A novel parameter-free form for the path-integral (PI) partition function is proposed, which enables calculations of accurate quantum-mechanical averages. The developed approach is demonstrated to achieve convergence with $P \lesssim \hbar \omega/k_B T$, where $P$ is the number of classical beads, $\omega$ is the largest characteristic frequency in the system and $T$ is the temperature. Any technique for sampling of the phase space can be utilized, including molecular dynamics (MD) and Monte Carlo simulations with any choice for thermostat or barostat. No a priori system-dependent information is required and the method can be easily applied to large and strongly anharmonic systems. The efficiency of the method is demonstrated for 1D model systems, Morse quantum liquid, and for \textit{ab initio} PIMD simulations for N$_2$ and C$_6$H$_6$ molecules. In all of these cases, the developed approach requires roughly an order of magnitude fewer beads than conventional PIMD simulations at the same level of accuracy, thus significantly extending the applicability of PI methods to realistic systems.

The quantum nature of nuclear motions can have a vital role in the structure, stability, and thermodynamics of molecular and condensed-matter systems. The standard approach to take nuclear quantum effects (NQE) into account is the Feynman-Kac imaginary-time path integrals \cite{1,2}. This method maps a quantum system into $P$ copies of classical subsystems (“beads”) interacting with each other \textit{via} harmonic springs \cite{3}. Incorporation of PI molecular dynamics (MD) techniques into \textit{ab initio} calculations offers a straightforward way to study NQE in different chemical and physical systems \cite{4-20}. Unfortunately, conventional PIMD simulations require exceedingly large number of beads ($P \gg \hbar \omega/k_B T$) to accurately capture NQE, resulting in considerable computational cost even at room temperature due to the rather high internal vibrational frequencies $\omega$ of many systems of interest.

The need for large $P$ stems from the second-order expansion of the $\exp(-\beta (K + V))$ operator utilized in conventional PI simulations, where $\beta$ is the inverse temperature, and $K$ and $V$ are the kinetic and potential energy operators, respectively. While for $P \to \infty$, convergence to full quantum statistics is guaranteed, this is not the case for reasonable finite $P$. In this case, the properties obtained in conventional PI simulations are often far from the correct quantum result and effectively correspond to semi-classical regime. To alleviate this problem, a number of promising high-order methods have been developed. Most of them are based on the work of Takahashi and Imada (TI) \cite{21}, who proposed a fourth-order decomposition scheme valid for the trace of $\exp(-\beta (K + V))$. The convergence of the TI estimator for the total internal energy can be achieved with a factor of four fewer beads compared to the conventional second-order PI scheme \cite{8}. However, the TI propagator depends upon derivatives of the potential energy, making its application exceedingly costly for realistic systems. The necessity to deal with the high-order derivatives within TI based PIMD simulations is usually avoided by treating the propagator terms containing forces as weight factors \cite{4,15,22,23}. Ceriotti et al. demonstrated \cite{24} that for large and/or strongly quantum systems, a large number of beads is required to keep the fluctuations in the re-weighted average under control.

Another very promising way to improve the convergence of PIMD simulations is based on the generalized Langevin equation (GLE) thermostat, in particular with the so-called colored-noise thermostat (CNT) \cite{25,26}. The developed PI-GLE scheme is able to decrease considerably the number of beads required for accurate PIMD simulations \cite{27-29}. However, ensuring the convergence of computed properties while keeping the efficiency of sampling of the phase space can prove challenging for PI-GLE methods. Furthermore, a priori information about the system needs to be introduced \textit{via} parameterization.

In this Letter, we propose a novel parameter-free form for the PI partition function and estimators to calculate converged thermodynamic averages from semi-classical (small $P$) path-integral simulations. Our method requires the same ingredients as the conventional PI simulations, but decreases the required number of classical beads by roughly an order of magnitude. A considerable advantage of the developed approach is that it can be incorporated with any kind of thermostat or barostat, as well as any phase-space sampling technique. The proposed method has been applied to study the thermodynamics of a quantum harmonic oscillator, double-well potential, and 64 Morse particles within periodic boundary conditions, as well as for \textit{ab initio} PIMD simulations for N$_2$ and C$_6$H$_6$ molecules at room temperature. For all the systems within the developed method, $P = 4$ to 8 is enough to recover the NQE contribution to the total energy within 2% of the fully converged quantum result.

The free energy of an arbitrary quantum system can
be written as an expansion in powers of $\hbar$ [30]

$$F = F_c + \frac{\hbar^2 \beta^2}{24} \sum_i \frac{\langle f_i^2 \rangle}{m_i} + o(\hbar^3),$$  

(1)

where $F_c$ is the classical free energy, $m_i$ is a particle mass, $f_i$ is the $i$-th force component, $\beta = 1/k_B T$ is the inverse temperature, and $\langle \ldots \rangle$ means thermodynamic averaging. Index $i$ run over all degrees of freedom in the system.

The first non-vanishing non-classical term in Eq. (1) is proportional to $\hbar^2$ and does not depend upon the statistics of particles being equally applicable to both bosonic and fermionic systems [31, 32]. It is also proportional to $\langle f_i^2 \rangle$, which means that in strongly interacting systems the NQE can be important even at relatively high temperatures. In fact, for many real molecules the internal vibrational frequencies are rather high. Thus, employing only the quasi-classical term in Eq. (1) without account for higher-order $o(\hbar^3)$ terms, which are unknown in general case, usually leads to an overestimation of the free energy and, as a result, to wrong thermodynamic averages obtained from it.

The situation can be greatly improved by generalization of Eq. (1) to the case of imaginary-time path-integral approach. The auxiliary system which is constructed in the PI method has a temperature $P$ times larger than the equilibrium temperature, where $P$ is the number of beads. In the limit $P \to \infty$ the quantum effects are fully recovered, while at finite $P$ they are captured only partially. The contribution from the $o(\hbar^3)$ terms decreases as $P$ grows, so the expression akin to that in Eq. (1) should become increasingly more accurate. This allows us to treat the PI auxiliary system as a semi-classical one and use an analogue of Eq. (1) to calculate its free energy, partition function and, as a result, all the thermodynamic averages.

To explain our proposal, we consider a quantum system consisting of a single particle in an external potential $U$. The PI partition function can be written as:

$$Z_{PI} = A \int dq_1 \ldots dq_P e^{-\beta U_{eff}(\{q_s\})},$$  

(2)

where $A$ is a normalization constant and $U_{eff}$ is the effective potential

$$U_{eff}(\{q_s\}) = \sum_{s=1}^{P} \frac{m \omega_s^2 (\bar{q}_s + 1 - \bar{q}_s)^2}{2} + \frac{P}{\beta} \sum_{s=1}^{P} U_s,$$  

(3)

where $\omega_s^2 = P/\beta^2$ is the chain frequency, $\bar{q}_s$ and $U_s$ are the particle coordinate vector and the potential energy for the beads, respectively.

As it follows from Eqs. (1) and (3), the quantum correction to the partition function can be written in a form

$$Z_q = \exp(-\beta F_q) = \exp \left\{ \frac{\hbar^2 \beta^3}{24P^3} \sum_{s=1}^{P} \frac{1}{m} \langle \tilde{f}_s^2 \rangle \right\},$$  

(4)

where the averaged square forces $\langle \tilde{f}_s^2 \rangle$ are those of the conventional PI approach.

The multiplier $P^{-3}$ in Eq. (4) appears due to the fact that the PI effective temperature is $PT$. The force $\tilde{f}$ in Eq. (4) is the same as in Eq. (1). It does not include the coupling term arising from $U_{eff}$. Indeed, such term gives non-zero coupling forces even for non-interacting particles. Thus, its inclusion into $\tilde{f}$ in Eq. (4) would lead to wrong non-zero free-energy correction for a non-interacting system as well as wrong translational motion of the center of mass of a multi-particle system in zero external field.

As a result, the final expression for the corrected PI partition function is

$$Z_{qPI} = Z_q Z_{PI}.$$  

(5)

From Eq. (5) one can derive estimators for any thermodynamic quantity which can be computed using conventional PI trajectories, either during or a posteriori PI simulations.

For the total energy $E$ one obtains

$$E_{qPI} = -\frac{\partial \ln Z_{qPI}}{\partial \beta} = E_{PI} + E_q,$$  

(6)

where

$$E_q = -\frac{\partial \ln Z_q}{\partial \beta} = \frac{\hbar^2 \beta^2}{8P^3} \sum_{s=1}^{P} \frac{1}{m} \langle \tilde{f}_s^2 \rangle$$

$$+ \frac{\hbar^2 \beta^3}{24P^3} \sum_{s=1}^{P} \frac{1}{m} \frac{\partial}{\partial \beta} \langle \tilde{f}_s^2 \rangle.$$  

(7)

The derivative of the average square force with respect to the inverse temperature can be found exactly using Eq. (2)

$$\frac{\partial}{\partial \beta} \langle \tilde{f}_s^2 \rangle = \langle \tilde{f}_s^2 \rangle \langle \epsilon \rangle - \langle \tilde{f}_s^2 \epsilon \rangle,$$  

(8)

where $\epsilon$ is a standard primitive energy estimator

$$\epsilon = \frac{3P}{2\beta} - \sum_{s=1}^{P} \left\{ \frac{m \omega_s^2 (\bar{q}_{s+1} - \bar{q}_s)^2}{2} - \frac{U_s}{P} \right\}.$$  

(9)

Eqs. (7) and (8) give the following expression for the total energy correction

$$E_q = \frac{\hbar^2 \beta^3}{24P^3} \sum_{s=1}^{P} \frac{1}{m} \left\{ \left( \frac{3}{2} \beta + \langle \epsilon \rangle \right) \langle \tilde{f}_s^2 \rangle - \langle \tilde{f}_s^2 \epsilon \rangle \right\}.$$  

(10)

The correction to the heat capacity $C_q$ can be obtained as a temperature derivative of $E_q$ (see supplemental material).

In the general case, for an arbitrary function of coordinates $\lambda(\vec{q})$, one can derive the corrected estimator by
using the following procedure. First the potential energy is rewritten as $U_i \rightarrow U_i + \alpha \lambda \langle \vec{q} \rangle$. Then the thermodynamic average for $\lambda$ is

$$\langle \lambda \rangle = -\frac{1}{\beta} \left[ \frac{\partial \ln Z_{\alpha \pi}}{\partial \alpha} \right]_{\alpha=0}$$

(11)

Following the scheme of the derivation of the total energy one obtains

$$\langle \lambda \rangle = \langle \xi_\lambda \rangle + \frac{\hbar^2 \beta^3}{24 P^3} \sum_{s=1}^{P} \frac{1}{m} \left( \left\langle \vec{f}_s \right\rangle^2 \langle \xi_\lambda \rangle \right)$$

$$- \langle \vec{f}_s^2 \xi_\lambda \rangle - \frac{\hbar^2 \beta^2}{12 P^3} \sum_{s=1}^{P} \frac{1}{m} \left( \vec{f}_s \frac{\partial \lambda}{\partial \vec{q}_s} \right),$$

(12)

where $\xi_\lambda$ is the standard primitive estimator for $\lambda$ in the conventional PI approach

$$\xi_\lambda = \frac{1}{P} \sum_{s=1}^{P} \lambda_s.$$

(13)

The generalization to the case of multi-particle system is trivial and requires a summation over all particles in the system.

In Eq. (12), a potential difficulty could lie in obtaining the derivative $\frac{\partial \lambda}{\partial \vec{q}_s}$, contained in the last term. For some properties of interest this derivative could be inaccessible directly, and might require approximations. However, in this Letter we concentrate our attention on the total energy and heat capacity, which require only the information about particle coordinates, forces, and potential energies.

To demonstrate the performance of the developed method for both harmonic and anharmonic systems we carried out PIMD simulations for one dimensional (1D) quantum harmonic oscillator (QHO) and double-well potential (DWP)

$$U_{\text{QHO}}(x) = \frac{k x^2}{2},$$

$$U_{\text{DWP}}(x) = \Delta \left[ 1 + \frac{x^2}{d^2} \left( \frac{x^2}{d^2} - 2 \right) \right],$$

(14)

where $k$ is the stiffness of QHO, $\Delta$ is the barrier height and $2d$ is the distance between the two minima in DWP. At small and moderate $\Delta/T$ ratios the DWP potential is strongly anharmonic, thus the combination of these two model systems represents two limiting cases of interest for real applications.

To avoid numerical errors due to the finiteness of the time step in PIMD simulations we choose the value of the time step that gives 200 points per period of classical oscillation within the interaction potential. We use the following set of units and parameters for the QHO and DWP: $\hbar = 1$, $k_B = 1$, and $m = 1$.

![QHO and DWP](image)

**FIG. 1.** (color online) The relative error in the NQE contribution to the total energy [(a),(b)] and constant volume heat capacity [(c),(d)] of 1D QHO and DWP at fixed temperature. The results are shown as a function of the number of beads with respect to the converged values. Blue circles are the results of the conventional PIMD approach (PI) and red triangles correspond to the developed method (qPI). For both PI and qPI calculations we use the same PIMD trajectories. The parameters of simulations are: $k = 1$ and $T = 0.2$ for QHO, and $\Delta = 1$, $d = 0.5$, and $T = 1.2$ for DWP.

Figure 1 shows the difference between the NQE contribution to the total energy [(a),(b)] and the constant volume heat capacity [(c),(d)] obtained for QHO and DWP within our method and with conventional PIMD estimators. The results are shown as a function of the number of beads with respect to the converged values. When using the developed estimators both the total energy and heat capacity converge with a factor of eight fewer beads compared to the standard PIMD approach.

The qPI approach is equally applicable to arbitrary large anharmonic systems. To demonstrate this we carried out PIMD simulations for 64 identical particles interacting via Morse potential within periodic boundary conditions. For convenience we chose the following form of the Morse potential

$$U(r) = D \left( 1 - e^{-a(r-r_{eq})} \right)^2 - D,$$

(15)

where $r_{eq}$ is the equilibrium inter-particle distance, $D$ is the well depth of the potential (chosen as a normalization constant for energy variables), and $a = 1$ which gives a reasonable damping for inter-particle interaction. The particles are enclosed in a box with a linear size $4r_{eq}$. The simulation temperature is chosen to be $T = 0.8D$ to mimic the behavior of a quantum liquid. The performance of both methods is shown in Fig. 2. Obviously, the qPI approach exhibits fast convergence with increase
in the number of beads, capturing the correct quantum result within few percent for \( P \geq 4 \). For instance, for \( P = 4 \), the PI simulation underestimates the NQE contribution to the total energy by 22% while the developed approach gives less than 3.5% error.

A very important aspect for PIMD simulations is the statistical convergence of thermodynamic averages. Figure 3 demonstrates the convergence of the total energy for 64 Morse particles in periodic boundary conditions with the number of simulation steps for \( P = 4 \) and 6. For details see Fig. 2.

![FIG. 2. (color online) The relative underestimation of the NQE contribution to the total energy of 64 Morse particles in periodic boundary conditions as a function of the number of beads at fixed temperature. Blue circles are the results of the conventional PIMD approach (PI) and red triangles represent the performance of the developed method (qPI). For both PI and qPI calculations we use same data. The parameters of the simulations are: \( D = 1 \), \( r_{eq} = 10 \), \( a = 1 \), box size is \( 4r_{eq} \), and \( T = 0.8 \).](image1)

![FIG. 3. (color online) The deviation of the total energy of 64 Morse particles in periodic boundary conditions from the converged results as a function of the number of simulation steps for \( P = 4 \) and 6. For details see Fig. 2.](image2)

<table>
<thead>
<tr>
<th>( P )</th>
<th>( \text{N}_2 ) (in meV)</th>
<th>( \text{C}_6\text{H}_6 ) (in meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>PI 59.4</td>
<td>qPI 124.6</td>
</tr>
<tr>
<td></td>
<td>PI 1081.8</td>
<td>qPI 2019.5</td>
</tr>
<tr>
<td>8</td>
<td>PI 94.7</td>
<td>qPI 121.5</td>
</tr>
<tr>
<td></td>
<td>C6H6 1549.8</td>
<td>1936.6</td>
</tr>
<tr>
<td>QHA</td>
<td>120.0</td>
<td>1933.9</td>
</tr>
</tbody>
</table>

TABLE I. The NQE contribution to the total energy for \( \text{N}_2 \) and \( \text{C}_6\text{H}_6 \) molecules at room temperature within the conventional approach (PI), the developed method (qPI), and quantum harmonic approximation (QHA). The accuracy of the simulations is approximately 0.5 meV per atom.

Clearly, within the developed approach even for \( P = 4 \) one obtains results in good agreement with the quantum harmonic approximation (QHA), while conventional PIMD underestimates the NQE contribution by approximately 50%. For the molecules studied herein, the rather high internal vibrational frequencies make QHA a good reference for NQE at room temperature. For larger molecules with many anharmonic degrees of freedom, it is evident that the qPI approach will be significantly more accurate than QHA and more efficient than conventional PI methods.

In summary, the developed parameter-free qPI approach to calculate quantum-mechanical averages considerably improves the efficiency of PI simulations. Using conventional PIMD trajectories we are able to decrease the number of required beads by roughly an order of magnitude. The proposed method is not a re-weighting scheme and thus it does not suffer from statistical convergence problem for large systems. The efficiency and accuracy of the qPI method can extend the applicability of PIMD to increasingly larger systems.


