), and an approach in which an effective potential is constructed such that the one- and two-particle high-temperature density matrices are reproduced exactly in the limit of small densities. We called this approach the effective propagator (EPr) method. The latter approach can be further reduced by only taking into account certain corrections on the diagonal of the high-temperature density matrix leading to the r-EPr method.

We emphasized the different spirit of EPr and HOA methods: In the EPr method, observables orthogonal in real space can be evaluated directly, whereas the HOA method requires effective estimators. The need to alter estimators even for radial distribution functions obtained in simulations taking into account quantum effects in an effective potential are discussed. We showed that the proper estimators lead to a very fast convergence to the quantum limit in a simple argon crystal.

For the linear monoatomic chain investigated in this study, we found that the corrections based on HOA vanish with P^{-4} while all other methods, PA, EPr, and r-EPr, have corrections in the order of P^{-2}. The prefactor is similar for PA and r-EPr and distinctly smaller for EPr. Both EPr and r-EPr, however, give rather accurate results at small P, e.g., the relative error in the thermal expectation value of the potential energy is smaller than 10% in those approaches, while PA and HOA differ by nearly 100% at low temperatures and $P=1$. The Trotter number where convergence starts is similar in all approaches. If one requires high accuracy, e.g., 1%, one needs to increase the Trotter number P linearly in all approaches.

The $1/P^4$ convergence of average potential energy, average kinetic energy, and average atomic volume was also obtained in HOA simulations for anharmonic systems, in which the interatomic potentials were singular at the origin. This comment applies to cases where the probability density vanishes in the singularity, which is not the case for the attractive or repulsive Coulomb potential. Our case studies included an HOA based virial expansion of gaseous ^{4}He and a Lennard-Jones model of solid argon.

What can we conclude for path integral simulations? The use of HOA is certainly a little more CPU time expensive than that of EPr, r-EPr, and PA, which all require approximately the same amount of computing. This is because in an HOA based simulation, we need derivatives of the interaction potential that are one order higher than those in simulations based on EPr, r-EPr, and PA. This makes HOA Monte Carlo simulations about twice as CPU time expensive than Monte Carlo simulations that are based on one of the other schemes discussed here. This factor of 2 can be reduced close to unity in path integral molecular dynamics by using multiple time-step algorithms, in which the correction terms do not have to be evaluated at every time step. But even in a Monte Carlo simulation, one is rewarded with the best convergence to the quantum limit in an HOA based path integral simulation. While EPr also results in a significant improvement with respect to PA, it is plagued with a tedious, nontrivial implementation procedure. Moreover, HOA is easily generalized to three-body forces, while the inclusion of three-body terms in EPr would require nontrivial generalizations. Nevertheless, EPr should be the method of choice for the simulation of dilute systems like the recently produced Bose-Einstein condensates. For dense systems, however, the HOA method seems to be the most efficient method in particular if high numerical accuracy is required.

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