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Generalized Fourth-Order Decompositions of Imaginary Time Path Integral: Implications of the Harmonic Oscillator†

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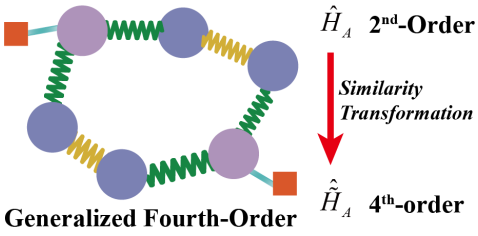
The imaginary time path integral formalism offers a powerful numerical tool for simulating thermodynamic properties of realistic systems. We show that, when second-order and fourth-order decompositions are employed, they share a remarkable unified analytic form for the partition function of the harmonic oscillator. We are then able to obtain the expression of the thermodynamic property and the leading error terms as well. In order to obtain reasonably optimal values of the free parameters in the generalized symmetric fourth-order decomposition scheme, we eliminate the leading error terms to achieve the accuracy of desired order for the thermodynamic property of the harmonic system. Such a strategy leads to an efficient fourth-order decomposition that produces third-order accurate thermodynamic properties for general systems.



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I. INTRODUCTION

Feynman's imaginary time path integral formulation has offered a powerful tool for computing quantum thermodynamic properties of physical systems [1, 2]. Adopting the isomorphism between the quantum partition function and the classical one of an enlarged system that consists of copies (also denoted beads) of the original one [3], scientists have made significant progress in developing efficient numerical algorithms of imaginary time path integral (PI) via Monte Carlo (MC) or molecular dynamics (MD) [4−10]. PIMC and PIMD have been widely used for realistic molecular systems from superfluid helium below 2.2 K to liquid water under ambient conditions.

Denote P the number of copies (beads) in the isomorphic classic system. Exact results are, in principle, achieved in the limit $P\to\infty$. The feasibility of numerical simulations of imaginary time path integral is then limited by the large value of P required for converged, reliable results. It becomes severe at low temperatures or when the interaction is strong. In comparison with the second-order $(\sim 1/P^2)$ Trotter decomposition [11] prevailingly used, fourth-order $(\sim 1/P^4)$ decomposition schemes considerably decrease the number of copies (beads) for obtaining converged results and lead to potentially more efficient approaches [5, 12−22]. Because the fourth-order decomposition scheme often involves adjustable parameters, it is important to know the optimal values of these parameters for practical purposes.

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The harmonic oscillator, a paradigmatic system where the analytical analysis is often available [2, 8, 9, 23], provides useful insight for choosing the optimal value of the free parameter as well as designing numerical algorithms [24, 25].

In the work, we use the generalized fourth-order decomposition scheme with the finite value of P to derive the expression of the partition function for the harmonic oscillator, and then show how to determine the optimal values for the free parameters. In Section II, we first give a brief review on previous works on fourth-order decompositions [13, 15, 17, 26], and then propose a generalized scheme, which in particular leads to more efficient fourth-order decompositions in light of rational design. We then derive in Section III a unified analytic form for the partition function of the harmonic oscillator, resorting to various second-order or fourth-order decompositions. The form of the partition function yields the analytical result of any thermodynamic properties with the finite number of copies involved in the isomorphic classical system. In Section IV, we first expand the analytical result of the thermodynamic property into a power series of $1/P$, and then obtain the optimal parameters by eliminating the leading error terms. Section V presents the comparison among different factorized decompositions for the numerical performance. Conclusion remarks and outlook follow in Section VI.

II. DECOMPOSITIONS FOR IMAGINARY TIME PATH INTEGRAL

Consider the partition function of a system described by the Hamiltonian,

$$\hat{H} = \hat{T} + \hat{V} = \frac{1}{2}\hat{\mathbf{p}}^T\mathbf{M}^{-1}\hat{\mathbf{p}} + V(\hat{\mathbf{x}}) \tag{1}$$

where $\mathbf{M}$ is the diagonal "mass matrix" with elements $\{m_i\}$, and $\hat{\mathbf{p}}$ and $\hat{\mathbf{x}}$ are the momentum and position operators. The partition function of the canonical ensemble in quantum mechanics is

$$Z = \mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\right) \tag{2}$$

where $\beta=1/k_\mathrm{B}T$ with k_B being the Boltzmann constant and T being the temperature.

Substituting a series of the resolution of identity operators, $\mathbf{I}=\int \mathrm{d}\mathbf{x}_j \left|\mathbf{x}_j\right\rangle \left\langle\mathbf{x}_j\right|$, into the configuration representation of Eq.(2), we obtain

$$Z = \int \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_P \prod_{j=1}^{P} \left\langle \mathbf{x}_j \right| \mathrm{e}^{-\varepsilon\hat{H}} \left| \mathbf{x}_{j+1} \right\rangle \tag{3}$$

where $\varepsilon=\beta/P$. Because the potential energy operator $\left(\hat{V}\right)$ and the kinetic energy operator $\left(\hat{T}\right)$ do not commute with each other, one has to use approximations to decouple them in $\mathrm{e}^{-\varepsilon\hat{H}}$ for numerical implementation. The simplest approximation is the Trotter decomposition [11],

$$\mathrm{e}^{-\varepsilon\hat{V}/2}\mathrm{e}^{-\varepsilon\hat{T}}\mathrm{e}^{-\varepsilon\hat{V}/2} = \mathrm{e}^{-\varepsilon\hat{H}+O\left(\varepsilon^3\right)} \tag{4}$$

which is prevailingly used in imaginary time path integral simulations. The decomposition defined in Eq.(4) is of second-order accuracy, *i.e.*, the error is of third-order and it often leads to a partition function of the first-order accuracy (*i.e.*, with the second-order error, $O\left(1/P^2\right)$), for general systems. This simple and user-friendly algorithm, however, often suffers from a slow numerical convergence with respect to P, the number of copies. For example, when the second-order Trotter decomposition is used, at least 48 copies (beads) in the isomorphic classic system have to be employed for obtaining converged results for liquid water at room temperature [8, 9, 27]. It is then expected that higher-order decompositions will accelerate the convergence rate. Below we introduce a generalized symmetric fourth-order decomposition scheme that is practically useful for general molecular systems.

A. Generalized symmetric fourth-order decompositions

Chin proposed that careful construction of the second-order decomposition can yield a third-order accurate partition function [15, 17, 28]. Consider the factorized symmetric second-order $\left(\varepsilon^2\right)$ decomposition,

$$\prod_{i=0}^{n} \exp\left(-\varepsilon t_i \hat{T}\right) \exp\left\{-\varepsilon v_i \hat{V}\right\} = \exp\left\{-\varepsilon \hat{H}_A\right\} \tag{5}$$

where the approximate Hamiltonian is

$$\begin{aligned} \hat{H}_A \;=\; & \hat{H} - e_{TVT}\varepsilon^2\left[\hat{T},\left[\hat{V},\hat{T}\right]\right] \\ & - e_{VTV}\varepsilon^2\left[\hat{V},\left[\hat{T},\hat{V}\right]\right] + O\left(\varepsilon^4\right) \end{aligned} \tag{6}$$

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In Eq.(5) the free parameters satisfy

$$\begin{aligned}\sum_{i=0}^{n} t_i &= 1\\ \sum_{i=0}^{n} v_i &= 1\end{aligned} \tag{7}$$

and the relations between $\{t_i,\ v_i\}$ and the coefficients of the errors $\{e_{TVT},\ e_{VTV}\}$ are

$$e_{TVT} = \sum_{i=0}^{n} t_i \sum_{j=i+1}^{n} t_j \sum_{k=j}^{n} v_k + \frac{1}{2}\sum_{i=0}^{n} {t_i}^2 \sum_{k=i}^{n} v_k - \frac{1}{6} \tag{8}$$

$$e_{VTV} = \sum_{i=0}^{n} t_i \sum_{j=i}^{n} v_j \sum_{k=j+1}^{n} v_k + \frac{1}{2}\sum_{i=0}^{n} t_i \sum_{j=i}^{n} {v_j}^2 - \frac{1}{6} \tag{9}$$

Since the decomposition in Eq.(5) is symmetric, for the elimination of the odd-order errors in the approximate Hamiltonian of Eq.(6), the number of splitting terms is reduced from $2n+2$ to $2n+1$. Using the freedom of parameters $\{t_i,\ v_i\}$, we suggest the following two decomposition schemes, one defined as $nT\,(n+1)\,V$ with

$$\begin{aligned}&t_0 = 0\\ &t_i = t_{n-i+1}, \quad i \in \{1, 2, \cdots, n\}\\ &v_i = v_{n-i}, \quad i \in \{0, 1, \cdots, n\}\end{aligned} \tag{10}$$

and the other $(n+1)\,TnV$ with

$$\begin{aligned}&t_i = t_{n-i}, \quad i \in \{0, 1, \cdots, n\}\\ &v_n = 0\\ &v_i = v_{n-i-1}, \quad i \in \{0, 1, \cdots, n-1\}\end{aligned} \tag{11}$$

Because of the invariance of the trace of a finite matrix under the similarity transformation [15], the partition function reads

$$\begin{aligned}Z &= \mathrm{Tr}\left[\left(\mathrm{e}^{-\varepsilon \hat{H}_A}\right)^P\right] = \mathrm{Tr}\left[\left(\mathrm{e}^{\varepsilon \hat{C}}\mathrm{e}^{-\varepsilon \hat{H}_A}\mathrm{e}^{-\varepsilon \hat{C}}\right)^P\right]\\ &= \mathrm{Tr}\left[\left(\exp\left(\varepsilon \hat{\tilde{H}}_A\right)\right)^P\right]\end{aligned} \tag{12}$$

where

$$\hat{\tilde{H}}_A \equiv \mathrm{e}^{\varepsilon \hat{C}}\hat{H}_A\mathrm{e}^{-\varepsilon \hat{C}} = \hat{H}_A + \varepsilon\left[\hat{C}, \hat{H}_A\right] + \frac{\varepsilon^2}{2}\left[\hat{C}, \left[\hat{C}, \hat{H}_A\right]\right] + \frac{\varepsilon^3}{3!}\left[\hat{C}, \left[\hat{C}, \left[\hat{C}, \hat{H}_A\right]\right]\right] + O(\varepsilon^4) \tag{13}$$

is the corrected approximate Hamiltonian, and $\hat{C}$ is a corrector whose explicit form is unnecessary in numerical simulations. With these results, Chin observed that

$$e_{TVT} + e_{VTV} = 0 \tag{14}$$

is required so that the symmetric second-order decomposition scheme of Eq.(5) leads to a third-order $\left(1/P^3\right)$ accurate partition function (that is, with the fourth-order error, $O\left(1/P^4\right)$). Eq.(14) is, however, never satisfied when factors $\{t_i,\ v_i\}$ are non-negative [15, 17, 29], which is a generalized conclusion of Suzuki's and Sheng's previous works [26, 30].

Moreover, because the evaluation of $\left[\hat{T}, \left[\hat{V}, \hat{T}\right]\right]$ involves higher-order derivatives of the potential beyond the Hessian and is not practically useful, Suzuki [12] and Chin [13] suggested that the term $\left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right]$ should be included in the decomposition for achieving the third-order accurate partition function with non-negative $\{t_i,\ v_i\}$. Note that $\left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right]$ can straightforwardly be evaluated as [5, 13]

$$\left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right] = \hbar^2 \mathbf{F}^T(\hat{\mathbf{x}})\mathbf{M}^{-1}\mathbf{F}(\hat{\mathbf{x}}) \tag{15}$$

where $\mathbf{F}(\hat{\mathbf{x}})$=$\nabla V(\hat{\mathbf{x}})$.

More recently we have proposed a generalized symmetric factorized fourth-order decomposition that yields the third-order accurate partition function. Such a decomposition reads

$$\prod_{i=0}^{n} \exp\left(-\varepsilon t_i \hat{T}\right) \exp\left\{-\varepsilon v_i \hat{V} - \varepsilon^3 c_i\left(e_{VTV} + e_{TVT}\right)\left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right]\right\} = \exp\left\{-\varepsilon \hat{H}'_A\right\} \tag{16}$$

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$$\hat{H}'_A = \hat{H} - e_{TVT}\varepsilon^2 \left(\left[\hat{T}, \left[\hat{V}, \hat{T}\right]\right] - \left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right] \right) + O\left(\varepsilon^4\right) \tag{17}$$

is the approximate Hamiltonian, the set of parameters $\{c_i\}$ satisfy

$$\sum_{i=0}^{n} c_i = 1 \tag{18}$$

and $\{t_i,\ v_i\}$ are nonnegative, satisfying Eq.(7), while $\{e_{TVT},\ e_{VTV}\}$ are defined in Eqs.(8)−(9). We then have a generalized symmetric $nT\left(n+1\right)V$ decomposition, where

$$c_i = c_{n-i} \tag{19}$$

and $\{t_i,\ v_i\}$ are set according to Eq.(10), and a generalized symmetric $\left(n+1\right)TnV$ decomposition, where

$$c_n = 0, \quad c_i = c_{n-i-1} \tag{20}$$

and $\{t_i,\ v_i\}$ are set according to Eq.(11). In the original fourth-order decomposition formulations of Refs.[17, 28] and applied to PIMC in Refs.[25, 31, 32], e_{TVT}=0. In contrast, no constraints for $\{e_{TVT},\ e_{VTV}\}$ in Eq.(16) are required, leaving more freedom for the optimization of the involved free parameters.

To show that Eq.(16) is indeed an effective fourth-order symmetric decomposition, we need to refer to Eqs.(12) and (13). Now, we apply the similarity transformation with the corrector

$$\hat{C}' = \varepsilon e_{TVT}\left[\hat{T}, \hat{V}\right] \tag{21}$$

and obtain

$$\begin{aligned} \hat{\hat{H}}'_A &= \hat{H} - e_{TVT}\varepsilon^2 \left(\left[\hat{T}, \left[\hat{V}, \hat{T}\right]\right] - \left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right] \right) \\ &\quad + \varepsilon^2 e_{TVT}\left[\left[\hat{T}, \hat{V}\right], \hat{H}\right] + O(\varepsilon^4) \\ &= \hat{H} + O(\varepsilon^4) \end{aligned} \tag{22}$$

As a consequence, the symmetric decomposition of Eq.(16) is effectively fourth-order accurate, with which the corresponding partition function is of third-order accuracy $\left(1/P^3\right)$.

B. Unified expression of the partition function of symmetric second-order and fourth-order decompositions

With the symmetric second-order decomposition of Eq.(5) and the generalized symmetric fourth-order decomposition of Eq.(16), the corresponding partition function with nP beads can be expressed in a unified form as

$$Z_{nP} \overset{\mathbf{x}_1 \equiv \mathbf{x}_{nP+1} \equiv \mathbf{x}}{=} \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2 \cdots \int \mathrm{d}\mathbf{x}_{nP} \left(\frac{1}{2\pi\varepsilon\hbar^2}\right)^{nNP/2} \left(\prod_{i=1}^{n} t'_i\right)^{-NP/2} |\mathbf{M}|^{nP/2} \mathrm{e}^{-\varepsilon H_{nP}} \tag{23}$$

where the effective potential reads

$$H_{nP} \overset{\mathbf{x}_1 \equiv \mathbf{x}_{nP+1} \equiv \mathbf{x}}{=} \frac{1}{2\varepsilon^2\hbar^2} \sum_{i=1}^{nP} \frac{1}{t'_i} (\mathbf{x}_{i+1} - \mathbf{x}_i)^T \mathbf{M} (\mathbf{x}_{i+1} - \mathbf{x}_i) + \sum_{i=1}^{nP} v'_i V(\mathbf{x}_i) + \kappa\varepsilon^2\hbar^2 \sum_{i=1}^{nP} c'_i \mathbf{F}^T(\mathbf{x}_i) \mathbf{M}^{-1} \mathbf{F}(\mathbf{x}_i) \tag{24}$$

The effective potential of the generalized symmetric $nT\left(n+1\right)V$ scheme with parameters satisfying Eqs.(10) and (19), can be recast to Eq.(24) with

$$\begin{aligned} t'_i &= t_{\mathrm{mod}\,(i-1,n)+1}, \\ v'_i &= \begin{cases} v_{\mathrm{mod}\,(i,n)}, & \mathrm{mod}(i,n) \neq 0 \\ 2v_0 = 2v_n, & \mathrm{mod}(i,n) = 0 \end{cases} \\ c'_i &= \begin{cases} c_{\mathrm{mod}\,(i,n)}, & \mathrm{mod}(i,n) \neq 0 \\ 2c_0 = 2c_n, & \mathrm{mod}(i,n) = 0 \end{cases} \end{aligned} \tag{25}$$

and e_{TVT}+e_{VTV}=κ. Similarly, the effective potential of the generalized symmetric $\left(n+1\right)TnV$ scheme with parameters satisfying Eqs.(11) and (20), can be recast into Eq.(24) with

$$\begin{aligned} t'_i &= \begin{cases} t_{\mathrm{mod}\,(i,n)} & \mathrm{mod}\,(i,n) \neq 0 \\ 2t_0 = 2t_n & \mathrm{mod}\,(i,n) = 0 \end{cases} \\ v'_i &= v_{\mathrm{mod}\,(i,n)} \\ c'_i &= c_{\mathrm{mod}\,(i,n)} \end{aligned} \tag{26}$$

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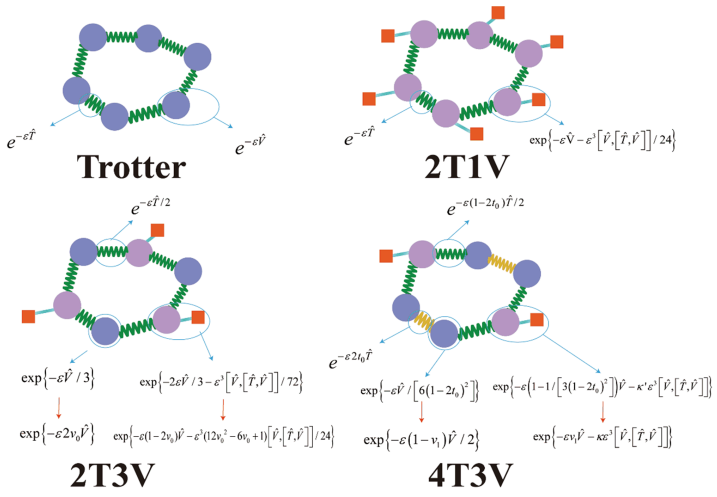

FIG. 1 A schematic representation of Totter decomposition [11], generalized decomposition [1], decomposition [12, 13], and its generalization, as well as decomposition [35] and its generalization when six copies (beads) are used.

and $e_{TVT}+e_{VTV}=\kappa$. Eqs.(25) and (26) indicate

$$\left.\begin{array}{l} t'_j = t'_{j+nl} \\ v'_j = v'_{j+nl} \\ c'_j = c'_{j+nl} \end{array}\right\} \quad \begin{array}{c} l \in \{0,1,2,\cdots,P-1\}, \\ j \in \{1,2,\cdots,n\} \end{array} \tag{27}$$

Note that when the second-order decomposition scheme of Eq.(5) is used, κ=0 in Eq.(24).

A schematic representation of decomposition schemes is presented in FIG. 1.

III. QUANTUM PARTITION FUNCTION OF THE HARMONIC OSCILLATOR

In numerical implementations of Eq.(16), the values of its adjustable parameters $\{t_i,\ v_i,\ c_i\}$ should be given. Unfortunately, no straightforward and exact procedures are available to determine them for general systems. We thus examine the harmonic oscillator (HO) and acquire the optimal values of these parameters and hope that they work reasonably well for other systems.

For the HO system with potential

$$V(x) = \frac{m\omega^2 x^2}{2} \tag{28}$$

the exact partition function is known to be

$$Z_{\mathrm{HO}} = \frac{1}{2\sinh(u/2)} \tag{29}$$

Here and throughout the paper the unitless parameter

$$u = \beta\hbar\omega \tag{30}$$

is used. With the partition function we readily obtain the internal energy,

$$E_{\mathrm{HO}} = -\frac{\partial}{\partial\beta}\ln Z_{\mathrm{HO}} = \frac{\hbar\omega}{2}\coth\left(\frac{u}{2}\right) \tag{31}$$

and other thermodynamic properties [2, 23, 33].

As we apply the expression of the partition function for the decomposition scheme with finite P, Eq.(23) to HO, the corresponding effective potential defined by Eq.(24), becomes

$$\begin{aligned} H_{nP}(\mathbf{x}) &\overset{x_1\equiv x_{nP+1}\equiv x}{=} m\omega^2\left[\frac{P^2}{2u^2}\sum_{i=1}^{nP}\frac{1}{t'_i}(x_{i+1}-x_i)^2 + \sum_{i=1}^{nP}\left(\frac{v'_i}{2}+\kappa\frac{u^2}{P^2}c'_i\right){x_i}^2\right] \\ &= m\omega^2\left(\mathbf{x}^T\mathbf{\Lambda}(n,P)\,\mathbf{x}\right) \end{aligned} \tag{32}$$

where $\mathbf{x}=[x_1,x_2,\cdots x_{nP}]^T$ is the nP-dimensional coordinate vector, and $\mathbf{\Lambda}(n,P)$ is the nP-dimensional coefficient

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matrix

$$\mathbf{\Lambda}(n,P)=\begin{bmatrix} D_1 & -d_1 & & & & & -d_{nP} \\ -d_1 & D_2 & -d_2 & & & & \\ & -d_2 & D_3 & \ddots & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & \ddots & \ddots & \ddots & \\ & & & & \ddots & \ddots & -d_{nP-1} \\ -d_{nP} & & & & & -d_{nP-1} & D_{nP} \end{bmatrix} \tag{33}$$

with elements

$$d_i = P^2/\left(2u^2 t_i'\right),\ d_0 = d_{nP},\ D_i = d_{i-1} + d_i + v_i'/2 + \kappa u^2 c_i'/P^2 \tag{34}$$

Therefore, the quantum partition function of the system described by the Hamiltonian Eq.(23) becomes a multidimensional Gaussian integral,

$$Z_{nP} = \int \mathrm{d}\mathbf{x}\Big(\frac{m}{2\pi\varepsilon\hbar^2}\Big)^{nP/2}\left(\prod_{i=1}^{nP} t_i'\right)^{-1/2} \exp\left[-\varepsilon\omega^2\left(\mathbf{x}^T\mathbf{\Lambda}(n,P)\,\mathbf{x}\right)\right] \tag{35}$$

Inspired by Ref.[34], we recast Eq.(35) into

$$\begin{aligned} Z_{nP} &= \int \mathrm{d}x \int \mathrm{d}\mathbf{x}'\Big(\frac{m}{2\pi\varepsilon\hbar^2}\Big)^{nP/2}\left(\prod_{i=1}^{nP} t_i'\right)^{-1/2} \exp\left\{-\varepsilon m\omega^2 D_1 x^2\right\}\exp\left\{-\varepsilon m\omega^2\left(\mathbf{x}'^T\mathbf{A}(n,P)\,\mathbf{x}' + \mathbf{x}'^T\mathbf{B}\right)\right\} \\ &= \int \mathrm{d}x\Big(\frac{m}{2\pi\varepsilon\hbar^2}\Big)^{nP/2}\left(\prod_{i=1}^{nP} t_i'\right)^{-1/2}\left[\frac{\pi^{nP-1}}{(\varepsilon m\omega^2)^{nP-1}A(n,P)}\right]^{1/2}\exp\left\{-\varepsilon m\omega^2 D_1 x^2\right\}\exp\left\{-\frac{\varepsilon m\omega^2}{4}\mathbf{B}^T[\mathbf{A}(n,P)]^{-1}\mathbf{B}\right\} \end{aligned} \tag{36}$$

where $\mathbf{x}'=[x_2, x_3, \cdots x_{nP}]^T$ is an $(nP-1)$-dimensional vector,

$$\mathbf{B} = -2x[d_1, 0, 0, \cdots, 0, d_{nP}]^T \tag{37}$$

is another $(nP-1)$-dimensional vector with only two non-zero elements, and $\mathbf{A}(n,P)$ is an $(nP-1)$-dimensional symmetric tridiagonal matrix,

$$\mathbf{A}(n,P) = \begin{bmatrix} D_2 & -d_2 & & & & & \\ -d_2 & D_3 & -d_3 & & & & \\ & -d_3 & D_4 & \ddots & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & \ddots & \ddots & \ddots & \\ & & & & \ddots & \ddots & -d_{nP-1} \\ & & & & & -d_{nP-1} & D_{nP} \end{bmatrix} \tag{38}$$

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which is the submatrix of matrix $\mathbf{\Lambda}(n,P)$ of Eq.(33) with the first row and column deleted, corresponding to the (1,1) minor the matrix $\mathbf{\Lambda}(n,P)$. By using Eq.(27), we express $\mathbf{A}(n,P)$ in terms of $\{d_i,\ D_i;\ \ i=1,2,\cdots,n\}$ such that Eq.(38) becomes

$$\mathbf{A}(n,1)=\begin{bmatrix} D_2 & -d_2 & & \\ -d_2 & D_3 & \ddots & \\ & \ddots & \ddots & -d_{n-1} \\ & & -d_{n-1} & D_n \end{bmatrix} \tag{39}$$

when P=1,

$$\mathbf{A}(n,2)=\begin{bmatrix} D_2 & -d_2 & & & & & & \\ -d_2 & D_3 & \ddots & & & & & \\ & \ddots & \ddots & -d_{n-1} & & & & \\ & & -d_{n-1} & D_n & -d_n & & & \\ & & & -d_n & D_1 & -d_1 & & \\ & & & & -d_1 & D_2 & \ddots & \\ & & & & & \ddots & \ddots & -d_{n-1} \\ & & & & & & -d_{n-1} & D_n \end{bmatrix} \tag{40}$$

when P=2,

$$\mathbf{A}(n,3)=\begin{bmatrix} D_2 & -d_2 & & & & & & & & \\ -d_2 & D_3 & \ddots & & & & & & & \\ & \ddots & \ddots & -d_{n-1} & & & & & & \\ & & -d_{n-1} & D_n & -d_n & & & & & \\ & & & -d_n & D_1 & -d_1 & & & & \\ & & & & -d_1 & D_2 & \ddots & & & \\ & & & & & \ddots & \ddots & -d_{n-1} & & \\ & & & & & & -d_{n-1} & D_n & -d_n & \\ & & & & & & & -d_n & D_1 & -d_1 \\ & & & & & & & & -d_1 & D_2 \end{bmatrix} \tag{41}$$

when P=3, and so forth. Its determinant, $A(n,P)=|\mathbf{A}(n,P)|$, is evaluated as

$$A(n,P)=\left(\prod_{i=1}^{n} d_i\right)^{P-1}\frac{\sinh(P\alpha)}{\sinh\alpha}A(n,1) \tag{42}$$

of which the derivation is demonstrated in Appendix A. In Eq.(42) the value of α is determined by the equality,

$$\cosh\alpha=\frac{\Lambda(n,1)}{2\left(\prod_{i=1}^{n} d_i\right)}+1 \tag{43}$$

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TABLE I The corresponding value of α of several representative decompositions defined in Eq.(43), which is used in the unified form of the partition function $Z_{nP}=[2\sinh(P\alpha/2)]^{-1}$.

Factorized decompositions	Corresponding α
Trotter [11]	$\alpha_{\rm Tro}=\text{arc cosh}\left(1+\frac{u^2P^{-2}}{2}\right)$
3-term ($g2T1V$[a])	$\alpha_{\rm TI}=\text{arc cosh}\left(1+\frac{u^2P^{-2}}{2}+\frac{u^4P^{-4}}{24}\right)$
5-term ($2T3V$[b], $3T2V$ [13, 35], $g2T3V$, $g3T2V$)	$\alpha_5=\text{arc cosh}\left(\frac{D_1D_2-2d_1d_2}{2d_1d_2}\right)$
7-term ($3T4V$[35], $4T3V$ [13, 35], $g4T3V$[c])	$\alpha_7=\text{arc cosh}\left(\frac{D_1D_2D_3-D_3{d_1}^2-D_1{d_2}^2-D_2{d_3}^2}{2d_1d_2d_3}\right)$

[a] See Ref.[5]. $g2T1V$ decomposition is equivalent to $g2V1T$ in the evaluation of thermodynamic properties, demonstrated in Ref.[15]. g stands for the generalized fourth-order decomposition, which leads to the third-order partition function.
[b] Also denoted the Suzuki-Chin decomposition in the literature. See Refs.[12, 13].
[c] The $g4T3V$ decomposition is equivalent to $g4V3T$ in the evaluation of thermodynamic properties.

with $\Lambda(n,1)$ being the determinant of $\mathbf{\Lambda}(n,P)$ in Eq.(33) at P=1. The definition of α depends on the decomposition of choice, and its explicit forms corresponding to several representative decompositions are summarized in Table I and will be discussed in Section IV.

Since vector $\mathbf{B}$ of Eq.(36) defined in Eq.(37) includes but two non-zero elements, only the (1, 1), (1, $nP-1$), ($nP-1$, 1), and ($nP-1$, $nP-1$) elements of the inverse of matrix $\mathbf{A}(n,P)$ are involved in the final output of the multidimensional Gaussian integral [34] in Eq.(36), which are related to the (1, 1), (1,$nP-1$), ($nP-1$, 1), and ($nP-1$, $nP-1$) cofactors of matrix $\mathbf{A}(n,P)$, respectively. The results of the four cofactors are presented in Appendix B.

Substituting the determinant of $\mathbf{A}(n,P)$ of Eq.(42) as well as the four cofactors into Eqs.(B1)−(B2) of Appendix B, *i.e.*, an equivalent expression of Eq.(36), we finally achieve

$$Z_{nP}=\frac{1}{2\sinh(P\alpha/2)} \tag{44}$$

It is remarkable that for the harmonic oscillator, the quantum partition function with all the different decomposition schemes assumes such a simple expression, which provides a convenient means to optimize the free parameters for the decomposition schemes.

The analytic expression of the partition function allows us, through elementary mathematical manipulations, to obtain all thermodynamic quantities for the harmonic oscillator. For instance, the internal energy is

$$E=-\frac{1}{Z_{nP}}\frac{\partial Z_{nP}}{\partial\beta}=\frac{P\coth(P\alpha/2)}{2}\frac{\partial\alpha}{\partial\beta} \tag{45}$$

the (Helmholtz) free energy is

$$A=-\frac{1}{\beta}\ln Z_{nP}=\frac{1}{\beta}\ln[\sinh(P\alpha/2)] \tag{46}$$

and the heat capacity reads

$$\begin{aligned}C_V&=k\beta^2\frac{\partial^2}{\partial\beta^2}\ln Z_{nP}\\&=k\beta^2\left[\frac{P^2}{4\sinh^2(P\alpha/2)}\left(\frac{\partial\alpha}{\partial\beta}\right)^2-\frac{P}{2\tanh(P\alpha/2)}\frac{\partial^2\alpha}{\partial\beta^2}\right]\end{aligned} \tag{47}$$

IV. PARAMETER OPTIMIZATION

Our aim is to achieve an efficient factorization scheme for general systems. We can expand the analytic partition function of the harmonic oscillator into a power series of $1/P$, so that we may optimize the free parameters by requiring vanishing errors to the desired order. It is straightforward to carry out the similar error analysis for any thermodynamic properties, as their analytic forms (*e.g.*, Eqs.(45)−(47)) for the harmonic oscillator are available. The conclusion should be the same because all thermodynamic properties are functionals of the partition function.

We take the 7-term decomposition, with the number of copies (beads) being $3P$, as an example. Substitution of

$$\begin{aligned}\Lambda(3,1)\ =\ &D_1D_2D_3-D_3{d_1}^2-D_1{d_2}^2\\&-D_2{d_3}^2-2d_1d_2d_3\end{aligned} \tag{48}$$

into Eq.(43) yields

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$$\alpha_7 = \operatorname{arc\,cosh}\left(\frac{D_1D_2D_3 - D_3{d_1}^2 - D_1{d_2}^2 - D_2{d_3}^2}{2d_1d_2d_3}\right) \tag{49}$$

To be specific, when using the generalized $4T3V$ decomposition

$$\begin{aligned}
&\mathrm{e}^{-\varepsilon t_0\hat{T}}\exp\left\{-\varepsilon\frac{1-v_1}{2}\hat{V} - c_0\kappa\varepsilon^3\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon(1-2t_0)\hat{T}/2}\exp\left\{-\varepsilon v_1\hat{V} - (1-2c_0)\kappa\varepsilon^3\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\\
&\times\mathrm{e}^{-\varepsilon(1-2t_0)\hat{T}/2}\exp\left\{-\varepsilon\frac{1-v_1}{2}\hat{V} - c_0\kappa\varepsilon^3\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon t_0\hat{T}}\\
=&\exp\left\{-\varepsilon\hat{H} + \frac{\varepsilon^3}{24}\left[(2-3v_1)(1-2t_0)^2 + 4{t_0}^2 - 4t_0\right]\left(\left[\hat{T},\left[\hat{V},\hat{T}\right]\right] - \left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right) + O\left(\varepsilon^5\right)\right\}
\end{aligned} \tag{50}$$

where $0<v_1<1$, $0<t_0<1/2$, $0\leq c_0\leq 1/2$, and the parameters of Eq.(49) are

$$\begin{aligned}
&d_1 = d_2 = \frac{P^2}{(1-2t_0)u^2}, \quad d_3 = \frac{P^2}{4t_0u^2},\\
&D_1 = 2d_1 + \frac{v_1}{2} + (1-2c_0)\kappa\frac{u^2}{P^2}, \quad D_2 = D_3 = d_1 + d_3 + \frac{1-v_1}{4} + c_0\kappa\frac{u^2}{P^2}
\end{aligned} \tag{51}$$

and

$$\kappa = \frac{1}{24}\left[\left(12{t_0}^2 - 1\right)(1-v_1) + (2-6t_0)(1-v_1)^2 + {v_1}^2\right] \tag{52}$$

By virtue of the relation in Eq.(45), the internal energy of the generalized $4T3V$ decomposition is obtained, whose series expansion of $1/P$ is

$$E_{g4T3V} = \frac{\hbar\omega}{2}\coth\left(\frac{u}{2}\right) + \frac{\hbar\omega u^4\left(u - 5\sinh(u)\right)}{5760P^4\sinh^2(u/2)}\Psi + O\left(\frac{1}{P^6}\right) \tag{53}$$

where Ψ, the coefficient of the fourth-order $(1/P^4)$ error, is

$$\begin{aligned}
\Psi =& 720{t_0}^4(v_1-1)(v_1-2c_0-1) - 360{t_0}^3(v_1-1)^2(6c_0+1)\\
&-60{t_0}^2\left[2 + {v_1}^2(9-54c_0) - 20c + 3a^3(4c_0-1) + v_1(60c_0-8)\right]\\
&+90t_0(v_1-1)\left[-3 + v_1(9-30c) + 10c_0 + 6{v_1}^2(4c_0-1)\right]\\
&-45{v_1}^3(4c_0-1) + 90{v_1}^2(3c_0-1) - 30v_1(5c_0-2) + 30c_0 - 13
\end{aligned} \tag{54}$$

The free energy, obtained via the thermodynamic relation in Eq.(46), can be expanded as

$$A_{g4T3V} = \frac{\hbar\omega}{u}\ln\left[2\sinh\left(\frac{u}{2}\right)\right] - \frac{\hbar\omega u^4\coth(u/2)}{2880P^4}\Psi + O\left(\frac{1}{P^6}\right) \tag{55}$$

Because any thermodynamic property is a functional of the partition function, it is evident that the fourth-order error is removed for all thermodynamic properties when we set Ψ=0. That is, it is adequate to use the free energy or internal energy to do the analysis. Consider the evaluation of $\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]$ (*i.e.*, Eq.(15)) and its derivative

$$\frac{\partial}{\partial x_j}\left[\hat{V}\left[\hat{T},\hat{V}\right]\right] = \hbar^2\sum_{l=1}^{N}\mathcal{H}_{jl}(\hat{\mathbf{x}})\cdot\frac{\nabla_l V(\hat{\mathbf{x}})}{m_l} = \hbar^2\sum_{l=1}^{N}\mathcal{H}_{jl}(\hat{\mathbf{x}})\frac{F_l(\hat{\mathbf{x}})}{m_l} \tag{56}$$

where $H_{jl}(\hat{\mathrm{x}})$ is the element of the Hessian matrix and $\mathbf{F}(\hat{\mathbf{x}})$=$\nabla V(\hat{\mathbf{x}})$ is the force vector. Both Eq.(15) and Eq.(56)

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are often numerically expensive in the fourth-order PIMD simulation of general molecular systems. Parameter c_0 is set to zero in Eq.(50) for less computational cost. In order to remove the fourth-order error, we set Ψ=0, yielding an equation between the two parameters, v_1 and t_0,

$$\begin{aligned}&720{t_0}^4(v_1-1)^2-360{t_0}^3(v_1-1)^2-60{t_0}^2\left[2-8v_1+9{v_1}^2-3{v_1}^3\right]\\&-90t_0(v_1-1)^2(2v_1-1)-13+60v_1-90{v_1}^2+45{v_1}^3=0\end{aligned}\tag{57}$$

According to the relation above, v_1 can be expressed as a function of t_0, which is demonstrated in FIG. 2. If Eq.(57) is satisfied, we require $0<t_0<t_{\max}$ to keep v_1 positive, where

$$\begin{aligned}t_{\max}=&\frac{1}{8}-\frac{1}{24}\left[\frac{4\left(9\sqrt{2230}-425\right)^{1/3}}{5^{2/3}}-4\left(45\sqrt{2230}-2125\right)^{-1/3}+25\right]^{1/2}\\&+\frac{1}{4}\left\{\begin{array}{l}\dfrac{1}{9}\left[\left(45\sqrt{2230}-2125\right)^{-1/3}-\dfrac{\left(9\sqrt{2230}-425\right)^{1/3}}{5^{2/3}}\right]+\dfrac{25}{18}\\+\dfrac{13}{2}\left[\dfrac{4\left(9\sqrt{2230}-425\right)^{1/3}}{5^{2/3}}-\dfrac{4}{\left(45\sqrt{2230}-2125\right)^{1/3}}+25\right]^{-1/2}\end{array}\right\}^{1/2}\\\approx&\,0.453031\end{aligned}\tag{58}$$

We plot in FIG. 3 the internal energy of the harmonic oscillator as a function of t_0 with ω=1 and β=8. FIG. 3 shows that there exists a specific value of t_0 that produces the closest result to the exact energy when the number of beads is small, *i.e.*, t_0=0.209114, with the corresponding v_1.

When t_0=0 or 1/2, the generalized $4T3V$ decomposition of Eq.(50) is reduced to the generalized $2T3V$ decomposition of Eq.(D11) of Appendix D, or generalized $2T1V$ decomposition of Eq.(C3) of Appendix C, respectively. When v_1=0, c_0=1/2 or v_1=1, c_0=0, the generalized $4T3V$ decomposition becomes the generalized $3T2V$ decomposition of Eq.(D10) of Appendix D, or generalized $2T1V$ decomposition of Eq.(C3) of Appendix C, respectively.

It is important to note that, the partition function corresponding to the generalized $4T3V$ decomposition of Eq.(50) is the same as that corresponding to the generalized $3T4V$ decomposition. Actually, when n is odd, a generalized symmetric $(n+1)TnV$ decomposition, such as generalized $4T3V$ in Eq.(50) and the generalized $2T1V$ in Eq.(C3) of Appendix C, can be transformed to a generalized symmetric $nT(n+1)V$ decomposition, in terms of the similarity transformation with a corrector,

$$\begin{aligned}\exp\left(-\varepsilon\hat{C}\right)&=\exp\left(-\varepsilon t_n\hat{T}\right)\left[\prod_{i=n-1}^{(n+1)/2}\exp\left\{-\varepsilon v_i\hat{V}\right\}\exp\left(-\varepsilon t_i\hat{T}\right)\right]\exp\left\{-\frac{\varepsilon v_{(n-1)/2}\hat{V}}{2}\right\}\\&=\left[\prod_{i=0}^{(n-3)/2}\exp\left(-\varepsilon t_i\hat{T}\right)\exp\left\{-\varepsilon v_i\hat{V}\right\}\right]\exp\left(-\varepsilon t_{(n-1)/2}\hat{T}\right)\exp\left\{-\frac{\varepsilon v_{(n-1)/2}\hat{V}}{2}\right\}\end{aligned}\tag{59}$$

The equivalence relation of the RHS of Eq.(59) is obtained with the relation of the coefficients $\{t_i,\ v_i,\ c_i\}$ in Eq.(11) and Eq.(20). It is straightforward to use Eq.(12) and Eq.(59) to show that the generalized symmetric $(n+1)\,TnV$ decomposition and the generalized symmetric $nT\,(n+1)\,V$ decomposition yield the same partition function when n is odd. In comparison, such a relation, however, does not apply when n is even.

As a special case for the generalized $4T3V$ decomposition, where v_1=1−1/$\left[3\,(1-2t_0)^2\right]$ is used to eliminate the

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third-order term of the RHS of Eq.(50), the original $4T3V$ decomposition of Ref.[35] reads

$$\begin{aligned}
&\mathrm{e}^{-\varepsilon t_0\hat{T}}\exp\left\{-\frac{\varepsilon}{6(1-2t_0)^2}\hat{V}-c_0\kappa\varepsilon^3\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon(1-2t_0)\hat{T}/2}\\
&\times\exp\left\{-\varepsilon\left[1-\frac{1}{3(1-2t_0)^2}\right]\hat{V}-(1-2c_0)\,\kappa\varepsilon^3\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon(1-2t_0)\hat{T}/2}\\
&\times\exp\left\{-\frac{\varepsilon}{6(1-2t_0)^2}\hat{V}-c_0\kappa\varepsilon^3\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon t_0\hat{T}}\\
&=\mathrm{e}^{-\varepsilon\hat{H}+O(\varepsilon^5)}
\end{aligned}\tag{60}$$

where

$$\kappa=\frac{1-12(1-2t_0)^2t_0}{72(1-2t_0)^3}\tag{61}$$

In Eq.(60), $0<t_0<1/2-\sqrt{3}/6$ and $0\le c_0\le 1/2$ are the two parameters required for the evaluation of α_7 of Eq.(49) as well as thermodynamic properties. The series expansion of the free energy is

$$A_{4T3V}=\frac{\hbar\omega}{u}\ln\left[2\sinh\left(\frac{u}{2}\right)\right]-\frac{\hbar\omega u^4\coth(u/2)}{8640(1-2t_0)^4P^4}\Upsilon+O\left(\frac{1}{P^6}\right)\tag{62}$$

where

$$\Upsilon=11-18t_0+144{t_0}^2-552{t_0}^3+576{t_0}^4+10c_0\left(-1+18-108{t_0}^2+168{t_0}^3+576{t_0}^4-1728{t_0}^5+1152{t_0}^6\right)\tag{63}$$

When we set c_0=0 in Eq.(63) and optimize the parameters by eliminating the leading error, the fourth-order error is removed with

$$\begin{aligned}
t_0=&\frac{1}{96}\left\{-16\left(\frac{450}{15+\sqrt{285}}\right)^{1/3}+8\left[60\left(15+\sqrt{285}\right)\right]^{1/3}+145\right\}^{1/2}+\frac{23}{96}-\frac{1}{48\sqrt{2}}\left\{8\left(\frac{450}{15+\sqrt{285}}\right)^{1/3}\right.\\
&\left.-4\left[60\left(15+\sqrt{285}\right)\right]^{1/3}+2375\left[-16\left(\frac{450}{15+\sqrt{285}}\right)^{1/3}+8\left[60\left(15+\sqrt{285}\right)\right]^{1/3}+145\right]^{-1/2}+145\right\}^{1/2}\\
\approx&\ 0.142326
\end{aligned}\tag{64}$$

Similarly, the optimization of the parameters included in the 5-term decompositions (the generalized $2T3V$ decomposition and that in the asymmetric generalized $3T2V$ decomposition) are interpreted in Appendix D.

V. COMPARISON AMONG DIFFERENT DECOMPOSITION SCHEMES FOR PIMD

We compare the efficiency of the original $4T3V$ of Ref.[35], our generalized symmetric $4T3V$ scheme, with optimal factors obtained in Section IV, as well as the generalized symmetric $2T3V$ scheme of Eq.(D3) in Appendix D, for the PIMD calculation of thermodynamic properties of the harmonic oscillator with ω=1 at β=8. The factor-fixed original $2T3V$ decomposition of Eq.(D9) developed by Suzuki [12] and Chin [13], asymmetric $3T2V$ decomposition of Eq.(D11) in Appendix D, generalized $2T1V$ decomposition of Eq.(C3) of Appendix C (equivalent to the Takahashi-Imada decomposition [5]), and conventional second-order Trotter decomposition of Eq.(4) are also presented for the purpose of comparison.

It is suggested in Ref.[19] that Eq.(56) can be efficiently evaluated by finite differences along the force vector in fourth-order PIMD,

$$\frac{\partial}{\partial x_j}\left[\hat{V}\left[\hat{T},\hat{V}\right]\right]=\lim_{\eta\to0}\frac{1}{2\eta\delta}\left[F_j\left(\hat{\mathbf{x}}+\eta\delta\hat{\mathbf{u}}\right)-F_j\left(\hat{\mathbf{x}}-\eta\delta\hat{\mathbf{u}}\right)\right]\tag{65}$$

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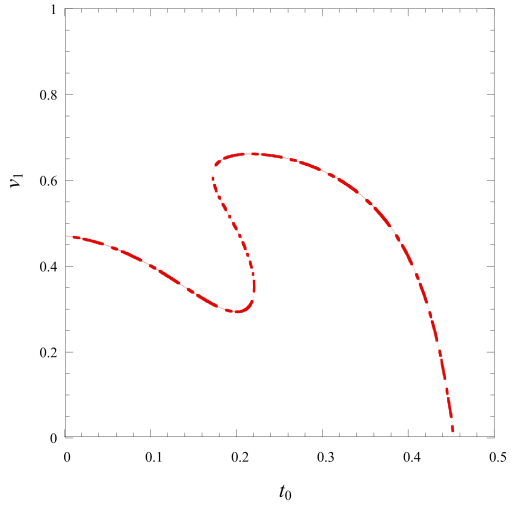

FIG. 2 Relation in Eq.(57) of the parameters, v_1 and t_0, in the generalized $4T3V$ factorization for the elimination of the fourth-order error in the series expansion of the free energy or internal energy.

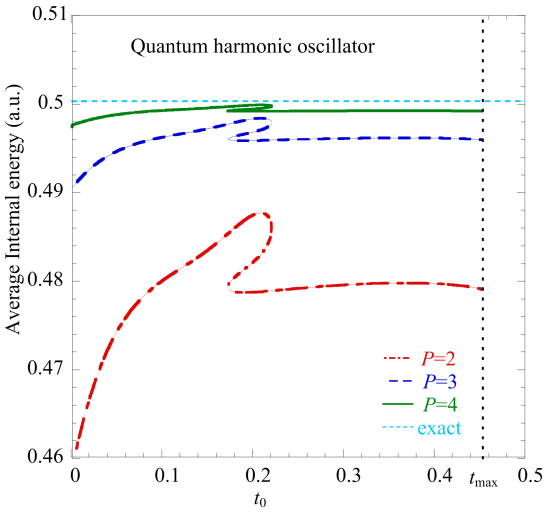

FIG. 3 Relation between the value of the parameter t_0 and the internal energy of the harmonic oscillator at ω=1, β=8, when P is fixed. Atom units (a.u.) are used.

where

$$u_j = \frac{F_j(\hat{\mathbf{x}})}{m_j}$$
$$\delta = \frac{1}{NP}\mathbf{F}^T(\hat{\mathbf{x}})\mathbf{M}^{-1}\mathbf{F}(\hat{\mathbf{x}}) \tag{66}$$

and η is a reasonable small scalar number determining the displacement along the force vector. The same idea was earlier used in imaginary time path integral investigations of the heat capacity and equilibrium isotope effects [36, 37] and also implemented in the linearized semiclassical initial value representation (LSC-IVR) in Ref.[27]. When the trick of Eq.(65) is used, the direct computation of the Hessian matrix of Eq.(56) is avoided for general molecular systems. It is important to note that two additional evaluations of the force vector are involved each time when the finite difference approach Eq.(65) is invoked. One should seriously consider such additional effort for the comparison among different decomposition schemes. Concretely, the 5-term decompositions (the generalized and original $2T3V$), with parameter c_0=0, invoke the force vector evaluation 4 times every 2 beads per step; and the 7-term decompositions (the original decomposition and the generalized $4T3V$ decomposition), invoke the force vector evaluation 5 times every 3 beads per step.

In FIG. 4, the results of the internal energy and heat capacity of the harmonic oscillator, obtained by different decomposition schemes, are compared with the same number of times of the force vector evaluation per step. FIG. 4(a) shows that the number of times of the force vector evaluation required for achieving the internal energy result of the same accuracy has the ascending order for different decomposition schemes, $g4T3V \approx 4T3V < g2T3V \approx g3T2V < 2T3V < g2T1V <$Trotter. Here g stands for the generalized decomposition where the similarity transformation is taken into account. The fourth-order decompositions ($g4T3V$, $4T3V$, $g2T3V$, and $g3T2V$) with their optimal factors perform better than the factor-fixed $2T3V$ and generalized $2T1V$ decomposition, because the thermodynamic properties obtained with the former four decompositions are of fifth-order accuracy while the latter two ones are only third-order accurate (for the harmonic oscillator). The 7-term decompositions, including the original and generalized $4T3V$ decompositions, with parameter c_0=0, are more efficient than the 5-term ones ($g2T3V$ and $g3T2V$), because less extra calculation effort is introduced by the finite difference approach Eq.(65) when the same number of beads is used.

FIG. 4(b) presents the numerical performance of different decomposition schemes for studying the heat capacity due to the change of the number of times of the force vector evaluation per step. The evaluation of the heat capacity requires more beads (more times of the force vector evaluation) to achieve converged results. The ascending order of computational effort for achieving the same accuracy for the heat capacity is $g4T3V < 4T3V < g2T3V \approx g3T2V < 2T3V < g2T1V <$Trotter. The optimization of the additional free parameter

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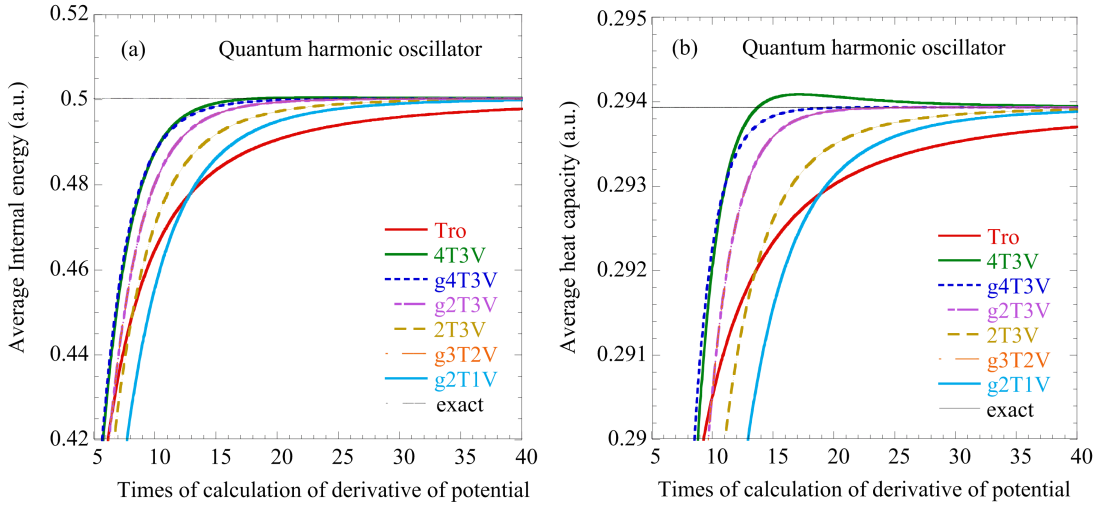

FIG. 4 Analytic results for the quantum harmonic oscillator at ω=1, β=8 with the same times of the force vector evaluation per step. (a) The average internal energy. (b) The heat capacity. "Tro" stands for the Trotter decomposition. g stands for the generalized fourth-order decomposition. Atom units (a.u.) are used.

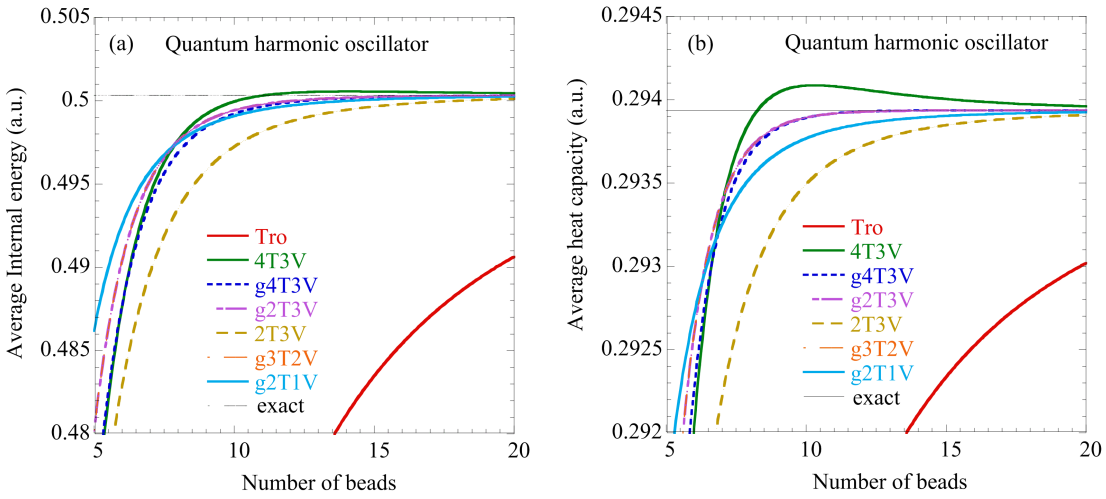

FIG. 5 Same as in FIG. 4, but with the same number of beads. (a) The average internal energy. (b) The heat capacity.

in $g4T3V$ leads to better performance over the original $4T3V$ decomposition [35]. FIG. 4 suggests that the generalized symmetric $4T3V$ decomposition with the optimal parameter t_0=0.209114 and its corresponding v_1 is the most efficient scheme that should be recommended for future applications.

In comparison to FIG. 4, FIG. 5 demonstrates the same results as functions of the number of beads. FIG. 5 indicates that it is inherently misleading to use the number of beads to count the efficiency. The superiority of the fourth-order decomposition over the traditional second-order Trotter decomposition is exaggerated when the additional effort of using Eq.(65) is not considered.

VI. CONCLUSION REMARKS

In the work we present a framework of symmetric decompositions for achieving the third-order $\left(1/P^3\right)$ accurate partition function for general systems. Such generalized fourth-order $\left(1/P^4\right)$ symmetric decomposition schemes lead to thermodynamic properties of the third-order $\left(1/P^3\right)$ accuracy. In comparison with the conventional fourth-order decomposition that includes the same number of splitting terms for $\mathrm{e}^{-\beta\hat{H}/P}$, the generalized decomposition has an additional free parameter to be adjusted.

We first derive an analytic unified form of the harmonic oscillator partition function (Eq.(44) with Table

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I) for all the (generalized) decomposition schemes as a function of (n, P). The form yields analytical results of the free energy, internal energy, heat capacity, and other thermodynamic properties. We then obtain the power series expansion of $(1/P)$ of the thermodynamic properties. By requiring eliminating error to the desired order, we optimize the free parameters of the generalized symmetric fourth-order decomposition scheme. While the factor-fixed decompositions proposed in the literature lead to the third-order $(1/P^3)$ accurate thermodynamic property, the generalized symmetric decomposition (with 7 terms) with optimal factors is capable of producing the same thermodynamic property of the fifth-order $(1/P^5)$ accuracy. We expect that the general symmetric decomposition scheme will be practically useful for imaginary time path integral simulations of realistic molecular systems.

Supplementary materials: Three sections are included: proof of Eq.(A10) with mathematic induction, evaluation of the determinant of $\mathbf{A}(n, P)$ from the recurrence relation, evaluation of the four cofactors in Eq.(B1).

VII. ACKNOWLEDGMENTS

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APPENDIX A: Evaluation of the determinant of matrix $\mathbf{A}(n, P)$

As demonstrated in FIG. 6 and FIG. 7, the evaluation of $A(n, P)$ requests

$$A(n,P)=A(n,1)\,G(n,P-1)-T(n)\,d_n{}^2A(n,P-1) \quad \text{(A1)}$$

$$G(n,P)=G(n,1)\,G(n,P-1)-Y(n)\,d_n{}^2A(n,P-1) \quad \text{(A2)}$$

where $G(n,P)=|\mathbf{G}(n,P)|$ is the determinant of an (nP)-dimensional symmetric tridiagonal matrix, which

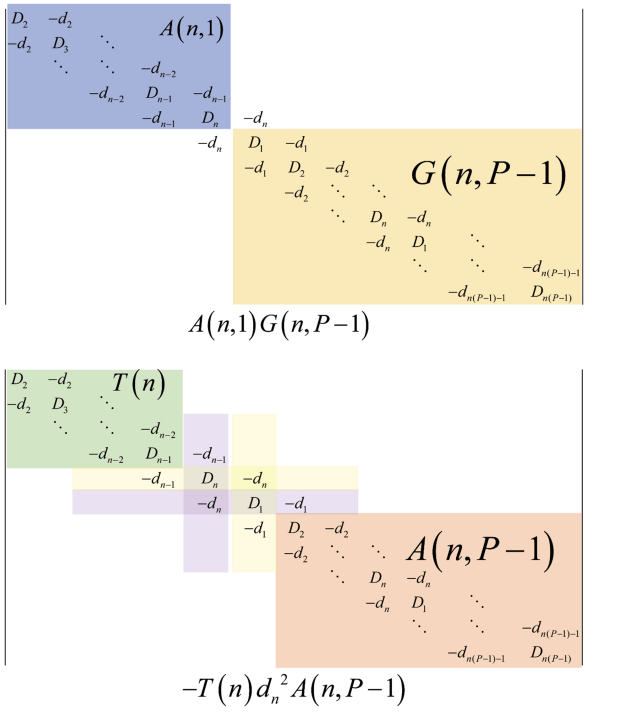

FIG. 6 Both $G(n, P-1)$ and $A(n, P-1)$ are employed in the expansion of the determinant, $A(n, P)$. Since $A(n, P)$ is a tridiagonal determinant, in addition to $A(n, P)\,G(n, P-1)$, the second term of Eq.(A1) of Appendix A corresponds to the multiplication of the $(n+1, n)$ element of $A(n, P)$, $-d_n$, and the $(n+1, n)$ cofactor that is equal to $T(n)\,d_n A(n, P-1)$.

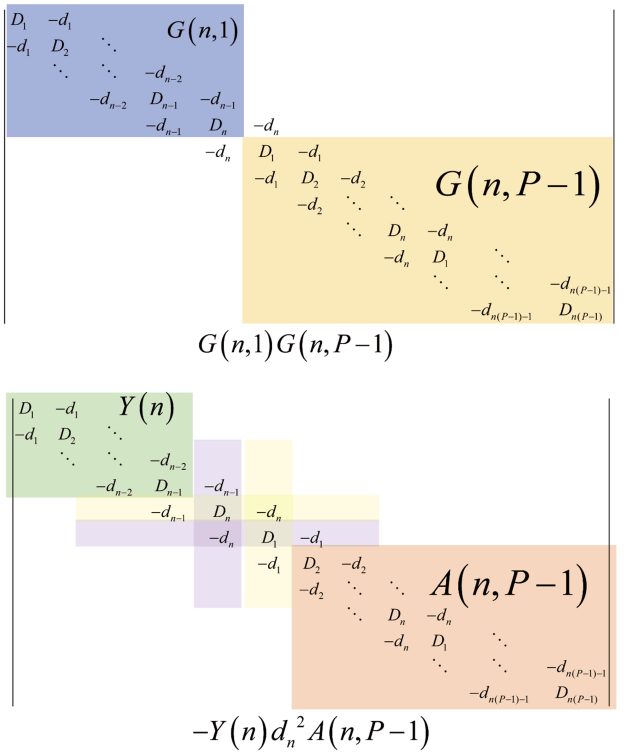

FIG. 7 Similar to FIG. 6, but for the expansion of $G(n, P)$ in Eq.(A2) of Appendix A.

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is the same as $\mathbf{\Lambda}(n,P)$ of Eq.(33) except that the $(1,nP)$ and $(nP,1)$ elements of $\mathbf{G}(n,P)$ are zero. For instance, we have

$$\mathbf{G}(n,1)=\begin{bmatrix} D_1 & -d_1 & & \\ -d_1 & D_2 & \ddots & \\ & \ddots & \ddots & -d_{n-1} \\ & & -d_{n-1} & D_n \end{bmatrix} \tag{A3}$$

when P=1,

$$\mathbf{G}(n,2)=\begin{bmatrix} D_1 & -d_1 & & & & & & \\ -d_1 & D_2 & \ddots & & & & & \\ & \ddots & \ddots & -d_{n-1} & & & & \\ & & -d_{n-1} & D_n & -d_n & & & \\ & & & -d_n & D_1 & -d_1 & & \\ & & & & -d_1 & D_2 & \ddots & \\ & & & & & \ddots & \ddots & -d_{n-1} \\ & & & & & & -d_{n-1} & D_n \end{bmatrix} \tag{A4}$$

when P=2,

$$\mathbf{G}(n,3)=\begin{bmatrix} D_1 & -d_1 & & & & & & & & \\ -d_1 & D_2 & \ddots & & & & & & & \\ & \ddots & \ddots & -d_{n-1} & & & & & & \\ & & -d_{n-1} & D_n & -d_n & & & & & \\ & & & -d_n & D_1 & -d_1 & & & & \\ & & & & -d_1 & D_2 & \ddots & & & \\ & & & & & \ddots & \ddots & -d_{n-1} & & \\ & & & & & & -d_{n-1} & D_n & -d_n & \\ & & & & & & & -d_n & D_1 & -d_1 \\ & & & & & & & & -d_1 & D_2 \end{bmatrix} \tag{A5}$$

when P=3, and so forth. In Eq.(A1),

$$T(n)=\begin{vmatrix} D_2 & -d_2 & & \\ -d_2 & D_3 & \ddots & \\ & \ddots & \ddots & -d_{n-2} \\ & & -d_{n-2} & D_{n-1} \end{vmatrix} \tag{A6}$$

is an $(n-2)$-dimensional determinant, the $(n-1,\ n-1)$ minor of matrix $\mathbf{A}(n,1)$. Specifically, we define

$$\begin{aligned} T(1)&=0 \\ T(2)&=1 \end{aligned} \tag{A7}$$

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for consistence. In Eq.(A2),

$$Y(n)=\begin{vmatrix} D_1 & -d_1 & & \\ -d_1 & D_2 & \ddots & \\ & \ddots & \ddots & -d_{n-2} \\ & & -d_{n-2} & D_{n-1} \end{vmatrix} \tag{A8}$$

is an $(n-1)$-dimensional determinant, the (n,n) minor of matrix $\mathbf{G}(n,1)$. For the purpose of consistence, we define

$$Y(1)=1 \tag{A9}$$

As shown in Section S1 of the Supplementary materials, it is straightforward to derive

$$\left(A(n,1)\,Y(n)-G(n,1)\,T(n)\right)\,{d_n}^2=\left(\prod_{i=1}^{n}d_i\right)^2 \tag{A10}$$

with mathematical induction. Eq.(A1) is then recast into a recurrence relation

$$\begin{aligned} A(n,P) &= \left(G(n,1)-T(n)\,{d_n}^2\right)A(n,P-1) \\ &\quad -\left(\prod_{i=1}^{n}d_i\right)^2 A(n,P-2) \end{aligned} \tag{A11}$$

for $P>2$. We show in Section S2 of the Supplementary materials that the solution to the characteristic equation for Eq.(A11) leads to

$$A(n,P)=\left(\prod_{i=1}^{n}d_i\right)^{P-1}\frac{\sinh(P\alpha)}{\sinh\alpha}A(n,1) \tag{A12}$$

where α is given by

$$\cosh\alpha=\frac{G(n,1)-T(n)\,{d_n}^2}{2\left(\prod_{i=1}^{n}d_i\right)} \tag{A13}$$

which depends on the decomposition of choice.

Eq.(A13) can be further simplified. As demonstrated in FIG. 8, $G(n,1)$, the determinant of matrix $\mathbf{G}(n,1)$, in Eq.(A3) is

$$G(n,1)=D_1A(n,1)-d_1^2A^{(1,1)}(n,1) \tag{A14}$$

where $A^{(1,1)}(n,1)$ is the (1,1) minor of matrix $\mathbf{A}(n,1)$.

As demonstrated in FIG. 9, $\Lambda(n,1)$, the determinant of matrix $\mathbf{\Lambda}(n,P)$ of Eq.(33) in the main text when

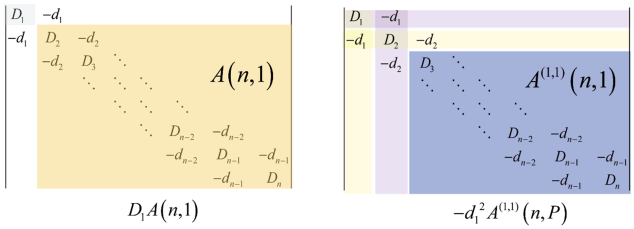

FIG. 8 Similar to FIG. 6, but for the expansion of $G(n,1)$ of Eq.(A14) of Appendix A.

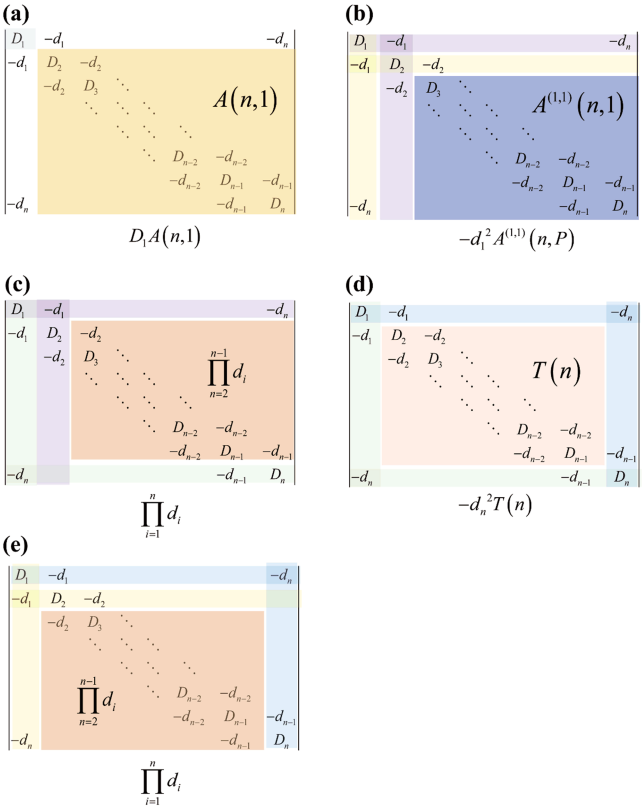

FIG. 9 Similar to FIG. 6, but for the expansion of $\Lambda(n,1)$ of Eq.(A15) of Appendix A. Note that five terms are in the expansion.

$P=1$, is expressed as

$$\begin{aligned} \Lambda(n,1) &= D_1A(n,1)-{d_1}^2A^{(1,1)}(n,P) \\ &\quad +\prod_{i=1}^{n}d_i-{d_n}^2T(n)+\prod_{i=1}^{n}d_i \end{aligned} \tag{A15}$$

Substitution of Eq.(A14) into Eq.(A15) yields

$$\Lambda(n,1)=G(n,1)-T(n)\,{d_n}^2-2\left(\prod_{i=1}^{n}d_i\right) \tag{A16}$$

By substituting Eq.(A16) into Eq.(A13), we achieve Eq.(43) in the main text.

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APPENDIX B: Four cofactors of matrix $\mathbf{A}(n,P)$

Define $A^{(1,1)}(n,P)$, $A^{(1,nP-1)}(n,P)$, $A^{(nP-1,1)}(n,P)$ and $A^{(nP-1,nP-1)}(n,P)$ as the (1,1), (1,nP−1), (nP−1,1), and $(nP-1,nP-1)$ minors of matrix $\mathbf{A}(n,P)$, respectively. The corresponding four cofactors of matrix $\mathbf{A}(n,P)$ are $A^{(1,1)}(n,P)$, $(-1)^{nP}A^{(1,nP-1)}(n,P)$, $(-1)^{nP}A^{(nP-1,1)}(n,P)$ and $A^{(nP-1,nP-1)}(n,P)$, with which the partition function of Eq.(36) in the main text can be recast into

$$Z_{nP}=\int \mathrm{d}x\left(\frac{\varepsilon m\omega^2}{\pi A(n,P)}\right)^{1/2}\left(\prod_{i=1}^{n}d_i\right)^{P/2}\exp\left\{-\varepsilon m\omega^2 D_1 x^2\right\}\exp\left\{-\frac{\varepsilon m\omega^2 x^2}{A(n,P)}\Phi(n,P)\right\} \tag{B1}$$

where

$$\begin{aligned}\Phi(n,P) &= d_1^2A^{(1,1)}(n,P)+d_1d_n\left[(-1)^{nP}A^{(1,nP-1)}(n,P)+(-1)^{nP}A^{(nP-1,1)}(n,P)\right]\\ &\quad +d_n^2A^{(nP-1,nP-1)}(n,P)\end{aligned} \tag{B2}$$

We can evaluate the four cofactors with the similar strategy to that in Appendix A for the determinant of $\mathbf{A}(n,P)$.

$$A^{(1,1)}(n,P)=\left(G(n,1)-T(n)\,{d_n}^2\right)A^{(1,1)}(n,P-1)-\left(\prod_{i=1}^{n}d_i\right)^2A^{(1,1)}(n,P-2) \tag{B3}$$

$$(-1)^{nP}A^{(1,nP-1)}(n,P)=(-1)^{nP}A^{(nP-1,1)}(n,P)=(-1)^{nP}\left[\prod_{i=2}^{n-1}(-d_i)\right]^P=\frac{1}{d_1d_n}\left(\prod_{i=1}^{n}d_i\right)^P \tag{B4}$$

$$\begin{aligned}A^{(nP-1,nP-1)}(n,P) &= \left(G(n,1)-T(n)\,{d_n}^2\right)A^{[n(P-1)-1,n(P-1)-1]}(n,P-1)\\ &\quad -\left(\prod_{i=1}^{n}d_i\right)^2A^{[n(P-2)-1,n(P-2)-1]}(n,P-2)\end{aligned} \tag{B5}$$

More details are presented in Section S3 of the Supplementary materials.

APPENDIX C: Parameter-fixed 3-term decompositions

Consider the 3-term decomposition. When using the second-order Trotter decomposition in Eq.(4), according to Eq.(A16) and Eq.(A7), we specifically define

$$\Lambda(1,1)=D_1-{d_1}^2=\frac{P^2}{u^2}+\frac{1}{2}-{d_1}^2 \tag{C1}$$

with $d_1{=}P^2/\left(2u^2\right)$. Substitution of Eq.(C1) into Eq.(43) leads to the definition of α_{Tro},

$$\alpha_{\mathrm{Tro}}=\operatorname{arc\,cosh}\left(1+\frac{u^2P^{-2}}{2}\right) \tag{C2}$$

which was obtained by Kamibayashi in Ref.[34].

When the generalized $2T1V$ fourth-order decomposition (which is also the Takahashi-Imada decomposition of Ref.[5]),

$$\mathrm{e}^{-\varepsilon\hat{T}/2}\exp\left\{-\varepsilon\hat{\mathrm{V}}-\frac{\varepsilon^3}{24}\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon\hat{T}/2}=\exp\left\{-\varepsilon\hat{H}+\frac{\varepsilon^3}{24}\left(\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]-\left[\hat{T},\left[\hat{V},\hat{T}\right]\right]\right)+O(\varepsilon^5)\right\}. \tag{C3}$$

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is used, substitution of

$$\Lambda\left(1,1\right)=D_1-{d_1}^2=\frac{P^2}{u^2}+\frac{1}{2}+\frac{u^2}{24P^2}-{d_1}^2 \tag{C4}$$

into Eq.(43) yields

$$\alpha_{\rm TI}=\operatorname{arc\,cosh}\left(1+\frac{u^2}{2P^2}+\frac{u^4}{24P^4}\right) \tag{C5}$$

In the symmetric 3-term decompositions above, all the parameters are fixed.

APPENDIX D: Optimization of the parameters in the generalized 5-term decomposition scheme

We consider the 5-term decomposition scheme with the number of beads being $2P$. Substitution of

$$\Lambda\left(2,1\right)=D_1D_2-\left(d_1+d_2\right)^2 \tag{D1}$$

into Eq.(43) produces

$$\alpha_5=\operatorname{arc\,cosh}\left(\frac{D_1D_2-{d_1}^2-{d_2}^2}{2d_1d_2}\right) \tag{D2}$$

Specifically, for the generalized $2T3V$ decomposition,

$$\begin{aligned}
&\exp\left\{-\varepsilon v_0\hat{V}-\varepsilon^3\frac{c_0}{24}(12{v_0}^2-6v_0+1)\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon\hat{T}/2}\\
&\times\exp\left\{-\varepsilon(1-2v_0)\hat{V}-\varepsilon^3\frac{1-2c_0}{24}(12{v_0}^2-6v_0+1)\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon\hat{T}/2}\\
&\times\exp\left\{-\varepsilon v_0\hat{V}-\varepsilon^3\frac{c_0}{24}(12{v_0}^2-6v_0+1)\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\\
=\ &\exp\left\{-\varepsilon\hat{H}+\frac{\varepsilon^3}{24}\left(6v_0-1\right)\left(\left[\hat{T},\left[\hat{V},\hat{T}\right]\right]-\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right)+O(\varepsilon^5)\right\}
\end{aligned} \tag{D3}$$

where $0<v_0<1/2$ and $0\leq c_0\leq1/2$ are required to keep the coefficients positive, and the parameters required in the evaluation of Eq.(D2) are

$$\begin{aligned}
&d_1=d_2=\frac{P^2}{u^2},\qquad D_1=\frac{2P^2}{u^2}+v_0+\frac{c_0}{12}(12{v_0}^2-6v_0+1)\frac{u^2}{P^2}\\
&D_2=\frac{2P^2}{u^2}+\frac{1-2v_0}{2}+\frac{1-2c_0}{24}(12{v_0}^2-6v_0+1)\frac{u^2}{P^2}
\end{aligned} \tag{D4}$$

The expansion of the internal energy is

$$E_{g2T3V}=\frac{\hbar\omega}{2}\coth\left(\frac{u}{2}\right)+\frac{\hbar\omega u^4\left[u-5\sinh\left(u\right)\right]}{5760P^4\sinh^2\left(u/2\right)}\Theta+O\left(\frac{1}{P^6}\right) \tag{D5}$$

and that of the free energy is

$$A_{g2T3V}=\frac{\hbar\omega}{u}\ln\left[2\sinh\left(\frac{u}{2}\right)\right]-\frac{\hbar\omega u^4\coth\left(u/2\right)}{2880P^4}\Theta+O\left(\frac{1}{P^6}\right) \tag{D6}$$

where

$$\Theta=2-30v_0+180{v_0}^2-360{v_0}^3+15c_0\left(-1+10v_0-36{v_0}^2+48{v_0}^3\right) \tag{D7}$$

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We set c_0=0 such that Eq.(56) is evaluated once every two beads per step. The fourth-order error in Eq.(D5) and in Eq.(D6) can be removed by setting Θ=0, which produces

$$v_0 = \frac{1}{2} - \frac{1}{6}\left(2 - \frac{1}{\sqrt[3]{5}}\right) \approx 0.264134 \tag{D8}$$

Note that, when v_0=0 or 1/2, the generalized $2T3V$ decomposition of Eq.(D3) is reduced to the generalized $2T1V$ decomposition in Eq.(C3) of Appendix C.

The original $2T3V$ decomposition, the Suzuki-Chin decomposition developed by Suzuki [12] and Chin [13], is a special case of Eq.(D3), the generalized one,

$$\begin{aligned} &\exp\left\{-\frac{\varepsilon\hat{V}}{6} - \frac{c_0\varepsilon^3}{144}\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon\hat{T}/2}\exp\left\{-\frac{2\varepsilon\hat{V}}{3} - \frac{(1-c_0)\,\varepsilon^3}{72}\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\} \\ &\times\mathrm{e}^{-\varepsilon\hat{T}/2}\exp\left\{-\frac{\varepsilon\hat{V}}{6} - \frac{c_0\varepsilon^3}{144}\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\} \\ &= \mathrm{e}^{-\varepsilon\hat{H}+O(\varepsilon^5)} \end{aligned} \tag{D9}$$

where v_0=1/6 is used to eliminate the third-order term of the RHS of Eq.(D3), all coefficients are fixed except for c_0. A similar form of α_5 to Eq.(D2) for the original decomposition was obtained by Kamibayashi in Ref.[34]. Parameter c_0 is often set as zero for PIMD simulations.

The generalized symmetric $3T2V$ decomposition reads

$$\begin{aligned} &\mathrm{e}^{-\varepsilon t_0\hat{T}}\exp\left\{-\frac{\varepsilon\hat{V}}{2} - \frac{\varepsilon^3}{48}(12{t_0}^2 - 6t_0 + 1)\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon(1-2t_0)\hat{T}} \\ &\times\exp\left\{-\frac{\varepsilon\hat{V}}{2} - \frac{\varepsilon^3}{48}(12{t_0}^2 - 6t_0 + 1)\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon t_0\hat{T}} \\ &= \left\{-\varepsilon\hat{H} + \frac{\varepsilon^3}{12}\left(6{t_0}^2 - 6t_0 + 1\right)\left(-\left[\hat{T},\left[\hat{V},\hat{T}\right]\right] + \left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right) + O(\varepsilon^5)\right\} \end{aligned} \tag{D10}$$

where $0<t_0<1/2$, and the two terms including $\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]$ are symmetrically distributed. Because the finite-difference approach, Eq.(65), is used for the PIMD implementation, $\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]$ (Eq.(15)) as well as its derivative with respect to the coordinate (Eq.(56)) has to be evaluated twice every two beads per step for Eq.(D10). As comparison, the generalized decomposition of Eq.(D3) (with c_0=0 and other optimal factors) requests the evaluation of $\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]$ and its derivative only once every two beads. Eq.(D10) is then more computationally expensive in the PIMD simulation in comparison with the generalized $2T3V$ decomposition of Eq.(D3).

We can break the symmetry and construct the generalized asymmetric $3T2V$ decomposition

$$\mathrm{e}^{-\varepsilon t_0\hat{T}}\exp\left\{-\frac{\varepsilon\hat{V}}{2} - \frac{\varepsilon^3}{24}(12{t_0}^2 - 6t_0 + 1)\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right\}\mathrm{e}^{-\varepsilon(1-2t_0)\hat{T}}\mathrm{e}^{-\varepsilon\hat{V}/2}\mathrm{e}^{-\varepsilon t_0\hat{T}} = \exp\left\{-\varepsilon\hat{H}_{g3T2V}\right\} \tag{D11}$$

such that the evaluation of $\left[\hat{V},\left[\hat{T},\hat{V}\right]\right]$ and its derivative is requested only once every two beads per step. In Eq.(D11), the approximate Hamiltonian is

$$\hat{H}_{g3T2V} = \hat{H} - \frac{\varepsilon^2}{12}\left(6{t_0}^2 - 6t_0 + 1\right)\left(-\left[\hat{T},\left[\hat{V},\hat{T}\right]\right] + \left[\hat{V},\left[\hat{T},\hat{V}\right]\right]\right) - \varepsilon^4\hat{\Pi} + O(\varepsilon^5) \tag{D12}$$

where $-\varepsilon^4\hat{\Pi}$ is the fourth-order error with the expression of $\hat{\Pi}$ presented by

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$$\hat{\Pi} = e_1 \left[\hat{T}, \left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right]\right] + e_2 \left[\hat{V}, \left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right]\right] \quad \text{(D13)}$$

with e_1 and e_2 as two coefficients. Note that $\left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right]$ commutes with $\hat{V}$, *i.e.*,

$$\left[\hat{V}, \left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right]\right] = 0 \quad \text{(D14)}$$

It is easy to verify from Eq.(13) that the fourth-order error of Eq.(D12) can be eliminated by the similarity transformation of Eq.(12), with a corrector,

$$\hat{C}_{g3T2V} = \frac{\varepsilon^3}{12}\left(6{t_0}^2 - 6t_0 + 1\right)\left[\hat{V}, \hat{T}\right] - e_1 \left[\hat{V}, \left[\hat{T}, \hat{V}\right]\right] \quad \text{(D15)}$$

The generalized asymmetric $3T2V$ decomposition of Eq.(D11) then yields the third-order $\left(1/P^3\right)$ accurate partition function for general systems.

When applying the asymmetric $3T2V$ decomposition to the harmonic oscillator, we evaluate α_5 of Eq.(D2) with the parameters,

$$\begin{aligned} d_1 &= \frac{P}{2t_0 u} \\ d_2 &= \frac{P}{2(1-t_0)u} \\ D_1 &= d_1 + d_2 + \frac{u}{4P} \\ D_2 &= d_1 + d_2 + \frac{u}{4P} + \frac{1}{24}(12{t_0}^2 - 6t_0 + 1)\frac{u^3}{P^3} \end{aligned} \quad \text{(D16)}$$

Expansion of the internal energy of the generalized $3T2V$ decomposition in the power series expansion of $1/P$ produces

$$E_{g3T2V} = \frac{\hbar\omega}{2}\coth\left(\frac{u}{2}\right) + \frac{\hbar\omega u^4\left[u - 5\sinh(u)\right]}{2880P^4\sinh^2(u/2)}\Xi + O\left(\frac{1}{P^6}\right) \quad \text{(D17)}$$

while the expansion of the free energy leads to

$$A_{g3T2V} = \frac{\hbar\omega}{u}\ln\left[2\sinh\left(\frac{u}{2}\right)\right] - \frac{\hbar\omega u^4\coth(u/2)}{1440P^4}\Xi + O\left(\frac{1}{P^6}\right) \quad \text{(D18)}$$

where

$$\Xi = 1 - 15t_0 + 60{t_0}^2 - 90{t_0}^3 + 45{t_0}^4 \quad \text{(D19)}$$

The fourth-order error is eliminated in Eq.(D17) as well as Eq.(D18) by setting Eq.(D19) to be equal to zero, yielding

$$t_0 = \frac{1}{2} - \frac{1}{30}\sqrt{15\left(5 + 2\sqrt{5}\right)} \approx 0.102673 \quad \text{(D20)}$$

$$t_0 = \frac{1}{2} - \frac{1}{30}\sqrt{15\left(5 - 2\sqrt{5}\right)} \approx 0.406204 \quad \text{(D21)}$$

Our numerical tests of several typical systems show that Eq.(D21) leads to more accurate results than Eq.(D20), for the generalized asymmetric $3T2V$ decomposition of Eq.(D11). When we employ the generalized asymmetric $3T2V$ decomposition, we always use Eq.(D21) for the value of t_0.

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