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Generalization of the Linearized Approximation to the Semiclassical Initial Value Representation for Reactive Flux Correlation Functions

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The semiclassical (SC) initial value representation (IVR) provides a general and practical approach for including quantum effects in classical molecular dynamics simulations. The linearized approximation (LA) to the SC-IVR simplifies the description much further, reducing it to the well-known classical Wigner model (i.e., a classical trajectory calculation with a Wigner distribution of initial conditions); the LA is able to describe quantum effects well for short times ($t \lesssim \hbar\beta$) but not so for longer times. It is shown here how the full SC-IVR approach, which *is* able to describe quantum effects for long times, can be cast in a form very similar in structure to the LA, with specific application to flux correlation functions relevant to chemical reaction rates. This formulation may thus make it possible to carry out full SC-IVR calculations while still retaining much of the simplifying aspects of its linearized approximation.

I. Introduction

There has been a rebirth of interest among several research groups in using semiclassical (SC) theory as a practical way for including quantum interference and tunneling effects in classical molecular dynamics (CMD) simulations.[1-8] These recent efforts make use of an initial value representation (IVR)[9] to implement the semiclassical approximation, thus reducing the calculation to an average over the initial conditions of classical trajectories. The primary difference of an SC-IVR calculation from a conventional CMD one is that there is phase information in the semiclassical calculation, from which the quantum effects arise but which also makes the calculation more difficult. Applications[1-8] to a number of simple molecular systems have shown that the SC-IVR provides a very useful description of essentially all quantum effects in molecular dynamics, so there is an intense ongoing effort to make these calculations as practical as possible so that they can be used for more complex molecular systems.

In a previous paper[6f] it was shown that a particular kind of *linearization* of the general SC-IVR expression for the reactive flux correlation function (which is related[10] to thermal rate constants for chemical reactions) leads to an extremely simple result for the correlation function, namely, the classical Wigner model that has been obtained many times before from a variety of approaches.[11-14] Within this approximation the only difference from a conventional CMD, or classical trajectory calculation, is that the initial conditions are weighted by the Wigner function corresponding to the Boltzmannized flux operator rather than the classical Boltzmann and flux functions themselves. (This is reviewed in section II below.) This linearized approximation to the SC-IVR is thus practical for systems with many degrees of freedom, and in fact it has been applied[6f,i] to

several problems involving a reaction coordinate (or a two level system[6h]) coupled to an infinite bath of harmonic oscillators and found to give excellent results for the thermal rate constant (by comparison to accurate quantum path integral calculations[15,16]). A more detailed study,[6g] however, showed that though the linearized approximation to the SC-IVR describes quantum effects in the flux correlation function accurately for *short* times ($t \lesssim \hbar\beta$), its description of longer time dynamics is that of classical, not quantum, mechanics. This means that it is good for describing quantum effects in direct barrier-crossing dynamics, i.e., transition state theory-type dynamics,[17] but not for describing quantum effects in more complex phenomena, e.g., recrossing dynamics that violate transition-state theory behavior.

Because the linearized approximation to the SC-IVR, i.e., the classical Wigner model, does some things quite well, it is desirable to exploit its possibilities and build thereon. In this paper I thus show how the full SC-IVR expression for the flux correlation function can be written in the same form as its linearized approximation, with a generalized distribution function replacing the Wigner function. This development is carried out in section II, and section III concludes with a discussion of further ways one may be able to simplify and implement it.

II. SC-IVR for the Flux-Side Correlation Function

The flux-side correlation function is defined by the following quantum trace expression:[10]

$$C_{fs}(t) = \text{Tr}[\hat{F}(\beta)\, e^{i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar}] \tag{2.1}$$

The thermal rate constant $k(T)$ for a chemical reaction is given by its long time limit

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$$k(T) = Q_r(T)^{-1} \lim_{t \to \infty} C_{fs}(t) \qquad (2.2)$$

where Q_r is the reactant partition function (per unit volume for a bimolecular reaction). In eq 2.1 $\hat{H}$ is the total molecular Hamiltonian and $\hat{h} = h(\mathbf{q})$ is a Heaviside function that is 0 (1) on the reactant (product) side of a surface that divides reactants from products, where $\mathbf{q}$ denotes all the coordinates of the system. $\hat{F}(\beta)$ is the Boltzmannized flux operator,

$$\hat{F}(\beta) \equiv e^{-(\beta/2)\hat{H}} \hat{F} e^{-(\beta/2)\hat{H}} \qquad (2.3)$$

where β is related to temperature in the usual way, $\beta = (k_B T)^{-1}$, and $\hat{F}$ is the flux operator

$$\hat{F} = \frac{i}{\hbar}[\hat{H}, \hat{h}] \qquad (2.4)$$

The standard expression for the coordinate space, or Van Vleck SC-IVR for the time evolution operator, is[6a]

$$e^{-i\hat{H}t/\hbar} = \int d\mathbf{p}_0 \int d\mathbf{q}_0 \left[\left| \frac{\partial \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)}{\partial \mathbf{p}_0} \right| / (2\pi i \hbar)^F \right]^{1/2} \times$$
$$e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{q}_t\rangle\langle\mathbf{q}_0| \quad (2.5)$$

where the integration variables $(\mathbf{p}_0, \mathbf{q}_0)$ are the initial conditions for classical trajectories, $\mathbf{q}_t \equiv \mathbf{q}(\mathbf{p}_0, \mathbf{q}_0, t)$ is the coordinate at time t that results from these initial conditions, and S_t the action integral along it,

$$S_t(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t dt' [\mathbf{p}(t') \cdot \dot{\mathbf{q}}(t') - H] \qquad (2.6)$$

(F is the number of degrees of freedom of the system.) For present purposes, however, it is useful for the moment to consider trajectories running backward in time from t to 0; thus, the operator

$$e^{i\hat{H}t/\hbar} \equiv e^{-iH(0-t)/\hbar} \qquad (2.6a)$$

propagates from t to 0, and use of eq 2.5 gives

$$e^{i\hat{H}t/\hbar} = \int d\mathbf{p}_t \int d\mathbf{q}_t \left[\left| \frac{\partial \mathbf{q}_0(\mathbf{p}_t, \mathbf{q}_t)}{\partial \mathbf{p}_t} \right| / (2\pi i \hbar)^F \right]^{1/2} \times$$
$$e^{iS_{-t}(\mathbf{p}_t, \mathbf{q}_t)/\hbar} |\mathbf{q}_0\rangle\langle\mathbf{q}_t| \quad (2.6b)$$

where here $(\mathbf{p}_t, \mathbf{q}_t)$ are thought of as the initial conditions and $\mathbf{q}_0 \equiv \mathbf{q}_0(\mathbf{p}_t, \mathbf{q}_t)$ the final position; the action integral S_{-t} is

$$S_{-t}(\mathbf{p}_t, \mathbf{q}_t) = \int_t^0 dt' [\mathbf{p}(t') \cdot \dot{\mathbf{q}}(t') - H] \qquad (2.7)$$

where the integrand is the trajectory determined by the "initial conditions" $(\mathbf{p}_t, \mathbf{q}_t)$. By adjointing eq 2.6b, one has

$$e^{-i\hat{H}t/\hbar} = \int d\mathbf{p}_t' \int d\mathbf{q}_t' \left[\left| \frac{\partial \mathbf{q}_0(\mathbf{p}_t', \mathbf{q}_t')}{\partial \mathbf{p}_t'} \right| / (-2\pi i \hbar)^F \right]^{1/2} \times$$
$$e^{-iS_{-t}(\mathbf{p}_t', \mathbf{q}_t')/\hbar} \cdot |\mathbf{q}_t'\rangle\langle\mathbf{q}_0'| \quad (2.8)$$

where we have used primed variables as the integration variables and $\mathbf{q}_0' \equiv \mathbf{q}_0(\mathbf{p}_t', \mathbf{q}_t')$. (Equation 2.8 is also obtainable directly from the "standard" expression, eq 2.5, by using Liouville's theorem, i.e., that $\int d\mathbf{p}_0 \int d\mathbf{q}_0 = \int d\mathbf{p}_t \int d\mathbf{p}_t$, and also that $\partial q_t/\partial p_0 = -\partial q_0/\partial p_t$.)

Equations 2.6b and 2.8 are now used for the propagators in the flux correlation function, eq 2.1, to give

$$C_{fs}(t) = \frac{\int d\mathbf{q}_t \int d\mathbf{p}_t \int d\mathbf{p}_t'}{(2\pi\hbar)^F} \left| \frac{\partial \mathbf{q}_0(\mathbf{p}_t, \mathbf{q}_t)}{\partial \mathbf{p}_t} \right|^{1/2} \left| \frac{\partial \mathbf{q}_0(\mathbf{p}_t', \mathbf{q}_t)}{\partial \mathbf{p}_t'} \right|^{1/2} \times$$
$$h(\mathbf{q}_t)\langle\mathbf{q}_0'|\hat{F}(\beta)|\mathbf{q}_0\rangle e^{i[S_{-t}(\mathbf{p}_t, \mathbf{q}_t) - S_{-t}(\mathbf{p}_t', \mathbf{q}_t)]/\hbar} \quad (2.9)$$

with $\mathbf{q}_0 = \mathbf{q}_0(\mathbf{p}_t, \mathbf{q}_t)$, $\mathbf{q}_0' = \mathbf{q}_0(\mathbf{p}_t', \mathbf{q}_t)$. Next one performs a sum and difference transformation of the integration variables $\mathbf{p}_t$ and $\mathbf{p}_t'$.

$$\mathbf{p}_t = \bar{\mathbf{p}}_t - \frac{\Delta\mathbf{p}}{2}$$

$$\mathbf{p}_t' = \bar{\mathbf{p}}_t + \frac{\Delta\mathbf{p}}{2}$$

to give

$$C_{fs}(t) = \frac{\int d\mathbf{q}_t \int d\bar{\mathbf{p}}_t}{(2\pi\hbar)^F} \int d\Delta\mathbf{p} \left| \frac{\partial \mathbf{q}_0^+}{\partial \bar{\mathbf{p}}_t} \right|^{1/2} \left| \frac{\partial \mathbf{q}_0^-}{\partial \bar{\mathbf{p}}_t} \right|^{1/2}$$
$$h(\mathbf{q}_t) \langle\mathbf{q}_0^+|\hat{F}(\beta)|\mathbf{q}_0^-\rangle e^{i[S_{-t}^- - S_{-t}^+]/\hbar} \quad (2.10a)$$

where

$$\mathbf{q}_0^\pm = \mathbf{q}_0\left(\bar{\mathbf{p}}_t \pm \frac{\Delta\mathbf{p}}{2}, \mathbf{q}_t\right) \qquad (2.10b)$$

$$S_{-t}^\pm = S_{-t}\left(\bar{\mathbf{p}}_t \pm \frac{\Delta\mathbf{p}}{2}, \mathbf{q}_t\right) \qquad (2.10c)$$

Finally, we use Liouville's theorem to change integration variables in eq 2.10a from $(\bar{\mathbf{p}}_t, \mathbf{q}_t)$ to $(\mathbf{p}_0, \mathbf{q}_0)$, which are connected to $(\bar{\mathbf{p}}_t, \mathbf{q}_t)$ by the trajectory from 0 to t, giving

$$C_{fs}(t) = \frac{\int d\mathbf{p}_0 \int d\mathbf{q}_0}{(2\pi\hbar)^F} h[\mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)] F_{eff}(\mathbf{p}_0, \mathbf{q}_0) \qquad (2.11a)$$

where

$$F_{eff}(\mathbf{p}_0, \mathbf{q}_0) = \int d\Delta\mathbf{p} \left| \frac{\partial \mathbf{q}_0^+}{\partial \bar{\mathbf{p}}_t} \right|^{1/2} \left| \frac{\partial \mathbf{q}_0^-}{\partial \bar{\mathbf{p}}_t} \right|^{1/2} \times$$
$$\langle\mathbf{q}_0^+|\hat{F}(\beta)|\mathbf{q}_0^-\rangle e^{i[S_{-t}^- - S_{-t}^+]/\hbar} \quad (2.11b)$$

with $\mathbf{q}_t = \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$, $\bar{\mathbf{p}}_t(\mathbf{p}_0, \mathbf{q}_0)$, and $\mathbf{q}_0^\pm$ and $S_{-t}^\pm$ from eqs 2.10b and 2.10c. The meaning of eq 2.11 is indicated pictorially in Figure 1. Given initial conditions $(\mathbf{p}_0, \mathbf{q}_0)$ (at time $t = 0$), one integrates to time t, arriving at the phase point $(\bar{\mathbf{p}}_t, \mathbf{q}_t)$; one now integrates back to time 0 with "initial conditions" (at time t) $(\bar{\mathbf{p}}_t \pm \Delta\mathbf{p}/2, \mathbf{q}_t)$ arriving at positions $\mathbf{q}_0^\pm$. The action integrals $S_{-t}^\pm$ are along the two "backward" trajectories.

The linearized approximation[6f] is obtained by linearizing $\mathbf{q}_0^\pm$ and $S_{-t}^\pm$ in the variable $\Delta\mathbf{p}$:

$$\mathbf{q}_0^\pm \equiv \mathbf{q}_0\left(\bar{\mathbf{p}}_t \pm \frac{\Delta\mathbf{p}}{2}, \mathbf{q}_t\right)$$

$$\cong \mathbf{q}_0(\bar{\mathbf{p}}_t, \mathbf{q}_t) \pm \frac{1}{2} \frac{\partial \mathbf{q}_0(\mathbf{p}_t, \mathbf{q}_t)}{\partial \bar{\mathbf{p}}_t} \cdot \Delta\mathbf{p} \qquad (2.12a)$$

$$S_{-t}^\pm \equiv S_{-t}\left(\bar{\mathbf{p}}_t \pm \frac{\Delta\mathbf{p}}{2}, \mathbf{q}_t\right)$$

$$\cong S_{-t}(\bar{\mathbf{p}}_t, \mathbf{q}_t) \pm \frac{1}{2}\mathbf{p}_0(\bar{\mathbf{p}}_t, \mathbf{q}_t) \cdot \frac{\partial \mathbf{q}_0(\bar{\mathbf{p}}_t, \mathbf{q}_t)}{\partial \bar{\mathbf{p}}_t} \cdot \Delta\mathbf{p} \qquad (2.12b)$$
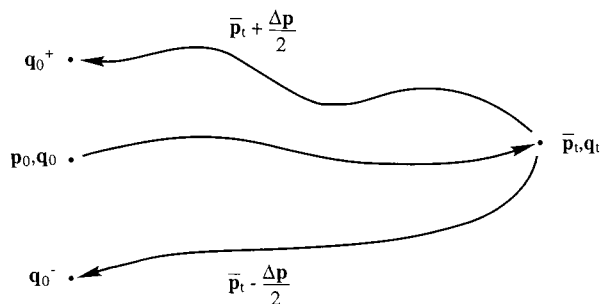
Figure 1. Schematic depiction of the classical trajectories relevant to eq 2.11. The trajectory begins at time 0 with initial conditions $(\mathbf{q}_0, \mathbf{p}_0)$ and evolves to the phase point $(\mathbf{q}_t, \bar{\mathbf{p}}_t)$ at time t; two trajectories are then integrated backward in time, from t to 0, starting from position $\mathbf{q}_t$ but with momenta $\bar{\mathbf{p}}_t \pm \Delta\mathbf{p}/2$, arriving at positions $\mathbf{q}_0^{\pm}$.

and we note that $\mathbf{q}_0(\bar{\mathbf{p}}_t, \mathbf{q}_t)$ and $\bar{\mathbf{p}}_0(\mathbf{p}_t, \mathbf{q}_t)$ are equal to $\mathbf{q}_0$ and $\mathbf{p}_0$, respectively, the integration variables in eq 2.11a. With the linearized approximations in eq 2.12, and neglecting the $\Delta\mathbf{p}$ dependence of the Jacobian determinants in eq 2.11b, the function F_{eff} of eq 2.11b becomes

$$F_{\text{eff}}(\mathbf{p}_0, \mathbf{q}_0) \cong \int d\Delta\mathbf{p} \; |\frac{\partial \mathbf{q}_0}{\partial \bar{\mathbf{p}}_t}| \left\langle \mathbf{q}_0 + \frac{1}{2}\frac{\partial \mathbf{q}_0}{\partial \bar{\mathbf{p}}}\cdot\Delta\mathbf{p} \right| \hat{F}(\beta) \left| \mathbf{q}_0 - \right.$$
$$\left. \frac{1}{2}\frac{\partial \mathbf{q}_0}{\partial \bar{\mathbf{p}}_t}\cdot\Delta\mathbf{p} \right\rangle e^{-i\mathbf{p}_0\cdot(\partial \mathbf{q}_0/\partial \bar{\mathbf{p}}_t)\,\Delta\mathbf{p}/\hbar}. \quad (2.13a)$$

Changing integration variables from $\Delta\mathbf{p}$ to $\Delta\mathbf{q}$,

$$\Delta\mathbf{q} \equiv \frac{\partial \mathbf{q}_0}{\partial \bar{\mathbf{p}}_t}\cdot\Delta\mathbf{p} \quad (2.13c)$$

then gives the Wigner function[18] for F_{eff} in this linearized approximation,

$$F_{\text{w}}(\mathbf{p}_0, \mathbf{q}_0) \equiv \int d\Delta\mathbf{q} \left\langle \mathbf{q}_0 + \frac{1}{2}\Delta\mathbf{q} \right| \hat{F}(\beta) \left| \mathbf{q}_0 - \frac{1}{2}\Delta\mathbf{q} \right\rangle e^{-i\mathbf{p}_0\cdot\Delta\mathbf{q}/\hbar}$$
$$(2.13c)$$

The linearized approximation has the great advantage that the Jacobian factor $|\partial \mathbf{q}_0(\mathbf{p}_t, \mathbf{q}_t)/\partial \mathbf{p}_t|$ completely cancels out; not only does this simplify matters by not having to calculate it but it also eliminates problems that arise in long-time and/or chaotic dynamics when this factor becomes very large. The fact that it totally cancels out in the linearized approximation suggests that its effects may be small even in the full version of the SC-IVR if it is handled appropriately.

Equation 2.11 is thus the desired result of the present work. It expresses the full SC-IVR for the flux-side correlation function, i.e., there are no approximations involved in going from eq 2.9 to eq. 2.11, in precisely the same form as its linearized approximation, with the function $F_{\text{eff}}(\mathbf{p}_0, \mathbf{q}_0)$ replacing the Wigner function. This formulation also suggests a convenient way of evaluating eq 2.11. Using Monte Carlo sampling based on the Wigner function $F_{\text{w}}(\mathbf{p}_0, \mathbf{q}_0)$, eq 2.11a can be written as

$$C_{\text{fs}}(t) = C_{\text{fs}}^{\text{LA}}(t)\cdot\Delta C(t) \quad (2.14a)$$

where $C_{\text{fs}}^{\text{LA}}(t)$ is the linearized approximation for the correlation function (i.e., the classical Wigner model) and the correction factor $\Delta C(t)$ is given by a Monte Carlo average of

$$[F_{\text{eff}}(\mathbf{p}_0, \mathbf{q}_0)/F_{\text{w}}(\mathbf{p}_0, \mathbf{q}_0)] \quad (2.14b)$$

Another possibly useful variation is to use the Kubo version of $\hat{F}(\beta)$ rather than the split operator version in eq 2.3. This is[19]

$$\hat{F}_{\text{Kubo}}(\beta) = \frac{i}{\hbar\beta}[\hat{h}, e^{-\beta\hat{H}}]$$

so that eq 2.11b becomes

$$F_{\text{eff}}(\mathbf{p}_0, \mathbf{q}_0) = \frac{i}{\hbar\beta}\int d\Delta\mathbf{p} \; |\frac{\partial \mathbf{p}_0^+}{\partial \bar{\mathbf{p}}_t}|^{1/2} |\frac{\partial \mathbf{q}_0^-}{\partial \bar{\mathbf{p}}_t}|^{1/2} (h(\mathbf{q}_0^+) - h(\mathbf{q}_0^-))$$
$$\langle \mathbf{q}_0^+ | e^{-\beta H} | \mathbf{q}_0^- \rangle \; e^{i[S_{-t}^- - S_{-t}^+]/\hbar} \quad (2.11c)$$

with $\mathbf{q}_t = \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$, $\bar{\mathbf{p}}_t = \mathbf{p}_t(\mathbf{p}_0, \mathbf{q}_0)$. In this case one would first integrate the trajectory with initial conditions $(\mathbf{p}_0, \mathbf{q}_0)$ from 0 to t. From eq 2.11a, it is required that $\mathbf{q}_t$ be on the product side of the dividing surface. One then integrates from t back to 0, with initial conditions $(\bar{\mathbf{p}}_t \pm \Delta\mathbf{p}/2, \mathbf{q}_t)$; $\mathbf{q}_0^+$ and $\mathbf{q}_0^-$ must lie on different sides of the dividing surface, or else the integrand of eq 2.11c is zero. These conditions, along with the matrix element of the Boltzmann operator, limit the range of the integration variables.

Finally, it is useful to illustrate the basic result for F_{eff}, eq 2.11b, for the elementary example of a one-dimensional free particle. Here, the $0 \rightarrow t$ trajectory gives

$$q_t = q_0 + p_0\left(\frac{t}{m}\right)$$
$$\bar{p}_t = p_0$$

and the two backward trajectories, $t \rightarrow 0$, give

$$q_0^{\pm} = q_t + \left(\bar{p}_t \pm \frac{\Delta p}{2}\right)\left(-\frac{t}{m}\right)$$

so that

$$q_0^{\pm} = q_0 \mp \frac{\Delta p}{2}\frac{t}{m}$$

and

$$S_{-t}^{\pm} = -\frac{t}{2m}\left(p_0 \pm \frac{\Delta p}{2}\right)^2$$

With the split operator version of $\hat{F}(\beta)$, for example, eq 2.11b thus gives

$$F_{\text{eff}}(p_0, q_0) = \int d\Delta p \; \frac{t}{m}\frac{m}{\pi\hbar^2\beta}\frac{\Delta pt}{mi\hbar\beta} \times$$
$$\exp\left\{\frac{-m}{\hbar^2\beta}\left[2q_0^2 + \frac{1}{2}\left(\frac{\Delta pt}{m}\right)^2\right]\right\} e^{-itp_0\Delta p/(\hbar m)}$$

or with the change of integration variable to $\Delta q = \Delta pt/m$,

$$F_{\text{eff}}(p_0, q_0) = \int d\Delta q \; \frac{m}{\pi\hbar^2\beta}\frac{\Delta q}{mi\hbar\beta} \times$$
$$\exp\left[\frac{-m}{\hbar^2\beta}\left(2q_0^2 + \frac{1}{2}\Delta q^2\right)\right] e^{-ip_0\Delta q/\hbar}$$

which is identical to the Wigner function in this case. The

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important thing to notice is that the integration over Δp (or Δq) is well localized.

III. Concluding Remarks

The purpose of this short note has been to show that the SC-IVR expression for the flux-side correlation function can be cast in a form very similar to its linearized approximation. This suggests new computational approaches that may have advantages over existing ones. We also note some similarities in structure of the present formulation to the "forward−backward" IVR presented before,[6m] though it is not equivalent to it. At the present time one is still investigating various strategies for implementing the SC-IVR approach, so various formulations may suggest useful approaches or other approximations.

For example, it may be useful to make *part* of the linearized approximation but not all of it. Thus, suppose one neglects the $\Delta \mathbf{p}$ dependence in the Jacobian factors in eq 2.11b but retains it elsewhere, then

$$\frac{\partial \mathbf{q}_0^{\pm}}{\partial \bar{\mathbf{p}}_t} = \frac{\partial \mathbf{q}_0(\bar{\mathbf{p}}_t, \mathbf{q}_t)}{\partial \bar{\mathbf{p}}_t} = -\frac{\partial \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)}{\partial \mathbf{p}_0}$$

so that one can change integration variables in eq 2.11b from $\Delta \mathbf{p}$ to $\Delta \mathbf{q}$,

$$\Delta \mathbf{q} \equiv \frac{\partial \mathbf{q}_0(\bar{\mathbf{p}}_t, \mathbf{q}_t)}{\partial \mathbf{p}_t} \cdot \Delta \mathbf{p}$$

$$= -\frac{\partial \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)}{\partial \mathbf{p}_0} \cdot \Delta \mathbf{p}$$

and the expression for the effective distribution function becomes

$$F_{\text{eff}}(\mathbf{p}_0, \mathbf{q}_0) = \int d\Delta \mathbf{q} \, \langle \mathbf{q}_0^{+} | \hat{F}(\beta) | \mathbf{q}_0^{-} \rangle \cdot e^{i[S_{-t}^{-} - S_{-t}^{+}]/\hbar} \quad (3.1)$$

with $\mathbf{q}_0^{\pm}$ and $S_{-t}^{\pm}$ still given by eqs 2.10b and 2.10c, and

$$\bar{\mathbf{p}}_t = \mathbf{p}_t(\mathbf{p}_0, \mathbf{q}_0)$$

$$\mathbf{q}_t = \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$$

$$\Delta \mathbf{p} = -\left(\frac{\partial \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)}{\partial \mathbf{p}_0}\right)^{-1} \cdot \Delta \mathbf{q}$$

One expects the dependence on the Jacobian factor, $\partial \mathbf{q}_t / \partial \mathbf{p}_0$, to be weak, since there is no dependence at all in the linearized approximation.

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