On the Relation between the Semiclassical Initial Value Representation and an Exact Quantum Expansion in Time-Dependent Coherent States†

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Received: February 21, 2002; In Final Form: April 23, 2002

The Herman−Kluk (HK) or coherent state initial value representation (IVR) of semiclassical (SC) theory expresses a time-evolving wave function as a sum (integral) over the initial conditions of classically evolved coherent states (aka minimum uncertainty wave packets). An *exact* expansion of the wave function can also be made in terms of these same coherent states, thinking of them simply as a (time-dependent) basis set. This paper shows the precise set of approximations that are necessary to degenerate the exact expansion into the SC-IVR result. As a byproduct, we also obtain a generalization of the HK "prefactor".

I. Introduction

The initial value representation (IVR) of semiclassical (SC) theory[1] is undergoing a great deal of attention at present as a potentially practical way for adding quantum mechanical effects to classical molecular dynamics (MD) simulations of complex molecular processes.[2] The attractiveness of the approach is that essentially all quantum mechanical effects in chemical systems are described well by SC theory—as has been verified by application to a number of "small molecule" problems[2] (where its accuracy can be checked by comparing to quantum calculations)—and it has also been shown to be applicable to model problems involving many degrees of freedom[2] (e.g., an "interesting" degree of freedom or two coupled to a "bath" of harmonic modes). Classical MD simulations are of course widely used to model a host of molecular phenomena, e.g., chemical reactions is solution, clusters, solids, proteins, so if the SC-IVR approach can indeed be made practical, it should be extremely useful.

The SC-IVR represents a time-evolving wave function as an integral over the initial conditions of classical trajectories. For example, the Herman−Kluk[3,4] (HK), or coherent state IVR expresses a time-dependent wave function as follows

$$\psi(q,t) \equiv \langle q|e^{-i\hat{H}t/\hbar}|\psi_i\rangle = (2\pi\hbar)^{-1}\int dq_0 \int dp_0 \langle q|q_t,p_t\rangle\langle q_0,p_0|\psi_i\rangle \times e^{iS_t(q_0,p_0)/\hbar} C_t^{HK}(q_0,p_0) \quad (1.1)$$

where $|\psi_i>$ is the initial wave function at $t = 0$, (q_0,p_0) are initial coordinates and momenta for classical trajectories, (q_t,p_t) are the values at time t that evolve from them [and thus $q_t = q_t(q_0,p_0)$ and $p_t = p_t(q_0,p_0)$], and $S_t(q_0,p_0)$ is the classical action along this trajectory,

$$S_t(q_0,p_0) = \int_0^t dt' [p_{t'}^2/2m - V(q_{t'})] \quad (1.2)$$

where H is the classical Hamiltonian function

$$H(p,q) = p^2/2m + V(q) \quad (1.3)$$

(To keep the notation as simple as possible, we write all expressions for a one-dimensional system with the above Cartesian Hamiltonian; generalization to the multidimensional case is straightforward.) $\langle q|q_t,p_t\rangle$ in eq 1.1 is a coherent state[5] wave function,

$$\langle q|q_t,p_t\rangle = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\left[-\frac{\gamma}{2}(q-q_t)^2 + \frac{i}{\hbar}p_t(q-q_t)\right] \quad (1.4)$$

where γ is the parameter that tunes between the coordinate ($\gamma\rightarrow\infty$) and momentum space ($\gamma\rightarrow 0$) limits of the coherent state. $C_t^{HK}(q_0,p_0)$ in eq 1.1 is the HK prefactor[3,4]

$$C_t^{HK}(q_0,p_0) = \left[\frac{1}{2}\left(M_{qq} + M_{pp} + \frac{\hbar\gamma}{i}M_{qp} + \frac{i}{\hbar\gamma}M_{pq}\right)\right]^{1/2} \quad (1.5)$$

where M_{qq}, etc., are the monodromy matrices

$$M_{qq} = \frac{\partial q_t}{\partial q_0} \qquad M_{qp} = \frac{\partial q_t}{\partial p_0}$$

$$M_{pq} = \frac{\partial p_t}{\partial q_0} \qquad M_{pp} = \frac{\partial p_t}{\partial p_0} \quad (1.6)$$

Thinking of the coherent states of eq 1.1 as simply a time-dependent basis set,

$$\phi_{q_0,p_0}(q,t) \equiv \langle q|q_t(q_0,p_0),p_t(q_0,p_0)\rangle \quad (1.7a)$$

the IVR expansion of the wave function in eq 1.1 thus has the form

$$\psi(q,t) = \int dq_0 \int dp_0\, \phi_{q_0,p_0}(q,t) A_{q_0,p_0}(t) \quad (1.7b)$$

where the coefficients are given by

$$A_{q_0,p_0}(t) = (2\pi\hbar)^{-1}\langle q_0,p_0|\psi_i\rangle e^{iS_t(q_0,p_0)/\hbar} C_t^{HK}(q_0,p_0) \quad (1.7c)$$

Several authors, however—inspired primarily by Heller's very influential work[6] using coherent states (aka Gaussian wave

† Part of the special issue "John C. Tully Festschrift".

10.1021/jp020500+ CCC: $22.00
Published on Web 06/17/2002

packets) in the mid 1970s—have considered an *exact* expansion of the wave function in the form of eq 1.7b, with the time-dependent coefficients determined by substituting this expansion into the Schrödinger equation. (The expansion can be exact because coherent states form an overcomplete set.) Work by Sawada et al.[7] is the first work of this kind that we are aware of; more recently, Martinez[8] has developed approaches that start with this premise, and most recently, Child and Shalashilin[9] have been pursuing this approach.

The purpose of this paper is to show the relation between this exact expansion of the wave function in time-dependent coherent states and the above IVR approximation, i.e., to show what approximations one must make to the exact formulation in order to obtain the IVR result. It is also hoped, of course, that once one understands this connection more clearly that one may be able to see improvements to the IVR approach that might be useful, and this is indeed the case: a generalization of the HK prefactor (eq 1.5) is suggested.

In concluding this Introduction, it should also be noted that Grossmann and Xavier[10a] have shown that the HK-IVR can be derived by starting with Weissman's[11] SC expression for coherent state matrix elements of the propagator and using the stationary phase approximation to transform to the coordinate space representation of the propagator. Simultaneous with this, Sun[10b] showed another route for obtaining the HK-IVR from Weissman's result. In addition, Miller[12] has recently shown that the HK-IVR can also be obtained by applying a modified Filinov transformation[13] to the coordinate space, or Van Vleck IVR[14] of the propagator. The present paper, showing how the HK-IVR can be obtained from the exact expansion of the wave function in coherent states, is different from these and thus provides further insight into the basic nature of this semiclassical approximation.

II. The Exact Expansion

To make the connection with the IVR expression (eq 1.1) as close as possible, the exact expansion of the time-dependent wave function is written in the same form as eq 1.1,

$$\psi(q,t) = (2\pi\hbar)^{-1}\int \mathrm{d}q_0 \int \mathrm{d}p_0\, \langle q|q_t,p_t\rangle\langle q_0,p_0|\psi_i\rangle \mathrm{e}^{iS_t(q_0,p_0)/\hbar} C_t(q_0,p_0) \tag{2.1}$$

where all quantities are the same as in eq 1.1, except for the coefficients $C_t(q_0,p_0)$, which are to be determined here by substituting this expansion into the time-dependent Schrödinger equation,

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\psi(q,t) = \hat{H}\,\psi(q,t) \tag{2.2}$$

Because of the completeness relation of coherent states,

$$\hat{1} = (2\pi\hbar)^{-1}\int \mathrm{d}q_0 \int \mathrm{d}p_0\, |q_0,p_0\rangle\langle q_0,p_0| \tag{2.3}$$

one easily sees (by setting $t = 0$ in eq 2.1) that the initial value of C_t is unity,

$$C_0(q_0,p_0) = 1 \tag{2.4}$$

The development is now quite standard and straightforward, so we only sketch some of the intermediate steps: the time derivative of the wave function (the LHS of eq 2.2) involves three factors,

$$\frac{\partial}{\partial t}\langle q|q_t,p_t\rangle = \left[\gamma(q-q_t)\dot{q}_t + \frac{\mathrm{i}}{\hbar}\dot{p}_t(q-q_t) - \frac{\mathrm{i}}{\hbar}p_t\dot{q}_t\right]\langle q|q_t,p_t\rangle \tag{2.5a}$$

$$\frac{\partial}{\partial t}\mathrm{e}^{\mathrm{i}S_t(q_0,p_0)/\hbar} = \frac{\mathrm{i}}{\hbar}[p_t^{\,2}/2m - V(q_t)]\mathrm{e}^{\mathrm{i}S_t(q_0,p_0)/\hbar} \tag{2.5b}$$

$$\frac{\partial}{\partial t}C_t(q_0,p_0) \equiv \dot{C}_t(q_0,p_0) \tag{2.5c}$$

and the Hamiltonian, of course, operates (the RHS of eq 2.2) only on the coherent state "basis function"

$$\begin{aligned}\hat{H}\langle q|q_t,p_t\rangle &\equiv \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + V(q)\right]\langle q|q_t,p_t\rangle \\ &= \left[p_t^{\,2}/2m - \frac{\hbar^2\gamma^2}{2m}(q-q_t)^2 + \frac{\hbar^2\gamma}{2m} + \frac{\mathrm{i}\hbar\gamma}{m}p_t(q-q_t) + V(q)\right]\langle q|q_t,p_t\rangle\end{aligned} \tag{2.5d}$$

Inserting the expansion eq 2.1 into the Schrödinger equation (eq 2.2), using eq 2.5, and then projecting with respect to the time-dependent coherent state corresponding to another initial phase point (q_0',p_0'), $\langle q_t(q_0',p_0'), p_t(q_0',p_0')|$, leads to the following set of linear equations for the expansion coefficients $C_t(q_0,p_0)$:

$$\begin{aligned}&\int dq_0 \int \mathrm{d}p_0\, \langle q_t',p_t'|q_t,p_t\rangle \mathrm{e}^{\mathrm{i}S_t(q_0,p_0)/\hbar}\langle q_0,p_0|\psi_i\rangle \mathrm{i}\hbar\dot{C}_t(q_0,p_0) = \\ &\int \mathrm{d}q_0 \int \mathrm{d}p_0 \Big\{\langle q_t',p_t'|V|q_t,p_t\rangle - V'(q_t)\langle q_t',p_t'|q-q_t|q_t,p_t\rangle - \\ &\qquad \frac{\hbar^2\gamma^2}{2m}\langle q_t',p_t'|(q-q_t)^2|q_t,p_t\rangle + \\ &\qquad \left(\frac{\hbar^2\gamma}{2m} - V(q_t)\right)\langle q_t',p_t'|q_t,p_t\rangle\Big\}\mathrm{e}^{iS_t(q_0,p_0)/\hbar}\langle q_0,p_0|\psi_i\rangle C_t(q_0,p_0)\end{aligned} \tag{2.6}$$

where $(q_t',p_t') = (q_t(q_0',p_0'),\ p_t(q_0',p_0'))$, and the fact that $\dot{q}_t = p_t/m$ and $\dot{p}_t = -V'(q_t)$ has been used (since q_t and p_t follow a classical trajectory).

Equation 2.6 involves a matrix element of the potential, $\langle q_t',p_t'|V|q_t,p_t\rangle$, and for "real" applications (i.e., other than to model problems), one will not be able to evaluate this analytically. To make further progress, therefore, one expands $V(q)$ to second order about q_t (in the spirit of Heller's original semiclassical approaches[6]); the required matrix elements are then easily evaluated analytically, so that eq 2.6 becomes

$$\begin{aligned}&\int \mathrm{d}q_0' \int dp_0' \,\langle q_t,p_t|q_t',p_t'\rangle \mathrm{e}^{\mathrm{i}S_t(q_0',p_0')/\hbar} \times \\ &\qquad \langle q_0',p_0'|\psi_i\rangle \mathrm{i}\hbar\dot{C}_t(q_0',p_0') = \\ &\qquad \int \mathrm{d}q_0' \int \mathrm{d}p_0' \,\langle q_t,p_t|q_t',p_t'\rangle\left[\frac{\hbar^2\gamma}{4m} + \frac{K(q_t')}{4\gamma} + \right. \\ &\qquad \left.\frac{1}{8}\left(K(q_t') - \frac{\hbar^2\gamma^2}{m}\right)\left(q_t' - q_t - \frac{\mathrm{i}}{\hbar\gamma}(p_t' - p_t)\right)^2\right] \times \\ &\qquad \mathrm{e}^{\mathrm{i}S_t(q_0',p_0')/\hbar}\langle q_0',p_0'|\psi_i\rangle C_t(q_0',p_0')\end{aligned} \tag{2.7}$$

where $K(q) = V''(q)$ is the force constant (matrix, in general), and for later notational convenience, we have interchanged (q_0,p_0) and (q_0',p_0'). [And we remind the reader again that $(q_t,p_t) \equiv (q_t(q_0,p_0),\ p_t(q_0,p_0))$ and $(q_t',p_t') \equiv (q_t(q_0',p_0'),\ p_t(q_0',p_0'))$.]

III. Approximations

As noted, except for the quadratic expansion of $V(q)$ about the position q_t, eq 2.7 is the exact equation that determines the

coefficients $C_t(q_0,p_0)$. If the phase space integrals in eq 2.7 were evaluated on a grid of phase points, it would become a set of first-order linear equations for the coefficients, their number being the number of phase points, i.e., the number of trajectories that are integrated. As is typical of quantum mechanics, every basis function $|q_t(q_0,p_0),p_t(q_0,p_0)\rangle$ (and thus every trajectory) is coupled to every other one. In the SC approximation (eq 1.1), however, the coefficient $C_t^{HK}(q_0,p_0)$ of eq 1.5 is determined only by the phase point (q_0,p_0) itself, with no coupling between different trajectories. The question we wish to address is how this comes about; i.e., what approximations to the exact equation for the coefficients (eq 2.7) are necessary in to order to obtain the SC approximation to them (eq 1.5).

The key approximation is to assume that $C_t(q_0,p_0)$ is a slowly varying function of (q_0,p_0). This is suggested by the fact that the HK prefactor (eq 1.5) depends only on the monodromy matrices, which themselves are often assumed to be weak functions of the initial conditions (q_0,p_0).[15,16] The approximation to eq 2.7, therefore, is to replace $C_t(q_0',p_0')$ by $C_t(q_0,p_0)$ on both right- and left-hand sides of eq 2.7. (Note also that the overlap factor $\langle q_t',p_t'|q_t,p_t\rangle$ tends to keep (q_0',p_0') close to (q_0,p_0), which helps to justify the approximation.) $C_t(q_0,p_0)$ can then be brought outside of the phase space integrals and eq 2.7 rearranged to read

$$i\hbar\dot{C}_t(q_0,p_0)/C_t(q_0,p_0) \equiv \Delta V_t(q_0,p_0) = \frac{1}{4\gamma}\left(K(q_t)+\frac{\hbar^2\gamma^2}{m}\right)+\frac{1}{8}\left(K(q_t)-\frac{\hbar^2\gamma^2}{m}\right)I_2(q_0,p_0)/I_0(q_0,p_0) \quad (3.1)$$

where we have also replaced $K(q_t')$ by $K(q_t)$ (which is consistent with the similar approximation to C_t) and where the integrals I_n are

$$I_n(q_0,p_0) \equiv \int dq_0' \int dp_0' \left[q_t'-q_t-\frac{i}{\hbar\gamma}(p_t'-p_t)\right]^n \times \langle q_t,p_t|q_t',p_t'\rangle e^{iS_t(q_0',p_0')/\hbar}\langle q_0',p_0'|\psi_i\rangle \quad (3.2)$$

Once the RHS of eq 3.1 has been computed, it is a trivial matter to obtain the coefficient by integration,

$$C_t(q_0,p_0) = \exp\left[-\frac{i}{\hbar}\int_0^t dt'\Delta V_{t'}(q_0,p_0)\right] \quad (3.3)$$

the notation suggesting that it can be combined with the factor involving the classical action and thought of as providing a "quantum correction" to the potential,

$$e^{iS_t(q_0,p_0)/\hbar}C_t(q_0,p_0) = \exp\left\{-\frac{i}{\hbar}\int_0^t dt'[p_{t'}^2/2m - V(q_{t'}) - \Delta V_{t'}(q_0,p_0)]\right\} \quad (3.4)$$

In the harmonic limit $[V(q) = (1/2)m\omega^2q^2,\ \gamma = m\omega/\hbar]$, eq 3.1 gives $\Delta V = \hbar\omega/2$, the zero point energy (as is well-known). In general, however, ΔV of eq 3.1 is complex.

Taking the initial state $|\psi_i\rangle$ to be the coherent state $|q_i,p_i\rangle$, and using the standard expression for the overlap of two coherent states,

$$\langle q,p|q',p'\rangle = \exp\left[-\frac{\gamma}{4}(q-q')^2-\frac{1}{4\hbar^2\gamma}(p-p')^2+\frac{i}{2\hbar}(p+p')(q-q')\right] \quad (3.5)$$

eq 3.2 for the integrals I_n becomes

$$I_n(q_0,p_0) = \int dq_0' \int dp_0' \left[q_t'-q_t-\frac{i}{\hbar\gamma}(p_t'-p_t)\right]^n \times \exp\left[-\frac{\gamma}{4}(q_t-q_t')^2-\frac{1}{4\hbar^2\gamma}(p_t-p_t')^2-\frac{\gamma}{4}(q_0'-q_i)^2-\frac{1}{4\hbar^2\gamma}(p_0-p_i)^2+\frac{i}{\hbar}S_t(q_0',p_0')+\frac{i}{2\hbar}(p_t+p_t')(q_t-q_t')+\frac{i}{2\hbar}(p_0'+p_i)(q_0'-q_i)\right] \quad (3.6)$$

The IVR result for the coefficient C_t is then obtained by expanding the integrand of eq 3.6 about the phase point (q_0,p_0); specifically, one changes integration variables

$$q_0' = q_0 + \Delta q$$
$$p_0' = p_0 + \Delta p \quad (3.7a)$$

so that

$$\int dq_0' \int dp_0' \rightarrow \int d\Delta q \int d\Delta p \quad (3.7b)$$

and expands $q_t' \equiv q_t(q_0+\Delta q,p_0+\Delta p)$ and $p_t' \equiv p_t(q_0+\Delta q,p_0+\Delta p)$ to first order in Δq and Δp,

$$q_t' = q_t + M_{qq}\Delta q + M_{qp}\Delta p$$
$$p_t' = p_t + M_{pq}\Delta q + M_{pp}\Delta p \quad (3.7c)$$

where $M_{qq} = \partial q_t/\partial q_0$, etc., are the monodromy matrices of eq 1.6. (Note that this is very reminiscent of the "linearization approximation"[17,18] used in another context of IVR theory.) With this approximation, the integrand of eq 3.6 becomes a 2d Gaussian integral in Δq and Δp that can be evaluated analytically. The calculation is tedious but straightforward (the algebra is similar to that involved in carrying out a Filinov transformation[10,11] of the IVR integrand), and one obtains the following result for the required ratio I_2/I_0

$$\frac{I_2}{I_0} = \frac{2}{\gamma}\frac{\left(M_{qq}+\frac{\hbar\gamma}{i}M_{qp}-M_{pp}-\frac{i}{\hbar\gamma}M_{pq}\right)}{\left(M_{qq}+\frac{\hbar\gamma}{i}M_{qp}+M_{pp}+\frac{i}{\hbar\gamma}M_{pq}\right)} \quad (3.8)$$

Using this result in eq 3.1 gives

$$\frac{i\hbar\dot{C}_t(q_0,p_0)}{C_t(q_0,p_0)} = \frac{1}{2\gamma}\frac{\left[K(q_t)\left(M_{qq}+\frac{\hbar\gamma}{i}M_{qp}\right)+\frac{\hbar^2\gamma^2}{m}\left(M_{pp}+\frac{i}{\hbar\gamma}M_{pq}\right)\right]}{\left(M_{qq}+\frac{\hbar\gamma}{i}M_{qp}+M_{pp}+\frac{i}{\hbar\gamma}M_{pq}\right)} \quad (3.9)$$

which one can verify—by direct differentiation of eq 1.5, using the known expression for derivatives of the monodromy matrix

$$\frac{d}{dt}\begin{pmatrix}M_{qq}, M_{qp}\\ M_{pq}, M_{pp}\end{pmatrix} = \begin{pmatrix}0, \frac{1}{m}\\ -K(q_t), 0\end{pmatrix}\begin{pmatrix}M_{qq}, M_{qp}\\ M_{pq}, M_{pp}\end{pmatrix} \quad (3.10)$$

—is identical to the Herman−Kluk prefactor (eq 1.5).

In summary, therefore, we have shown that the Herman−Kluk IVR (eqs 1.1−1.5) is obtained from the *exact* expansion

in time-dependent coherent states (eq 2.7) by assuming that only values of (q_0',p_0') infinitesimally close to (q_0,p_0) contribute to the integrals in eq 2.7 and then by approximating the integrands accordingly. If it were really true that only values of (q_0',p_0') close to (q_0,p_0) contribute, then this should of course make it relatively easy to solve the exact quantum equations for the coefficients (eq 2.7). This is what Child and Shalashilin[9] are in fact suggesting, and it remains to be seen whether this is the case.

IV. Concluding Remarks

The primary objective of this paper has been to show precisely how the SC-IVR approximation for the time evolution of a wave function (eq 1.1) is obtained from the exact description (eq 2.7). Having accomplished this, one wonders if it is possible to "back up" a bit, e.g., to make the local approximation that leads to eqs 3.1−3.3, but no further ones. The suggestion is that one evaluate the integrals $I_n(q_0,p_0)$ defined by eq 3.2, e.g., by Monte Carlo averaging over (q_0',p_0'), which might be very efficient if the averaging is dominated by values of (q_0',p_0') that are close to (q_0,p_0). The prefactor would then be obtained by eq 3.3.

A very attractive feature of the above suggestion is that no monodromy matrices are involved! Since their calculation is the major additional effort of an SC-IVR calculation beyond a strictly classical molecular dynamics simulation, this is very appealing. The effect of nearby trajectories on the one with initial conditions (q_0,p_0), which is accounted for in the HK approximation by the monodromy matrix (cf. eq 1.5), is replaced by a phase space average; the ratio I_2/I_0 is seen to have the form of a second moment

$$\frac{I_2(q_o,p_0)}{I_0(q_o,p_0)} = \left\langle \left[q_t' - q_t - \frac{\mathrm{i}}{\hbar\gamma}(p_t' - p_t) \right]^2 \right\rangle \qquad (4.1)$$

with respect to the following complex weight function

$$\rho(q_0',p_0') \propto \langle q_t,p_t|q_t',p_t'\rangle \mathrm{e}^{\mathrm{i}S_t(q_0',p_0')/\hbar} \langle q_0',p_0'|\psi_i\rangle \qquad (4.2)$$

Whether it is easier to compute the phase space average over (q_0',p_0') in eqs 3.1 and 3.2—for each value of (q_0,p_0)—rather than the monodromy matrix is not at all clear, however. If the calculation were done in the most naïve fashion—i.e., to carry out an independent Monte Carlo average over (q_0',p_0') for each value of (q_0,p_0)—then it would certainly seem not to be. If, however, one stored the trajectory information from each set of (Monte Carlo selected) initial conditions and used the same set of trajectories for the (q_0',p_0') averages in eqs 3.1 and 3.2 as for the IVR average over (q_0,p_0) in eq 1.1, then it might in fact be practical.

Finally, there is the question of whether the prefactor given by eqs 3.1−3.3 is better, i.e., gives better agreement with exact quantum mechanics, than the Herman−Kluk prefactor of eq 1.5, but this must await test calculations.

Acknowledgment. This work has been supported in part by the National Science Foundation under Grant No. CHE-0096576 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE AC03-76SF00098.

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