Effective potential analytic continuation calculations of real time quantum correlation functions: Asymmetric systems

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We apply the effective potential analytic continuation (EPAC) method to one-dimensional asymmetric potential systems to obtain the real time quantum correlation functions at various temperatures. Comparing the EPAC results with the exact results, we find that for an asymmetric anharmonic oscillator the EPAC results are in very good agreement with the exact ones at low temperature, while this agreement becomes worse as the temperature increases. We also show that the EPAC calculation for a certain type of asymmetric potentials can be reduced to that for the corresponding symmetric potentials.

I. INTRODUCTION

The imaginary time path integral formalism\textsuperscript{1} has been an important tool for studying static or dynamical properties of quantum statistical mechanical systems. The static properties have successfully been calculated by means of the path integral Monte Carlo (PIMC) or path integral molecular dynamics (PIMD) technique\textsuperscript{2,3}. However, these numerical methods have difficulties in computing the dynamical properties such as the real time quantum correlation functions, because the analytic continuation from the imaginary time to the real time is a non-trivial procedure in the numerical calculations\textsuperscript{4,5,6}.

As new quantum dynamics methods to calculate the real time quantum correlation functions at finite temperature, the centroid molecular dynamics (CMD) method\textsuperscript{7} and the effective potential analytic continuation (EPAC) method\textsuperscript{8} have recently been proposed. Both the methods use effective potentials, which can be numerically calculated by means of the PIMC or PIMD technique. In computing the real time quantum correlation functions, the CMD method uses the effective classical potential\textsuperscript{1,9,10}, while the EPAC method uses the standard effective potential which appears in the effective action formalism\textsuperscript{11,12}. The effective potentials have been extensively used as powerful tools in the calculations of the static properties\textsuperscript{9,10,11,12,13,14}, so that they are expected to be effective also for the calculations of the dynamical properties. In practice, the CMD method has been tested in low-dimensional systems\textsuperscript{7,13,14,15,16,17,18} and applied to various many-body molecular systems to yield many promising results\textsuperscript{19,20}. On the other hand, it has already been shown that the EPAC method works well in a one-dimensional symmetric double well system\textsuperscript{8}. This success suggests that the EPAC should be very useful for the calculation of quantum dynamics of the systems in which quantum coherence is significant.

Most of actual potentials appearing in chemical systems and condensed matter systems have asymmetric shapes. For example, asymmetric double well potentials have been widely used to describe the proton transfer reactions\textsuperscript{21}.

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or the first-order phase transitions \[22, 23\]. The other asymmetric potentials such as the Morse potential have also been very important and have been repeatedly used in chemical physics as a realistic model of the intramolecular vibration.

In the present paper, the EPAC method is therefore applied to the evaluation of real time quantum correlation functions for one-dimensional asymmetric systems. We investigate whether the EPAC method can successfully reproduce the exact correlation functions for the Morse potential. We also show that the EPAC calculation for a certain type of asymmetric potentials can be reduced to that for the corresponding symmetric potentials. This property is called the \textit{decoupling property}, which is quite useful for the discussion of the asymmetrization effect in the quantum statistical systems, for instance, the enhancement or suppression of the transition rate in chemical reaction \[21\]. Furthermore, the decoupling property can aid us in reducing the computational cost required on the PIMD/PIMC calculation. In this paper, we analytically prove that this property holds, followed by the numerical examination of it.

In Sec. II, we summarize the definition of a couple of types of effective potentials and review our EPAC method. Moreover, we explicitly present the standard effective potential and the EPAC position autocorrelation function for a harmonic oscillator as the simplest example. The EPAC analyses of one-dimensional systems with asymmetric potentials are shown in Sec. III. After showing the decoupling property of linear terms appearing in the classical potentials, we present the EPAC results for the asymmetric harmonic/anharmonic oscillators. The conclusions are given in Sec. IV.

**II. EFFECTIVE POTENTIAL ANALYTIC CONTINUATION METHOD**

**A. Effective potentials and analytic continuation**

We first introduce the effective classical potential defined by Feynman \[1\]. Consider a quantum system where a quantum particle of mass \(m\) moves in a one-dimensional potential \(V(q)\) at temperature \(T\). The quantum canonical partition function of this system is expressed in terms of the imaginary time path integral

\[
Z_{\beta} = \int_{-\infty}^{\infty} dq \int_{q(0)=q}^{q(\beta\hbar)=q} Dq \ e^{-S_E/\hbar},
\]

where \(\beta = 1/k_B T\) and \(S_E\) is the Euclidean action functional

\[
S_E[q] = \int_{0}^{\beta\hbar} d\tau \left[ \frac{1}{2} m \dot{q}^2 + V(q) \right].
\]

After a Fourier decomposition of the periodic paths \(q(\tau) = (1/\beta\hbar) \sum_{n=-\infty}^{\infty} e^{-i\omega_n \tau} \tilde{q}(\omega_n)\) with the Matsubara frequencies \(\omega_n = 2\pi n/\beta\hbar\), we get \[24\]

\[
Z_{\beta} = \sqrt{\frac{m}{2\pi\beta\hbar^2}} \int_{-\infty}^{\infty} dq_0 \prod_{n=1}^{\infty} \frac{m\omega_n^2}{\pi\beta\hbar^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d(\text{Re}\tilde{q}(\omega_n)) d(\text{Im}\tilde{q}(\omega_n)) \ e^{-S_E/\hbar},
\]

where \(q_0\) is the path centroid (zero mode): \(q_0 = \tilde{q}(\omega_0)/\beta\hbar\). Inserting an identity \(1 = \int_{-\infty}^{\infty} dq_c \delta(q_0 - q_c)\) into the integral in Eq. \[3\] and integrating out all the Fourier modes, we obtain

\[
Z_{\beta} = \sqrt{\frac{m}{2\pi\beta\hbar^2}} \int_{-\infty}^{\infty} dq_c \ e^{-\beta V_{\beta}(q_c)}. \tag{4}
\]

Here \(V_{\beta}(q_c)\) is the effective classical potential \[1, 2, 10\], which is a function of the position centroid variable \(q_c\). Among the integration of all the Fourier modes, the zero mode integral \(\int_{-\infty}^{\infty} dq_0\) yields only the replacement \(q_0 \rightarrow q_c\), so that the effective classical potential \(V_{\beta}(q_c)\) does not contain the fluctuation effect of the zero mode \(q_0\). Therefore the effective classical potential contains only the quantum fluctuation effects of \(\tilde{q}(\omega_n \neq 0)\) modes.
Another type of effective potential \[11, 12\] is briefly summarized next. At first, consider the quantum canonical partition function represented in terms of an imaginary time path integral in the presence of a constant external source \(J\),

\[
Z_\beta(J) = \int_{-\infty}^{\infty} dq \int_{q(0)=q}^{q(\beta\hbar)=q} Dq \ e^{-S_E/\hbar} e^{\beta J q_0} = e^{\beta w_\beta(J)},
\]

where \(w_\beta(J)\) is the generating function for the connected Green functions with zero energy. From Eqs. \((4)\) and \((5)\), the generating function is written in terms of \(V^c_\beta(q_c)\),

\[
w_\beta(J) = \frac{1}{\beta} \log \left[ \int_{-\infty}^{\infty} dq_c \ e^{-\beta V^c_\beta(q_c)} e^{\beta J q_c} \right].
\]

This can be rewritten in the phase-space centroid representation,

\[
w_\beta(J) = \frac{1}{\beta} \log \left[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_c dp_c \ \frac{m}{2\pi\beta\hbar^2} \ e^{\beta J q_c} \ e^{-\beta (p_c^2/2m + V^c_\beta(q_c))} \right],
\]

where \(p_c\) is the momentum centroid variable. The “conventional” effective potential \(V_\beta(Q)\) is defined as the Legendre transform of the generating function \(w_\beta(J)\) \[11, 12\],

\[
V_\beta(Q) = \sup_J \left\{ JQ - w_\beta(J) \right\}.
\]

We refer to this effective potential as the standard effective potential. This is the leading order of the derivative expansion of the effective action, and contains the effects of both quantum fluctuation and thermal fluctuation in the quantum statistical system. The static properties of the system can be reproduced from \(V_\beta(Q)\) straightforwardly \[11, 12\]. For example, one can evaluate the expectation value of the position operator \(\hat{q}\) using the relation

\[
\langle \hat{q} \rangle_\beta = Q_{\min},
\]

where \(Q_{\min}\) is the position of the standard effective potential minimum. The value of \(Q_{\min}\) is determined by the stationary condition \(\partial V_\beta/\partial Q |_{Q=Q_{\min}} = 0\). In the low temperature limit, the two effective potentials are identical \[25, 26, 27\], while the ground state energy of the quantum system is given by the minimum value of \(V_\beta(Q)\) \[12, 14\],

\[
E_0 = \langle 0 | \hat{H} | 0 \rangle = \lim_{\beta \to \infty} V_\beta(Q_{\min}).
\]

On the other hand, one can also calculate the dynamical properties such as real time quantum correlation functions from the standard effective potential \(V_\beta(Q)\). Using the effective action formalism \[11, 12\], at first imaginary time quantum correlation functions are directly obtained from the standard effective potential \(V_\beta(Q)\) with the leading order derivative expansion. Then by means of the analytic continuation \[28\] real time quantum correlation functions can be readily obtained from the imaginary time quantities. This is the EPAC \[8\], an approximation method based on the effective action formalism. Following the EPAC method, for example, the real time position autocorrelation function \(C_\beta(t) = \langle \hat{q}(t)\hat{q}(0) \rangle_\beta\) can be expressed as

\[
C_\beta(t) \simeq C^{AC}_\beta(t) = \left( \frac{\hbar}{2m\omega_\beta} \ coth \frac{\beta h \omega_\beta}{2} \right) \ cos \omega_\beta t - i \left( \frac{\hbar}{2m\omega_\beta} \right) \ sin \omega_\beta t + Q^2_{\min},
\]

where \(\omega_\beta\) is the effective frequency,

\[
\omega_\beta = \sqrt{\frac{1}{m} \ \frac{\partial^2 V_\beta}{\partial Q^2} |_{Q=Q_{\min}}}.\]
FIG. 1: The inverse temperature $\beta$ dependence of $V_\beta(q_c = 0)$, $V_\beta(Q = 0)$, and $\omega_\beta$ for the quantum harmonic oscillator with the parameters $\hbar = k_B = m = \omega = 1$. Note that $\omega_\beta$ of the harmonic oscillator is independent of the temperature.

B. Example: harmonic oscillator

To illustrate the characteristics of the standard effective potential $V_\beta(Q)$ and the EPAC correlation function, here we explicitly present the results for a simple system: a quantum harmonic oscillator whose classical potential is given by

$$V(q) = \frac{1}{2} m \omega^2 q^2.$$  \hspace{1cm} (13)

In this system the effective classical potential can be written as

$$V_\beta^c(q_c) = \frac{1}{2} m \omega^2 q_c^2 + \frac{1}{\beta} \log \left( \frac{\sinh(\beta \hbar \omega/2)}{\beta \hbar \omega/2} \right).$$  \hspace{1cm} (14)

Then we can evaluate the generating function $w_\beta(J)$ from Eqs. (6) and (14),

$$w_\beta(J) = \frac{1}{2} m \omega^2 J^2 - \frac{1}{\beta} \log \left( 2 \sinh \frac{\beta \hbar \omega}{2} \right),$$  \hspace{1cm} (15)

to obtain eventually the standard effective potential as the Legendre transform of $w_\beta(J)$

$$V_\beta(Q) = \frac{1}{2} m \omega^2 Q^2 + \frac{1}{\beta} \log \left( 2 \sinh \frac{\beta \hbar \omega}{2} \right).$$  \hspace{1cm} (16)

The minimum of $V_\beta(Q)$ is located at the point $Q = Q_{\text{min}} = 0$, and the effective frequency is temperature-independent: $\omega_\beta = \omega$. This potential minimum $V_\beta(Q = 0)$ is equal to the free energy of the quantum harmonic oscillator.

In fact, in the low temperature limit, the potential minimum $V_\beta(Q = 0)$ is equal to that of the effective classical potential $V_\beta^c(q_c = 0)$, and they give the ground state energy of the quantum harmonic oscillator,

$$\lim_{\beta \to \infty} V_\beta(Q = 0) = \lim_{\beta \to \infty} V_\beta^c(q_c = 0) = \frac{\hbar \omega}{2}.$$  \hspace{1cm} (17)

On the other hand, in the high temperature limit ($\beta \to 0$), these effective potentials exhibit quite different features. The standard effective potential minimum $V_\beta(Q = 0)$ diverges to negative infinity, while the effective classical potential
minimum $V'_{\beta}(q_c = 0)$ converges to zero. This is because the standard effective potential $V_{\beta}(Q)$ includes the effects of both quantum fluctuation and thermal fluctuation, while the effective classical potential $V'_{\beta}(q_c)$ includes the effect of quantum fluctuation only. In Fig. 11 we show the inverse temperature $\beta$ dependence of $V'_{\beta}(q_c = 0)$, $V_{\beta}(Q = 0)$, and $\omega_{\beta}$ with the parameters $\hbar = k_B = m = \omega = 1$.

Finally we obtain the EPAC position autocorrelation function for the quantum harmonic oscillator

$$C^{A\beta}_{\text{AC}}(t) = \left( \frac{\hbar}{2m\omega} \coth \frac{\beta \omega}{2} \right) \cos \omega t - i \left( \frac{\hbar}{2m\omega} \right) \sin \omega t.$$ (18)

This is equal to the exact correlation function. The EPAC method is thus exact for harmonic systems as well as the CMD [29].

III. APPLICATION TO ASYMMETRIC SYSTEMS

In our previous paper [8], the usefulness of the EPAC method has been shown for a $Z_2(q \leftrightarrow -q)$ symmetric double well potential system in comparison with the CMD result. We expect that the EPAC method may also be useful for general anharmonic quantum systems. In the present section, we embark on a project to investigate how the EPAC method works in a $Z_2$ asymmetric system with the classical potential [7, 15],

$$V(q) = \frac{1}{2} q^2 + \frac{1}{10} q^3 + \frac{1}{100} q^4,$$ (19)

where natural units $\hbar = k_B = m = 1$ are employed. This potential is given by a polynomial approximation to a Morse potential,

$$V(q) = \frac{25}{2} \left( 1 - e^{(1/5)q} \right)^2,$$ (20)

regarding $q$ as the small deviation from the minimum $q = 0$ [30]. This polynomial approximation is very good for $\beta \gtrsim 10$. The Morse potential [20] corresponds to, for example, the parameters denoting the intramolecular vibration of the HCl molecule [31]. For this system the inverse temperature $\beta = 10$ corresponds to the temperature $T \sim 400$ K.

On the other hand, by a variable shift $x = q + \frac{5}{2}$, we can transform the potential [19] to the form

$$\bar{V}(x) = \frac{125}{64} - \frac{5}{4} x + \frac{1}{8} x^2 + \frac{1}{100} x^4,$$ (21)

which is a potential asymmetricized by the linear term $-\frac{5}{4} x$ only. Such additional linear terms exhibit interesting feature in the effective potential analyses; they are irrelevant both to the path integral calculation [3] and to the Legendre transformation [8]. This property ensures that the standard effective potential for the asymmetric potential [21] can readily be given by that for the corresponding symmetric potential without the linear term. This is the decoupling property, which has been discussed for other types of effective potentials in the context of the nonperturbative renormalization group [23, 32]. In the following we give a proof of this property for the standard effective potential, and then apply it to the evaluation of the standard effective potentials for an asymmetric harmonic oscillator and the asymmetric anharmonic oscillator [21].

A. Decoupling property of the additional linear term

Consider a quantum system described by a classical potential of the form

$$V(q) = U(q) + fq,$$ (22)
where \( U(q) \) is any classical potential and \( f \) is a constant. The effective classical potential can be written as

\[
V^*_\beta(q_c) = U^*_\beta(q_c) +fq_c,
\]

(23)

where \( U^*_\beta(q_c) \) is the effective classical potential for \( U(q) \). This is because in the Euclidean action \( S_E \) the linear term consists of only the zero mode \( q_0 \),

\[
\int_0^{\beta\hbar} d\tau f q(\tau) = f\beta\hbar q_0,
\]

(24)

and never generate or receive any quantum correction when we integrate out all the Fourier modes to evaluate the effective classical potential.

Next, from Eqs. (16) and (23) the generating function for \( V(q) \) is given as

\[
w_\beta(J) = \frac{1}{\beta} \log \left[ \sqrt{\frac{m}{2\pi\beta\hbar^2}} \int_{-\infty}^{\infty} dq_c e^{-\beta U^*_\beta(q_c)} e^{\beta (J-f)q_c} \right].
\]

(25)

Supposing that \( w^U_\beta \) is the generating function for \( U(q) \), an evident relation \( w_\beta(J) = w^U_\beta(J-f) \) holds. Furthermore, supposing \( J^*(Q) \) is the solution of the equation \( Q = \partial w_\beta / \partial J \) and \( J^*_U(Q) \) is that of \( Q = \partial w^U_\beta / \partial J \), we get a relation \( J^*(Q) = J^*_U(Q) + f \). The standard effective potential for \( V(q) \) can therefore be written as

\[
V_\beta(Q) = \left\{ JQ - w_\beta(J) \right\}|_{J=J^*(Q)}
= J^*_U(Q)Q +fq - \frac{1}{\beta} \log \left[ \sqrt{\frac{m}{2\pi\beta\hbar^2}} \int_{-\infty}^{\infty} dq_c e^{-\beta U^*_\beta(q_c)} e^{\beta (J-f)q_c} \right]
= U_\beta(Q) +fq,
\]

(26)

where \( U_\beta(Q) \) is the standard effective potential for \( U(q) \). Equations (23) and (26) ensure that the functional form of the linear term remains unchanged through the path integration and the Legendre transformation, and that it never generates any quantum or thermal correction to \( U(q) \). That is, the linear term in the classical potential decouples from the effective potential calculations.

Using Eq. (26), we can directly obtain the standard effective potential \( V_\beta(Q) \) from \( U_\beta(Q) \). This means that we have only to carry out the path integration and the Legendre transformation for \( U(q) \). This decoupling property is especially useful when \( U(q) \) is a \( Z_2(q \leftrightarrow -q) \) symmetric potential, because we can simply discuss the asymmetrization effect as the additional linear term effect on \( U_\beta(Q) \). Furthermore, the \( Z_2 \) symmetry reduces the computational cost required on the PIMD/PIMC calculation for the \( Z_2 \) symmetric \( U(q) \). This is because the required cite number in \( q_c \) space is reduced by half by the \( Z_2 \) symmetry.

**B. Asymmetric harmonic oscillator**

As a simple example of the system with the additional linear term, we consider an asymmetric harmonic oscillator

\[
V(q) = \frac{1}{2} m \omega^2 q^2 + f q.
\]

(27)

From Eqs. (16) and (26) we readily obtain the standard effective potential

\[
V_\beta(Q) = \frac{1}{2} m \omega^2 Q^2 + f Q + \frac{1}{\beta} \log \left( 2 \sinh \frac{\beta \hbar \omega}{2} \right).
\]

(28)

The minimum of \( V_\beta(Q) \) is at the point \( Q = Q_{min} = -f/m \omega^2 \), and the effective frequency is still temperature-independent: \( \omega_\beta = \omega \). The value \( Q_{min} \) coincides with the exact position expectation value \( \langle \hat{q} \rangle_\beta \), while the minimum
value,
\[ V_\beta(Q_{\text{min}}) = -\frac{f^2}{2m\omega^2} + \frac{1}{\beta} \log \left( 2 \sinh \frac{\beta \hbar \omega}{2} \right), \] (29)
gives the exact ground state energy in the low temperature limit,
\[ E_0 = \lim_{\beta \to \infty} V_\beta(Q_{\text{min}}) = -\frac{f^2}{2m\omega^2} + \frac{\hbar \omega}{2}. \] (30)

The EPAC position autocorrelation function is then obtained as
\[ C_\beta^{AC}(t) = \left( \frac{\hbar}{2m\omega} \coth \frac{\beta \hbar \omega}{2} \right) \cos \omega t - i \left( \frac{\hbar}{2m\omega} \right) \sin \omega t + \frac{f^2}{m^2\omega^4}. \] (31)
This present result is also equal to the exact correlation function.

C. Asymmetric anharmonic oscillator

In this section we attempt to apply the EPAC method to the asymmetric anharmonic system with the potential \( V(q) \). To obtain the parameters \( Q_{\text{min}} \) and \( \omega_\beta \) needed for the EPAC correlation function \( (11) \), now we propose the following computational schemes.

\textbf{Scheme (A).} By carrying out the path integration and the Legendre transformation for the classical asymmetric potential \( V(q) \), we obtain the standard effective potential \( V_\beta(Q) \). We then fix the parameters \( Q_{\text{min}} \) and \( \omega_\beta \) by minimizing \( V_\beta(Q) \).

\textbf{Scheme (B).} We first carry out the path integration and the Legendre transformation for the symmetric part in the converted potential \( \bar{U}(x) \),
\[ \bar{U}(x) = \frac{125}{64} + \frac{1}{8} x^2 + \frac{1}{100} x^4, \] (32)
to obtain the symmetric standard effective potential \( \bar{V}_\beta(X) \). Using Eq. \( (26) \) with \( f = -\frac{5}{4} \), we can write the asymmetric standard effective potential as
\[ \bar{V}_\beta(X) = \bar{U}_\beta(X) - \frac{5}{4} X. \] (33)

We then obtain the minimum point \( X_{\text{min}} \) and the effective frequency \( \bar{\omega}_\beta \) by minimizing \( \bar{V}_\beta(X) \). The parameters \( Q_{\text{min}} \) and \( \omega_\beta \) are obtained from the relations \( Q_{\text{min}} = X_{\text{min}} - \frac{5}{2} \) and \( \omega_\beta = \bar{\omega}_\beta \).

In the following we perform the numerical calculation with scheme (A) to test the EPAC method itself. The numerical calculation with scheme (B) is also performed to check the decoupling property \( (26) \). To evaluate the standard effective potentials \( V_\beta(Q) \) in scheme (A) and \( \bar{U}_\beta(X) \) in scheme (B) using Eqs. \( (6) \) and \( (8) \), we need to precompute the effective classical potentials \( V_\beta^c(q_c) \) and \( \bar{U}_\beta^c(x_c) \), respectively. Employing the PIMD technique and the fitting procedure described in Ref. \( [33] \), we calculated \( V_\beta^c(q_c) \) and \( \bar{U}_\beta^c(x_c) \) at the inverse temperature \( \beta = 0.1, 1, 10, \) and 100. We then calculated the standard effective potential \( V_\beta(Q) \) and \( \bar{U}_\beta(X) \) by carrying out the numerical integration \( [30] \) and the numerical Legendre transformation \( [31] \). As for scheme (A), Fig. \( 2 \) shows the evaluated effective potentials for the asymmetric potential \( V(q) \) \( [Eq. \ 19] \). As seen in Fig. \( 2(a) \) and \( 2(b) \), at the low temperature \( \beta = 100 \), the standard effective potential \( V_\beta(Q) \) has almost the same shape as the effective classical
FIG. 2: The inverse temperature $\beta$ dependence of the effective potentials for the asymmetric classical potential \[19\]: (a) the effective classical potential $V_\beta^c(q_c)$ and (b) the standard effective potential $V_\beta(Q)$. In this plot we set $V_\beta^c(0) = 0$ and $V_\beta(Q_{min}) = 0$.

Potential $V_\beta^c(q_c)$. This is a general property of the effective potentials \[25, 26, 27\]. With regard to Scheme (B), the evaluated effective potentials for the symmetric part $\bar{U}(x)$ [Eq. \[32\]] are shown in Fig. 3. It is also seen in this figure that $\bar{U}_\beta(x_c)$ and $\bar{U}_\beta(X)$ have more similar shape at lower temperature, as in Fig. 2.

Next we evaluated the parameters $Q_{min}$ and $\omega_\beta$. With scheme (A) we directly obtained them from the computed $V_\beta(Q)$, while in scheme (B) they were obtained from the evaluated effective potential $\bar{U}_\beta(X)$ using the relations $Q_{min} = X_{min} - \frac{1}{2}$ and $\omega_\beta = \bar{\omega}_\beta$. Figure 4 shows $Q_{min}$ and $\omega_\beta$ calculated by means of scheme (A) and (B), and also shows the exact result

$$\langle \hat{q} \rangle_\beta = \frac{1}{Z_\beta} \sum_n e^{-\beta E_n} \langle n | \hat{q} | n \rangle,$$

where the energy eigenstates $|n\rangle$ and the energy eigenvalues $E_n$ were obtained by a numerical integration of the Schrödinger equation. In this figure, we also plotted the effective frequency of the symmetric effective potential $\bar{U}_\beta(X)$: $\bar{\omega}_\beta = \sqrt{\partial^2 \bar{U}_\beta(X)/\partial X^2}|_{X=0}$. It is found that at each temperature the quantities computed in scheme (B) are in very good agreement with the corresponding ones in scheme (A). This indicates that the relation \[26\] actually holds in the numerical PIMD calculation and the numerical Legendre transformation. We can also see that each $Q_{min}$ agrees very well with the corresponding exact value $\langle \hat{q} \rangle_\beta$; the effective potential approach to such a static property works successfully in this asymmetric system.

Here we give a comment on the asymmetrization effect. As seen in Fig. 4 each effective frequency $\omega_\beta(= \bar{\omega}_\beta)$ is larger than $\omega_\beta^s$ at each temperature, that is, the asymmetrization effect enhances the effective frequency of the system. This property can be simply understood as follows: For the weakly anharmonic system, the symmetric standard effective potential $\bar{U}_\beta(X)$ can be well approximated by a power series expansion to the fourth order, $\bar{U}_\beta(X) =$
FIG. 3: The inverse temperature $\beta$ dependence of the effective potentials for the symmetric classical potential (32): (a) the effective classical potential $\bar{U}_c^\beta(x_c)$ and (b) the standard effective potential $\bar{U}_\beta^\beta(X)$. In this plot we set $\bar{U}(0) = 0$, $\bar{U}_c^\beta(0) = 0$, and $\bar{U}_\beta^\beta(X_{\min}) = 0$.

FIG. 4: The inverse temperature $\beta$ dependence of the minimum point $Q_{\min}$ and the effective frequency $\omega_\beta$. The exact position expectation value $\langle \hat{q} \rangle_\beta$ and the effective frequency of the symmetric effective potential $\omega_s^\beta$ are also plotted.
\[ C + \frac{1}{4} \omega_\beta^2 X^2 + \frac{1}{4} \lambda_\beta X^4 \] with a constant \( C \) and a positive coupling constant \( \lambda_\beta \). Then the asymmetric standard effective potential can be written as \( \tilde{V}_\beta(X) = C - \frac{1}{2} X + \frac{1}{4} \omega_\beta^2 X^2 + \frac{1}{4} \lambda_\beta X^4 \). Supposing \( X_{\text{min}} \) is the minimum point of \( \tilde{V}_\beta(X) \), we obtain the effective frequency of \( \tilde{V}_\beta(X) \) as \( \tilde{\omega}_\beta = \sqrt{\omega_\beta^2 + 3 \lambda_\beta X_{\text{min}}} \). Since the parameters \( \omega_\beta^2 \) and \( \lambda_\beta \) are positive, we get an inequality \( \tilde{\omega}_\beta \geq \omega_\beta^2 \), where the equality holds in the harmonic limit \( \lambda_\beta \to 0 \). Figure 4 also shows that \( \omega_\beta^2 = \tilde{\omega}_\beta \) becomes closer to \( \omega_\beta^2 \) as the temperature increases. This implies that the standard effective potentials \( \tilde{U}_\beta(X), \tilde{V}_\beta(X) \), and \( V_\beta(Q) \) become effectively harmonic ones at the higher temperature.

Finally we constructed the EPAC position autocorrelation functions \( C^{AC}_\beta(t) \) using the computed quantities \( Q_{\text{min}} \) and \( \omega_\beta \). Figure 5 shows the real part of \( C^{AC}_\beta(t) \) together with the real part of the exact quantum position autocorrelation function,

\[
C_\beta(t) = \frac{1}{2\beta} \sum_n \sum_m e^{-\beta E_n} e^{-i(E_m - E_n)t/\hbar} |\langle m|\hat{q}|n \rangle|^2,
\]

at the inverse temperature \( \beta = 0.1, 1, \) and 10. We can see that each EPAC correlation function reproduces well the exact correlation function at \( t = 0 \); the static property \( C_\beta(0) \) can be approximated very well by only two quantities \( Q_{\text{min}} \) and \( \omega_\beta \),

\[
C_\beta(0) \approx C^{AC}_\beta(0) = \frac{\hbar}{2m\omega_\beta} \coth \frac{\beta\omega_\beta}{2} + Q_{\text{min}}^2.
\]

This means that the leading order derivative expansion employed in the EPAC is very good in the calculation of the static property \( C_\beta(0) \). The value \( C^{AC}_\beta(0) \) can be improved by employing the higher order derivative expansion; it should become exact in the infinite order expansion if the expansion is a converging one. On the other hand, as the time \( t \) increases, each EPAC correlation function deviates from the exact one. Such deviation becomes larger at the higher temperature. In particular, at \( \beta = 0.1 \) [Fig. 5(a)], the exact correlation function \( C_\beta(t) \) damps rapidly with time, whereas the EPAC correlation function \( C^{AC}_\beta(t) \) shows stable oscillation. This damping behavior comes from the fact that the exact correlation function \( C_\beta(t) \) consists of the many oscillation modes with the frequencies \( \omega_{m,n} = (E_m - E_n)/\hbar \), and oscillation modes with high energies contribute to Eq. \( 35 \) more at higher temperature. On the other hand, the EPAC correlation function consists of only one oscillation mode with the frequency \( \omega_\beta \) at any temperature, so that it always exhibits a single-mode oscillation. As the temperature lowers [Fig. 5(b) and 5(c)], the EPAC correlation function \( C^{AC}_\beta(t) \) becomes closer to the exact \( C_\beta(t) \). This is because at lower temperature, almost only one oscillation mode contributes to Eq. \( 35 \) to make the exact \( C_\beta(t) \) show a quasi-single-mode oscillation. This property generally holds for a weakly anharmonic system though it does not hold for strongly anharmonic systems such as deep double well systems.

The results shown in Fig. 5 imply that the leading order derivative expansion employed in the EPAC method becomes worse at longer time and at higher temperature. To reproduce the damping behavior of the exact \( C_\beta(t) \) at high temperature, we need the higher order derivative expansion of the effective action. However, our calculation at lower temperature \( \beta = 10 \) [Fig. 5(c)] corresponds to, for example, the dynamics of the intramolecular vibration of the HCl molecule at temperature \( T \sim 400 \) K. Therefore our EPAC method even in the present form should work very well for such chemical systems in the realistic temperature region.

Finally we mention the applicability of the EPAC method to a nonpolynomial potential, in particular, an asymptotically sublinear potential such as \( \lim_{|q| \to \infty} V(q)/|q| \leq 0 \). Most of the actual potentials appearing in chemical systems and condensed matter systems have this type of potential shape, for example, the Morse potential, the Lenard-Jones potential, and other intramolecular and intermolecular potentials. An important property of these potentials is that they represent the dissociation in the long distance limit. It is quite nontrivial to make the dissociation effect involved in the effective potential approach. In fact, some difficulties have already been pointed out. From the chemical interest, this is a challenging subject to be examined.
FIG. 5: The real part of the exact quantum position autocorrelation function $C_\beta(t)$ and the real part of the EPAC position autocorrelation function $C^{AC}_\beta(t)$: (a) at $\beta = 0.1$, (b) at $\beta = 1$, and (c) at $\beta = 10$.

IV. CONCLUDING REMARKS

In the present work we have focused on the EPAC analyses of one-dimensional asymmetric systems. At first, for the asymmetric harmonic oscillator (27), we have analytically shown that the exact real time position autocorrelation function is derived by means of the EPAC method. As for the asymmetric anharmonic oscillator (19), we could obtain the EPAC correlation function numerically. In this case, at first we have computed the standard effective potential $V_\beta(Q)$ by means of the PIMD technique and the numerical Legendre transformation. Then we have obtained the position of the effective potential minimum $Q_{\text{min}}$ and the effective frequency $\omega_\beta$ which are needed to construct the EPAC position autocorrelation function $C^{AC}_\beta(t)$. It has been shown that the static properties of this asymmetric system, $\langle \hat{q} \rangle_\beta$ and $C_\beta(0)=\langle \hat{q}(0)\hat{q}(0)\rangle_\beta$, are well reproduced by $Q_{\text{min}}$ and $C^{AC}_\beta(0)$, respectively. As for a long time behavior, we have found that at lower temperature the EPAC correlation function $C^{AC}_\beta(t)$ agrees with the exact $C_\beta(t)$ very well, whereas the EPAC result becomes worse as the temperature increases. This is because the EPAC method approximates the multimode contribution to the exact real time correlation function by the single-mode contribution with the effective frequency $\omega_\beta$. In a chemical aspect, however, it is quite remarkable that a good agreement of the EPAC correlation function with the exact one is achieved for the realistic potential in the realistic temperature region.

We have also shown that a linear term in a classical potential is irrelevant to the effective potential calculation. For a classical potential $V(q) = U(q) + f q$, the standard effective potential is given by $V_\beta(Q) = U_\beta(Q) + f Q$. We have
proved this decoupling property analytically, and have also checked it numerically by calculating $V_\beta(Q)$ and $U_\beta(Q)$ independently.

In the present work, it has been shown that the EPAC method is practically applicable to simple systems with single degree of freedom. More important applications in chemical physics are, however, to the systems with many degrees of freedom. For such applications, there are a couple of obstacles to be overcome. The first one is the computation of the generating function $w_\beta(J)$. To obtain $w_\beta(J)$ using Eq. (6), we need to precompute the effective classical potential $V_\beta(q_c)$ itself. However, this precomputation evidently demands more computational efforts as the system are more complicated. For many-body systems, Eq. (7) rather than Eq. (6) will be useful for more efficient evaluation of $w_\beta(J)$, because the CMD sampling can be used to calculate the statistical-mechanical average of $e^{\beta J q_c}$ appearing in the right-hand side of Eq. (7) [33]. That is, we can use the numerical techniques developed in the CMD calculations for many-body systems [19, 20]. The second obstacle is the evaluation of the standard effective potential $V_\beta(Q)$ in many-body systems, i.e., the multidimensional Legendre transformation of $w_\beta(J)$ [Eq. (8)]. This transformation will also require heavier computations for larger systems. It is quite important to solve these numerical problems lying in the practical calculations for many-body systems. We are presently developing the numerical schemes along this line.

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