A Semiclassical Initial-Value Representation for Quantum Propagator and Boltzmann Operator

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Starting from the position-momentum integral representation, we apply the correction operator method to the derivation of a uniform semiclassical approximation for the quantum propagator and then extend it to approximate the Boltzmann operator. In this approach, the involved classical dynamics is determined by the method itself instead of given beforehand. For the approximate Boltzmann operator, the corresponding classical dynamics is governed by a complex Hamiltonian, which can be described as a pair of real Hamiltonian systems. It is demonstrated that the semiclassical Boltzmann operator is exact for linear systems. A quantum propagator in the complex time is thus proposed and preliminary numerical results show that it is a reasonable approximation for calculating thermal correlation functions of general systems. © 2018 Wiley Periodicals, Inc.

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Introduction

Compared to the classical analogue, the many-particle quantum dynamics is hardly reachable because of its nonlocal features. There has been considerable effort to explore simple yet accurate approximations for the quantum propagator based on local classical dynamics, which leads to different versions of so called semiclassical propagators. Of all these semiclassical treatments, the very first was due to van Vleck[1] who obtained an approximate quantum propagator or Green's function by virtue of a time-dependent Wentzel-Kramers-Brillouin method.[2–4] In van Vleck's formula, it is required to calculate the classical trajectories with the given initial and final positions. This root-search problem limits van Vleck's approximation as a useful tool.

To overcome this difficulty, several semiclassical propagators based on classical trajectories starting from the given initial position and momentum have initially been proposed by Miller et al.,[5–11] among which the most popular is the Herman-Kluk (HK) semiclassical propagator.[11–14] In the HK approximation, one needs to calculate the classical trajectories associated with the stability matrices and their contributions by integration over the phase space. The HK propagator was first suggested as an approximate alternative of the traditional van Vleck formula (11), which was later shown to be one of the initial-value representation (IVR) variants, displaying an excellent numerical performance.[12–14] Notwithstanding the good accuracy of the HK approximation, there were serious debates over whether it is semiclassically rigorous.[15–18] It was Kay[19] that elaborated an elegant scheme based on the correction operator method developed by Pollak and coworkers,[20–22] which led to the derivation of the HK propagator as a uniform semiclassical IVR and thus finally resolved the debate. Further, the procedure used by Kay can give the high-order corrections systematically.

When one is interested in quantum thermodynamics or quantum evolution in the imaginary time instead of the real-time dynamics, the problem of nonlocality seems less severe except for very low temperatures. Indeed, the numerical path integral techniques[23–25] have been frequently used to compute the exact quantum Boltzmann distribution and thus the thermodynamic properties of many-particle systems. However, it becomes difficult to give convergent results as temperature gets low or the imaginary time is long. Several approximate methods have also been developed to evaluate the quantum partition function and the Boltzmann density matrices.[26–34] These methods can roughly be classified as two kinds. One is based on the variational principle in which the system is treated as an effective harmonic oscillator with the frequency (matrix) to be optimized.[26–28] The other is based on an approximate imaginary-time evolution. A representative of the latter is the thermal Gaussian approximation originally proposed by Metiu,[29] which has been further developed and applied to the studies of quantum thermodynamics of clusters and molecular liquids.[30–34]

As the Boltzmann operator can be regarded as a quantum system evolving in the imaginary time, it seems that the real-time IVR for the quantum propagator can directly be extended to the imaginary time. The HK propagator, for instance, was indeed converted into an imaginary-time version and used to calculate the Boltzmann matrix.[35] Associated with extending the dynamics to the imaginary time, the classical momentum is mapped to a

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purely imaginary variable and the corresponding classical dynamics corresponds to a real time motion on an inverted potential-energy surface. One may notice that, the so-obtained imaginary-time HK formula fails to produce the identity operator as time becomes zero, which corresponds to the infinite temperature limit. This intrinsic inconsistency is rooted in the nonexistence of the physical coherent state for some complex phase-space points from the classical evolution in the imaginary time. This issue, as we will address in the article, is the main obstacle for developing the imaginary-time semiclassical IVR. We will clarify and to some extent, how to get rid of the difficulty by using different representations. One may also develop a scheme using real momentum and position variables with the current method, as shown in section "Mixed position-momentum propagator in imaginary time" of this work. But then the accuracy will be a serious issue.

We organize the article as follows. In section "Correction operator approach for deriving semiclassical quantum propagators," we will show how to systematically develop the semiclassical IVR for the quantum propagator, following the reasoning of Kay. In section "Mixed position-momentum propagator in imaginary time," we will formally extend the result to the imaginary-time evolution for the Boltzmann operator, pointing out a caveat that a conceptual problem exists in such an extension. In section "Harmonic oscillator and parabolic barrier," we will show that the imaginary-time semiclassical IVR is exact for harmonic oscillators. In section "Nonlinear systems," we will also demonstrate that it gives good results for nonlinear systems, such as the double-well system and the Eckart potential.

Correction Operator Approach for Deriving Semiclassical Quantum Propagators

Propagator in the position-momentum representation

Miller first showed that the semiclassical evolution may be expressed in the mixed position-momentum (PM) integral representation.[7,8] The semiclassical propagator may also directly be derived with path integral, which is one of the earliest semiclassical IVR in the PM representation.[36,37] To demonstrate Kay's scheme, we first work out the PM-IVR in real time with correction operator method and then to acquire the imaginary-time version. Because Kay intended to give a proof of the semiclassical rigorousness of the Herman-Kluk IVR, he started from an integral coherent-state representation for the propagator. His procedure consists of two key steps. One is to use the correction operator method[20–22] to find an equivalent Schrödinger equation and the other is to make a semiclassical expansion for the Schrödinger equation. To derive the PM-IVR, we will start from a mixed position-momentum integral representation. Moreover, unlike Kay, we will not assume the *rules* or equations of motion for classical dynamics beforehand, instead, we will *derive* them according to the requirement that the correction operator should vanish for reproducing an exact quantum propagator. To be specific, let us consider an N-dimensional system described by the time-independent Hamiltonian $\hat{H}=\hat{\boldsymbol{p}}^T(2M)^{-1}\hat{\boldsymbol{p}}+V(\hat{\boldsymbol{q}})$ with M being the mass matrix. Suppose the quantum propagator $U(t)=e^{-i\hat{H}t/\hbar}$ assumes the following form in a mixed position-momentum integral representation,

$$U_{PM}(t)=\frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}R_t\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,|\,, \tag{1}$$

where the integration is over the "phase space" described by ($\boldsymbol{q}$, $\boldsymbol{p}$). Here, the scalar function R_t and the phase-space point ($\boldsymbol{q}_t$, $\boldsymbol{p}_t$) are the functions of time t and the starting point ($\boldsymbol{q}$, $\boldsymbol{p}$), which are yet to be determined. However, the position-momentum integral representation of eq. 1 involves the position eigenstate at time zero and the momentum eigenstate at time t. It is also required that $U_{PM}(t)$ satisfies the correct initial condition, that is, $U_{PM}(0)=I$. Now, we can define the correction operator $\hat{C}(t)\equiv i\hbar\partial U_{PM}/\partial t-\hat{H}U_{PM}$,[20] which measures the deviation of the quantum propagator $U_{PM}(t)$ from the exact one and can be used to find a systematic improvement when U_{PM} is an approximate one. Given the expression of $U_{PM}(t)$, $\hat{C}(t)$ now reads

$$\hat{C}(t)=\frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}R_t\left[i\hbar\frac{\dot{R}_t}{R_t}-\dot{\boldsymbol{p}}_t\cdot\hat{\boldsymbol{q}}-\frac{1}{2}\boldsymbol{p}_t^TM^{-1}\boldsymbol{p}_t-V(\hat{\boldsymbol{q}})\right]|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,|\,, \tag{2}$$

where in the derivation the relation

$$\frac{\partial}{\partial t}|\,\boldsymbol{p}_t\rangle=\frac{i}{\hbar}\dot{\boldsymbol{p}}_t\cdot\hat{\boldsymbol{q}}\,|\,\boldsymbol{p}_t\rangle$$

is used. Further, when the potential energy operator $V(\hat{\boldsymbol{q}})$ is expanded around the position $\boldsymbol{q}_t$ at time t and substituted into eq. 2, there yields

$$\hat{C}(t)=\frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}R_t\hat{F}_t\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,|\,, \tag{3}$$

where the operator $\hat{F}_t$ in the integrand is

$$\begin{aligned}\hat{F}_t=&i\hbar\frac{\dot{R}_t}{R_t}-\dot{\boldsymbol{p}}_t\cdot\hat{\boldsymbol{q}}-\frac{1}{2}\boldsymbol{p}_t^TM^{-1}\boldsymbol{p}_t-V(\boldsymbol{q}_t)-\nabla_{\boldsymbol{q}_t}V(\boldsymbol{q}_t)\cdot(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)\\&-\frac{1}{2}(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)^T\nabla_{\boldsymbol{q}_t}\nabla_{\boldsymbol{q}_t}^TV(\boldsymbol{q}_t)(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)-V_1(\hat{\boldsymbol{q}},\boldsymbol{q}_t)\end{aligned} \tag{4}$$

with $V_1(\hat{\boldsymbol{q}},\boldsymbol{q}_t)$ being the high-order contributions to $V(\hat{\boldsymbol{q}})$. To go further, we regard the operator $\hat{F}_t$ as a sum of the series of $\hat{\boldsymbol{q}}-\boldsymbol{q}_t$. Note that an exact propagator means a vanishing correction operation $\hat{C}$ and vice versa. To obtain an exact propagator, therefore, it is required that all coefficients of the powers of $\hat{\boldsymbol{q}}-\boldsymbol{q}_t$ in eq. 4 vanish. This seems to provide a straight way toward a systematic semiclassical approximation whenever the functions R_t, $\boldsymbol{q}_t$ and $\boldsymbol{p}_t$ are known. Leaving aside the zero-order term for the moment, we first consider the linear term in $\hat{\boldsymbol{q}}-\boldsymbol{q}_t$. As its coefficient becomes 0, there is

$$\dot{\boldsymbol{p}}_t=-\nabla_{\boldsymbol{q}_t}V(\boldsymbol{q}_t), \tag{5}$$

which gives one of the equations of motion for the phase-space point ($\boldsymbol{q}_t$, $\boldsymbol{p}_t$). Of course, one needs the other independent

equation to fully determine the "classical evolution." Although it cannot be provided by the vanishing first-order term and may take different forms, a simple and convenient choice is

$$\dot{\boldsymbol{q}}_t = M^{-1}\dot{\boldsymbol{p}}_t. \tag{6}$$

We thus obtain the traditional classical dynamics ($\boldsymbol{q}_t$, $\boldsymbol{p}_t$) described by the Hamilton's equation. It should be pointed out that if one starts from the coherent state representation in eq. 2 as in the derivation of the Herman-Kluk propagator by Kay, then one may naturally obtain the Hamilton's equation from the requirement that the coefficients of $\hat{\boldsymbol{q}}-\boldsymbol{q}_t$ in the correction operator $\hat{C}(t)$ vanish. This observation will also be clarified when we analyze the position-coherent-state semiclassical propagator[12,13,38] in the next section. We now consider to find the expressions of powers of $\hat{\boldsymbol{q}}-\boldsymbol{q}_t$ acting on the "basis" $|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|$, which can conveniently be dealt with later. To this end, we use the relation

$$\nabla_{\boldsymbol{p}}\langle\boldsymbol{q}|\boldsymbol{p}_t\rangle = \frac{i}{\hbar}\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\boldsymbol{q}\langle\boldsymbol{q}|\boldsymbol{p}_t\rangle$$

to establish the following one

$$\nabla_{\boldsymbol{p}}\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,| = \frac{i}{\hbar}\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\hat{\boldsymbol{q}}\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,|,$$

or

$$\hat{\boldsymbol{q}}\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,| = -i\hbar\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)^{-1}\nabla_{\boldsymbol{p}}\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,|,$$

which can be viewed as the expression of the position operator in the mixed position-momentum representation. With this result, we introduce the classical action S_t and define $A_t \equiv S_t - \boldsymbol{q}_t\cdot\boldsymbol{p}_t$ to obtain

$$(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,| = -i\hbar\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)^{-1}e^{-\frac{i}{\hbar}A_t}\nabla_{\boldsymbol{p}}\left[e^{\frac{i}{\hbar}A_t}|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|\right]. \tag{7}$$

Therefore, the operator $(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)$ acting on $|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|$ can be replaced by an alternative displayed above. This result shows that the operation of powers of $(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)$ on the basis $|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|$ brings about contributions of high orders in $\hbar$, which may be a suitable starting point for a systematic perturbation treatment. For instance, the second-order term reads

$$\begin{aligned}&(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)^T\nabla_{\boldsymbol{q}_t}\nabla_{\boldsymbol{q}_t}^T V(\boldsymbol{q}_t)(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,|\\ &= -i\hbar e^{-\frac{i}{\hbar}A_t}\mathrm{Tr}\left\{\nabla_{\boldsymbol{q}_t}\nabla_{\boldsymbol{q}_t}^T V(\boldsymbol{q}_t)\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)^{-1}\nabla_{\boldsymbol{p}}\boldsymbol{q}_t^T\right\}\left[e^{\frac{i}{\hbar}A_t}|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|\right]\\ &-\hbar^2 e^{-\frac{i}{\hbar}A_t}\mathrm{Tr}\left\{\nabla_{\boldsymbol{q}_t}\nabla_{\boldsymbol{q}_t}^T V(\boldsymbol{q}_t)\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)^{-1}\nabla_{\boldsymbol{p}}\left[e^{-\frac{i}{\hbar}A_t}\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)^{-1}\nabla_{\boldsymbol{p}}\right]^T\right\}\\ &\left[e^{\frac{i}{\hbar}A_t}|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|\right].\end{aligned} \tag{8}$$

Upon substituting all the results for powers of $(\hat{\boldsymbol{q}}-\boldsymbol{q}_t)$ into eq. 3, the correction operator assumes the following form

$$\hat{C}(t) = \frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}e^{-\frac{i}{\hbar}A_t}R_tG_t\left(\nabla_{\boldsymbol{p}}\right)\left[e^{\frac{i}{\hbar}A_t}|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|\right], \tag{9}$$

where the operator function G_t is a sum of a series of the gradient operator $\nabla_{\boldsymbol{p}}$ and other given functions, whose explicit expression can in principle be worked out by repeated use of eq. 7. Then, we take integration by parts for eq. 9 and assume that $|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|$ vanish at the infinite boundaries to obtain

$$\hat{C}(t) = \frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}e^{-\frac{i}{\hbar}A_t}R_tG_t\left(-\overleftarrow{\nabla}_{\boldsymbol{p}}\right)\left[e^{\frac{i}{\hbar}A_t}|\boldsymbol{p}_t\rangle\langle\boldsymbol{q}|\right], \tag{10}$$

where $\overleftarrow{\nabla}_{\boldsymbol{p}}$ denotes the gradient operation on the function to the left. For an exact quantum propagator, there must be $\hat{C}(t)=0$, which means a vanishing integrand in eq. 10 and further results in

$$G_t\left(-\nabla_{\boldsymbol{p}}\right)R_te^{-\frac{i}{\hbar}A_t} = 0. \tag{11}$$

This is an alternative Schrödinger equation for the quantum propagator based on the mixed position-momentum integral representation, defined by eq. 2. We would like to stress again that we may explicitly obtain the operator $G_t(-\nabla_{\boldsymbol{p}})$ and then make a rigorous semiclassical treatment for eq. 11 as Kay did. But here for simplicity, we only consider the operator G_t containing terms up to the first-order in $\hbar$. Then eq. 11 becomes

$$\left\{i\hbar\frac{\dot{R}_t}{R_t} + \dot{A}_t + \frac{1}{2}i\hbar\mathrm{Tr}\left[\nabla_{\boldsymbol{q}_t}\nabla_{\boldsymbol{q}_t}^T V(\boldsymbol{q}_t)\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)^{-1}\nabla_{\boldsymbol{p}}\boldsymbol{q}_t^T\right]\right\}R_te^{-\frac{i}{\hbar}A_t} = 0. \tag{12}$$

Suppose $R_t = e^{\frac{i}{\hbar}A_t}\widetilde{R}_t$. Inserting into eq. 12, we readily obtain the equation for $\widetilde{R}_t$,

$$\begin{aligned}\frac{1}{\widetilde{R}_t}\frac{\partial}{\partial t}\widetilde{R}_t &= -\frac{1}{2}\mathrm{Tr}\left[\nabla_{\boldsymbol{q}_t}\nabla_{\boldsymbol{q}_t}^T V(\boldsymbol{q}_t)\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)^{-1}\nabla_{\boldsymbol{p}}\boldsymbol{q}_t^T\right]\\ &= \frac{1}{2}\frac{d}{dt}\mathrm{Tr}\ln\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right).\end{aligned} \tag{13}$$

With the initial condition $R_0 = \exp(-i\boldsymbol{q}\cdot\boldsymbol{p}/\hbar)[\widetilde{R}_0 = 1]$, eq. 13 gives

$$\widetilde{R}_t = \left[\det\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)\right]^{1/2}.$$

However, the equation of motion method can be used to calculate the stability matrix elements in R_t,

$$\nabla_{\boldsymbol{p}}\dot{\boldsymbol{q}}_t = M^{-1}\nabla_{\boldsymbol{p}}\boldsymbol{p}_t, \tag{14}$$

$$\nabla_{\boldsymbol{p}}\dot{\boldsymbol{p}}_t = -\nabla_{\boldsymbol{p}_t}\nabla_{\boldsymbol{p}_t}^T V(\boldsymbol{q}_t)\nabla_{\boldsymbol{p}}\boldsymbol{q}_t \tag{15}$$

with the initial condition $\nabla_{\boldsymbol{p}}\boldsymbol{q}_0 = 0$ and $\nabla_{\boldsymbol{p}}\boldsymbol{p}_0 = I$. Substituting R_t into eq. 1, we finally obtain the semiclassical position-momentum propagator,

$$U_{PM}(t) = \frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}\left[\det\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_t^T\right)\right]^{1/2}e^{\frac{i}{\hbar}(S_t-\boldsymbol{q}_t\cdot\boldsymbol{p}_t)}\,|\,\boldsymbol{p}_t\rangle\langle\boldsymbol{q}\,|. \tag{16}$$

With the same procedure we can also find a similar semiclassical propagator based on the momentum (at time 0) -position (at time t) integral representation, namely,

$$U_{PM,1}(t)=\frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}\left[\det\left(\nabla_{\boldsymbol{q}_t}\boldsymbol{q}_t^T\right)\right]^{1/2}e^{\frac{i}{\hbar}(S_t+\boldsymbol{q}_t\cdot\boldsymbol{p}_t)}\,|\,\boldsymbol{q}_t\rangle\langle\boldsymbol{p}\,|\,. \tag{17}$$

Mixed position-coherent-state semiclassical propagator

Before turning to the semiclassical approximation in the imaginary time, we will discuss the issue of the classical dynamics in the semiclassical propagator in a mixed position-coherent-state representation.[12,13,38] We now consider the quantum propagator in the position-coherent-state representation, that is

$$U_{AF}(t)=\frac{1}{(2\pi\hbar)^{N}}(\pi\hbar)^{N/4}(\det\Gamma)^{-1/4}\int d\boldsymbol{q}d\boldsymbol{p}R_t\,|\,g(\boldsymbol{q}_t,\boldsymbol{p}_t)\rangle\langle\boldsymbol{q}\,|\,, \tag{18}$$

where the wave function of the coherent-state is defined by

$$\langle\boldsymbol{x}|g(\boldsymbol{q},\boldsymbol{p})\rangle=\frac{1}{(\pi\hbar)^{N/4}}(\det\Gamma)^{1/4}e^{-\frac{1}{2\hbar}(\boldsymbol{x}-\boldsymbol{q})^T\Gamma(\boldsymbol{x}-\boldsymbol{q})+\frac{i}{\hbar}\boldsymbol{p}\cdot(\boldsymbol{x}-\boldsymbol{q})}$$

with Γ being the positive, diagonal Gaussian width matrix. With this expression we can, of course, utilize Kay's scheme to find a semiclassical expression of R_t. Here we will not repeat the whole procedure, but only focus on how to derive the classical dynamics in the approximation which was presumably chosen as the traditional one in Kay's work. As described above, we first find the expression for the correction operator $\hat{C}(t)\equiv i\hbar\partial U_{AF}/\partial t-\hat{H}U_{AF}$ and then expand the potential energy operator $V(\hat{\boldsymbol{q}})$ around $\boldsymbol{q}_t$. As explained in the previous section for the PM semiclassical propagator, it is required that the first-order contribution of $\hat{\boldsymbol{q}}-\boldsymbol{q}_t$ in the integrand of the correction operator is 0. Then, we obtain

$$i\Gamma\dot{\boldsymbol{q}}_t-\dot{\boldsymbol{p}}_t-i\Gamma M^{-1}\boldsymbol{p}_t-\nabla_{\boldsymbol{q}_t}V(\boldsymbol{q}_t)=0. \tag{19}$$

If we assume that the position $\boldsymbol{q}_t$ and momentum $\boldsymbol{p}_t$ are real, then eq. 19 immediately results in the Hamilton's equation represented by eqs. 5 and 6. In this case one obtains

$$R_t=\left\{\det\left[\nabla_{\boldsymbol{p}}\left(\boldsymbol{p}_t^T-i\Gamma\boldsymbol{q}_t^T\right)\right]\right\}^{1/2}e^{\frac{i}{\hbar}S_t}, \tag{20}$$

which leads to the semiclassical position-coherent-state propagator. If, however, we do not impose the real domain on $\boldsymbol{q}_t$ and $\boldsymbol{p}_t$, one may obtain different approximate propagators. Because the semiclassical IVR for the imaginary, as well as the complex-time evolution will be our focus, we will not explore this interesting issue in the article, although it does deserve a further investigation.

Mixed Position-Momentum Propagator in Imaginary Time

We have so far explained how to systematically derive semiclassical IVR series for the quantum propagator, following the derivation of HK approximation by Kay. Although the higher order contributions are not shown and analyzed here, they can in principle be obtained. No matter how accurate these semiclassical IVRs are, they are appealing in the sense that the involved classical dynamics is genuine Newtonian. Now we may wonder whether the semiclassical IVR is also valid by making a change of variables $t=-i\hbar\beta$ for the imaginary time propagator or the Boltzmann operator (Here, $\beta=1/k_BT$ is the inverse temperature with k_B being the Boltzmann constant). It seems that the imaginary time result comes out naturally whenever the time t is replaced by $-i\hbar\beta$ in the expression of the semiclassical IVR. But doing so results in a classical evolution with complex trajectories. To see this point clearly, we formally apply the procedure in the previous section to the Boltzmann operator.

The Boltzmann operator $\rho(\beta)=e^{-\beta\hat{H}}$ may be viewed as a quantum system $\hat{H}$ evolving in the imaginary time $t=-i\hbar\beta$. The analogue of $\rho(\beta)$ to eq. 1 is

$$\rho_{PM}(\beta)=\frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}R_\beta\,|\,\boldsymbol{p}_\beta\rangle\langle\boldsymbol{q}\,|\,. \tag{21}$$

The Boltzmann operator obeys the Bloch equation, that is, $\partial\rho/\partial\beta=-\hat{H}\rho$. The corresponding correction operator $\hat{C}(\beta)=\partial\rho_{PM}/\partial\beta+\hat{H}\rho_{PM}$ then reads

$$\hat{C}(\beta)=\frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{q}d\boldsymbol{p}R_\beta\left[\frac{\dot{R}_\beta}{R_\beta}+\frac{i}{\hbar}\dot{\boldsymbol{p}}_\beta\cdot\hat{\boldsymbol{q}}+\frac{1}{2}\boldsymbol{p}_\beta^TM^{-1}\boldsymbol{p}_\beta+V(\hat{\boldsymbol{q}})\right]\,|\,\boldsymbol{p}_\beta\rangle\langle\boldsymbol{q}\,|\,. \tag{22}$$

From here, the dot sign $\dot{}$ denotes the derivative with respect to the imaginary time β. The correction operator has been used to develop a frozen Gaussian evolution for the Boltzmann operator.[39] Although the thermal frozen Gaussian evolution can be regarded as an imaginary time IVR, it is not obtained from a direct extension of the real-time counterpart and a unified IVR for both the real and imaginary time is not studied. Here, we adopt a method that may deal with the real and imaginary time on the same footing, which can hopefully lead to a more consistent unified semiclassical approximation with high accuracy. To the correction operator given by eq. 22, we can repeat what we did above for the real time evolution, the result for the imaginary time evolution may have different physical interpretation. For instance, the derived "classical" equation under the requirement of vanishing linear term of $\hat{\boldsymbol{q}}-\boldsymbol{q}_\beta$ in the integrand of the correction operator is

$$\dot{\boldsymbol{p}}_\beta=i\hbar\nabla_{\boldsymbol{q}_\beta}V(\boldsymbol{q}_\beta). \tag{23}$$

It is no longer the Hamilton's equation with a real potential energy. However, if we introduce a complex Hamiltonian $\widetilde{H}=-i\hbar H$, then we may formally reobtain one of the conventional Hamilton's equations,

$$\dot{\boldsymbol{p}}_\beta=-\nabla_{\boldsymbol{q}}\widetilde{H}. \tag{24}$$

In this case, the counterpart of eq. 6 may be chosen as

$$\dot{\boldsymbol{q}}_\beta = -i\hbar M^{-1}\boldsymbol{p}_\beta = \nabla_{\boldsymbol{p}}\widetilde{H}. \tag{25}$$

As a consequence, the action S_β becomes

$$\begin{aligned} S_\beta &= \int_0^{-i\hbar\beta} dt' \left[\frac{1}{2}\dot{\boldsymbol{q}}_{t'}^T M \dot{\boldsymbol{q}}_{t'} - V(\boldsymbol{q}_{t'})\right] \\ &= i\hbar\int_0^{\beta} d\tau \left[\frac{1}{2\hbar^2}\dot{\boldsymbol{q}}_\tau^T M \dot{\boldsymbol{q}}_\tau + V(\boldsymbol{q}_\tau)\right] \\ &= -i\hbar\int_0^{\beta} d\tau \left[\frac{1}{2}\boldsymbol{p}_\tau^T M^{-1}\boldsymbol{p}_\tau - V(\boldsymbol{q}_\tau)\right]. \end{aligned} \tag{26}$$

Now it becomes clear that as time changes from the real to the imaginary, the involved "classical" dynamics extends from the real to the complex space. Here we should stress that this result is a formal consequence of the starting ansatz eq. 21 and its validity is a subtle issue. Before proceeding, we also like to point out that if we begin with the position-coherent-state semiclassical propagator or the HK propagator, the corresponding eq. 19 that determines the equations of classical motion will, upon setting $t = -i\hbar\beta$, become

$$-\frac{\Gamma}{\hbar}\dot{\boldsymbol{q}}_\beta - \frac{i}{\hbar}\dot{\boldsymbol{p}}_\beta - i\Gamma M^{-1}\boldsymbol{p}_\beta - \nabla_{\boldsymbol{q}_\beta}V(\boldsymbol{q}_\beta) = 0. \tag{27}$$

When real trajectories are required, we readily obtain $\dot{\boldsymbol{q}}_\beta = -\hbar\Gamma^{-1}\nabla_{\boldsymbol{q}_\beta}V(\boldsymbol{q}_\beta)$ and $\dot{\boldsymbol{p}}_\beta = -\hbar\Gamma M^{-1}\boldsymbol{p}_\beta$, that is, the position and momentum evolve independently. However, the equation of the motion for the position is similar to that discussed in the method of thermal Gaussian evolution.[32] Moreover, the momentum assumes an analytic solution, $\boldsymbol{p}_\beta = e^{-\hbar\Gamma M^{-1}\beta}\boldsymbol{p}$. We can go further to have the Bloch equation in the coherent-state-position representation, as explained before for the real time propagator. Unlike the corresponding Schrödinger equation, however, the so obtained Bloch equation denies a straight semiclassical expansion (with $\hbar$ being the small parameter). Conversely, we could not find a position-coherent-state IVR approximation with real dynamics for the Boltzmann operator.

Return to the PM-IVR. A complex trajectory, of course, is not physically appealing. But it can fortunately be transformed into a pair of real trajectories.[40,41] To this end, we decompose the complex Hamiltonian $\widetilde{H}$ and the trajectories ($\boldsymbol{q}_\beta$, $\boldsymbol{p}_\beta$) into real and imaginary parts in such a way that $\widetilde{H} = H_1 + iH_2$, $\boldsymbol{q} = \boldsymbol{q}_1 + i\boldsymbol{p}_2$, and $\boldsymbol{p} = \boldsymbol{p}_1 + i\boldsymbol{q}_2$. It is straightforward to transform a general Hamiltonian $H = \boldsymbol{p}^T(2M)^{-1}\boldsymbol{p} + V(\boldsymbol{q})$ to the complex one $-i\hbar H$ and to obtain $H_1 = \hbar\boldsymbol{p}_1^T M^{-1}\boldsymbol{q}_2 + \hbar\Im(V(\boldsymbol{q}_1 + i\boldsymbol{p}_2))$. According to the Hamilton's equations and the Cauchy-Riemann condition, we readily derive two pairs of new Hamilton's equations,

$$\dot{\boldsymbol{q}}_{1(2)} = \nabla_{\boldsymbol{p}_{1(2)}}\widetilde{H}_1, \tag{28}$$

$$\dot{\boldsymbol{p}}_{1(2)} = -\nabla_{\boldsymbol{q}_{1(2)}}\widetilde{H}_1, \tag{29}$$

where only the real (or imaginary) part of the complex Hamiltonian is needed. The stability matrix can be calculated similarly. With the complex Hamiltonian a formal development for the semiclassical approximation is straightforward and parallel to what we have done for the real time $U_{PM}(t)$, which yields the thermal density matrix

$$\langle \boldsymbol{x}'|\rho_{PM}(\beta)|\boldsymbol{x}\rangle = \frac{1}{(2\pi\hbar)^{N/2}}\int d\boldsymbol{p}\left[\det\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_\beta^T\right)\right]^{1/2} e^{\frac{i}{\hbar}\left[S_\beta + (\boldsymbol{x}' - \boldsymbol{x}_\beta)\cdot\boldsymbol{p}_\beta\right]}. \tag{30}$$

Note that the classical evolution starts from real variables $\boldsymbol{x}$ and $\boldsymbol{p}$. Consequently, the integration in eq. 30 is carried out over the real axis. However, the variables $\boldsymbol{x}_\beta$ and $\boldsymbol{p}_\beta$ become complex for finite temperatures. This may cause a convergence problem in numerical implementation because of the oscillatory integrand. To reduce the difficulty, we can use hermicity of the Boltzmann operator $e^{-\beta\hat{H}}$ to have a symmetric version of eq. 30, namely

$$\begin{aligned} \langle \boldsymbol{x}'|\rho_{PM}(\beta)|\boldsymbol{x}\rangle &= \int d\boldsymbol{q}\langle \boldsymbol{x}'|\rho_{PM}(\beta/2)|\boldsymbol{q}\rangle\langle \boldsymbol{q}|\rho_{PM}^\dagger(\beta/2)|\boldsymbol{x}\rangle \\ &= \frac{1}{(2\pi\hbar)^N}\int d\boldsymbol{q}d\boldsymbol{p}d\overline{\boldsymbol{p}}\left[\det\left(\nabla_{\boldsymbol{p}}\boldsymbol{p}_{\beta/2}^T\right)\right]^{1/2}\left[\det\left(\nabla_{\overline{\boldsymbol{p}}}\overline{\boldsymbol{p}}_{\beta/2}^T\right)^*\right]^{1/2} \\ &\quad e^{\frac{i}{\hbar}\left[S_{\beta/2} - \overline{S}_{\beta/2}^* + (\boldsymbol{x}' - \boldsymbol{q}_{\beta/2})\cdot\boldsymbol{p}_{\beta/2} - (\boldsymbol{x} - \overline{\boldsymbol{q}}_{\beta/2})\cdot\overline{\boldsymbol{p}}_{\beta/2}\right]}. \end{aligned} \tag{31}$$

Here, a pair of trajectories starting from ($\boldsymbol{q}$, $\boldsymbol{p}$) and ($\overline{\boldsymbol{q}}$,$\overline{\boldsymbol{p}}$), respectively, are launched and they evolve for a duration of $\beta/2$, ending at ($\boldsymbol{q}_{\beta/2}$, $\boldsymbol{p}_{\beta/2}$) and ($\overline{\boldsymbol{q}}_{\beta/2}$,$\overline{\boldsymbol{p}}_{\beta/2}$) with actions $S_{\beta/2}$ and $\overline{S}_{\beta/2}$. Compared to eq. 30, eq. 31 entails an integration in triple dimensions.

We would like to point out a caveat in the PM-IVR approximation eq. 21 of the Boltzmann operator in which $|\boldsymbol{p}_\beta\rangle$ is implicitly assumed to be the eigenstate of the momentum operator. This assumption may be questionable and needs to be further scrutinized when $\boldsymbol{p}_\beta$ is complex. In Ref. [42], Zhao and Miller suggested a semiclassical position representation for the Boltzmann operator where the equation of motion is eqs. 23 and 25, but with a pure imaginary momentum variable $\boldsymbol{q}_\beta$. Although the position variable $\boldsymbol{q}_\beta$ is real in their scheme and it is free from the conceptual problem to regard $|\boldsymbol{q}_\beta\rangle$ as the eigenstate of the position operator, the integration with respect to $\boldsymbol{p}$ is performed over the imaginary axis and one may notice that the semiclassical approximation fails to produce the exact Boltzmann operator for the quantum harmonic oscillator.

Now, we show that the PM density operator leads to the classical Boltzmann distribution in the limit $\hbar \to 0$. To this end, we should transform the PM operator into the Wigner function that may be viewed as a quasi-distribution in quantum phase space and demonstrate the latter gives the classical Boltzmann distribution as $\hbar \to 0$. Although eq. 30 is equally eligible, here eq. 31 is used to evaluate the Wigner distribution function of the Boltzmann operator ρ, which is defined by

$$\rho_W(\boldsymbol{q}_c, \boldsymbol{p}_c) \equiv \frac{1}{(2\pi\hbar)^N}\int d\boldsymbol{r}e^{\frac{i}{\hbar}\boldsymbol{r}\cdot\boldsymbol{p}_c}\left\langle \boldsymbol{q}_c - \frac{\boldsymbol{r}}{2}|\,\rho|\boldsymbol{q}_c + \frac{\boldsymbol{r}}{2}\right\rangle. \tag{32}$$

Replacing ρ by ρ_{PM}, we may obtain the PM approximation for the Wigner distribution, namely

$$\rho_{W,PM}(\boldsymbol{q}_c,\boldsymbol{p}_c) \equiv \frac{1}{(2\pi\hbar)^N}\int d\boldsymbol{r}d\boldsymbol{q}e^{\frac{i}{\hbar}\boldsymbol{r}\cdot\boldsymbol{p}_c}\left\langle \boldsymbol{q}_c-\frac{\boldsymbol{r}}{2}\right| \rho_{PM}(\beta/2)|\boldsymbol{q}\rangle\left\langle \boldsymbol{q}\right| \rho^{\dagger}_{PM}(\beta/2)|\boldsymbol{q}_c+\frac{\boldsymbol{r}}{2}\rangle. \quad (33)$$

In the classical limit ($\hbar \to 0$), we readily work out the trajectory and the action associated with the initial point ($\boldsymbol{q}$, $\boldsymbol{p}$), keeping up to the first order in $\hbar$,

$$\boldsymbol{q}_{\beta/2} = \boldsymbol{q} - \frac{i}{2}\beta\hbar M^{-1}\boldsymbol{p},$$

$$\boldsymbol{p}_{\beta/2} = \boldsymbol{p} + \frac{i}{2}\beta\hbar\nabla_{\boldsymbol{q}}V(\boldsymbol{q}),$$

and

$$S_{\beta/2} = -\frac{i}{2}\beta\hbar\left[\frac{1}{2}\boldsymbol{p}^T M^{-1}\boldsymbol{p} - V(\boldsymbol{q})\right],$$

and that with the initial point ($\overline{\boldsymbol{q}}$,$\overline{\boldsymbol{p}}$). These relations and a straightforward algebra allow us to obtain the following results

$$\nabla_{\boldsymbol{p}}\boldsymbol{p}^T_{\beta/2} \approx I,$$

$$\nabla_{\overline{\boldsymbol{p}}}\overline{\boldsymbol{p}}^T_{\beta/2} \approx I$$

and

$$\begin{aligned} S_{\beta/2} - \overline{S}^*_{\beta/2} + \left(\boldsymbol{q}_c - \frac{\boldsymbol{r}}{2} - \boldsymbol{q}_{\beta/2}\right)\cdot\boldsymbol{p}_{\beta/2} - \left(\boldsymbol{q}_c + \frac{\boldsymbol{r}}{2} - \overline{\boldsymbol{q}}_{\beta/2}\right)\cdot\overline{\boldsymbol{p}}_{\beta/2} \\ = \frac{i}{2}\beta\hbar\left(\boldsymbol{p}^T M^{-1}\boldsymbol{p} + \overline{\boldsymbol{p}}^T M^{-1}\overline{\boldsymbol{p}}\right) + i\beta\hbar V(\boldsymbol{q}) + (\boldsymbol{q}_c - \boldsymbol{q}) \\ \cdot\left[\boldsymbol{p} - \overline{\boldsymbol{p}} + i\beta\hbar\nabla_{\boldsymbol{q}}V(\boldsymbol{q})\right] - \frac{\boldsymbol{r}}{2}(\boldsymbol{p} + \overline{\boldsymbol{p}}). \end{aligned}$$

Inserting into the PM approximation eq. 31 and substituting the result into eq. 33, we obtain

$$\begin{aligned} \rho_{W,PM}(\boldsymbol{q}_c,\boldsymbol{p}_c) = \frac{1}{(2\pi\hbar)^{2N}}\int d\boldsymbol{q}d\boldsymbol{p}d\overline{\boldsymbol{p}}\delta \\ [\boldsymbol{p}_c - (\boldsymbol{p}+\overline{\boldsymbol{p}})/2]e^{\frac{i}{\hbar}(\boldsymbol{q}_c-\boldsymbol{q})\cdot}\left[\boldsymbol{p} - \overline{\boldsymbol{p}} + i\beta\hbar\nabla_{\boldsymbol{q}}V(\boldsymbol{q})\right] \\ e^{-\frac{1}{4}\beta\left(\boldsymbol{p}^T M^{-1}\boldsymbol{p} + \overline{\boldsymbol{p}}^T M^{-1}\overline{\boldsymbol{p}}\right) - \beta V(\boldsymbol{q})} \end{aligned} \quad (34)$$

after finishing the integration over $\boldsymbol{r}$. The remaining integration can be completed by making of change of variables such as $\widetilde{\boldsymbol{p}}_1 = (\boldsymbol{p}+\overline{\boldsymbol{p}})/2$ and $\widetilde{\boldsymbol{p}}_2 = (\boldsymbol{p}-\overline{\boldsymbol{p}})/2$, and the classical result ($\hbar \to 0$) is

$$\rho_{W,PM}(\boldsymbol{q}_c,\boldsymbol{p}_c) = e^{-\frac{1}{2}\beta\boldsymbol{p}_c^T M^{-1}\boldsymbol{p}_c - \beta V(\boldsymbol{q}_c)} = e^{-\beta H(\boldsymbol{q}_c,\boldsymbol{p}_c)}, \quad (35)$$

which is the classical Boltzmann distribution except for the unconsidered normalization constant.

Harmonic Oscillator and Parabolic Barrier

We use the semiclassical imaginary-time propagator eq. 30 to calculate the Boltzmann operator of the harmonic oscillator defined by $\hat{H} = \hat{p}^2/(2m) + m\omega^2\hat{q}^2/2$. In this case, one readily obtains $H_1 = \hbar q_2 p_1/m + \hbar m\omega^2 q_1 p_2$. As a consequence, the equations of motion read

$$\dot{q}_1 = \hbar\frac{q_2}{m}, \quad \dot{q}_2 = \hbar m\omega^2 q_1,$$

$$\dot{p}_1 = -\hbar m\omega^2 p_2, \quad \dot{p}_2 = -\hbar\frac{p_1}{m},$$

with the initial condition $q_1 = x$, $p_1 = p$, and $q_2 = p_2 = 0$. There linear differential equations assume the following analytic solutions

$$q_{1,\beta} = x\cosh(\hbar\omega\beta), \quad q_{2,\beta} = m\omega x\sinh(\hbar\omega\beta),$$

$$p_{1,\beta} = p\cosh(\hbar\omega\beta), \quad p_{2,\beta} = -p\frac{\sinh(\hbar\omega\beta)}{m\omega},$$

and the corresponding action S_β is

$$S_\beta = \frac{i}{4m\omega}\sinh(2\hbar\omega\beta)\left(m^2\omega^2x^2 - p^2\right) + xp\sinh^2(\hbar\omega\beta).$$

Inserting these results into eq. 30 and noticing that $q_\beta = q_{1,\beta} + ip_{2,\beta}$ and $p_\beta = p_{1,\beta} + iq_{2,\beta}$, we readily carry out the integration and obtain

$$\langle x'|\rho_{PM}(\beta)|x\rangle = \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\hbar\omega\beta)}} \exp\left\{-\frac{m\omega}{2\hbar\sinh(\hbar\omega\beta)}\left[\left(x^2+x'^2\right)\cosh(\hbar\omega\beta) - 2xx'\right]\right\}, \quad (36)$$

which is exact.

For the parabolic barrier described by $\hat{H} = \hat{p}^2/(2m) - m\omega^2\hat{q}^2/2$, the corresponding trajectory and the action can be calculated similarly,

$$q_{1,\beta} = x\cos(\hbar\omega\beta), \quad q_{2,\beta} = -m\omega x\sin(\hbar\omega\beta),$$

$$p_{1,\beta} = p\cos(\hbar\omega\beta), \quad p_{2,\beta} = -p\frac{\sin(\hbar\omega\beta)}{m\omega},$$

and

$$S_\beta = -\frac{i}{4m\omega}\sin(2\hbar\omega\beta)\left(m^2\omega^2x^2 + p^2\right) - xp\sin^2(\hbar\omega\beta).$$

As these expressions are inserted into eq. 30, we find that only if $2\hbar\omega\beta < \pi$ or $\beta < \pi/(2\hbar\omega)$, the integrand (of variable p) is bounded, which gives a finite result for the integral over p,

$$\langle x'|\rho_{PM}(\beta)|x\rangle = \sqrt{\frac{m\omega}{2\pi\hbar\sin(\hbar\omega\beta)}} \exp\left\{-\frac{m\omega}{2\hbar\sin(\hbar\omega\beta)}\left[\left(x^2+x'^2\right)\cos(\hbar\omega\beta) - 2xx'\right]\right\}. \quad (37)$$

When $\beta > \pi/(2\hbar\omega)$, however, the integrand on the right-hand side of eq. 30 is unbounded and the integral is divergent. This means that the expression is no longer valid. To obtain the

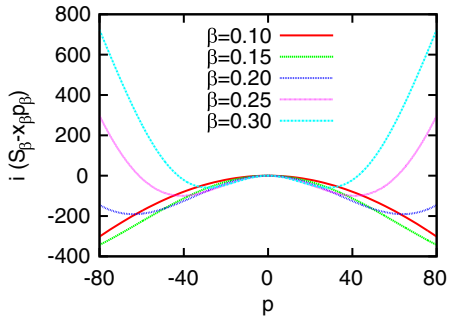

Figure 1. The regulated action $i(S_\beta - x_\beta\, p_\beta)$ as a function of the initial momentum p for calculating the matrix element $\langle 0|\, \rho_{PM}(\beta)|\, 0\rangle$ at different temperatures. The potential is $x^2(1 + x^2/8)/2$ and all quantities are in arbitrary unit. [Color figure can be viewed at wileyonlinelibrary.com]

correct result in this case, we may resort to the Trotter expansion[43] to divide β into K pieces such that $\overline{\beta} \equiv \beta/K < \pi/(2\hbar\omega)$ and for each imaginary time $\overline{\beta}$, we can apply eq. 37.

Nonlinear Systems

To check the applicability of the semiclassical imaginary-time propagator for nonlinear systems, we first investigate the one-dimensional systems with the potential

$$V(q) = -\frac{\lambda}{2}q^2\left(1 - \frac{\lambda q^2}{8}\right), \tag{38}$$

where λ is a parameter indicating a double-well system ($\lambda = 1$) or a single-well one ($\lambda = -1$).

For nonlinear systems, an analytic examination as we show for the harmonic and parabolic potentials will be difficult and tedious even if not impossible. Thus, we adopt an analysis for the applicability of the method based on numerical solutions for eqs. 26, 28, and 29. The simulations are done with a unit mass $m = 1$. Further, the Planck constant $\hbar$ is set to unit. We first check the momentum dependence of the exponential factor in the integrand of eq. 30,

$$W_{\beta,x,x'}(p) = i\left[S_\beta + \left(x' - x_\beta\right)\cdot p_\beta\right] \tag{39}$$

which is essentially the regulated action determining the convergence of the integration. Interestingly, the regulated action $W_{\beta,0,0}(p)$ is real for systems with potential eq. 38. Figure 1 depicts these quantities in the calculation of the matrix element $\langle 0|\, \rho_{PM}(\beta)|\, 0\rangle$ at different temperatures for the single-well potential in eq. 38 with $\lambda = -1$. We observe that the regulated action as a function of the initial momentum may be well-approximated with a quadratic form at a temperature as high

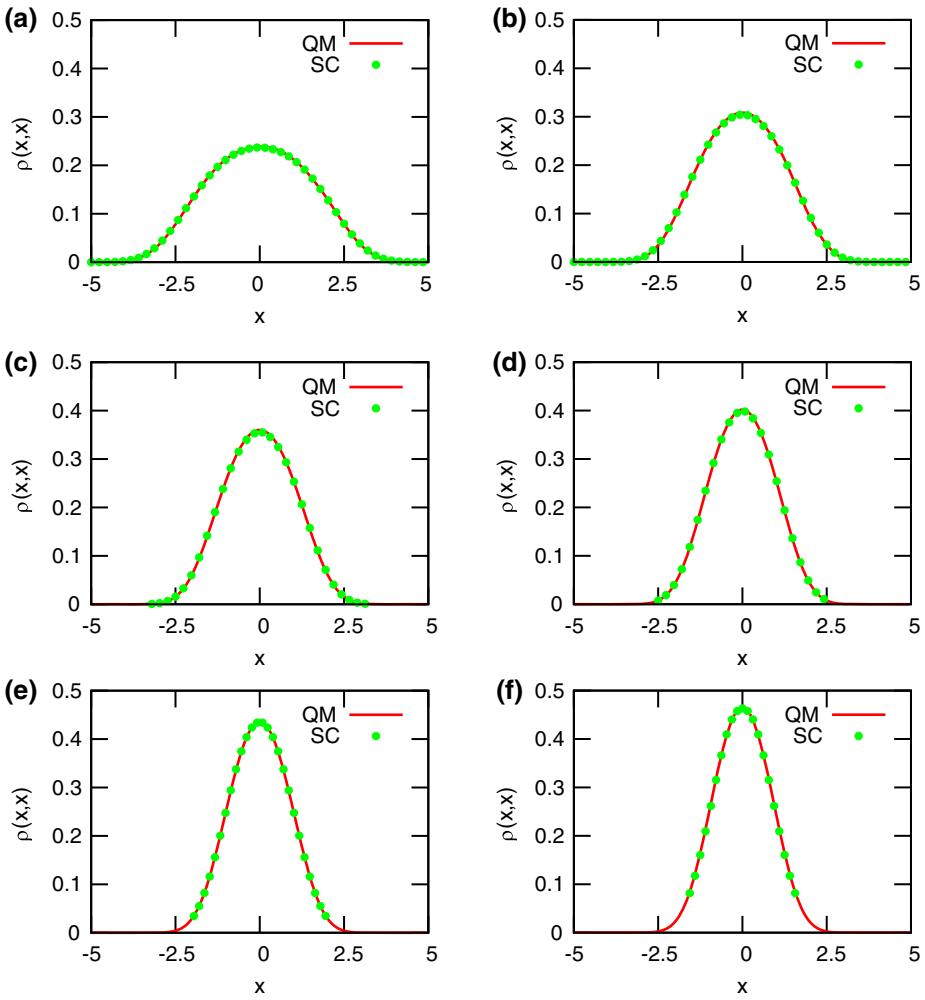

Figure 2. The principal-diagonal matrix elements of the density operator for the potential $V(x) = x^2(1 + x^2/8)/2$ at different temperatures. From panel (a) to (f), β changes from 0.2 to 1.2 in step of 0.2. [Color figure can be viewed at wileyonlinelibrary.com]

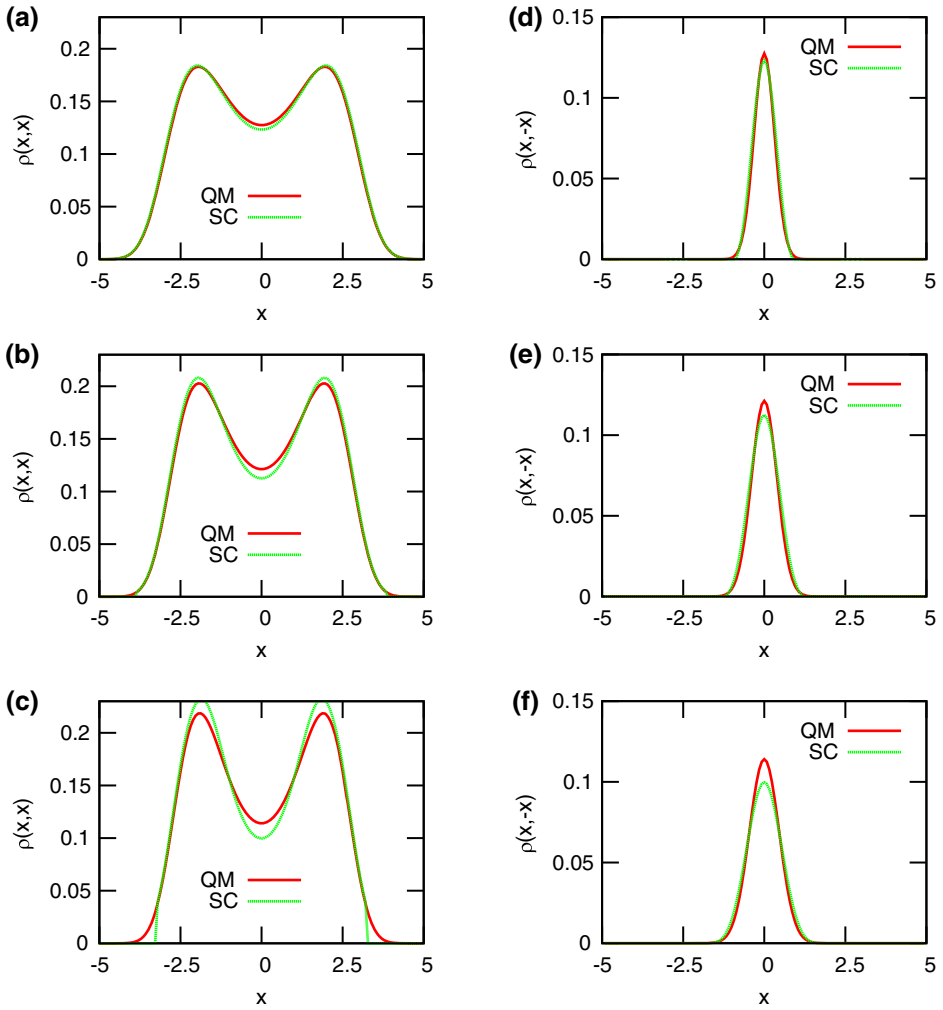

Figure 3. Symmetric (left) and antisymmetric (right) parts of the density matrix for the potential $V(x) = -x^2(1 - x^2/8)/2$. From top to bottom, β changes from 0.4 to 0.8 in step of 0.2. [Color figure can be viewed at wileyonlinelibrary.com]

as 10, which corresponds to the results for a certain harmonic oscillator. In calculating $\langle x|\, \rho_{PM}(\beta)|\, x\rangle (x \neq 0)$, the regulated action assumes complex contributions, while its real part is still of an approximately quadratic form. When temperature decreases, the regulated action gradually deviates the quadratic form and are no longer bounded when $\beta \geq 0.2$. It indicates that, strictly speaking, the integration in eq. 30 only converges for $\beta \leq 0.2$ when using the PM-IVR approximation. However, we should keep in mind that the semiclassical method is only an effective theory which works well for weak anharmonicities. For a nonlinear and bounded system, a trajectory starting with a larger momentum could reach the position with higher potential energy and feel a stronger effective nonlinearity. Consequently, the semiclassical approximation may fail for a trajectory with a large initial momentum.

However, the most significant population distribution locates around the bottom part of the potential well. Because the average energy at equilibrium is $E_{eq} = \left\langle \hat{H} e^{-\beta \hat{H}} \right\rangle / Z_\beta$, only the density matrix elements $\langle x|\, \rho(\beta)|\, x\rangle$ with $V(x) - V(x_{min}) < 2E_{eq}$ assume significant values. Here, x_{min} is the position corresponding to the minimum potential energy. As a result, we may obtain reasonable approximations by integrating over the initial momentum with the range $\left[-2\sqrt{mE_{eq}}, 2\sqrt{mE_{eq}}\right]$ instead of $[-\infty, \infty]$.

As we have used a harmonic approximation for the potential in the derivation of the semiclassical propagator, we use the classical and harmonic approximation to E_{eq}, resulting in $E_{eq} \approx 1/\beta$. Thus, we can use the small momentum approximation for the upper and the lower limits of the integration in eq. 30, namely, replacing the integration range with $\left[-2\sqrt{m/\beta}, 2\sqrt{m/\beta}\right]$.

With this treatment, we may obtain reliable density operators for lower temperatures. Calculated results for the full density

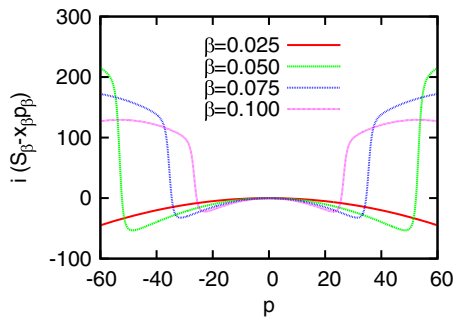

Figure 4. The regulated action $i(S_\beta - x_\beta\, p_\beta)$ as a function of the initial momentum p for calculating the matrix element $\langle 0|\, \rho_{PM}(\beta)|\, 0\rangle$ at different temperatures for the Eckart potential $8/\pi \mathrm{sech}^2(\sqrt{\pi}x/3)$. All quantities are in arbitrary unit. [Color figure can be viewed at wileyonlinelibrary.com]

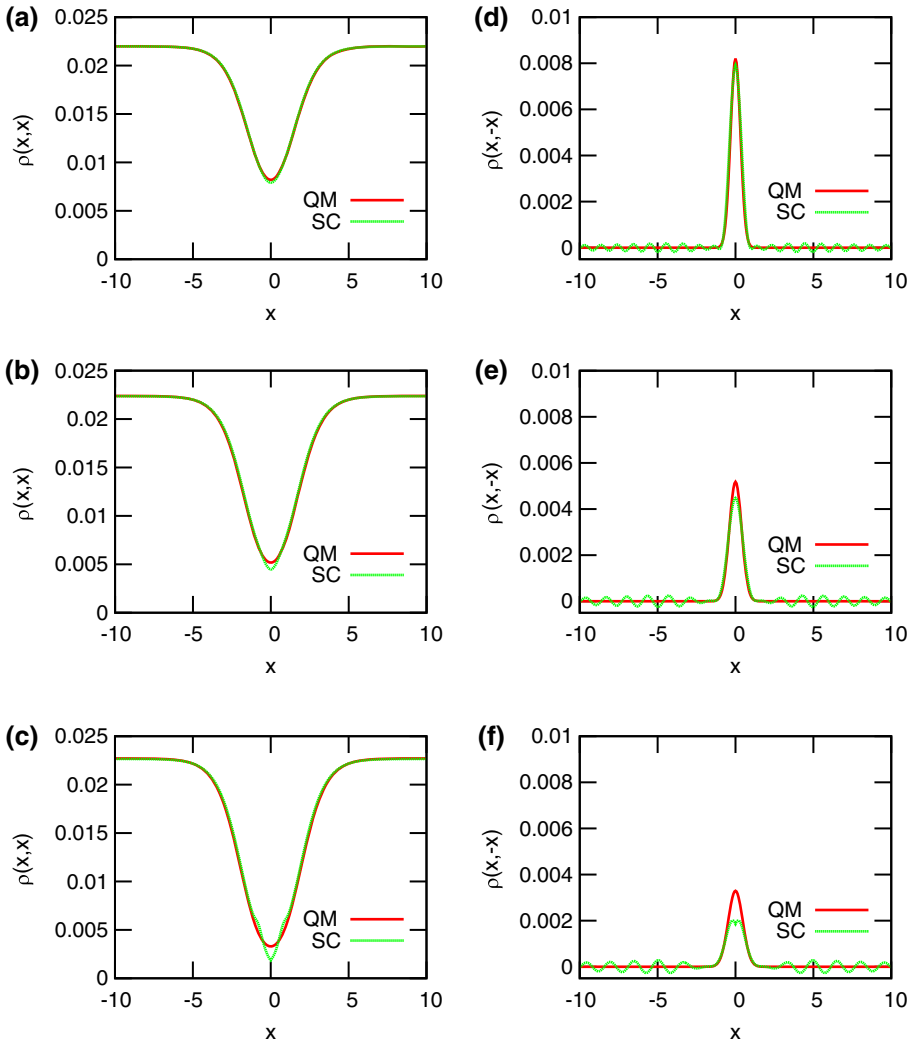

Figure 5. Symmetric (left) and antisymmetric (right) parts of the density matrix for the Eckart potential $8/\pi \mathrm{sech}^2(\sqrt{\pi}x/3)$. The results are calculated with the coordinate range [−24, 24] and β changes from 0.4 to 0.8 in step of 0.2 from top to bottom. [Color figure can be viewed at wileyonlinelibrary.com]

matrix reveal that the largest errors occur along the principal-diagonal direction. Following Ref. [39], we will scrutinize the principal diagonal $\langle x|\ \rho_{PM}(\beta)|\ x\rangle$ and the off-diagonal $\langle x|\ \rho_{PM}(\beta)|\ -x\rangle$ matrix elements of the thermal density matrix. To demonstrate the applicability at low temperatures, we show the results for the principal-diagonal matrix elements of the density operator in Figure 2. The matrix elements for the regions beyond the two outmost points assume anomalous results due to the convergence issue and are not shown in the plots. The exact quantum mechanical calculations are also presented to verify the semiclassical approximation. One observes that the semiclassical results agree well with the exact ones up to $\beta = 1.2$ for the bottom part of the potential. It is also noticed that the reliable range shrinks as the temperature decreases.

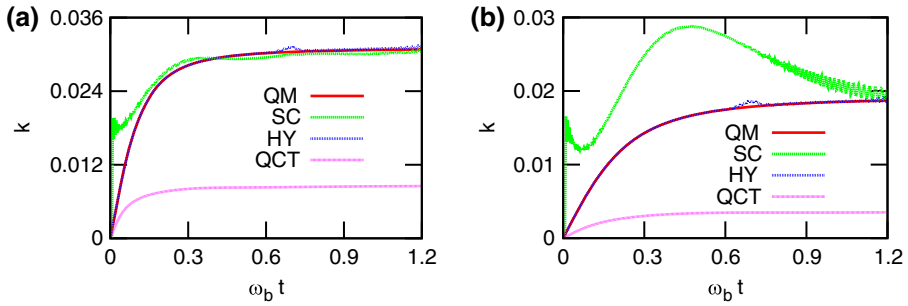

Figure 6. The PM-IVR approximation of reaction rate for the Eckart potential $8/\pi \mathrm{sech}^2(\sqrt{\pi}x/3)$ compared to the quantum mechanical results. QM: the exact quantum mechanical results. SC: the PM-IVR approximation. HY: the combination of the imaginary-time PM-IVR approximation and the exact real-time quantum mechanical propagation. QCT: the quasiclassical trajectory starting with the exact quantum mechanical density matrix. The temperature is $\beta = 0.2$ for plot (a) and $\beta = 0.4$ for plot (b). The time in the *x*-axis is rescaled with the harmonic vibration frequency of the inverted potential barrier. [Color figure can be viewed at wileyonlinelibrary.com]

The PM semiclassical propagator can be applied to systems with stronger nonlinearity, for example, the double-well systems which serve as prototypes to describe the quantum tunneling. Here, parameters $\lambda = 1$ is chosen for describing the potential energy in eq. 38. In this case, there are two eigenstates below the barrier height. When β is larger than three, 95% of the population is distributed among the two lowest eigenstates. For this system, the initial-momentum dependence of the regulated action behaves similarly with that depicted in Figure 1. That is, the exponential factor in the integration of eq. 30 becomes unbounded for $\beta \geq 0.2$, and we should carefully deal with the integration there. With the same argument and treatment for the single-well potential, we may overcome this limitation and obtain reliable results for lower temperatures. The results for the principal diagonal and off-diagonal matrix elements are presented in Figure 3. The deviations from the exact results are small for $\beta = 0.4$. The differences become larger for $\beta = 0.6$, but the maximum relative error is still less than 7.5%. Even for a lower temperature of $\beta = 0.8$, we still can obtain qualitative results for the density operator with the PM-IVR approximation.

We further apply the PM-IVR approximation to the Eckart potential

$$V(x) = V_0 \,\mathrm{sech}^2\left(\frac{x}{a}\right), \tag{40}$$

where $V_0 = 8/\pi$ and $a = 3/\sqrt{\pi}$ are the parameters controlling the height and the width of the potential barrier, respectively. Compared to the potentials with quadruple nonlinearity, the regulated action for the Echart potential shows a different temperature and initial-momentum dependence. Strictly speaking, according to Figure 4 the integration to calculate $\langle 0|\, \rho_\beta |\, 0\rangle$ will diverge for $\beta \geq 0.05$. However, the restriction of the integration range of the momentum yields reasonable results for lower temperatures. As depicted in Figure 5, for $\beta = 0.4$ the PM-IVR results agree well with the quantum mechanical ones. When the temperature decreases, for example, $\beta = 0.6$, the semiclassical approximation only slightly deviates from the exact one for a small top part of the potential and produces almost exact results for the rest part. For an even lower temperature, $\beta = 0.8$, the deviation around the top becomes bigger but is still acceptable as a semiclassical approximation.

The good approximation of the density matrix at high temperatures allows us to simulate the reaction rate for the barrier crossing. Here, the rate constant will be calculated in light of the side-side correlation function[44] defined as

$$C_s(t) = -\mathrm{Tr}\left[h(-\hat{s})e^{i\hat{H}t_c^*/\hbar}h(\hat{s})e^{i\hat{H}t_c/\hbar}\right],$$

or

$$C_s(t) = \int_0^\infty ds \int_{-\infty}^0 ds' \left|\left\langle s'\right| e^{-i\hat{H}t_c/\hbar}\left|s\right\rangle\right|^2,$$

where $t_c = t - i\hbar\beta/2$ and the $h(q)$ is the Heaviside step function, $h(q) = 1$ for $q > 0$ and $h(q) = 0$ for $q < 0$. With the partition function Q of the reactant, the reaction rate constant k can be computed according to

$$kQ = \lim_{t\to\infty} \frac{d}{dt} C_s(t).$$

When applying the PM semiclassical propagator, we may choose a specific path for the complex time from $t_c = 0$ to $t_c = t - i\hbar\beta/2$. For simplicity, we let the time t_0 first go from $t_c = 0$ only on an imaginary clock to $t_m = -i\hbar\beta/2$ and then go only on a real clock to $t_c = t - i\hbar\beta/2$ with fixed imaginary time.

The results for the reaction rate constants are presented in Figure 6. Through the plots, we find that the PM-IVR approximation for both the imaginary- and real-time yields a rate close to the exact one when $\beta = 0.2$. At lower temperatures, for example, $\beta = 0.4$, the derivative of the side-side correlation function based on the pure PM-IVR treatment does not approach to a plateau for reading a reaction rate. To check the reason of the deviation and to verify the applicability of the imaginary-time PM method, we also show the results with a semiclassical propagation at the imaginary time and a quantum mechanical evolution at the real time. Figure 6 depicts that this hybrid approach gives identical results to the pure quantum mechanical calculations both at $\beta = 0.2$ and $\beta = 0.4$. Further simulations demonstrate that the hybrid approach can provide reaction rate constants with errors smaller than 5% up to $\beta = 1.6$. Supplemented to the above results, we further perform the quasiclassical trajectory (QCT) simulations with the quantum mechanical density matrices. In the QCT calculations, density matrix is transformed to the Wigner function and the rate constant is calculated in the light of side-side correlation function. The results show that the rate constants calculated with the QCT method are significantly smaller than the quantum mechanical results, which indicates the importance of the quantum effect for the current Eckart potential model.

Summary

The semiclassical methods are powerful tools to approximate the real-time dynamics and have been extended to the imaginary time for calculating the Boltzmann operator. In developing rigorous semiclassical approximations of the quantum Boltzmann operator, there are two important issues to hold, namely, the recovery of the identity operator at the zero imaginary-time and the exactness for the quantum harmonic oscillator. The available approaches in the literature may fail to satisfy one or the other requirement, which limits the applications of the imaginary-time semiclassical approximations. In this article, we have first derived a position-momentum and a mixed coherent-state-position representation for the quantum propagator basing on the correction operator method. In the derivation, the equations of motion for the classical dynamics are determined by the condition of the vanishing first-order correction instead of a set of preselected ones. The same reasoning has been applied to derive a consistent semiclassical position-momentum representation for the Boltzmann operator which produces the identity operator at the zero imaginary-time. The suggested semiclassical Boltzmann operator is exact for the quantum

harmonic oscillator and correct for the quantum parabolic barrier down to a critical temperature. Numerical simulations show that the semiclassical approximation is reliable for high to intermediate temperatures for nonlinear systems. Combined with the real-time propagation, the obtained semiclassical Boltzmann operator can be used to calculate the reaction rate constants of chemical reactions.

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Keywords: correction operator · Boltzmann operator · imaginary-time semiclassical approximation · semiclassical dynamics

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