Systematic Improvement of Initial Value Representations of the Semiclassical Propagator†

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A systematic method is developed to obtain increasingly accurate semiclassical initial value representation (IVR) approximations to the exact quantum propagator. The main result is a series of correction terms of increasing order in a "correction operator", which describes the difference between the exact evolution equation and the equation obeyed by the semiclassical propagator. Each term in the series involves only phase space integrals of classical trajectories and is therefore, in principle, amenable to numerical computation. The properties of the "correction operator" are studied for three different representations of the semiclassical propagator. For initial times, we find that the propagator suggested recently by Baranger et al. is superior to a thawed Gaussian propagator or the Herman−Kluk propagator.

I. Introduction

A major advance in semiclassical theory has been the formulation of initial value representations (IVR) of the semiclassical propagator. Recent reviews of the history of the semiclassical IVR have been given by Grossmann[1] and Baranger et al.[2] Instead of a double-ended boundary value problem as in the VanVleck−Gutzwiller propagator,[3,4] the IVR allows one to express a semiclassical approximation to the propagator that depends only on the initial conditions in phase space and the classical trajectory initiated at the point. This simple structure is very convenient for Monte Carlo computations, especially if one computes thermal averages, such as thermal correlation functions. The Boltzmann factor usually prevents the need for integration for times that are too long, and the semiclassical IVR computation can be converged numerically. In addition, as pointed out by Miller,[5,6] in contrast to the Van Vleck−Gutzwiller semiclassical propagator, the prefactor of the IVR representation does not diverge. Heller suggested in 1975[7] to use thawed Gaussians as an approximate semiclassical propagator. In 1984, Herman and Kluk[8] derived an IVR of the semiclassical propagator. The practical usefulness of the Herman−Kluk propagator was first pointed out by Kay,[9−11] who showed that it could lead to rather accurate approximation of exact quantum results. These initial studies were then followed by the work of Tannor, Grossmann, and others[12−19] who applied the propagator to a number of problems, including the collinear hydrogen exchange reaction, which eluded a "good" semiclassical solution for decades.

At present, the semiclassical IVR is the most powerful and perhaps also promising tool for computation of quantum effects in "large" systems. But the IVR does have drawbacks. Perhaps the most serious one is that, to date, it is an uncontrollable approximation. Correction terms to the approximation have not been derived, so one does not have an objective handle that could be used to assess the quality of the approximation. The propagator is not unique. One may write down infinitely many IVR representations of an IVR semiclassical propagator, all of which have the nice properties that their stationary phase limit reduces to the correct Van Vleck−Gutzwiller result and they are unitary in the stationary phase sense. This multiplicity has led recently to a new derivation of an IVR propagator by Baranger et al.[2] that differs from the Herman−Kluk and thawed Gaussian propagators. A lively discussion on the merits of the differing propagators has recently taken place.[2,20,21]

A different critique of the Herman−Kluk (HK) propagator was presented recently in ref 22. In a previous study of the initial time dependence of operators in phase space,[23] we found that for short times the classical propagator is exact. For example, for a coordinate-dependent operator, the first three initial time derivatives are given exactly by classical mechanics. In ref 22, it was shown that the HK propagator was already not exact for short times, introducing spurious terms that are on the order of $\hbar$. However, for longer times, the classical approximation of course fails, while the HK propagator remained reasonably accurate, following correctly the quantum coherences. It is therefore of interest to compare the short-time properties of the Herman−Kluk, Heller, and Baranger et al. propagators.

The main purpose of the present paper is to show that one can readily derive systematic correction terms to the semiclassical IVR propagator, which are functions only of the underlying classical trajectories and their properties. This result allows, for the first time, a systematic examination of the quality of the semiclassical IVR representation. It should also help to eliminate the controversy as to which is the "best" method. The "best" semiclassical IVR will be the one for which the corrections are "smallest" so that the series of correction terms converges most rapidly. We will show that, at least for short propagation times, the leading order "correction" operator is, in a sense, smallest for the Baranger et al. (BEA) propagator.

The systematic correction of semiclassical IVR approximations to the propagator is presented in section II. Then, in section III, we review briefly the BEA and thawed Gaussian (TG)

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propagators and derive an explicit expression for their respective "correction operator". The comparison between the initial time properties of the BEA, TG, and HK propagators is presented in section IV, and we end with a discussion of the implication of our results on future uses of the semiclassical initial value representation.

II. Systematic Improvement of Semiclassical IVR Propagators

We assume a system described by the Hamiltonian operator $\hat{H}$. The equation of motion for the propagator

$$\hat{K} = e^{-(i/\hbar)Ht} \tag{2.1}$$

is, of course,

$$i\hbar\frac{\partial}{\partial t}\hat{K} = \hat{H}\hat{K} \tag{2.2}$$

We then assume that there exists an approximation to the exact propagator, denoted as $\hat{K}_0$, which obeys the equation of motion:

$$i\hbar\frac{\partial}{\partial t}\hat{K}_0(t) = \hat{H}\hat{K}_0(t) + \hat{C}(t) \tag{2.3}$$

where the known "correction operator", $\hat{C}$, is hopefully a small correction only. This form is motivated by a previous result for the HK propagator, which has this structure.[22] We also assume that at time $t = 0$ the operator $\hat{K}_0 = \hat{I}$. We will now show that one can construct a hopefully convergent series of operators, the error of which will be of increasing power in the correction operator.

We note that the exact propagator is unitary

$$\hat{K}\hat{K}^{\dagger} = \hat{I} \tag{2.4}$$

but that this is not necessarily the case for the approximate propagator, $\hat{K}_0$. Expanding the exact propagator in a series

$$\hat{K} = \hat{K}_0(\hat{I} + \delta\hat{K}_1 + \delta\hat{K}_2 + ...) \tag{2.5}$$

where we assume that the nth term ($\delta\hat{K}_n$) is on the order of the nth power of the correction operator, we readily find

$$i\hbar\frac{\partial}{\partial t}(\delta\hat{K}_1 + \delta\hat{K}_2 + ... + \delta\hat{K}_n + ...) = -\hat{K}_0^{-1}\hat{C}(\hat{I} + \delta\hat{K}_1 + \delta\hat{K}_2 + ... + \delta\hat{K}_n + ...) \tag{2.6}$$

If the approximate propagator is unitary for all times, then $\hat{K}_0^{-1} = \hat{K}_0^{\dagger}$ and the solution of eq 2.6 may be represented in terms of the time-ordered exponential operator

$$\hat{K}(t) = \hat{K}_0(t)\, e_+^{i/\hbar\int_0^t dt'\hat{K}_0^{\dagger}(t')\hat{C}(t')} \tag{2.7}$$

The semiclassical IVR propagators to be discussed in this paper are, however, not unitary, so one must work a bit more. The unitarity of the exact propagator and eq 2.5 imply that

$$\hat{K}_0^{-1} = (I + \delta\hat{K}_1 + ... + \delta\hat{K}_n + ...)(I + \delta\hat{K}_1^{\dagger} + ... + \delta\hat{K}_n^{\dagger} + ...)\hat{K}_0^{\dagger} \tag{2.8}$$

We therefore find from eq 2.6 that the first two correction terms to the propagator take the form

$$\delta\hat{K}_1(t) = \frac{i}{\hbar}\int_0^t dt'\, \hat{K}_0^{\dagger}(t')\hat{C}(t') \tag{2.9}$$

$$\delta\hat{K}_2(t) = \frac{i}{\hbar}\int_0^t dt'\, ((\delta\hat{K}_1(t') + \delta\hat{K}_1^{\dagger}(t'))\hat{K}_0^{\dagger}(t')\hat{C}(t') + \hat{K}_0^{\dagger}(t')\hat{C}(t')\delta\hat{K}_1(t')) \tag{2.10}$$

and derivation of higher order correction terms is straightforward but increasingly lengthy. An explicit expression for the correction operator of the HK propagator has been derived in ref 22. In the next section, we derive the correction operator for the BEA and TG propagators.

III. The Correction Operator

A. The Baranger et al. Propagator. In this first paper, we will restrict ourselves to one-dimensional systems (with unit mass), governed by the Hamiltonian operator:

$$\hat{H} = \frac{\hat{p}^2}{2} + V(\hat{q}) \tag{3.1}$$

where $\hat{p}$ and $\hat{q}$ are the momentum and coordinate operators, respectively, obeying the commutation relation

$$[\hat{q}, \hat{p}] = i\hbar \tag{3.2}$$

The coherent state representation of the BEA semiclassical IVR propagator may be deduced from eq 4.55 of ref 2 to be

$$\hat{K}_B \equiv e_B^{-i\hat{H}t/\hbar} = \int_{-\infty}^{\infty}\frac{dp\,dq}{2\pi\hbar}D(p,q,t)\, e^{(i/\hbar)(\iota(p,q,t)+S_{\tilde{H}}(p,q,t))}|g(p,q,t)\rangle\langle g(p,q,0)| \tag{3.3}$$

The coordinate representation of the Gaussian wave packets with the time-dependent real width parameter, $\Gamma(t)$, is

$$\langle x|g(p,q,t)\rangle = \left(\frac{\Gamma(t)}{\pi}\right)^{1/4} e^{-[\Gamma(t)/2][x-q(t)]^2+(i/\hbar)p(t)[x-q(t)]} \tag{3.4}$$

Here, $q(t)$ and $p(t)$ are the classically evolved values of the coordinate and the momentum, respectively, given that at time $t = 0$ $q(0) = q$ and $p(0) = p$. That is, $q(t)$ and $p(t)$ obey Hamilton's equations of motion

$$\dot{q}(t) = \frac{\partial\tilde{H}}{\partial p} = p(t) \tag{3.5}$$

$$\dot{p}(t) = -\frac{\partial\tilde{H}}{\partial q} = -\tilde{V}'(q) \tag{3.6}$$

where the dot denotes time differentiation and the coherent state representation of the Hamiltonian is

$$\tilde{H} = \langle g(p,q,0)|H|g(p,q,0)\rangle = \frac{1}{2}p^2 + \frac{\hbar^2\Gamma(0)}{4} + \tilde{V}(q) \tag{3.7}$$

with the transformed potential

$$\tilde{V}(q) \equiv \left(\frac{\Gamma(0)}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}dx\, e^{-\Gamma(0)(x-q)^2}V(x) \tag{3.8}$$

The classical action is

$$S_{\tilde{H}}(p,q,t) = \int_0^t dt'\, \{p(t')\dot{q}(t') - \tilde{H}[p(t'),q(t')]\} \tag{3.9}$$

and the added exponential term, which results from the semiclassical estimate of the coherent state propagator,[2] is

$$\iota(p,q,t) = \frac{1}{2}\int_0^t \mathrm{d}t' \left(\frac{1}{2\Gamma(0)}\frac{\partial^2\tilde{H}}{\partial q^2} + \frac{\hbar^2\Gamma(0)}{2}\frac{\partial^2\tilde{H}}{\partial p^2}\right) \tag{3.10}$$

The preexponential factor is

$$D(p,q,t) = \frac{1}{\sqrt{m_{qq} + im_{qp}}}\left(\frac{\Gamma(0)}{\Gamma(t)}\right)^{1/4} \tag{3.11}$$

where the time-dependent width parameter, $\Gamma(t)$, is determined by

$$\Gamma(t) \equiv \Gamma(0)\frac{1-\gamma(t)}{1+\gamma(t)} \tag{3.12}$$

and

$$\gamma(t) \equiv \frac{m_{qq} + im_{qp} + im_{pq} - m_{pp}}{m_{qq} + im_{qp} - im_{pq} + m_{pp}} \tag{3.13}$$

The m_{kl}'s are the elements of the monodromy matrix:

$$m_{qq} \equiv \frac{\partial q(t)}{\partial q} \tag{3.14}$$

$$m_{qp} \equiv \hbar\Gamma(0)\frac{\partial q(t)}{\partial p} \tag{3.15}$$

$$m_{pq} \equiv \frac{1}{\hbar\Gamma(0)}\frac{\partial p(t)}{\partial q} \tag{3.16}$$

$$m_{pp} \equiv \frac{\partial p(t)}{\partial p} \tag{3.17}$$

The width parameter $\Gamma(0)$ is a free parameter, the magnitude of which is typically chosen according to some physical consideration of the problem being studied.

At time $t = 0$, the prefactor $D(p,q,0) = 1$ and the actions $S_{\tilde{H}}(p,q,0) = \iota(p,q,t) = 0$. Therefore, the operator reduces to the identity operator, as it should.

B. The Thawed Gaussian Propagator. As shown by Baranger et al.,[2] Heller's suggestion to use a thawed Gaussian propagator leads to a form that is very similar to the BEA propagator:

$$\hat{K}_{\mathrm{TG}} = \int_{-\infty}^{\infty}\frac{\mathrm{d}p\,\mathrm{d}q}{2\pi\hbar}D(p,q,t)\,\mathrm{e}^{(i/\hbar)S_H(p,q,t)}|g(p,q,t)\rangle\langle g(p,q,0)| \tag{3.18}$$

The main difference between this operator and the BEA operator is that here the classical trajectories obey Hamilton's equations of motion for the Weyl symbol of the Hamiltonian, which in our case is just the classical Hamiltonian

$$H_{\mathrm{c}}(p,q) = \frac{1}{2}p^2 + V(q) \tag{3.19}$$

Thus the action in eq 3.18 is the classical action

$$S_H(p,q,t) = \int_0^t \mathrm{d}t'\,\{p(t')\dot{q}(t') - H_{\mathrm{c}}[p(t'),q(t')]\} \tag{3.20}$$

The prefactor $D(p,q,t)$ has the same form as in eq 3.11; however, the time dependence is obtained through the classical trajectories governed by H_{c} instead of $\tilde{H}$. The added exponential term $\iota(p,q,t)$ does not appear here.

C. The Correction Operator. We shall first derive the correction operator for the BEA propagator. We note a few useful identities. The coherent state matrix element of the Hamiltonian operator is

$$\begin{aligned}\langle x|\hat{H}|g(p,q,t)\rangle &= \left(-\frac{\hbar^2}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)\langle x|g(p,q,t)\rangle \\ &= \left(V(x) + \frac{\hbar^2}{2}\left(\Gamma(t) - \left[\frac{i}{\hbar}p(t) - \Gamma(t)(x-q(t))^2\right]^2\right)\right)\langle x|g(p,q,t)\rangle\end{aligned} \tag{3.21}$$

from which we deduce that

$$\hat{H}|g(p,q,t)\rangle = \left(V(\hat{q}) + \frac{\hbar^2}{2}\left(\Gamma(t) - \left(\frac{ip(t)}{\hbar} - \Gamma(t)[\hat{q} - q(t)]\right)^2\right)\right)|g(p,q,t)\rangle \tag{3.22}$$

Considering explicitly the time derivative of the semiclassical propagator, eq 3.3, one finds

$$i\hbar\frac{\partial}{\partial t}\hat{K}_{\mathrm{B}} = \int_{-\infty}^{\infty}\frac{\mathrm{d}p\,\mathrm{d}q}{2\pi\hbar}\left(i\hbar\frac{\frac{\partial D(p,q,t)}{\partial t}}{D(p,q,t)} - \frac{\partial}{\partial t}(\iota(p,q,t) + S_{\tilde{H}}(p,q,t)) + i\hbar\frac{\frac{\partial}{\partial t}|g(p,q,t)\rangle}{|g(p,q,t)\rangle}\right)D(p,q,t)\,\mathrm{e}^{(i/\hbar)(\iota(p,q,t)+S_{\tilde{H}}(p,q,t))}|g(p,q,t)\rangle\langle g(p,q,0)| \tag{3.23}$$

noting that

$$\frac{\partial}{\partial t}(\iota(p,q,t) + S_{\tilde{H}}(p,q,t)) = \frac{p(t)^2}{2} - \tilde{V}(q(t)) + \frac{\tilde{V}''(q(t))}{4\Gamma(0)} \tag{3.24}$$

that

$$i\hbar\frac{\frac{\partial D(p,q,t)}{\partial t}}{D(p,q,t)} = \frac{\hbar^2\Gamma(t)}{4} + \frac{\tilde{V}''(q(t))}{4\Gamma(t)} \tag{3.25}$$

and that

$$i\hbar\frac{\frac{\partial}{\partial t}|g(p,q,t)\rangle}{|g(p,q,t)\rangle} = \frac{1}{4}\left(\hbar^2\Gamma(t) - \frac{\tilde{V}''(q(t))}{\Gamma(t)}\right)(1 - 2\Gamma(t)(\hat{q} - q(t))^2) + (\hat{q} - q(t))(\tilde{V}'(q(t)) + i\hbar p(t)\Gamma(t)) + p(t)^2 \tag{3.26}$$

Using the identity

$$\left(\hbar^2\Gamma(t)^2 - i\hbar\frac{\partial\Gamma}{\partial t}\right) = \tilde{V}''[q(t)] \tag{3.27}$$

inserting eqs 3.22–3.24 into eq 3.21, using eq 3.20, and rearranging gives the modified equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{K}_{\mathrm{B}} = \hat{H}\hat{K}_{\mathrm{B}} + \hat{C}_{\mathrm{B}}(t) \tag{3.28}$$

where the "correction operator" $\hat{C}_{\mathrm{B}}(t)$ is found to be

$$\hat{C}_{\rm B}(t) = \int_{-\infty}^{\infty} \frac{{\rm d}p\,{\rm d}q}{2\pi\hbar}\Big(\tilde{V}[q(t)] + \tilde{V}'[q(t)][\hat{q} - q(t)] + \frac{\tilde{V}''[q(t)]}{2}[\hat{q} - q(t)]^2 - V(\hat{q}) - \frac{1}{4\Gamma(0)}\tilde{V}''[q(t)]\Big) D(p,q,t)\, {\rm e}^{(i/\hbar)(\iota(p,q,t)+S_{\tilde{H}}(p,q,t))}|g(p,q,t)\rangle\langle g(p,q,0)| \quad (3.29)$$

We note that for a harmonic potential the correction operator is identically zero, as it should be; the semiclassical IVR propagator is exact for harmonic systems.

Derivation of the correction operator for the thawed Gaussian propagator follows similar lines, and one finds

$$\hat{C}_{\rm TG}(t) = \int_{-\infty}^{\infty} \frac{{\rm d}p\,{\rm d}q}{2\pi\hbar}\Big(V[q(t)] + V'[q(t)][\hat{q} - q(t)] + \frac{V''[q(t)]}{2}[\hat{q} - q(t)]^2 - V(\hat{q})\Big)D(p,q,t)\, {\rm e}^{(i/\hbar)S_H(p,q,t)}|g(p,q,t)\rangle\langle g(p,q,0)| \quad (3.30)$$

This form is especially transparent; using the Taylor expansion

$$V(\hat{q}) = V(q(t) + [\hat{q} - q(t)]) = V(q(t)) + V'[q(t)][\hat{q} - q(t)] + \frac{1}{2}V''[q(t)][\hat{q} - q(t)]^2 + ... \quad (3.31)$$

one notes that the leading order term in the correction operator involves the cubic derivative of the potential. Clearly, for harmonic systems, the correction operator is identically zero.

Finally, we note also the correction operator found in ref 22 for the HK propagator:

$$\hat{C}_{HK}(t) = \int_{-\infty}^{\infty} \frac{{\rm d}p\,{\rm d}q}{2\pi\hbar}\Big(\frac{\hbar^2\Gamma(0)^2}{2}[\hat{q} - q(t)]^2 - \frac{\hbar^2\Gamma(0)}{2} + i\hbar\frac{\dot{R}(p,q,t)}{R(p,q,t)} + V[q(t)] + V'[q(t)][\hat{q} - q(t)] - V(\hat{q})\Big) R(p,q,t)\, {\rm e}^{(i/\hbar)S(p,q,t)}|g(p,q,t)\rangle\langle g(p,q,0)| \quad (3.32)$$

where

$$R(p,q,t) = \frac{1}{\sqrt{2}}(m_{pp} - im_{qp} + m_{qq} + im_{pq})^{1/2} \quad (3.33)$$

so that

$$\dot{R}(p,q,t) = \frac{1}{4R(p,q,t)}\Big(- i\frac{V''[q(t)]}{\hbar\Gamma(0)}(m_{qq} - im_{qp}) - i\hbar\Gamma(0)(m_{pp} + im_{qp})\Big) \quad (3.34)$$

For the HK propagator, the classical trajectories evolve on the "bare" potential, $V(q)$, and not on the coherent state averaged potential, $\tilde{V}(q)$.

IV. Initial Time Properties

A. Initial Time Correction Operator. To get a better feeling for the correction operator in the various representations, it is useful to study its initial time properties. Using the identity

$$V(\hat{q}) = \int_{-\infty}^{\infty} \frac{{\rm d}p\,{\rm d}q}{2\pi\hbar}({\rm e}^{-1/(2\Gamma(0))(d^2/{\rm d}q^2)}\tilde{V}(q))|g(p,q,0)\rangle\langle g(p,q,0)| \quad (4.1)$$

one readily finds for the BEA correction operator that at $t = 0$

$$\hat{C}_{\rm B}(0) = \int_{-\infty}^{\infty} \frac{{\rm d}p\,{\rm d}q}{2\pi\hbar}\Big(\tilde{V}(q) - \frac{\tilde{V}''(q)}{2\Gamma(0)} + \frac{\tilde{V}^{(4)}(q)}{8\Gamma(0)^2} - {\rm e}^{-1/(2\Gamma(0)){\rm d}^2/{\rm d}q^2}\tilde{V}(q)\Big)|g(p,q,0)\rangle\langle g(p,q,0)| \quad (4.2)$$

The initial time correction operator is not zero only if the potential has terms on the order of q^6 or higher. The leading order term will then be on the order of $\Gamma(0)^{-3}$. Because, typically, one chooses $\Gamma(0)$ to be inversely proportional to $\hbar$, this means that the correction operator is on the order of $\hbar^3$. We also note that the initial time correction operator is Hermitian.

The initial time correction operator for the thawed Gaussian propagator is

$$\hat{C}_{TG}(0) = \int_{-\infty}^{\infty} dq\sqrt{\frac{\Gamma(0)}{\pi}}e^{-\Gamma(0)(\hat{q}-q)^2}\sum_{j=2}^{\infty}\frac{\frac{d^{2j}V(q)}{dq^{2j}}}{(2j)!}(\hat{q} - q)^{2j} \quad (4.3)$$

demonstrating that this correction operator becomes nonzero when the nonlinearity of the potential is quartic or higher. This then implies a leading order term that goes as $\Gamma(0)^{-2}$ or on the order of $\hbar^2$. This is a first indication that the BEA correction operator is *smaller* than the Heller thawed Gaussian correction operator.

For the sake of completeness, we also write down the HK initial time correction operator (eq 2.15 of ref 22):

$$\hat{C}_{\rm HK}(0) = \frac{3}{2}\tilde{V}(\hat{q}) - V(\hat{q}) - \sqrt{\frac{\Gamma(0)}{\pi}}\int_{-\infty}^{\infty}{\rm d}q\,{\rm e}^{-\Gamma(0)(\hat{q}-q)^2}\Gamma(0)V(q)(\hat{q} - q)^2 \quad (4.4)$$

This operator also becomes nonzero when the anharmonicity is quartic or higher. Thus, it will be on the order of $\hbar^2$ and so inferior to the BEA but similar to the TG propagator.

B. Initial Time Derivative of an Operator. We will consider the time evolution of a Hermitian operator, $O(\hat{p},\hat{q})$. The exact time evolution of the operator under the Hamiltonian $\hat{H}$ is

$$O(\hat{p},\hat{q},t) = {\rm e}^{(it/\hbar)\hat{H}}\,O(\hat{p},\hat{q},0)\,{\rm e}^{-(it/\hbar)\hat{H}} = \hat{K}^\dagger(t)O(\hat{p},\hat{q},0)\hat{K}(t) \quad (4.5)$$

The semiclassical IVR time evolution of the operator is given by replacing the quantum evolution operator with its semiclassical IVR counterpart, denoted as $\hat{K}_j$, where the subscript j denotes any one of the three propagators that we have been considering. The approximate time derivative of the operator is then found by using eq 2.3:

$$i\hbar\dot{O}(\hat{p},\hat{q},t)_j = \hat{K}_j^\dagger(t)[O(\hat{p},\hat{q},0),\hat{H}]\hat{K}_j(t) + \hat{K}_j^\dagger(t)O(\hat{p},\hat{q},0)\hat{C}_j(t) - \hat{C}_j^\dagger(t)O(\hat{p},\hat{q},0)\hat{K}_j(t) \quad (4.6)$$

At the initial time, $t = 0$, the semiclassical IVR propagator, as noted above, is the identity operator. In other words, the initial time derivative of an Hermitian operator $O(\hat{p},\hat{q})$ is

$$i\hbar\dot{O}(\hat{p},\hat{q},t)|_{t=0} = [O(\hat{p},\hat{q}),\hat{H} + \hat{C}_j(0)] \tag{4.7}$$

If the operator O depends only on the coordinates, then O will commute with $\hat{C}(0)$ and the initial time derivative obtained from the semiclassical IVR propagator is exact. If however the operator O depends also on the momentum operator, then the commutator $[O(\hat{p},\hat{q}),\hat{C}(0)] \neq 0$ and the initial time derivative obtained from the semiclassical IVR propagator is no longer exact.

Consider the simple case of $O(\hat{p},\hat{q}) = \hat{p}$. The Wigner representation of an operator is defined as[26]

$$O(p,q)_{\rm W} = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} {\rm d}\xi\ {\rm e}^{ip\xi/\hbar} \left\langle q - \frac{\xi}{2}\middle|O(\hat{p},\hat{q})\middle|q + \frac{\xi}{2}\right\rangle \tag{4.8}$$

The exact initial time derivative of the momentum operator is $i\hbar\dot{\hat{p}} = [\hat{p},\hat{H}]$. In the Wigner representation, one then finds that the initial time derivative is

$$\dot{p}|_{t=0} = -V'(q) \tag{4.9}$$

and this is of course also the exact classical result.

When one uses the semiclassical IVR propagator, then one must also consider the commutator $[\hat{p},\hat{C}(0)]$. Some straightforward algebra, using the definition of eq 4.8, shows that

$$i\hbar[\hat{p},\hat{C}_j(0)]_{\rm W} = -\frac{1}{2\pi\hbar}\hbar^2\frac{{\rm d}C_j(q)}{{\rm d}q} \tag{4.10}$$

where $C_j(q)$ is the Wigner representation of the operator $\hat{C}_j(0)$. Clearly, the order of accuracy of the initial time derivative for the three propagators is that the accuracy of the BEA operator is greater than that of the HK and TG propagators.

Finally, we note that if one uses the leading order correction to the semiclassical IVR, one readily finds that the initial time derivative of the operator is now exact for all representations. Specifically, using eqs 2.3 and 2.8, one finds

$$i\hbar\frac{\partial}{\partial t}(\hat{K}_j(\hat{I} + \delta\hat{K}_{1j}))|_{t=0} = \hat{H} \tag{4.11}$$

which is of course the exact result. If however one estimates the second initial time derivative, one will find again an error but now of order $\hat{C}(0)^2$. If one employs also the second-order correction to the semiclassical IVR, one will find that also the second initial time derivative is exact.

IV. Discussion

The central result of this paper is the development of a perturbation series for the semiclassical IVR propagator in terms of the known "correction operator". As one increases the order of the terms, one will increase the accuracy of the approximate propagator. Each added term ensures the exactness of a higher order initial time derivative of the propagator. Because numerical computations show that often the error in the semiclassical propagator remains relatively small for rather long times, one may expect that the perturbation series will converge rather rapidly. It is remarkable that the convergence of the series implies obtaining exact quantum mechanical results using only classical trajectories and the linearized motion about them.

The analytical results derived in this paper are also useful in determining the relative merits of different semiclassical IVR propagators. We have seen that the BEA propagator leads to a correction operator which, at least for short times, depends on the sixth order of the nonlinearity in the potential. The thawed Gaussian and the HK propagators involve the fourth order. In this sense, the BEA propagator is the most accurate. We do note that all semiclassical IVR propagators considered in this paper are not unitary. Moreover, the operator definition of the propagators, as used in this paper, also does not conserve the norm, that is, $\langle g(p,q)|\hat{K}_j\hat{K}_j^\dagger|g(p,q)\rangle$ does not necessarily equal unity for all times.[27] In other words, normalization is not a sufficient condition for preferring one propagator to the other. All operators considered are unitary in the stationary phase sense.

From a practical point of view, the BEA form is not very convenient for numerical computations because it involves trajectories on the coherent state averaged potential. This implies that for large scale systems it is no longer possible to carry out computations on the fly. Because the thawed Gaussian and the HK propagators involve trajectories on the bare potentials but give a similar initial time correction operator, we would conclude that either one of them would do. In practice, one should use either of them and then study which leads to a smaller first-order correction term.

We have not presented here any numerical computations. This is left for future work. We do note that each added term in the "correction operator" series involves an additional phase space integration of oscillatory integrands, so we do not expect that it will be easy to always converge the series. However, computing the first-order term should not be too difficult, and it should indicate the quality of the approximation obtained through the leading term, which involves the semiclassical IVR propagator only.

One of the major drawbacks of all semiclassical IVR approximations is that thus far they have not been sufficient for accounting for deep tunneling phenomena. It remains an open question for future study whether the systematic correction method presented in this paper will turn out to be a practical method that can extend the semiclassical IVR propagators also to deep tunneling problems.

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(27) In fact, Baranger et al. provide two different forms for their semiclassical propagator. One is given in their eq 4.29; the other is the operator form used in this paper, which is consistent with their eq 4.55. The two representations are not identical for anharmonic potentials.