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QUANTUM-CLASSICAL WIGNER – LIOUVILLE EQUATION

КВАНТОВО-КЛАСИЧНЕ РІВНЯННЯ ВІГНЕРА – ЛІУВІЛЛЯ

We consider a quantum system that is partitioned into a subsystem and a bath. Starting from the Wigner transform of the von Neumann equation for the quantum mechanical density matrix of the entire system, the quantum-classical Wigner – Liouville equation is obtained in the limit where masses M of the bath particles are large compared to the masses m of the subsystem particles. The structure of this equation is discussed and it is shown how the abstract operator form of the quantum-classical Liouville equation is obtained by taking the inverse Wigner transform on the subsystem. Solutions in terms of classical trajectory segments and quantum transition or momentum jumps are described.

Розглянуто квантову систему, розділену на підсистему та термостат. Після застосування перетворень Вігнера до рівняння фон Неймана для квантово-механічної матриці щільності системи одержано квантово-класичне рівняння Вігнера – Ліувілля у границі, де маси M частинок термостату великі у порівнянні з масами m частинок підсистеми. Обговорено структуру цього рівняння і показано, як можна отримати абстрактну операторну форму квантово-класичного рівняння Ліувілля за допомогою зворотного перетворення Вігнера на підсистемі. Розв'язки описано в термінах класичних сегментів траєкторії та квантового переходу або імпульсних стрибків.

1. Introduction. There are many circumstances when a mixed quantum-classical approach to the dynamics of a system is appropriate. If one considers proton or electron transfer processes in condensed phases, the quantum character of the proton or electron must be taken into account but the solvent in which these transfer reactions take place may often be approximated by classical mechanics. There are also compelling practical reasons for exploring such mixed schemes: it is impossible to simulate the full quantum dynamics for a large many-body system. However, it may be possible to mix classical molecular dynamics of the solvent with quantum evolution of some degrees of freedom.

Quantum dynamics in classical environments is often carried out using mean field theories or surface-hopping algorithms [1]. Mixed quantum-classical dynamics can also be described using a quantum-classical Liouville equation [2–6]. This equation may be derived from the full quantum mechanical von Neumann equation for the density matrix,

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)] \,, \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the system. The system is assumed to be composed of a subsystem and a bath or environment. The partial Wigner transform is first taken over the environmental degrees of freedom,

$$\hat{\rho}_W(R, P) = (2\pi\hbar)^{-\nu_h} \int dz e^{iP \cdot Z/\hbar} \left\langle R - \frac{Z}{2} \middle| \hat{\rho} \middle| R + \frac{Z}{2} \right\rangle, \tag{2}$$

where ν_h is the coordinate space dimension of the bath and, after introducing scaled variables similar to those used in the classical theory of Brownian motion, the evolution operator is expanded to first order in the small parameter $\mu = (m/M)^{1/2}$, where m and M, $M >> m$, are the masses of the particles in the quantum subsystem and bath, respectively. The quantum-classical Liouville equation takes the form [2–6],

$$\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2} \left(\left\{ \hat{H}_W, \hat{\rho}_W(t) \right\} - \left\{ \hat{\rho}_W(t), \hat{H}_W \right\} \right) \equiv$$

$$\equiv -i\hat{\mathcal{L}}\hat{\rho}_W(t) = -(\hat{H}_W, \hat{\rho}_W(t)), \tag{3}$$

where $\{\cdot, \cdot\}$ is the Poisson bracket and $(\cdot, \cdot)$ is the quantum-classical bracket. The quantum-classical Liouville operator is $\hat{\mathcal{L}}$. It has been proposed and used in various contexts [7]. This formulation of quantum-classical dynamics has proved useful as a theoretical basis for understanding the validity of existing surface hopping schemes and has provided a framework for constructing new surface-hopping algorithms for nonadiabatic dynamics [8]. The quantum-classical bracket that enters the quantum-classical Liouville equation does not have a Lie algebraic structure and this has implications for the dynamics and the structure of nonequilibrium statistical mechanics constructed in the framework of quantum-classical dynamics [9].

In this article we demonstrate some interrelations among various representations of the quantum-classical Liouville equation and indicate how it may be solved using surface-hopping trajectories.

2. Quantum-classical Wigner–Liouville equation. The dynamics of the entire quantum system, subsystem plus bath, is described by the von Neumann equation (1) for the density matrix. We may write the von Neumann equation in an equivalent form by taking its full Wigner transform to obtain the Wigner–Liouville equation [10–12],

$$\left[\frac{\partial}{\partial t} + i\mathcal{L}_\ell^{(0)} + i\mathcal{L}_h^{(0)} \right] \rho_W(p, P, r, R, t) =$$

$$= \int ds\, dS\, \omega(s, S, q, R) \rho_W(p - s, P - S, r, R, t).$$

Here we indicated Wigner transform variables as (p, r) for the subsystem and (P, R) for bath. The classical free streaming Liouville operators are $i\mathcal{L}_\ell^{(0)} = \dfrac{p}{m} \dfrac{\partial}{\partial r}$ and $i\mathcal{L}_h^{(0)} = \dfrac{P}{m} \dfrac{\partial}{\partial R}$. The kernel in the integral term is defined as

$$\omega(s, S, r, R) = \frac{2}{\hbar(\pi\hbar)^\nu} \int d\tilde{r}\, d\tilde{R}\, V(r - \tilde{r}, R - \tilde{R}) \sin\left(\frac{2(s\tilde{r} + S\tilde{R})}{\hbar} \right),$$

where ν is the coordinate space dimension of the entire system and the potential can be written as the sum of subsystem, bath and coupling contributions, $V = V_s + V_b + V_c$.

This equation is equivalent to the von Neumann equation and describes the quantum dynamics of the entire system. We now wish to take the limit where the bath degrees of freedom are treated classically. To this end we follow the procedure in Ref. [6] and introduce scaled coordinates as follows: we measure the energy in units ϵ_0, time in units $t_0 = \dfrac{\hbar}{\epsilon_0}$, length in units $\lambda_m = \left(\dfrac{\hbar^2}{m\epsilon_0} \right)^{1/2}$, momentum of the light subsystem particles in units of $p_m = \dfrac{m\lambda_m}{t_0} = (m\epsilon_0)^{1/2}$ and momentum of the heavy subsystem particles in units $P_M = (M\epsilon_0)^{1/2}$. The transformed variables are denoted by a prime: $p' = \dfrac{p}{p_m}$, $r' = \dfrac{r}{\lambda_m}$, $P' = \dfrac{P}{P_M}$, $R' = \dfrac{R}{\lambda_m}$ and $t' = t/t_0$. In these scaled coordinates the Wigner–Liouville equation takes the form,

$$\left[\frac{\partial}{\partial t'} + i\mathcal{L}_\ell^{(0)\prime} + \mu i\mathcal{L}_h^{(0)\prime} \right] \rho_W' =$$

$$= \int ds'\, dS'\, \omega'(s', S', r', R') \rho_W'(p' - s', P' - S', r', R', t'). \tag{4}$$

The quantum-classical limit of this equation is obtained by expanding the right-hand side of this equation to linear order in the small parameter μ. The Taylor expansion of $V'(r - \tilde{r}', R' - \mu\tilde{R}'')$ that appears in the definition of the kernel is

$$V'(r - \tilde{r}', R' - \mu\tilde{R}'') \approx V'(r - \tilde{r}', R') - \mu\frac{\partial V'(r - \tilde{r}', R')}{\partial R'}\tilde{R}'' + \mathcal{O}(\mu^2).$$

Keeping terms up to linear order in μ in the expression for ω', we obtain

$$\omega'(s', S', r', R') \approx \frac{2}{(\pi)^\nu} \int d\tilde{r}' d\tilde{R}'' V'(r' - \tilde{r}', R') \sin\left(2s'\tilde{r}' + 2S'\tilde{R}''\right) -$$

$$- \frac{2\mu}{(\pi)^\nu} \int d\tilde{r}' d\tilde{R}'' \frac{\partial V'(r' - \tilde{r}', R')}{\partial R'}\tilde{R}'' \sin\left(2s'\tilde{r}' + 2S'\tilde{R}''\right) + \mathcal{O}(\mu^2).$$

Next, using the fact that $\int d\tilde{R}'' \cos(2S'\tilde{R}'') = \pi^{\nu_h}\delta(S')$ and $\int d\tilde{R}'' \sin(2S'\tilde{R}'') = 0$, we may write this equation in the form,

$$\omega'(s', S', r', r') \approx \frac{2}{\pi^{\nu_\ell}} \int d\tilde{r}' V'(r' - \tilde{r}', R') \sin(2s'\tilde{r}')\delta(S') +$$

$$+ \frac{\mu}{\pi^{\nu_\ell}} \int d\tilde{r}' \frac{\partial V'(r' - \tilde{r}', R')}{\partial R'} \cos(2s'\tilde{r}')\frac{d\delta(S')}{dS'}.$$

Inserting this expression for ω' in the integral in Eq. (4) and simplifying, we obtain,

$$\left[\frac{\partial}{\partial t'} + i\mathcal{L}_\ell^{(0)'} + \mu i\mathcal{L}_h^{(0)'}\right]\rho_W' =$$

$$= \frac{2}{\pi^{\nu_\ell}} \int ds' \left[\int d\tilde{r}' V'(r' - \tilde{r}', R') \sin(2s'\tilde{r}')\right]\rho_W'(p' - s', P', r', R', t') +$$

$$+ \mu \int ds' \Delta F'_{R',s'} \frac{\partial}{\partial P'}\rho_W'(p' - s', P', r', R', t'),$$

where we have defined $\Delta F'_{R',s'} = \frac{1}{\pi^{\nu_\ell}}\frac{\partial}{\partial R'}\left[\int d\tilde{r}' \cos(2s'\tilde{r}')V'(r' - \tilde{r}', R')\right].$

Returning to the original unscaled coordinates we have the quantum-classical Wigner – Liouville equation,

$$\left[\frac{\partial}{\partial t} + i\mathcal{L}_\ell^{(0)} + i\mathcal{L}_h^{(0)}\right]\rho_W(p, P, r, R, t) =$$

$$= \frac{2}{\hbar(\pi\hbar)^{\nu_\ell}} \int ds \left[\int d\tilde{r} V(r - \tilde{r}, R) \sin\left(\frac{2s\tilde{r}}{\hbar}\right)\right]\rho_W(p - s, P, r, R, t) +$$

$$+ \int ds \Delta F(R, s)\frac{\partial}{\partial P}\rho_W(p - s, P, r, R, t), \tag{5}$$

with

$$\Delta F(R, s) = \frac{1}{(\pi\hbar)^{\nu_\ell}}\frac{\partial}{\partial R}\left[\int d\tilde{r} \cos(2s\tilde{r}/\hbar)V(r - \tilde{r}, R)\right].$$

This equation gives the dynamics of the quantum-classical system in terms of phase space variables (R, P) for the bath and the Wigner transform variables (r, p) for the quantum subsystem. The solution of this equation is difficult in general but this formulation of mixed quantum-classical dynamics may prove useful in some contexts, for example when the subsystem has a dense spectrum. However, in many cases the quantum subsystem can be described in terms of a few quantum states and in this case it may be

better to represent the quantum subsystem in terms of some suitable basis. The adiabatic basis is a particularly convenient basis for making connection to surface hopping schemes. To this end, we now show how to "undo" the Wigner transformation of the quantum subsystem degrees of freedom and obtain the quantum-classical Liouville equation (3) that is independent of the representation of the subsystem.

3. Partially undoing the Wigner transform. The quantum-classical Liouville equation (3) describes and abstract, representation free description of the dynamics, while in the quantum-classical Wigner – Liouville equation (5) the quantum subsystem is described in Wigner transform space. We now show that, as expected, if we undo the Wigner transform on the quantum degrees of freedom we recover the quantum-classical Liouville equation. The Wigner transform of a dynamical variable in the quantum subsystem can be written as,

$$A_W(r,p) = \int d\xi e^{ip\xi/\hbar} \left\langle r - \frac{\xi}{2} \middle| \hat{A} \middle| r + \frac{\xi}{2} \right\rangle \equiv \mathcal{W} \circ \left\langle r - \frac{\xi}{2} \middle| \hat{A} \middle| r + \frac{\xi}{2} \right\rangle,$$

while its inverse is defined by

$$\left\langle r - \frac{\xi}{2} \middle| \hat{A} \middle| r + \frac{\xi}{2} \right\rangle = \frac{1}{(2\pi\hbar)^{\nu_\ell}} \int dp e^{-ip\xi/\hbar} A_W(r,p) \equiv \mathcal{W}^{-1} \circ A_W(r,p).$$

A set of expressions analogous to Eq. (2) holds for the density matrix.

We may now apply $\mathcal{W}^{-1}$ to the quantum-classical Wigner – Liouville equation to obtain the desired result. First, we consider

$$\mathcal{W}^{-1} \circ \left\{ \frac{p}{m} \frac{\partial \rho_W(p,P,r,R)}{\partial r} \right\} = \frac{1}{(2\pi\hbar)^{\nu_\ell}} \int dp e^{-ip\xi/\hbar} \frac{p}{m} \frac{\partial \rho_W(p,P,r,R)}{\partial r} =$$

$$= \frac{i\hbar}{m} \frac{\partial}{\partial \xi} \frac{\partial}{\partial r} \left\langle r - \frac{\xi}{2} \middle| \hat{\rho}_W(P,R) \middle| r + \frac{\xi}{2} \right\rangle =$$

$$= \frac{i\hbar}{2m} \left[-\left(\frac{\partial^2}{\partial r^2} \left\langle \left(r - \frac{\xi}{2} \right) \middle| \right) \hat{\rho}_W(P,R) \middle| r + \frac{\xi}{2} \right\rangle + $$

$$+ \left\langle r - \frac{\xi}{2} \middle| \hat{\rho}_W(P,R) \left(\frac{\partial^2}{\partial r^2} \middle| \left(r + \frac{\xi}{2} \right) \right\rangle \right) \right] =$$

$$= \frac{i}{\hbar} \left\langle r - \frac{\xi}{2} \middle| \left[\frac{\hat{p}^2}{2m}, \hat{\rho}_W(P,R) \right] \middle| r + \frac{\xi}{2} \right\rangle.$$

To obtain the last line we inserted complete sets of states and used the identity,

$$\left\langle r \middle| \frac{\hat{p}^2}{2m} \middle| r' \right\rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \delta(r - r').$$

Next, consider the action of $\mathcal{W}^{-1}$ on the potential contribution,

$$\mathcal{W}^{-1} \circ c_1 \int ds \left[\int d\tilde{r} V(r - \tilde{r}, R) \sin(2s\tilde{r}/\hbar) \right] \rho_W(p - s, P, r, R, t) =$$

$$= \frac{1}{(2\pi\hbar)^{\nu_\ell}} \int dp e^{-ip\xi/\hbar} c_1 \int ds \left[\int d\tilde{r} V(r - \tilde{r}, R) \sin(2s\tilde{r}/\hbar) \right] \times$$

$$\times \rho_W(p - s, P, r, R, t) =$$

$$= c_1 \left[\int d\tilde{r} V(r - \tilde{r}, R) \int ds e^{-is\xi/\hbar} \sin(2s\tilde{r}/\hbar) \right] \times$$

$$\times \left\langle r - \frac{\xi}{2} \middle| \hat{\rho}_W(P,R) \middle| r + \frac{\xi}{2} \right\rangle,$$

where $c_1 = 2/(\hbar(\pi\hbar)^{\nu_\ell})$. Noting that

$$\int ds e^{-is\xi/\hbar} \sin\left(\frac{2s\tilde{r}}{\hbar}\right) = \frac{(2\pi\hbar)^{\nu_\ell}}{2i}\Big[\delta(\xi - 2\tilde{r}) - \delta(\xi + 2\tilde{r})\Big],$$

and carrying out the $\tilde{r}$ integration, the potential contribution becomes

$$\mathcal{W}^{-1} \circ c_1 \int ds \left[\int d\tilde{r} V(q - \tilde{r}, R) \sin\left(\frac{2s\tilde{r}}{\hbar}\right)\right] \rho_W(p - s, P, r, R, t) =$$

$$= -\frac{i}{\hbar}\left\langle r - \frac{\xi}{2}\left|\left[\hat{V}, \hat{\rho}_W(P, R)\right]\right|r + \frac{\xi}{2}\right\rangle.$$

Lastly, the term that involves ΔF can be analyzed as follows. Consider

$$\mathcal{W}^{-1} \circ \int ds \Delta F(R, s) \frac{\partial}{\partial P} \rho_W(p - s, P, r, R, t) =$$

$$= \int ds \Delta F(R, s) e^{-\frac{i}{\hbar}s\xi} \frac{\partial}{\partial P}\left\langle r - \frac{\xi}{2}\Big|\hat{\rho}_W(P, R, t)\Big|r + \frac{\xi}{2}\right\rangle.$$

Using the fact that

$$\int ds e^{-\frac{i}{\hbar}s\xi} \cos\left(\frac{2s\tilde{r}}{\hbar}\right) = \frac{(2\pi\hbar)^{\nu_\ell}}{2}\Big[\delta(\xi - 2\tilde{r}) + \delta(\xi + 2\tilde{r})\Big],$$

we may write

$$\int ds e^{-\frac{i}{\hbar}s\xi} \Delta F(R, s) = \frac{1}{(\pi\hbar)^{\nu_\ell}} \frac{\partial}{\partial R} \int d\tilde{r} V(r - \tilde{r}, R) \int ds e^{-\frac{i}{\hbar}s\xi} \cos\left(\frac{2s\tilde{r}}{\hbar}\right) =$$

$$= \frac{2^{\nu_\ell}}{2} \frac{\partial}{\partial R} \int d\tilde{r} V(r - \tilde{r}, R)\Big[\delta(\xi - 2\tilde{r}) + \delta(\xi + 2\tilde{r})\Big] =$$

$$= \frac{1}{2}\left[\frac{\partial V\left(r - \frac{\xi}{2}, R\right)}{\partial R} + \frac{\partial V\left(r + \frac{\xi}{2}, R\right)}{\partial R}\right].$$

Using these results this term becomes

$$\left\{\frac{1}{2}\left[\frac{\partial V\left(r - \frac{\xi}{2}, R\right)}{\partial R} + \frac{\partial V\left(r + \frac{\xi}{2}, R\right)}{\partial R}\right]\right\} \frac{\partial}{\partial P}\left\langle r - \frac{\xi}{2}\Big|\hat{\rho}_W(P, R, t)\Big|r + \frac{\xi}{2}\right\rangle =$$

$$= \frac{1}{2}\left\langle r - \frac{\xi}{2}\left|\left(\{\hat{V}, \hat{\rho}_W\} - \{\hat{\rho}_W, \hat{V}\}\right)\right|r + \frac{\xi}{2}\right\rangle,$$

where we have used the fact that

$$\{\hat{V}, \hat{\rho}_W\} - \{\hat{\rho}_W, \hat{V}\} = \frac{\partial\hat{V}}{\partial R}\frac{\partial\hat{\rho}_W}{\partial P} - \frac{\partial\hat{V}}{\partial P}\frac{\partial\hat{\rho}_W}{\partial R} - \frac{\partial\hat{\rho}_W}{\partial R}\frac{\partial\hat{V}}{\partial P} + \frac{\partial\hat{\rho}_W}{\partial P}\frac{\partial\hat{V}}{\partial R} =$$

$$= \frac{\partial\hat{V}}{\partial R}\frac{\partial\hat{\rho}_W}{\partial P} + \frac{\partial\hat{\rho}_W}{\partial P}\frac{\partial\hat{V}}{\partial R},$$

since $\hat{V}$ does not depend on P.

Collecting all of the expressions for the various terms we find that the inverse partial Wigner transform of the quantum-classical Wigner – Liouville equation in Eq. (5) is

$$\frac{\partial}{\partial t}\left\langle r - \frac{\xi}{2}\Big|\hat{\rho}_W(P, R, t)\Big|r + \frac{\xi}{2}\right\rangle =$$

$$= -\frac{i}{\hbar}\left\langle r-\frac{\xi}{2}\left|\left[\left(\frac{\hat{p}^2}{2m}+\hat{V}\right),\hat{\rho}_W(P,R)\right]\right|r+\frac{\xi}{2}\right\rangle -$$

$$-\frac{P}{M}\frac{\partial}{\partial R}\left\langle r-\frac{\xi}{2}\left|\hat{\rho}_W(P,R,t)\right|r+\frac{\xi}{2}\right\rangle +$$

$$+\frac{1}{2}\left\langle r-\frac{\xi}{2}\left|\left(\{\hat{V},\hat{\rho}_W\}-\{\hat{\rho}_W,\hat{V}\}\right)\right|r+\frac{\xi}{2}\right\rangle.$$

If we then use the definition of the partially Wigner transformed Hamiltonian, $\hat{H}_W = \dfrac{P^2}{2M}+\dfrac{\hat{p}^2}{2m}+\hat{V}$, we may write this equation in the form,

$$\left\langle r-\frac{\xi}{2}\left|\frac{\partial}{\partial t}\hat{\rho}_W(P,R,t)\right|r+\frac{\xi}{2}\right\rangle =$$

$$\left\langle r-\frac{\xi}{2}\left|\left[-\frac{i}{\hbar}\left[\hat{H}_W,\hat{\rho}_W(P,R)\right]+\frac{1}{2}\left(\{\hat{H}_W,\hat{\rho}_W\}-\{\hat{\rho}_W,\hat{H}_W\}\right)\right]\right|r+\frac{\xi}{2}\right\rangle.$$

Considering the operators inside the involved in these matrix elements, we have again obtained the quantum-classical Liouville equation (3) in its abstract form.

4. Solution of the Wigner–Liouville equation. In this section we shall contrast the solutions of the quantum-classical Wigner–Liouville equation (5) with those of the representation of the abstract quantum-classical Liouville equation (3) in the adiabatic basis.

We begin with the quantum-classical Wigner–Liouville equation and note that it can be written in a compact form as,

$$\left[\frac{\partial}{\partial t}+i\mathcal{L}_\ell+i\mathcal{L}_h\right]\rho_W(p,P,r,R,t)=\int ds\, K(s,P,r,R)\rho_W(p-s,P,r,R,t)\quad(6)$$

where $i\mathcal{L}_\ell = \dfrac{p}{m}\dfrac{\partial}{\partial r}+F_s(r)\dfrac{\partial}{\partial p}$ is the full classical Liouville operator for the subsystem and $i\mathcal{L}_h = \dfrac{P}{M}\dfrac{\partial}{\partial R}+F_b(R)\dfrac{\partial}{\partial P}$ is the full classical Liouville operator for the bath. Here $F_s(r) = -\dfrac{\partial V_s(r)}{\partial r}$ and $F_b(R) = -\dfrac{\partial V_b(R)}{\partial R}$. The kernel $K(s,P,r,R)$ is the sum of two contributions, $K = K_\ell + K_h$ with

$$K_h(s,P,r,R)=\left(-\frac{\partial}{\partial R}V_b(R)\right)\frac{\partial}{\partial P}\delta(s)-$$

$$-\frac{1}{(\pi\hbar)^{\nu_\ell}}\left(-\frac{\partial}{\partial R}\int d\tilde{r}\cos\left(\frac{2s\tilde{r}}{\hbar}\right)V(r-\tilde{r},R)\right)\frac{\partial}{\partial P},$$

$$K_\ell(s,P,r,R)=-\frac{\partial V_s(r)}{\partial r}\frac{d\delta(s)}{ds}+$$

$$+\frac{2}{\hbar(\pi\hbar)^{\nu_\ell}}\int ds\left[\int d\tilde{r}V(r-\tilde{r},R)\sin\left(\frac{2s\tilde{r}}{\hbar}\right)\right].$$

Equation (6) can be written in integral form as

$$\rho_W(p,P,r,R,t)=e^{-i(\mathcal{L}_\ell+\mathcal{L}_h)t}\rho_W(p,P,r,R,0)+$$

$$+\int\limits_0^t dt'\,e^{-i(\mathcal{L}_\ell+\mathcal{L}_h)(t-t')}\int ds\, K(s,P,r,R)\rho_W(p-s,P,r,R,t').$$

This equation may be iterated to obtain a formal solution for $\rho_W(p,P,r,R,t)$ which can, in principle, be computed by evaluating classical trajectory segments interspersed by

jumps in the momentum variables. Such a procedure may be useful for one-dimensional quantum subsystems embedded in a classical baths when the quantum subsystem has many closely spaced energy levels. However, the kernel in Eq. (6) is highly oscillatory and techniques for the solution of the integral equation need to be developed. Thus, so far no simulations of the quantum-classical Wigner – Liouville equation have been carried out using this method so its utility remains to be tested. Nevertheless, the equation may prove useful as a starting point for approximate solutions to quantum-classical dynamics, especially for cases when the subsystem spectrum is dense.

Although trajectory based methods for the solution of the quantum-classical Wigner – Liouville equation may have limited utility, if the quantum-classical Liouville equation in the adiabatic basis can be simulated from an ensemble of surface-hopping trajectories. The adiabatic states are the solution of the eigenvalue problem, $\hat{h}_W(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle$, where the Hamiltonian for the system with fixed values of the bath coordinates is $\hat{h}_W(R) = \dfrac{\hat{p}^2}{2m} + \hat{V}(\hat{q}, R)$. Note that the Wigner transformed Hamiltonian of the entire system is just the sum of the classical kinetic energy of the bath plus $\hat{h}_W(R)$, $\hat{H}_W(R, P) = \dfrac{P^2}{2M} + \hat{h}_W(R)$. Taking matrix elements of Eq. (3) and letting $\rho_W^{\alpha\alpha'}(R, P) = \langle \alpha; R|\hat{\rho}_W(R, P)|\alpha'; R\rangle$, we obtain

$$\frac{\partial \rho_W^{\alpha\alpha'}(R, P, t)}{\partial t} = \sum_{\beta\beta'} -i\mathcal{L}_{\alpha\alpha',\beta\beta'} \rho_W^{\beta\beta'}(R, P, t), \tag{7}$$

where the matrix elements of $i\mathcal{L}$ are

$$-i\mathcal{L}_{\alpha\alpha',\beta\beta'} = (-i\omega_{\alpha\alpha'} - iL_{\alpha\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'},$$

with $\omega_{\alpha\alpha'} = \dfrac{E_\alpha - E_{\alpha'}}{\hbar}$ and

$$J_{\alpha\alpha',\beta\beta'} = -\frac{P}{M}d_{\alpha\beta}\left(1 + \frac{1}{2}S_{\alpha\beta}\frac{\partial}{\partial P}\right)\delta_{\alpha'\beta'} - \frac{P}{M}d_{\alpha'\beta'}^*\left(1 + \frac{1}{2}S_{\alpha'\beta'}^*\frac{\partial}{\partial P}\right)\delta_{\alpha\beta}.$$

The quantity $S_{\alpha\beta}$ is defined as

$$S_{\alpha\beta} = (E_\alpha - E_\beta)d_{\alpha\beta}\left(\frac{P}{M}d_{\alpha\beta}\right)^{-1}.$$

This representation in the adiabatic basis is especially instructive for formulating the dynamics in terms of surface-hopping trajectories [6].

The solution of the quantum-classical Liouville equation (7) may be found by iteration to yield a representation of the dynamics as a sequence of terms involving increasing numbers of nonadiabatic transitions [6],

$$\rho_W^{\alpha_0\alpha_0'}(R, P, t) = e^{-i\mathcal{L}_{\alpha_0\alpha_0'}^0 t}\rho_W^{\alpha_0\alpha_0'}(R, P) +$$

$$+ \sum_{n=1}^{\infty} \sum_{(\alpha_1\alpha_1')\dots(\alpha_n\alpha_n')} \int\limits_0^{t_0} dt_1 \int\limits_0^{t_1} dt_2 \dots \int\limits_0^{t_{n-1}} dt_n \times$$

$$\times \prod_{k=1}^{n}\left[e^{-i\mathcal{L}_{\alpha_{k-1}\alpha_{k-1}'}^0 (t_{k-1}-t_k)} J_{\alpha_{k-1}\alpha_{k-1}',\alpha_k\alpha_k'}\right] \times$$

$$\times e^{-i\mathcal{L}_{\alpha_n\alpha_n'}^0 t_n}\rho_W^{\alpha_n\alpha_n'}(R, P, 0).$$

The successive terms in the series correspond to increasing numbers of nonadiabatic transitions. The first term that describes simple adiabatic dynamics. For example, the quantum-classical approximation to the population in state α at phase point (R, P) at time t is given by a sum of terms starting with adiabatic evolution on state α. Single nonadiabatic contributions appear next where transitions to states β, $\beta \neq \alpha$, occur at times t' intermediate between t and 0. Transitions are accompanied by continuous momentum changes in the environment specified by the term in J involving a momentum derivative. Since a single quantum transition takes place this contribution to $\rho_W^{\alpha\alpha}(R, P, t)$ must arise from an off-diagonal density matrix element, $\rho_W^{\alpha\beta}$ at time 0. During the portion of the evolution segment from t' to 0, the classical environmental phase space coordinates are propagated on the mean of the two α and β adiabatic surfaces and a phase factor $W_{\alpha\beta}$ contributes to the population in state α.

Efficient algorithms [8] to compute quantum-classical evolution based on these formulas have been constructed and used to determine mean values of observables [13] and chemical reaction rates [14].

5. Conclusion. Several forms of the quantum-classical Liouville equation were considered in this paper. These forms differ in the manner in which the quantum subsystem is represented. If one starts with a Wigner representation of the entire system, quantum subsystem plus bath, and takes the quantum-classical limit, the quantum-classical Wigner – Liouville equation is obtained. This equation may be of use for formal calculations where a phase space representation of the quantum subsystem is appropriate. It may also prove useful in studies where the spectrum of the quantum subsystem consists of many closely spaced levels. Undoing the Wigner representation of the quantum subsystem degrees of freedom leads to the quantum-classical Liouville equation where the description of the quantum subsystem is independent of any specific representation. If an adiabatic representation is chosen, the solution of the quantum-classical Liouville equation may be expressed in terms of surface-hopping trajectories.

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