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Thawed semiclassical IVR propagators

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Abstract

A general expression for thawed semiclassical initial-value representation propagators has been derived in the multidimensional form. The thawed Gaussian propagator of Heller and the coherent-state-averaged thawed Gaussian propagator of Baranger *et al* (2001 *J. Phys. A: Math. Gen.* **34** 7227) are some examples of the more general class. The derivation is based on the demand that the correction operator associated with the semiclassical propagator includes only cubic and higher-order terms of the averaged potential.

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1. Introduction

The term initial-value representation (IVR) for an approximate quantum propagator was originally coined by Miller [1]. Heller [2] in 1975, suggested an approximate propagator, of the Gaussian form with time-dependent coefficients, chosen to ensure that the propagator is exact in the harmonic limit. One version of such thawed Gaussian propagators was studied by Kay [3], who concluded that it is inferior to the Herman–Kluk [4] semiclassical initial value representation (SCIVR) propagator. The latter is an improvement of the frozen Gaussian SCIVR propagator proposed by Heller [5] in 1981.

Thawed Gaussian propagators are the subject of a thorough study presented recently by Baranger *et al* [6]. These authors derived an explicit expression for the thawed Gaussian suggested by Heller as well as a new SCIVR propagator (which we will refer to as the BEA propagator) in which the classical dynamics takes place on a coherent-state-averaged Hamiltonian. Baranger *et al* [6] did not provide a multidimensional generalization of their thawed Gaussian SCIVR propagators.

In the past few years, Pollak and co-workers [7–11] have shown that SCIVR propagators obey a time-dependent equation whose form is

$$i\hbar\frac{\partial\hat{K}_0(t)}{\partial t} = \hat{H}\hat{K}_0(t) + \hat{C}(t), \qquad \hat{K}_0(0) = \hat{I}, \tag{1.1}$$

where $\hat{H}$ is the Hamiltonian operator describing the system, $\hat{K}_0$ the SCIVR propagator and $\hat{C}$ is termed the 'correction operator'. SCIVR propagators are exact for harmonic systems and the correction operator vanishes in this limit. In this paper, we will use the known form of the correction operator to show how it can be used to derive a general class of thawed SCIVR propagators. The term 'thawed' implies that the width parameter appearing in the coherent states used to form the SCIVR propagator is time-dependent. Instead of starting with the exact quantum propagator and its representation in terms of coherent state path integrals, we will use the correction operator as our point of departure.

The main results of this paper are: (i) a multidimensional generalization of the thawed Gaussian propagators suggested by Baranger *et al* [6]; (ii) formulation of a generalized class of thawed SCIVR propagators and (iii) explicit formulae for the multidimensional form of the general class in terms of the monodromy matrices and the classical action function. The theory is presented in section 2 and the results are discussed in section 3.

2. Thawed SCIVR propagators

2.1. Preliminaries

We consider an N-dimensional system (with mass-weighted coordinates and momenta), governed by the Hamiltonian operator

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2} + V(\hat{\mathbf{q}}), \tag{2.1}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{q}}$ are N-dimensional vectors of the (mass-weighted) momentum and coordinate operators, respectively, obeying the commutation relation $[\hat{q}_i, \hat{p}_j] = \mathrm{i}\hbar\delta_{ij}$.

The general form of the SCIVR propagator can be written as

$$\hat{K}_0(t) = \int_{-\infty}^{\infty} \prod_{j=1}^{N} \left(\frac{\mathrm{d}p_j \mathrm{d}q_j}{2\pi\hbar}\right) R(\mathbf{p}, \mathbf{q}, t) \mathrm{e}^{(\mathrm{i}/\hbar)S(\mathbf{p},\mathbf{q},t)} |g(\mathbf{p}, \mathbf{q}, t)\rangle\langle g(\mathbf{p}, \mathbf{q}, 0)|. \tag{2.2}$$

The coordinate representation of the multidimensional Gaussian wavepackets is

$$\langle \mathbf{x}|g(\mathbf{p}, \mathbf{q}, t)\rangle = \left(\frac{\det(\underline{\Gamma}_r(\mathbf{p}, \mathbf{q}, t))}{\pi^N}\right)^{1/4} \mathrm{e}^{-(1/2)[\mathbf{x}-\mathbf{q}(t)]^{\mathrm{T}}\underline{\Gamma}(\mathbf{p},\mathbf{q},t)[\mathbf{x}-\mathbf{q}(t)]+(\mathrm{i}/\hbar)\mathbf{p}(t)\cdot[\mathbf{x}-\mathbf{q}(t)]}. \tag{2.3}$$

Here, $\underline{\Gamma}(\mathbf{p}, \mathbf{q}, t)$ is an $N \times N$-dimensional time- and phase-space-dependent matrix of complex width parameters. The term 'thawed' SCIVR propagator is used to indicate that the width matrix is time-dependent. The real and imaginary parts of the matrix, denoted by subscripts 'r' and 'i' ($\underline{\Gamma}_r(\mathbf{p}, \mathbf{q}, t)$, $\underline{\Gamma}_i(\mathbf{p}, \mathbf{q}, t)$), will be assumed to be symmetric. At time $t = 0$, the imaginary part will vanish and the real part will be a constant matrix with only positive eigenvalues. For the sake of brevity, henceforth we shall use the notation $\underline{\Gamma}_r(t)$ and $\underline{\Gamma}_i(t)$, keeping in mind that, in principle, the width matrices may also be dependent on the phase space variables.

At this point, we define a normalized averaging function $f(\mathbf{x} - \mathbf{q})$, which is even with respect to the argument. The classical analogue of the quantum Hamiltonian of equation (2.1) is

$$H_{cl} = \frac{\mathbf{p}_q^2}{2} + V(\mathbf{q}). \tag{2.4}$$

The averaged form of this classical Hamiltonian is then defined as

$$\widetilde{H}_{cl} = \frac{\mathbf{p}_q^2}{2} + \widetilde{V}(\mathbf{q}) \tag{2.5}$$

and $\widetilde{V}(\mathbf{q})$ is given by

$$\widetilde{V}(\mathbf{q}) = \int_{-\infty}^{\infty} \mathrm{d}\mathbf{x}\, f(\mathbf{q}-\mathbf{x})V(\mathbf{x}). \tag{2.6}$$

The classical (mass-weighted) coordinates and momenta $\mathbf{q}(t)$ and $\mathbf{p}(t)$ are N-dimensional vectors of the classically evolved values of the coordinate and momentum, respectively, given that at time $t = 0$, $\mathbf{q}(0) = \mathbf{q}$ and $\mathbf{p}(0) = \mathbf{p}$. That is, $\mathbf{q}(t)$ and $\mathbf{p}(t)$ obey Hamilton's equations of motion *on the averaged potential*

$$\dot{q}_j(t) = \frac{\partial \widetilde{H}_{cl}}{\partial p_j} = p_j(t), \tag{2.7}$$

$$\dot{p}_j(t) = -\frac{\partial \widetilde{H}_{cl}}{\partial q_j} = -\frac{\partial \widetilde{V}[\mathbf{q}(t)]}{\partial q_j}, \tag{2.8}$$

where the dot denotes time differentiation. Note the unitarity property of the Gaussian wavepackets, i.e.

$$\int_{-\infty}^{\infty} \prod_{j=1}^{N} \left(\frac{\mathrm{d}p_j \mathrm{d}q_j}{2\pi\hbar}\right) |g(\mathbf{p},\mathbf{q},t)\rangle\langle g(\mathbf{p},\mathbf{q},t)| = \underline{\hat{I}}. \tag{2.9}$$

The function $R(\mathbf{p},\mathbf{q},t)$ appearing in the SCIVR propagator (equation (2.2)) is termed the pre-exponential factor that at time $t = 0$ is unity: $R(\mathbf{p},\mathbf{q},0) = 1$. Similarly, the 'action function' $S(\mathbf{p},\mathbf{q},t)$ will vanish at the initial time $S(\mathbf{p},\mathbf{q},0) = 0$. These conditions assure that, at the initial time $t = 0$, the SCIVR operator reduces to the identity operator, as it should.

2.2. The correction operator

As shown in [11], the 'correction operator' has the form

$$\hat{C}(t) = \int_{-\infty}^{\infty} \prod_{j=1}^{N} \left(\frac{\mathrm{d}p_j \mathrm{d}q_j}{2\pi\hbar}\right) R(\mathbf{p},\mathbf{q},t)\mathrm{e}^{(\mathrm{i}/\hbar)S(\mathbf{p},\mathbf{q},t)}\Delta V(\hat{\mathbf{q}},t)|g(\mathbf{p},\mathbf{q},t)\rangle\langle g(\mathbf{p},\mathbf{q},0)| \tag{2.10}$$

and the potential difference operator $\Delta V(\hat{\mathbf{q}},t)$ is

$$\begin{aligned}\Delta V(\hat{\mathbf{q}},t) = {} & \nabla\widetilde{V}[\mathbf{q}(t)]\cdot(\hat{\mathbf{q}}-\mathbf{q}(t)) - V(\hat{\mathbf{q}}) - \frac{\partial S}{\partial t} + \frac{\mathbf{p}^{\mathrm{T}}\cdot\mathbf{p}}{2} + \mathrm{i}\hbar\frac{\dot{R}}{R} + \frac{\mathrm{i}\hbar}{4}\frac{\partial \log[\det \underline{\Gamma}_r(t)]}{\partial t} \\ & - \frac{\hbar^2}{2}\mathrm{Tr}[\underline{\Gamma}(t)] + \frac{\hbar^2}{2}(\hat{\mathbf{q}}-\mathbf{q}(t))^{\mathrm{T}}\underline{\Gamma}(t)\underline{\Gamma}(t)(\hat{\mathbf{q}}-\mathbf{q}(t)) \\ & - \frac{\mathrm{i}\hbar}{2}(\hat{\mathbf{q}}-\mathbf{q}(t))^{\mathrm{T}}\left[\frac{\partial}{\partial t}\underline{\Gamma}(t)\right](\hat{\mathbf{q}}-\mathbf{q}(t)).\end{aligned} \tag{2.11}$$

The averaged correction operator is defined as

$$\tilde{\hat{C}}(t) = \int_{-\infty}^{\infty} \mathrm{d}\hat{\mathbf{x}}\, f(\hat{\mathbf{x}} - \hat{\mathbf{q}})\hat{C}(t)$$

$$= \int_{-\infty}^{\infty} \prod_{j=1}^{N} \left(\frac{\mathrm{d}p_j \mathrm{d}q_j}{2\pi\hbar}\right) R(\mathbf{p}, \mathbf{q}, t)\mathrm{e}^{(\mathrm{i}/\hbar)S(\mathbf{p},\mathbf{q},t)} \widetilde{\Delta V}(\hat{\mathbf{q}}, t)|g(\mathbf{p}, \mathbf{q}, t)\rangle\langle g(\mathbf{p}, \mathbf{q}, 0)| \qquad (2.12)$$

and one readily finds that

$$\widetilde{\Delta V}(\hat{\mathbf{q}}, t) = \nabla\tilde{V}[\mathbf{q}(t)] \cdot (\hat{\mathbf{q}} - \mathbf{q}(t)) - \tilde{V}(\hat{\mathbf{q}}) - \frac{\partial S}{\partial t} + \frac{\mathbf{p}^{\mathrm{T}}(t) \cdot \mathbf{p}(t)}{2} + \mathrm{i}\hbar\frac{\dot{R}}{R} + \frac{\mathrm{i}\hbar}{4}\frac{\partial \log[\det \underline{\Gamma}_r(t)]}{\partial t}$$
$$- \frac{\hbar^2}{2}\mathrm{Tr}[\underline{\Gamma}(t)] + \frac{1}{2}\left\langle(\hat{\mathbf{x}} - \mathbf{q}(t))^{\mathrm{T}}\left[\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t)\right](\hat{\mathbf{x}} - \mathbf{q}(t))\right\rangle_f, \qquad (2.13)$$

where the brackets denote averaging with respect to the averaging function f.

2.3. The harmonic expansion

The general philosophy behind deriving thawed SCIVR propagators is to account exactly for the harmonic terms in the evolution equation. Expanding the averaged potential operator about the classical time-dependent coordinates:

$$\tilde{V}(\hat{\mathbf{q}}) = \tilde{V}(\mathbf{q}(t)) + \nabla\tilde{V}[\mathbf{q}(t)] \cdot (\hat{\mathbf{q}} - \mathbf{q}(t)) + \frac{1}{2}(\hat{\mathbf{q}} - \mathbf{q}(t))^{\mathrm{T}}\underline{\tilde{V}}''(\mathbf{q}(t))(\hat{\mathbf{q}} - \mathbf{q}(t)) + \tilde{V}_{nl}(\hat{\mathbf{q}}, \mathbf{q}(t)) \qquad (2.14)$$

(where $\underline{\tilde{V}}''(\mathbf{q}(t))$ is the matrix of the second derivatives of the averaged potential function) and noting that

$$\left\langle(\hat{\mathbf{x}} - \mathbf{q}(t))^{\mathrm{T}}\left[\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t)\right](\hat{\mathbf{x}} - \mathbf{q}(t))\right\rangle_f = (\hat{\mathbf{q}} - \mathbf{q}(t))^{\mathrm{T}}\left[\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t)\right]$$
$$\times (\hat{\mathbf{q}} - \mathbf{q}(t)) + \int_{-\infty}^{\infty} \mathrm{d}\mathbf{y}\, f(\mathbf{y})\mathbf{y}^{\mathrm{T}}\left[\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t)\right]\mathbf{y} \qquad (2.15)$$

allows us to rewrite the averaged potential difference operator appearing in equation (2.13) as the sum of four terms:

$$\widetilde{\Delta V}(\hat{\mathbf{q}}, t) = \left(-\frac{\partial S}{\partial t} + \frac{\mathbf{p}^{\mathrm{T}}(t) \cdot \mathbf{p}(t)}{2} - \tilde{V}(\mathbf{q}(t)) + \frac{1}{2}\int_{-\infty}^{\infty} \mathrm{d}\mathbf{y}\, f(\mathbf{y})\mathbf{y}^{\mathrm{T}}\left[\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t)\right]\mathbf{y}\right)$$
$$+ \left(\mathrm{i}\hbar\frac{\dot{R}}{R} + \frac{\mathrm{i}\hbar}{4}\frac{\partial \log[\det \underline{\Gamma}_r(t)]}{\partial t} - \frac{\hbar^2}{2}\mathrm{Tr}[\underline{\Gamma}(t)]\right)$$
$$+ \left(\frac{1}{2}(\hat{\mathbf{q}} - \mathbf{q}(t))^{\mathrm{T}}\left[\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t) - \underline{\tilde{V}}''(\mathbf{q}(t))\right](\hat{\mathbf{q}} - \mathbf{q}(t))\right)$$
$$+ \tilde{V}_{nl}(\hat{\mathbf{q}}, \mathbf{q}(t)). \qquad (2.16)$$

The thawed propagator is now derived by demanding that the first three terms in equation (2.16) vanish such that the correction operator is dependent only on the nonharmonic terms in the averaged potential. This can be effected, since at this point we have three as yet undetermined objects: the action function S, the prefactor function R and the width matrix $\underline{\Gamma}$. Thus, the width matrix is determined by demanding that the third term in the equation vanishes, i.e.

$$\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t) - \underline{\widetilde{V}}''(\mathbf{q}(t)) = 0. \tag{2.17}$$

Using the notation

$$\iota(\mathbf{p}(t),\mathbf{q}(t)) \equiv \frac{1}{2}\int_{-\infty}^{\infty}\mathrm{d}\mathbf{y}\, f(\mathbf{y})\mathbf{y}^{\mathrm{T}}\left[\hbar^2\underline{\Gamma}(t)\underline{\Gamma}(t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\underline{\Gamma}(t)\right]\mathbf{y} = \frac{1}{2}\int_{-\infty}^{\infty}\mathrm{d}\mathbf{y}\, f(\mathbf{y})\mathbf{y}^{\mathrm{T}}\underline{\widetilde{V}}''(\mathbf{q}(t))\mathbf{y}, \tag{2.18}$$

demanding that the first term on the rhs of equation (2.16) vanish and noting that, at the initial time, the thawed SCIVR propagator is the identity operator allow us to determine the action function as

$$S(\mathbf{p}(t),\mathbf{q}(t)) = \int_0^t \mathrm{d}t'\left[\frac{\mathbf{p}^{\mathrm{T}}(t')\cdot\mathbf{p}(t')}{2} - \widetilde{V}(\mathbf{q}(t')) + \iota(\mathbf{p}(t'),\mathbf{q}(t'))\right]. \tag{2.19}$$

Finally, demanding that the second term on the rhs of equation (2.16) vanishes determines the prefactor function as

$$R(\mathbf{p}(t),\mathbf{q}(t)) = \left(\frac{\det\underline{\Gamma}_r(0)}{\det\underline{\Gamma}_r(t)}\right)^{1/4}\exp\left(-\frac{\mathrm{i}\hbar}{2}\int_0^t \mathrm{d}\,t'\,\mathrm{Tr}[\underline{\Gamma}(t')]\right). \tag{2.20}$$

We have thus derived a generalized class of thawed SCIVR propagators that have the property that the initial time values of the elements of the width matrix are free parameters.

This generalized class is guaranteed to be exact for harmonic Hamiltonians. To prove this, we note that, after substituting equations (2.17), (2.19) and (2.20) into equation (2.11), one finds that the potential difference operator reduces to

$$\Delta V(\hat{\mathbf{q}},t) = \widetilde{V}[\mathbf{q}(t)] + \nabla\widetilde{V}[\mathbf{q}(t)]\cdot(\hat{\mathbf{q}} - \mathbf{q}(t)) + \frac{1}{2}(\hat{\mathbf{q}} - \mathbf{q}(t))^{\mathrm{T}}\widetilde{V}''[\mathbf{q}(t)](\hat{\mathbf{q}} - \mathbf{q}(t))$$
$$- \iota(\mathbf{p}(t),\mathbf{q}(t)) - V(\hat{\mathbf{q}}). \tag{2.21}$$

If the potential is harmonic, then the potential difference operator vanishes, since in this case one has that $\widetilde{V}[\mathbf{q}(t)] = V[\mathbf{q}(t)] + \iota(\mathbf{p}(t),\mathbf{q}(t))$.

2.4. Simplification using the monodromy matrices

In an attempt to simplify the computation of the prefactor appearing in the Herman–Kluk form for the propagator, Gelabert *et al* [12] provide a method that can be used also for the solution of equation (2.16). Using the ansatz

$$\mathrm{i}\hbar\underline{\Gamma}(t) = \underline{\dot{Q}}_t\underline{Q}_t^{-1} \tag{2.22}$$

and inserting it into equation (2.16), one readily finds that the matrix $\underline{Q}$ obeys the second-order differential equation in time:

$$\underline{\ddot{Q}}_t + \underline{\widetilde{V}}''(\mathbf{q}(t))\underline{Q}_t = 0. \tag{2.23}$$

The ansatz of equation (2.22) implies the two boundary conditions $\underline{Q}_0 = \underline{I}$ and $\underline{\dot{Q}}_0 = \mathrm{i}\hbar\underline{\Gamma}(0)$. Using the identity [12]

$$\det \underline{Q}_t = \exp\left[\int_0^t \mathrm{d}t' \,\mathrm{Tr}\, \underline{\dot{Q}}_t \underline{Q}_t^{-1}\right] = \exp\left[\mathrm{i}\hbar \int_0^t \mathrm{d}t' \,\mathrm{Tr}\, \underline{\Gamma}(t')\right], \tag{2.24}$$

the expression for the prefactor simplifies to

$$R(\mathbf{p}(t), \mathbf{q}(t)) = \left(\frac{\det \underline{\Gamma}_r(0)}{\det \underline{\Gamma}_r(t)}\right)^{1/4} \frac{1}{\sqrt{\det \underline{Q}_t}}. \tag{2.25}$$

The monodromy matrices are defined as

$$\underline{\widetilde{\mathbf{M}}}_{qq} = \frac{\partial \mathbf{q}_t(\mathbf{p}, \mathbf{q})}{\partial \mathbf{q}}, \tag{2.26}$$

$$\underline{\widetilde{\mathbf{M}}}_{qp} = \frac{\partial \mathbf{q}_t(\mathbf{p}, \mathbf{q})}{\partial \mathbf{p}}, \tag{2.27}$$

$$\underline{\widetilde{\mathbf{M}}}_{pq} = \frac{\partial \mathbf{p}_t(\mathbf{p}, \mathbf{q})}{\partial \mathbf{q}}, \tag{2.28}$$

$$\underline{\widetilde{\mathbf{M}}}_{pp} = \frac{\partial \mathbf{p}_t(\mathbf{p}, \mathbf{q})}{\partial \mathbf{p}}, \tag{2.29}$$

where the 'tilde' notation for the monodromy matrices stresses that the time evolution of the coordinates and momenta are obtained from the averaged potential energy surface as in equation (2.8). It is then straightforward to find that the matrix $\underline{Q}_t$ can be expressed in terms of the monodromy matrices as

$$\underline{Q}_t = \underline{\mathbf{M}}_{qq} + \mathrm{i}\hbar\underline{\mathbf{M}}_{qp}\underline{\Gamma}(0), \tag{2.30}$$

so that from Hamilton's equations of motion we also have that

$$\underline{\dot{Q}}_t = \underline{\mathbf{M}}_{pq} + \mathrm{i}\hbar\underline{\mathbf{M}}_{pp}\underline{\Gamma}(0), \tag{2.31}$$

thus completing the formulation of thawed SCIVR propagators.

2.5. *Thawed Gaussian propagators*

To complete the discussion, we consider two specific cases. The first is the thawed Gaussian propagator, which is obtained by choosing the averaging function to be

$$f_{TG}(\mathbf{x} - \mathbf{q}) = \delta(\mathbf{x} - \mathbf{q}), \tag{2.32}$$

where the 'delta' function is a product of the delta functions for each component separately. With this choice, the 'averaged' potential is just the bare potential so that the classical dynamics is determined by the usual classical Hamiltonian of the system. The ι function (equation (2.18)) vanishes in this case, so that the action function is also the 'standard' action function. The results of the previous subsection reduce to the one-dimensional form of the thawed Gaussian propagator as derived by Baranger *et al* [6]. This propagator has been termed thawed Gaussian owing to the fact that the width matrix is time-dependent—thawed—and the propagator is defined by coherent states that are Gaussian.

Baranger *et al* [6] also derived an SCIVR propagator using a Gaussian averaging function. Specifically, if one chooses

$$f_{BEA}(\mathbf{x}-\mathbf{q}) = \left(\frac{\det \underline{\Gamma}_r(0)}{(\pi)^N}\right)^{1/2} \exp(-(\mathbf{x}-\mathbf{q})^{\mathrm{T}}\underline{\Gamma}_r(0)(\mathbf{x}-\mathbf{q})), \tag{2.33}$$

then one regains what we termed [8] as their BEA propagator. In this case, our ι function defined in equation (2.18) is readily found to be

$$\iota(\mathbf{p}(t),\mathbf{q}(t)) = \tfrac{1}{4}\mathrm{Tr}[\underline{\widetilde{V}}''(\mathbf{q}(t))\underline{\Gamma}_r(0)^{-1}]. \tag{2.34}$$

Substituting this expression into the action function (2.19), one finds, in one dimension, that our action is identical to the sum of the Baranger *et al* action and their ι function. More specifically, Baranger *et al* have two contribution to their ι function. One is identical to equation (2.34), whereas the second contribution comes from the second derivative of the kinetic energy with respect to the momentum. At the same time, in their action term, one has the averaged Hamiltonian, rather than only the averaged potential as in our equation (2.19). If the Hamiltonian is quadratic in the momenta, then averaging over the momenta gives a term that exactly cancels out the momentum contribution to their ι function. A fact that emerges from all this is that, in one dimension, the resulting propagator as derived here is identical to the Baranger *et al* propagator. Finally, we do note that in principle one could choose, for the averaging function, a width matrix that is not identical to the real part of the width matrix appearing in the coherent states. This would then be a more general form of the BEA propagator.

3. Discussion

In this paper, we have derived explicit multidimensional expressions for a general class of thawed semiclassical IVR propagators. Using an averaging function, f, one obtains an averaged Hamiltonian, and then all the classical dynamics is carried out on the averaged Hamiltonian. We then showed that the propagator has the explicit form

$$\hat{K}_{f,0}(t) = \int_{-\infty}^{\infty}\prod_{j=1}^{N}\left(\frac{\mathrm{d}p_j\mathrm{d}q_j}{2\pi\hbar}\right)\left(\det[\underline{\mathbf{M}}_{qq} + \mathrm{i}\hbar\underline{\mathbf{M}}_{qp}\underline{\Gamma}(0)]\det\left[\underline{\mathbf{M}}_{pp} - \frac{\mathrm{i}}{\hbar}\underline{\mathbf{M}}_{pq}\underline{\Gamma}(0)^{-1}\right]\right)^{-1/4} \times \mathrm{e}^{(\mathrm{i}/\hbar)S(\mathbf{p},\mathbf{q},t)}|g(\mathbf{p},\mathbf{q},t)\rangle\langle g(\mathbf{p},\mathbf{q},0)|. \tag{3.1}$$

The action function S and the ι function that appears in the action function are given in equations (2.19) and (2.18), respectively. This generalized form reduces to the multidimensional version of the thawed Gaussian propagator when the averaging function is chosen to be a 'delta' function and reduces to the multidimensional version of the BEA propagator when the averaging function is a Gaussian with a width matrix identical to the initial time width matrix appearing in the coherent states.

The associated f averaged correction operator simplifies to

$$\widetilde{\hat{C}}(t) = \int_{-\infty}^{\infty}\prod_{j=1}^{N}\left(\frac{\mathrm{d}p_j\mathrm{d}q_j}{2\pi\hbar}\right)\widetilde{V}_{nl}(\hat{\mathbf{q}},\mathbf{q}(t))R(\mathbf{p},\mathbf{q},t)\mathrm{e}^{(\mathrm{i}/\hbar)S(\mathbf{p},\mathbf{q},t)}|g(\mathbf{p},\mathbf{q},t)\rangle\langle g(\mathbf{p},\mathbf{q},0)|, \tag{3.2}$$

showing explicitly that the transformed correction operator always vanishes for harmonic systems. In fact, the general class of thawed propagators was defined by demanding that the correction operator reduces to this simple form. We have also shown in equation (2.21) that the (untransformed) correction operator vanishes in the harmonic limit.

There is quite some controversy over the usefulness of thawed propagators. Kay's early computations [3] and, more recently, the work of Harabati *et al* [13] have shown that the thawed Gaussian propagator rapidly loses its unitarity, whereas the Herman–Kluk propagator is approximately unitary for rather long time periods. This seems to suggest that the whole discussion on thawed propagators is just a useless intellectual exercise. On the other hand, in the HK propagator, the monodromy matrices appear in the prefactor in the numerator. Thus, when treating a chaotic system, the exponential divergence of classical trajectories creates an exponent that increases exponentially in time, making any Monte Carlo evaluation of the propagator very difficult [14]. In the thawed propagators, the monodromy matrices appear in the denominator so that this rapid growth may not necessarily cause a problem. In this context, one should also note that, for thawed propagators, one is considering the classical dynamics on an averaged potential energy surface. This averaging would probably tend to 'smoothen' the surface and thus diminish the chaoticity.

As is evident, there is much freedom in the choice of thawed propagators. Both the averaging function and the initial value of the width matrix appearing in the coherent states are not defined uniquely. This freedom does imply that further studies are needed to elucidate what are the optimal width parameters and smoothing functions for different physically interesting cases. Ultimately, the 'best' propagator is the one for which the SCIVR series expansion discussed extensively in [9–11] converges most rapidly.

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