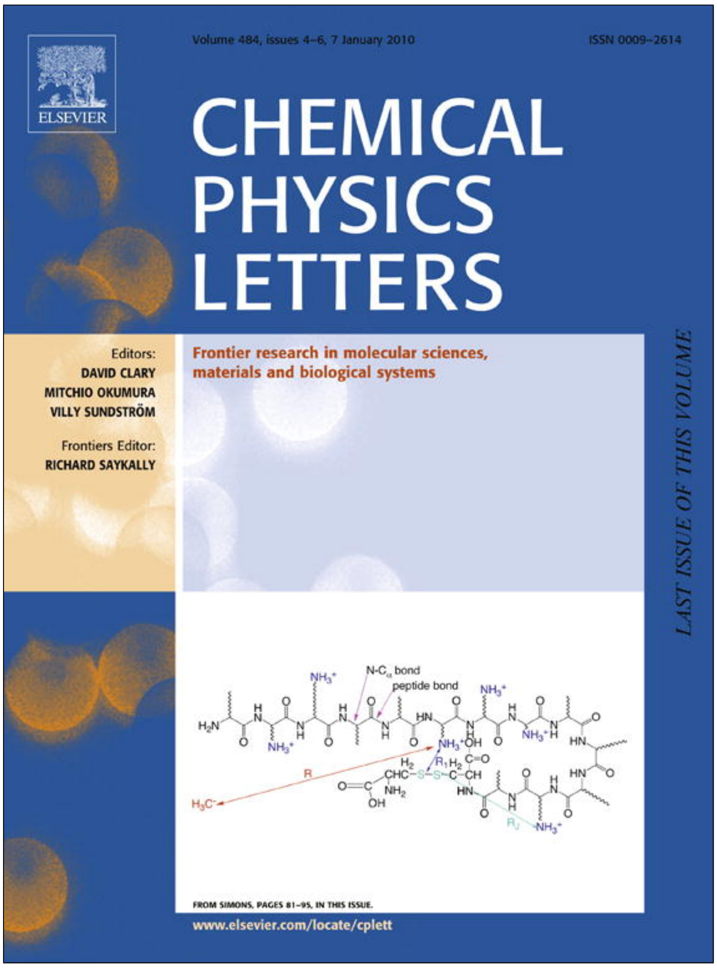
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Linearization approximations and Liouville quantum–classical dynamics

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ABSTRACT

We show that linearization methods, commonly used to approximate the evolution of the density operator in mixed quantum–classical systems, can be justified when a small parameter, the ratio of masses of the quantum subsystem and bath, is introduced. The same parameter enters in the derivation of the quantum–classical Liouville equation. Although its original derivation followed from a different formalism, here we show that the basis-free form of the quantum–classical Liouville equation for the density operator can also be obtained by linearization of the exact time evolution of this operator. These results show the equivalence among various quantum–classical schemes.

1. Introduction

Quantum–classical methods are currently the only viable computational tool to study the dynamics of relatively large systems in which the quantum properties of a subset of degrees of freedom play an important role. These methods usually start from a full quantum description of all the degrees of freedom and then partition them in two subsets (the quantum subsystem and the bath). A partial classical limit for the evolution of the bath is then taken and the way in which this is done distinguishes the various approaches [1–4]. Some approaches are derived from well-defined approximations to the quantum dynamics of the entire system, while others follow from physically motivated ansätze on the evolution equations. Since the various methods are based on rather different premises, even the relationships among those derived from well-defined approximations to the quantum dynamics have not been established. The analysis of these relationships is a worthwhile endeavor that can provide one with a better understanding of the relative merits of the approaches, help to clarify the different approximations on which they rely, and can lead to better algorithms for their simulation.

In the following we shall consider two such methods, the quantum–classical Liouville (QCL) approach and the family of techniques known as linearization methods (LM). Linearization methods start from a path integral representation of the Heisenberg time evolution of an operator. The forward and backward paths representing the propagators are expressed in terms of mean and difference variables, and the evolution is approximated via an expansion of the phase of the path integral to linear order in the difference variables. This approximation reduces the evolution of the path of the mean variables to a time stepping algorithm whose complexity is similar to that of classical mechanics. The advantages of this approach, which was originally devised for Born–Oppenheimer dynamics [5–9] and then generalized to non-adiabatic problems [10–13], have been demonstrated, but the approximation has been formally justified only for quantum systems bilinearly coupled to a bath of harmonic oscillators [14]. In Section 2 we show that the expansion in the difference variables is equivalent to an expansion in the mass ratio $\mu = (m/M)^{1/2}$ where m and M are the characteristic masses of the quantum subsystem and bath particles, respectively. This result is obtained without the introduction of a specific representation for the quantum subsystem and establishes the formal equivalence of different forms of mixed quantum–classical linearization methods that depend on a specific choice of basis. This equivalence implies that the accuracy of the calculations performed with these methods is the same, although the numerical efficiency of the various algorithms can vary considerably due to the choice of subsystem basis.

The control parameter μ also plays a key role in the derivation of the quantum–classical Liouville equation but the procedure to obtain this equation is very different from linearization methods. A partial Wigner transform of the density of the full system of the bath degrees of freedom is first taken. The exact evolution equation for this quantity is then expressed in terms of the quantum Liouville operator and the QCL evolution obtained, in scaled variables, via a first order expansion of this operator in the mass ratio [15]. In Section 3 we provide an alternative derivation of QCL that shows that it can be obtained from a linearization approximation. This is the main result of this work: the derivation unifies QCL equation and linearization methods showing that they can be obtained using the same framework. The link among LM and QCL

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approaches was investigated earlier by Shi and Geva [16] who examined the connection between the QCL equation and linearization within the influence functional formalism [17]. For two choices of basis for the quantum subsystem (adiabatic and diabatic), they demonstrated that the QCL equation could be obtained by linearizing the forward–backward action in the influence functional. Our derivation confirms these results, but it is more general since it is obtained in a basis-free form. This is an interesting technical point because, in general, after linearization it is not possible to prove equivalence in different representations simply via a standard transformation of the basis. The approximation affects both the dynamics and the representation of the system [18] and the properties of a fully quantum basis transformation may not be preserved. Due to this, for example, in [16] two distinct proofs were required depending on the representation of the electronic subsystem. In [19] an examination of the relative numerical performances of the QCL equation and the iterative linearized density matrix (ILDM) propagation [20] was made by directly comparing efficiencies and accuracies of the two algorithms based on these methods. The results showed the essential equivalence of the numerical performances of the QCL and ILDM algorithms. This equivalence too is explained by the connection among the methods described in this Letter.

2. Linearized approximations as mass ratio expansions

Consider a system described by the Hamiltonian, $\hat{H} = \frac{\hat{P}^2}{2M} + \hat{h}_q(\hat{p},\hat{r},\hat{R})$. In this expression, capital letters indicate the operators of the bath, while lower case letters are used for the quantum subsystem. The kinetic energy operator of the bath, $\hat{P}^2/2M$, has been isolated, while $\hat{h}_q(\hat{p},\hat{r},\hat{R})$ contains the kinetic energy of the quantum subsystem and all interaction terms, including, if present, external potentials. Below we choose a coordinate representation for the bath while the quantum subsystem is described by abstract operators. All dynamical properties of the system can be calculated in terms of the density operator, $\hat{\rho}$. In the Heisenberg representation, the time evolution of this operator from time 0 to time t is given by

$$\hat{\rho}(t) = e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}. \tag{1}$$

A convenient expression for the matrix element of the density in bath space can be obtained by inserting resolutions of the identity in the bath coordinate states; thus,

$$\langle R|\hat{\rho}(t)|\widetilde{R}\rangle = \int dR_0\, d\widetilde{R}_0 \langle R|e^{-\frac{i}{\hbar}\hat{H}t}|R_0\rangle\langle R_0|\hat{\rho}(0)|\widetilde{R}_0\rangle\langle\widetilde{R}_0|e^{\frac{i}{\hbar}\hat{H}t}|\widetilde{R}\rangle, \tag{2}$$

which is still an operator in the quantum subsystem space. Representing the propagators as path integrals in the bath's coordinates and momenta [21], the matrix element above can be written as

$$\begin{aligned}\langle R|\hat{\rho}(t)|\widetilde{R}\rangle \approx &\int dR_0 \ldots dR_{N-1}\frac{dP_1}{2\pi\hbar}\cdots\frac{dP_N}{2\pi\hbar}\int d\widetilde{R}_0\ldots d\widetilde{R}_{N-1}\\ &\times\frac{d\widetilde{P}_1}{2\pi\hbar}\cdots\frac{d\widetilde{P}_N}{2\pi\hbar}\times e^{-\frac{i\tau}{\hbar}\sum_{k=1}^{N}\frac{P_k^2}{2M}}e^{\frac{i}{\hbar}\sum_{k=1}^{N}P_k(R_k-R_{k-1})}e^{-\frac{i}{\hbar}\tau\hat{h}_q(R_N)}\ldots e^{-\frac{i}{\hbar}\tau\hat{h}_q(R_1)}\\ &\times\langle R_0|\hat{\rho}(0)|\widetilde{R}_0\rangle\times e^{\frac{i\tau}{\hbar}\sum_{k=1}^{N}\frac{\widetilde{P}_k^2}{2M}}e^{-\frac{i}{\hbar}\sum_{k=1}^{N}\widetilde{P}_k(\widetilde{R}_k-\widetilde{R}_{k-1})}e^{\frac{i}{\hbar}\tau\hat{h}_q(\widetilde{R}_1)}\ldots e^{\frac{i}{\hbar}\tau\hat{h}_q(\widetilde{R}_N)},\end{aligned} \tag{3}$$

The above expression (which employs a Trotter factorization of the Hamiltonian) becomes exact for $\tau \to 0$ (with $\tau = t/N$). This is the limit we shall consider here, though the symbol will be omitted from the equations. In the expression, we introduced the short hand notation $\hat{h}_q(R_k) = \hat{h}_q(\hat{p},\hat{r},R_k)$ and $R_N = R$, $\widetilde{R}_N = \widetilde{R}$. Note that the order of the exponentials of the quantum subsystem Hamiltonian must be preserved as these operators do not commute when evaluated at different bath positions. We now introduce mean, $\overline{R}_k = (R_k + \widetilde{R}_k)/2$, and difference, $\Delta R_k = R_k - \widetilde{R}_k$ variables (with similar expressions for the bath momenta). In these variables, the matrix element of the density operator is given by

$$\begin{aligned}\left\langle\overline{R}_N + \frac{\Delta R_N}{2}|\hat{\rho}(t)|\overline{R}_N - \frac{\Delta R_N}{2}\right\rangle = &\int d\overline{R}_0 d\Delta R_0\int\prod_{k=1}^{N-1}d\overline{R}_k\frac{d\overline{P}_k}{2\pi\hbar}\frac{d\overline{P}_N}{2\pi\hbar}\\ &\times\int\prod_{k=1}^{N-1}d\Delta R_k\frac{d\Delta P_k}{2\pi\hbar}\frac{d\Delta P_N}{2\pi\hbar}e^{\frac{i}{\hbar}\overline{P}_N\Delta R_N}e^{-\frac{i}{\hbar}\overline{P}_1\Delta R_0}e^{\frac{i}{\hbar}\sum_{k=1}^{N-1}(\overline{P}_{k+1}-\overline{P}_k)\Delta R_k}\\ &\times e^{-\frac{i}{\hbar}\sum_{k=1}^{N}\left[\tau\frac{\overline{P}_k}{M}-(\overline{R}_k-\overline{R}_{k-1})\right]\Delta P_k}e^{-\frac{i}{\hbar}\tau\hat{h}_q\left(\overline{R}_N+\frac{\Delta R_N}{2}\right)}\ldots e^{-\frac{i}{\hbar}\tau\hat{h}_q\left(\overline{R}_1+\frac{\Delta R_1}{2}\right)}\\ &\times\left\langle\overline{R}_0+\frac{\Delta R_0}{2}|\hat{\rho}(0)|\overline{R}_0-\frac{\Delta R_0}{2}\right\rangle e^{\frac{i}{\hbar}\tau\hat{h}_q\left(\overline{R}_1-\frac{\Delta R_1}{2}\right)}\ldots e^{\frac{i}{\hbar}\tau\hat{h}_q\left(\overline{R}_N-\frac{\Delta R_N}{2}\right)}.\end{aligned} \tag{4}$$

The integrals over the variables ΔP_k are representations of δ functions so they can be performed analytically and introduce a factor $\prod_{k=1}^{N}\delta\left[\tau\frac{\overline{P}_k}{M}-(\overline{R}_k-\overline{R}_{k-1})\right]$ in the integrand. The integral over ΔR_0 is, by definition [22], the partial Wigner transform with respect to the bath variables of the density at $t = 0$,

$$\hat{\rho}_W(\overline{R}_0,\overline{P}_1) = \int d\Delta R_0 e^{-\frac{i}{\hbar}\overline{P}_1\Delta R_0}\left\langle\overline{R}_0+\frac{\Delta R_0}{2}|\hat{\rho}(0)|\overline{R}_0-\frac{\Delta R_0}{2}\right\rangle. \tag{5}$$

Using these observations, Eq. (4) can be written as

$$\begin{aligned}\left\langle\overline{R}_N + \frac{\Delta R_N}{2}|\hat{\rho}(t)|\overline{R}_N - \frac{\Delta R_N}{2}\right\rangle = &\int d\overline{R}_0\int\prod_{k=1}^{N-1}d\overline{R}_k\frac{d\overline{P}_k}{2\pi\hbar}\frac{d\overline{P}_N}{2\pi\hbar}\\ &\times\prod_{k=1}^{N}\delta\left[\tau\frac{\overline{P}_k}{M}-(\overline{R}_k-\overline{R}_{k-1})\right]\int\prod_{k=1}^{N-1}d\Delta R_k e^{\frac{i}{\hbar}\overline{P}_N\Delta R_N}\\ &\times e^{-\frac{i}{\hbar}\tau\hat{h}_q(\overline{R}_N+\frac{\Delta R_N}{2})}\ldots e^{-\frac{i}{\hbar}\tau\hat{h}_q(\overline{R}_1+\frac{\Delta R_1}{2})}\hat{\rho}_W(\overline{R}_0,\overline{P}_1)\\ &\times e^{\frac{i}{\hbar}\tau\hat{h}_q(\overline{R}_1+\frac{\Delta R_1}{2})}\ldots e^{\frac{i}{\hbar}\tau\hat{h}_q(\overline{R}_N-\frac{\Delta R_N}{2})}.\end{aligned} \tag{6}$$

This result is exact. Note that if the path for the mean momenta is known, the presence of the delta function reduces the generation of the path for the mean coordinates to a sequence of classical-like steps. Unfortunately, the mean momentum path can only be calculated once the integral over the ΔR_k has been performed and, in general, this is impossible due to the implicit dependence of the quantum subsystem Hamiltonian on these variables. In linearization methods this difficulty is addressed in two steps. First, a basis is introduced for the quantum subsystem to resolve the operators still present in the path integral and turn $\hat{h}_q$ into a function, h_q, of the forward and backward path of the quantum subsystem and the mean and difference bath coordinates. Second, h_q is expanded to first order in the bath difference variables, at each point along the quantum forward and backward paths. This is the core of the linearized approximation. When the expansion is substituted in the path integral expression of the density matrix, the terms in the integrand that depend on ΔR_k can be combined to obtain a new set of delta functions that reduce also the succession of $\overline{P}_k$ to a classical-like evolution. The precise sequence of manipulations that produce the time-stepping prescription for generating the momentum path is different in the various LM and can produce algorithms with very different characteristics; however, the structure of the result and the two steps to linearization are common to all such methods. As an example, in the Appendix we summarize how these steps are realized in the linearized non-adiabatic dynamics method known as LAND-Map.

The truncation of the Taylor series expansion of h_q to linear order in the difference variable is usually justified in LM methods (see, for example, Refs. [10,11]) on the basis of arguments that involve the interference among the forward and backward paths in the Feynman representation of the time-evolved density. The idea is that, if the two paths are very different (i.e. for large values of the difference variables), the phase factors in the path integral oscillate wildly and interfere destructively. The most relevant contributions to the evolution of the density must then come from neighboring paths for which ΔR remains small and the approximation is accurate. More quantitative statements have been made only for very specific systems (in particular for a bath of harmonic oscillators bilinearly coupled to the quantum subsystem [14]). In contrast to these qualitative arguments, we now show that the expansion in ΔR is equivalent to an expansion of the quantum subsystem Hamiltonian to first order in the parameter $\mu = (m/M)^{1/2}$ and can therefore be justified on the basis of the relative magnitudes of the characteristic masses M and m. To this end, we consider again Eq. (6) and, in analogy with [15], introduce the energy ϵ_0, time $t_0 = \hbar/\epsilon_0$, and length $\lambda_m = (\hbar^2/m\epsilon_0)^{1/2}$ scales. We may then define the following set of dimensionless variables and operators: $\hat{r}' = \hat{r}/\lambda_m$, $R' = \overline{R}/\lambda_m$, $\hat{p}' = \hat{p}/p_m$ and $P' = \overline{P}/P_M$, together with the scaled time $t' = t/t_0$ and the scaled quantum subsystem Hamiltonian $\hat{h}'_q(\hat{r}', \hat{p}', R') = \hat{h}_q(\hat{r}, \hat{p}, R)/\epsilon_0$. Here $p_m = (m\lambda_m/t_0) = (m\epsilon_0)^{1/2}$ and $P_M = (M\epsilon_0)^{1/2}$. This scaling makes the momenta of all degrees of freedom in the system have the same order of magnitude. In the new variables, the time-evolved matrix element of the density operator (see Eq. (6)) is given by

$$\begin{aligned}\left\langle R'_N + \frac{\Delta R'_N}{2} \right| \hat{\rho}'(t') \left| R'_N - \frac{\Delta R'_N}{2} \right\rangle &= \int dR'_0 \int \prod_{k=1}^{N-1} dR'_k dP'_k dP'_N \\ &\times \prod_{k=1}^{N} \delta\left[\tau' \frac{\hbar P'_k}{\sqrt{\epsilon_0 M}} - \frac{\hbar(R'_k - R'_{k-1})}{\sqrt{\epsilon_0 m}}\right] \int \prod_{k=1}^{N-1} d\Delta R'_k e^{\frac{i}{\mu} P'_N \Delta R'_N} \\ &\times e^{\frac{i}{\mu}\sum_{k=1}^{N-1}(P'_{k+1} - P'_k)\Delta R'_k} e^{-i\tau' \hat{h}'_q\left(R'_N + \frac{\Delta R'_N}{2}\right)} \dots e^{-i\tau' \hat{h}'_q\left(R'_1 + \frac{\Delta R'_1}{2}\right)} \\ &\times \hat{\rho}'_W(R'_0, P'_1) e^{i\tau' \hat{h}'_q\left(R'_1 - \frac{\Delta R'_1}{2}\right)} \dots e^{i\tau' \hat{h}'_q\left(R'_N - \frac{\Delta R'_N}{2}\right)}. \end{aligned} \tag{7}$$

The mass ratio appears only in the phase factors in the second line of this equation. In the limit $\mu \to 0$ (i.e., when we expect the quantum–classical evolution equations to become accurate) this phase factor will oscillate very rapidly and complicate the evaluation of the integral. The effect of these oscillations can however be analyzed by performing (for $k = 1, \dots, N-1$) the change of variables $\Delta_k = \Delta R'_k/\mu$ to obtain

$$\begin{aligned}\left\langle R'_N + \mu\frac{\Delta_N}{2} \right| \hat{\rho}'(t') \left| R'_N - \mu\frac{\Delta_N}{2} \right\rangle &= \mu^{N-1} \int dR'_0 \int \prod_{k=1}^{N-1} dR'_k dP'_k dP'_N \\ &\times \prod_{k=1}^{N} \delta\left[\tau' \frac{\hbar P'_k}{\sqrt{\epsilon_0 M}} - \frac{\hbar(R'_k - R'_{k-1})}{\sqrt{\epsilon_0 m}}\right] \int \prod_{k=1}^{N-1} d\Delta_k e^{iP'_N \Delta_N} \\ &\times e^{-i\tau' \hat{h}'_q\left(R'_N + \mu\frac{\Delta_N}{2}\right)} \dots e^{-i\tau' \hat{h}'_q\left(R'_1 + \mu\frac{\Delta_1}{2}\right)} \\ &\times \hat{\rho}'_W(R'_0, P'_1) e^{i\tau' \hat{h}'_q\left(R'_1 - \mu\frac{\Delta_1}{2}\right)} \dots e^{i\tau' \hat{h}'_q\left(R'_N - \mu\frac{\Delta_N}{2}\right)}. \end{aligned} \tag{8}$$

The $\mu \to 0$ limit can now be used to justify truncation to first order in this parameter of the Taylor series expansion of the quantum subsystem Hamiltonian in the last line of the equation above

$$\begin{aligned}\left\langle R'_N + \mu\frac{\Delta_N}{2} \right| \hat{\rho}'(t') \left| R'_N - \mu\frac{\Delta_N}{2} \right\rangle &= \mu^{N-1} \int dR'_0 \int \prod_{k=1}^{N-1} dR'_k dP'_k dP'_N \\ &\times \prod_{k=1}^{N} \delta\left[\tau' \frac{\hbar P'_k}{\sqrt{\epsilon_0 M}} - \frac{\hbar(R'_k - R'_{k-1})}{\sqrt{\epsilon_0 m}}\right] \int \prod_{k=1}^{N-1} d\Delta_k e^{iP'_N \Delta_N} \\ &\times e^{i\sum_{k=1}^{N-1}(P'_{k+1} - P'_k)\Delta_k} e^{-i\tau'\left[\hat{h}'_q(R'_N) + \nabla\hat{h}'_q(R'_N)\mu\frac{\Delta_N}{2}\right]} \dots e^{-i\tau'\left[\hat{h}'_q(R'_1) + \nabla\hat{h}'_q(R'_1)\mu\frac{\Delta_1}{2}\right]} \\ &\times \hat{\rho}'_W(R'_0, P'_1) e^{i\tau'\left[\hat{h}'_q(R'_1) - \nabla\hat{h}'_q(R'_1)\mu\frac{\Delta_1}{2}\right]} \dots e^{i\tau'\left[\hat{h}'_q(R'_N) - \nabla\hat{h}'_q(R'_N)\mu\frac{\Delta_N}{2}\right]}. \end{aligned} \tag{9}$$

Returning to unscaled variables, this result can be written as

$$\begin{aligned}\left\langle \overline{R}_N + \frac{\Delta R_N}{2} \right| \hat{\rho}(t) \left| \overline{R}_N - \frac{\Delta R_N}{2} \right\rangle &= \int d\overline{R}_0 \int \prod_{k=1}^{N-1} d\overline{R}_k \frac{d\overline{P}_k}{2\pi\hbar} \frac{d\overline{P}_N}{2\pi\hbar} \\ &\times \prod_{k=1}^{N} \delta\left[\tau \frac{\overline{P}_k}{M} - (\overline{R}_k - \overline{R}_{k-1})\right] \int \prod_{k=1}^{N-1} d\Delta R_k e^{\frac{i}{\hbar}\overline{P}_N \Delta R_N} \\ &\times e^{\frac{i}{\hbar}\sum_{k=1}^{N-1}(\overline{P}_{k+1} - \overline{P}_k)\Delta R_k} \\ &\times e^{-\frac{i}{\hbar}\tau[\hat{h}_q(\overline{R}_1) + \nabla\hat{h}_q(\overline{R}_1)\frac{\Delta R_1}{2}]} \dots e^{-\frac{i}{\hbar}\tau\left[\hat{h}_q(\overline{R}_N) + \nabla\hat{h}_q(\overline{R}_N)\frac{\Delta R_N}{2}\right]} \\ &\times \hat{\rho}_W(\overline{R}_0, \overline{P}_1) e^{\frac{i}{\hbar}\tau\left[\hat{h}_q(\overline{R}_1) - \nabla\hat{h}_q(\overline{R}_1)\frac{\Delta R_1}{2}\right]} \dots e^{\frac{i}{\hbar}\tau\left[\hat{h}_q(\overline{R}_N) - \nabla\hat{h}_q(\overline{R}_N)\frac{\Delta R_N}{2}\right]}. \end{aligned} \tag{10}$$

Direct comparison of the equation above with (6) shows that the expansion of the quantum subsystem Hamiltonian in the (unscaled) difference variables is formally equivalent to an expansion in the parameter μ of the density matrix element in scaled variables. Since it holds for an abstract representation of the quantum subsystem, this result is independent of the specific choice of basis and, therefore, it can be used to justify any LM.

Finally, if we perform the change of variables $Y_k = \Delta R_k/\hbar$, Eq. (6) can also be written as

$$\begin{aligned}\left\langle \overline{R}_N + \frac{\hbar Y_N}{2} \right| \hat{\rho}(t) \left| \overline{R}_N - \frac{\hbar Y_N}{2} \right\rangle &= \int d\overline{R}_0 \int \prod_{k=1}^{N-1} d\overline{R}_k \frac{d\overline{P}_k}{2\pi} \frac{d\overline{P}_N}{2\pi\hbar} \\ &\times \prod_{k=1}^{N} \delta\left[\tau \frac{\overline{P}_k}{M} - (\overline{R}_k - \overline{R}_{k-1})\right] \int \prod_{k=1}^{N-1} dY_k e^{i\overline{P}_N Y_N} \\ &\times e^{i\sum_{k=1}^{N-1}(\overline{P}_{k+1} - \overline{P}_k)Y_k} \\ &\times e^{-\frac{i}{\hbar}\tau\hat{h}_q(\overline{R}_N + \frac{\hbar Y_N}{2})} \dots e^{-\frac{i}{\hbar}\tau\hat{h}_q(\overline{R}_1 + \frac{\hbar Y_1}{2})} \\ &\times \hat{\rho}_W(\overline{R}_0, \overline{P}_1) e^{\frac{i}{\hbar}\tau\hat{h}_q(\overline{R}_1 - \frac{\hbar\Delta Y_1}{2})} \dots e^{\frac{i}{\hbar}\tau\hat{h}_q\left(\overline{R}_N - \frac{\hbar Y_N}{2}\right)}. \end{aligned} \tag{11}$$

In these variables then, linearization is equivalent to a first order Taylor series expansion of $\hat{h}_q$ in $\hbar$. The mass scaling argument provides a more precise physical argument for the nature of the approximation, but the $\hbar$ expansion can be used to support linearization also for propagation of the bath variables in the absence of a quantum subsystem and/or to show how the full classical limit emerges from the linearization.

3. Quantum–classical Liouville equation from linearization

The scaling of variables and operators introduced in the previous section was used first in the derivation of the quantum–classical Liouville equation. The standard derivation of the QCL equation [15] follows from a partial Wigner representation of the density in the bath degrees of freedom and a first order expansion in the parameter μ of the quantum Liouville operator for the full system, when expressed in scaled variables/operators. In the following we show that the QCL equation can also be considered to be a linearized approximation to full quantum mechanics. To this end, we begin by casting the quantum time evolution equation for the density (the result can immediately be extended to generic operators) into an integro-differential form which is a convenient starting point for approximations. We then show that the QCL equation can be obtained from a linearization approximation to this equation.

Let us consider the time evolution of the density operator from time t to time $t + \tau$(τ is now an arbitrary infinitesimal time interval)

$$\hat{\rho}(t + \tau) = e^{-\frac{i}{\hbar}\hat{H}\tau} \hat{\rho}(t) e^{\frac{i}{\hbar}\hat{H}\tau}. \tag{12}$$

In the limit $\tau \to 0$ we can apply a Trotter factorization of the propagators in the equation above, $e^{\pm\frac{i}{\hbar}\hat{H}\tau} \approx e^{\pm\frac{i}{\hbar}\tau\frac{\hat{P}2}{2M}} e^{\pm\frac{i}{\hbar}\tau\hat{h}_q(\hat{p},\hat{r},\hat{R})}$, insert resolutions of the identity in the bath coordinates (to evaluate the contribution of the quantum subsystem Hamiltonian operator) and momentum states (to evaluate the contribution of the kinetic energy operator), and rewrite the density matrix element as

$$\langle R|\hat{\rho}(t+\tau)|\widetilde{R}\rangle = \int dR_0\, dP_0\, d\widetilde{R}_0\, d\widetilde{P}_0 e^{\frac{i}{\hbar}P_0(R-R_0)} e^{-\frac{i}{\hbar}\tau\frac{P_0^2}{2M}} e^{-\frac{i}{\hbar}\tau\hat{h}_q(\hat{p},\hat{r},R_0)} \times \langle R_0|\hat{\rho}(t)|\widetilde{R}_0\rangle e^{-\frac{i}{\hbar}\widetilde{P}_0(\widetilde{R}-\widetilde{R}_0)} e^{\frac{i}{\hbar}\tau\frac{\widetilde{P}_0^2}{2M}} e^{\frac{i}{\hbar}\tau\hat{h}_q(\hat{p},\hat{r},\widetilde{R}_0)}. \quad (13)$$

We now perform the change of variables $\overline{R}_0 = \frac{R_0+\widetilde{R}_0}{2}$, $\Delta R_0 = R_0 - \widetilde{R}_0$, along with similar variable changes for $R, \widetilde{R}, P_0, \widetilde{P}_0$. In the new variables, the density matrix element is

$$\left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t+\tau)|\overline{R} - \frac{\Delta R}{2}\right\rangle = \int d\overline{R}_0\, d\overline{P}_0\, d\Delta R_0\, d\Delta P_0 e^{\frac{i}{\hbar}\overline{P}_0(\Delta R-\Delta R_0)} \times e^{\frac{i}{\hbar}\Delta P_0(\overline{R}-\overline{R}_0)} \times e^{-\frac{i}{\hbar}\tau\frac{\overline{P}_0}{M}\Delta P_0} e^{-\frac{i}{\hbar}\tau\hat{h}_q\left(\hat{p},\hat{r},\overline{R}_0+\frac{\Delta R_0}{2}\right)} \times \langle \overline{R}_0 + \frac{\Delta R_0}{2}|\hat{\rho}(t)|\overline{R}_0 - \frac{\Delta R_0}{2}\rangle e^{\frac{i}{\hbar}\tau\hat{h}_q\left(\hat{p},\hat{r},\overline{R}_0-\frac{\Delta R_0}{2}\right)}. \quad (14)$$

This expression can be used to obtain the evolution equation for the density matrix elements. We expand the exponentials that depend on τ to first order in this parameter, e.g. $e^{-\frac{i}{\hbar}\tau\frac{\overline{P}_0}{M}\Delta P_0} \approx 1 - \frac{i}{\hbar}\tau\frac{\overline{P}_0}{M}\Delta P_0$. As a result of these expansions, the integral can be expressed (to first order in τ) as the sum of four contributions: $\langle\overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t+\tau)|\overline{R} - \frac{\Delta R}{2}\rangle = A + B + C_0 + C_1$, where

$$A = \int d\overline{R}_0\, d\overline{P}_0\, d\Delta R_0\, d\Delta P_0 e^{\frac{i}{\hbar}\overline{P}_0(\Delta R-\Delta R_0)} e^{\frac{i}{\hbar}\Delta P_0(\overline{R}-\overline{R}_0)} \times \left\langle \overline{R}_0 + \frac{\Delta R_0}{2}|\hat{\rho}(t)|\overline{R}_0 - \frac{\Delta R_0}{2}\right\rangle, \quad (15)$$

$$B = -\frac{i}{\hbar}\tau \int d\overline{R}_0\, d\overline{P}_0\, d\Delta R_0\, d\Delta P_0 e^{\frac{i}{\hbar}\overline{P}_0(\Delta R-\Delta R_0)} e^{\frac{i}{\hbar}\Delta P_0(\overline{R}-\overline{R}_0)} \frac{\overline{P}_0}{M} \times \Delta P_0 \left\langle \overline{R}_0 + \frac{\Delta R_0}{2}|\hat{\rho}(t)|\overline{R}_0 - \frac{\Delta R_0}{2}\right\rangle,$$

$$C_0 = -\frac{i}{\hbar}\tau \int d\overline{R}_0\, d\overline{P}_0\, d\Delta R_0\, d\Delta P_0 e^{\frac{i}{\hbar}\overline{P}_0(\Delta R-\Delta R_0)} e^{\frac{i}{\hbar}\Delta P_0(\overline{R}-\overline{R}_0)} \times \hat{h}_q\left(\hat{p},\hat{r},\overline{R}_0 + \frac{\Delta R_0}{2}\right) \left\langle \overline{R}_0 + \frac{\Delta R_0}{2}|\hat{\rho}(t)|\overline{R}_0 - \frac{\Delta R_0}{2}\right\rangle,$$

$$C_1 = \frac{i}{\hbar}\tau \int d\overline{R}_0\, d\overline{P}_0\, d\Delta R_0\, d\Delta P_0 e^{\frac{i}{\hbar}\overline{P}_0(\Delta R-\Delta R_0)} e^{\frac{i}{\hbar}\Delta P_0(\overline{R}-\overline{R}_0)} \times \left\langle \overline{R}_0 + \frac{\Delta R_0}{2}|\hat{\rho}(t)|\overline{R}_0 - \frac{\Delta R_0}{2}\right\rangle \hat{h}_q\left(\hat{p},\hat{r},\overline{R}_0 - \frac{\Delta R_0}{2}\right).$$

All integrals in A can be performed analytically: the integrals over $\overline{P}_0$ and ΔP are representations of δ functions in the arguments $(\Delta R - \Delta R_0)$ and $(\overline{R} - \overline{R}_0)$, respectively; these delta functions, in turn, allow one to perform the integrals over $\overline{R}_0$ and ΔR_0 to obtain

$$A = \left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle. \quad (16)$$

The same manipulations on C_0 and C_1 make it possible to write these terms as

$$C_0 = \hat{h}_q\left(\hat{p},\hat{r},\overline{R} + \frac{\Delta R}{2}\right)\left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle, \quad (17)$$

and

$$C_1 = \left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle \hat{h}_q\left(\hat{p},\hat{r},\overline{R} - \frac{\Delta R}{2}\right). \quad (18)$$

In term B in Eq. (15), note that the factor ΔP_0 appearing in the integral is proportional to the derivative of the integral with respect to $\overline{R}$; thus, taking into account the factor of proportionality, we have

$$B = -\tau\nabla_{\overline{R}} \int d\overline{R}_0\, d\overline{P}_0\, d\Delta R_0\, d\Delta P_0 e^{\frac{i}{\hbar}\overline{P}_0(\Delta R-\Delta R_0)} e^{\frac{i}{\hbar}\Delta P_0(\overline{R}-\overline{R}_0)} \times \frac{\overline{P}_0}{M}\left\langle \overline{R}_0 + \frac{\Delta R_0}{2}|\hat{\rho}(t)|\overline{R}_0 - \frac{\Delta R_0}{2}\right\rangle. \quad (19)$$

The integrals over ΔP_0 and $\overline{R}_0$ can again be performed, while the integral over ΔR_0 is the partial Wigner transform of the density operator in the bath variables so that

$$B = -\tau \int d\overline{P}_0 e^{\frac{i}{\hbar}\overline{P}_0\Delta R} \frac{\overline{P}_0}{M} \nabla_{\overline{R}}\hat{\rho}_W(\overline{R}, \overline{P}_0). \quad (20)$$

The partial Wigner transform of the density appears naturally as a consequence of the choice of the mean and difference variables.

The intermediate results obtained in Eqs. (16), (20), (17) and (18) can now be assembled to obtain the following expression for the finite difference approximation to the time derivative of the matrix element of the density:

$$\frac{1}{\tau}\left\{\left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t+\tau)|\overline{R} - \frac{\Delta R}{2}\right\rangle - \left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle\right\} = -\int d\overline{P}_0 e^{\frac{i}{\hbar}\overline{P}_0\Delta R} \frac{\overline{P}_0}{M}\nabla_{\overline{R}}\hat{\rho}_W(\overline{R}, \overline{P}_0) + \frac{i}{\hbar}\hat{h}_q\left(\hat{p},\hat{r},\overline{R} + \frac{\Delta R}{2}\right) \times \left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle - \frac{i}{\hbar}\left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle \times \hat{h}_q\left(\hat{p},\hat{r},\overline{R} - \frac{\Delta R}{2}\right). \quad (21)$$

Taking the limit $\tau \to 0$, multiplying both sides of the equation above by $e^{-\frac{i}{\hbar}\overline{P}\Delta R}$, and integrating the result over ΔR gives

$$\frac{\partial\hat{\rho}_W(\overline{R}, \overline{P})}{\partial t} = -\frac{\overline{P}}{M}\nabla_{\overline{R}}\hat{\rho}_W(\overline{R}, \overline{P}) + \frac{i}{\hbar}\int d\Delta R e^{-\frac{i}{\hbar}\overline{P}\Delta R}\hat{h}_q\left(\hat{p},\hat{r},\overline{R} + \frac{\Delta R}{2}\right) \times \left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle - \frac{i}{\hbar}\int d\Delta R e^{-\frac{i}{\hbar}\overline{P}\Delta R} \times \left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle \hat{h}_q\left(\hat{p},\hat{r},\overline{R} - \frac{\Delta R}{2}\right). \quad (22)$$

This integro-differential equation describes the full quantum evolution of the density matrix element. The main difficulty in solving Eq. (22) stems from the dependence of $\hat{h}_q(\hat{p},\hat{r},\overline{R} \pm \frac{\Delta R}{2})$ on the difference variable ΔR. The same scaling argument used to justify LM can be applied here to obtain a convenient approximation for the equation above. For example, linearizing the Hamiltonian $\hat{h}_q$ in the first integral one obtains,

$$\frac{i}{\hbar}\int d\Delta R e^{-\frac{i}{\hbar}\overline{P}\Delta R}\left[\hat{h}_q(\hat{p},\hat{r},\overline{R}) + \frac{\Delta R}{2}\nabla_R\hat{h}_q(\hat{p},\hat{r},\overline{R})\right]\left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle. \quad (23)$$

Substituting this expansion, and its analog for the last term in the right hand side of Eq. (22), results in four contributions to the evolution equation. The two zero order terms in ΔR can be trivially expressed as $-\frac{i}{\hbar}[\hat{h}_q(\hat{p},\hat{r},\overline{R}), \hat{\rho}_W(\overline{R}, \overline{P})]$, where $[.,.]$ is the quantum commutator. The contribution of the first order terms can be computed, for example, as follows:

$$\frac{i}{\hbar}\int d\Delta R e^{-\frac{i}{\hbar}\overline{P}\Delta R}\nabla_{\overline{R}}\hat{h}_q(\hat{p},\hat{r},\overline{R})\frac{\Delta R}{2}\left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle = \frac{1}{2}\nabla_{\overline{R}}\hat{h}_q(\hat{p},\hat{r},\overline{R})\nabla_{\overline{P}}\int d\Delta R e^{-\frac{i}{\hbar}\overline{P}\Delta R}\left\langle \overline{R} + \frac{\Delta R}{2}|\hat{\rho}(t)|\overline{R} - \frac{\Delta R}{2}\right\rangle = \frac{1}{2}\nabla_{\overline{R}}\hat{h}_q(\hat{p},\hat{r},\overline{R})\nabla_{\overline{P}}\hat{\rho}_W(\overline{R}, \overline{P}). \quad (24)$$

A similar treatment for the other first order term gives $1/2\nabla_{\overline{P}}\hat{\rho}_W(\overline{R}, \overline{P})\nabla_{\overline{R}}\hat{h}_q(\hat{p},\hat{r},\overline{R})$. Inserting the results above into Eq. (22), defining $\hat{H}_W(\overline{R}, \overline{P}) = \overline{P}^2/2M + \hat{h}_q(\hat{r},\hat{p},\overline{R})$ and noticing that

$$\frac{\overline{P}}{M}\nabla_{\overline{R}}\hat{\rho}_W(\overline{R},\overline{P}) = \frac{1}{2}\nabla_{\overline{P}}\hat{H}_W(\overline{R},\overline{P})\nabla_{\overline{R}}\hat{\rho}_W(\overline{R},\overline{P}) + \frac{1}{2}\nabla_{\overline{R}}\hat{\rho}_W(\overline{R},\overline{P})\nabla_{\overline{P}}\hat{H}_W(\overline{R},\overline{P}), \tag{25}$$

the terms in the equation can be appropriately rearranged to give

$$\frac{\partial\hat{\rho}_W(\overline{R},\overline{P})}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_W(\hat{p},\hat{r},\overline{R}),\hat{\rho}_W(\overline{R},\overline{P})\right] + \frac{1}{2}\left(\left\{\hat{H}_W(\overline{R},\overline{P}),\hat{\rho}_W(\overline{R},\overline{P})\right\} - \left\{\hat{\rho}_W(\overline{R},\overline{P}),\hat{H}_W(\overline{R},\overline{P})\right\}\right) \tag{26}$$

where $\{.,.\}$ is the classical Poisson bracket. This is the basis-independent mixed quantum–classical Liouville evolution equation for the partial Wigner transform of the density matrix as presented in [15].

4. Conclusions

In this Letter, a general connection between linearization and mass expansions was derived. This connection makes it possible to unify and establish the equivalence of mixed quantum–classical approaches based on these apparently different approximation schemes. In particular, we have shown that quantum–classical linearization methods can be derived from first order expansions of the quantum subsystem Hamiltonian in the mass ratio μ (or in $\hbar$) and that the quantum–classical Liouville equation can also be derived from a linearization of the propagator. The derivation of a linearized method is illustrated in the Appendix by considering the case of the LAND-Map algorithm. However, since our result does not rely on the specific choice of the quantum subsystem basis, similar proofs can be constructed for any linearized scheme as long as a coordinate-momentum representation of the bath is used. This includes, in particular, the linearization of the influence functional presented in [16]. In that work, in fact, a partial Wigner transform with respect to the bath degrees of freedom was employed to effectively introduce a momentum-coordinate representation of the initial density of the bath so the procedure is of the type indicated above. In more general terms, the analysis presented in this work implies that linearization schemes that differ only in the representation of the quantum subsystem are equivalent among themselves and to QCL. The result presented here also implies that, although the efficiency can vary, the accuracy of any algorithm based on linearization or quantum–classical Liouville methods is the same.

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Appendix A

To provide an example of the approximation described after Eq. (6), in this appendix we show how the linearization of the fully quantum evolution is performed in the specific case of LAND-Map, a recently developed linearized mixed quantum–classical method for simulating non-adiabatic dynamics. Here, we summarize only the parts of the derivation that are relevant to highlight the two steps for linearization described in the main text. A detailed description of the approach can be found in [12,13]. In LAND-Map, the classical bath is usually a set of nuclear coordinates, while the quantum subsystem is a set of discrete electronic states. These states are described at first in the diabatic basis, and then (without introducing approximations) in terms of a system of auxiliary harmonic oscillator states via the mapping Hamiltonian approach [23–26]. With this approach, the matrix element of the density operator for the full system at time t is written as

$$\begin{aligned}\left\langle \overline{R}_N+\frac{\Delta R_N}{2},\beta|\hat{\rho}(t)|\overline{R}_N-\frac{\Delta R_N}{2},\beta'\right\rangle &= \sum_{\alpha,\alpha'}\int d\overline{R}_0\int\prod_{k=1}^{N-1}d\overline{R}_k\frac{d\overline{P}_k}{2\pi\hbar}\frac{d\overline{P}_N}{2\pi\hbar}\\ &\times\prod_{k=1}^{N}\delta\left[\tau\frac{\overline{P}_k}{M}-(\overline{R}_k-\overline{R}_{k-1})\right]\int\prod_{k=1}^{N-1}d\Delta R_k e^{\frac{i}{\hbar}\overline{P}_N\Delta R_N}e^{\frac{i}{\hbar}\sum_{k=1}^{N-1}(\overline{P}_{k+1}-\overline{P}_k)\Delta R_k}\\ &\times\left\langle\beta\left|e^{-\frac{i}{\hbar}\tau\hat{h}_{mq}\left(\overline{R}_N+\frac{\Delta R_N}{2}\right)}\dots e^{-\frac{i}{\hbar}\tau\hat{h}_{mq}\left(\overline{R}_1+\frac{\Delta R_1}{2}\right)}\right|\alpha\right\rangle\langle\alpha|\hat{\rho}w(\overline{R}_0,\overline{P}_1)|\alpha'\rangle\\ &\times\left\langle\alpha'\left|e^{\frac{i}{\hbar}\tau\hat{h}_{mq}\left(\overline{R}_1-\frac{\Delta R_1}{2}\right)}\dots e^{-\frac{i}{\hbar}\tau\hat{h}_{mq}\left(\overline{R}_N-\frac{\Delta R_N}{2}\right)}\right|\beta'\right\rangle.\end{aligned} \tag{27}$$

where we indicate the mapping states with Greek letters. $\hat{h}_{mq}(R)$ is the mapping Hamiltonian

$$\hat{h}_{mq}(R) = \frac{1}{2}\sum_{\alpha}h_{\alpha,\alpha}(R)(\hat{q}_\alpha^2+\hat{p}_\alpha^2-\hbar)+\frac{1}{2}\sum_{\alpha,\beta}h_{\alpha,\beta}(R)(\hat{q}_\alpha\hat{q}_\beta+\hat{p}_\alpha\hat{p}_\beta). \tag{28}$$

where $h_{\alpha,\beta}(R)$ are the matrix elements of the quantum subsystem Hamiltonian in the diabatic basis computed at bath position R, and $\hat{q}_\alpha$ ($\hat{p}_\alpha$) are the position (momentum) operators of the mapping oscillators. Thanks to the fact that the mapping Hamiltonian is quadratic in the position and momentum mapping operators, the forward and backward transition amplitudes between quantum states α and β and α' and β' in Eq. (27) can be evaluated exactly via a path integral expression in the coherent state basis [27]. The steps involved in this evaluation are non-trivial (see Ref. [12]) but they provide the following explicit expression for the density matrix element

$$\begin{aligned}\left\langle \overline{R}_N+\frac{\Delta R_N}{2},\beta|\hat{\rho}(t)|\overline{R}_N-\frac{\Delta R_N}{2},\beta'\right\rangle &= \sum_{\alpha,\alpha'}\int d\overline{R}_0\int\prod_{k=1}^{N-1}d\overline{R}_k\frac{d\overline{P}_k}{2\pi\hbar}\frac{d\overline{P}_N}{2\pi\hbar}\\ &\times\prod_{k=1}^{N}\delta\left[\tau\frac{\overline{P}_k}{M}-(\overline{R}_k-\overline{R}_{k-1})\right]\int\prod_{k=1}^{N-1}d\Delta R_k e^{\frac{i}{\hbar}\overline{P}_N\Delta R_N}e^{\frac{i}{\hbar}\sum_{k=1}^{N-1}(\overline{P}_{k+1}-\overline{P}_k)\Delta R_k}\\ &\times\int dq_0dp_0e^{\frac{i}{\hbar}\Theta_{0\alpha}}G_0r_{0\alpha}e^{-\frac{i}{\hbar}\Theta_{t\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)}r_{t\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)\\ &\times\langle\alpha|\hat{\rho}w(\overline{R}_0,\overline{P}_1)|\alpha'\rangle\\ &\times\int dq_0'dp_0'e^{-\frac{i}{\hbar}\Theta_{0\alpha'}'}G_0'r_{0\alpha'}'e^{\frac{i}{\hbar}\Theta_{t\beta'}'\left(\left\{\overline{R}_k-\frac{\Delta R_k}{2}\right\}\right)}r_{t\beta'}'\left(\left\{\overline{R}_k-\frac{\Delta R_k}{2}\right\}\right).\end{aligned} \tag{29}$$

In the above equation, the integrals over the initial coordinates and momenta of the mapping states (e.g. $q_0=\{q_{0\lambda}\}$ and $p_0=\{p_{0\lambda}\}$ where λ goes from 1 to the number of electronic states) result from the coherent state path integral for the transition amplitudes. The functions required to compute the transition amplitudes (we focus on the forward transition amplitude as definitions for the backward transition amplitude are analogous) are:

1. the coherent state representation of the initial mapping state α, defined as the product $e^{\frac{i}{\hbar}\Theta_{0\alpha}}G_0r_{0\alpha}$ in the integrand, with

$$G_0 = e^{-1/2\sum_\lambda(q_{0\lambda}^2+p_{0\lambda}^2)},$$
$$r_{0,\alpha} = (q_{0,\alpha}^2+p_{0,\alpha}^2)^{1/2},$$
$$\Theta_{0\alpha} = \tan^{-1}\frac{p_{0,\alpha}}{q_{0,\alpha}};$$

2. the population of the final mapping state β, defined as

$$r_{t\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)=\left(q^2_{t,\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)+p^2_{t,\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)\right)^{1/2} \tag{30}$$

   if $\{q_t, p_t\}$ are the coordinate and momenta of the mapping states obtained by solving the classical evolution determined by the classical analog of the mapping Hamiltonian, Eq. (28);

3. the phase factor $e^{-\frac{i}{\hbar}\Theta_{t\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)}$, where

$$\begin{aligned}\Theta_{t,\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)&=\tan^{-1}\left(\frac{p_{0,\beta}}{q_{0,\beta}}\right)+\tau\sum_{k=1}^{N}h_{\beta,\beta}\left(\overline{R}_k+\frac{\Delta R_k}{2}\right)\\&\quad+\tau\sum_{k=1}^{N}\sum_{\lambda\neq\beta}\left[h_{\beta,\lambda}\left(\overline{R}_k+\frac{\Delta R_k}{2}\right)\frac{(p_{k\beta}p_{k\lambda}+q_{k\beta}q_{k\lambda})}{(p^2_{k\beta}+q^2_{k\beta})}\right]\\&=\tan^{-1}\left(\frac{p_{0,\beta}}{q_{0,\beta}}\right)+\tau\sum_{k=1}^{N}\theta_\beta\left(\overline{R}_k+\frac{\Delta R_k}{2}\right).\end{aligned} \tag{31}$$

   the last line in the equation above defines the function θ_β.

All quantities in Eq. (29) are functions, no longer operators, that depend on the forward and backward paths for the full system. This is the first step in the linearization method as described in the text. The phase factor in Eq. (31) contains, via the functions $h_{\beta,\lambda}(\overline{R}_k+\frac{\Delta R_k}{2})$, the implicit dependence of the matrix elements of the quantum subsystem Hamiltonian on the difference variables ΔR_k. The second step in the linearization approximation corresponds to the expansion of the Θ functions to linear order in the difference variables. Grouping terms of the same order in ΔR_k in the overall phase results in the following (linearized) expression for the matrix element of the density

$$\begin{aligned}\left\langle\overline{R}_N+\frac{\Delta R_N}{2},\beta|\hat{\rho}(t)|\overline{R}_N-\frac{\Delta R_N}{2},\beta'\right\rangle&=\sum_{\alpha,\alpha'}\int d\overline{R}_0\int\prod_{k=1}^{N-1}d\overline{R}_k\frac{d\overline{P}_k}{2\pi\hbar}\frac{d\overline{P}_N}{2\pi\hbar}\\&\times\prod_{k=1}^{N}\delta\left[\tau\frac{\overline{P}_k}{M}-(\overline{R}_k-\overline{R}_{k-1})\right]\int dq_0dp_0\int dq'_0dp'_0\int\prod_{k=1}^{N-1}d\Delta R_k e^{\frac{i}{\hbar}\overline{P}_N\Delta R_N}\\&\times e^{\frac{i}{\hbar}\sum_{k=1}^{N-1}\left[(\overline{P}_{k+1}-\overline{P}_k)-\tau\frac{\nabla\theta_\beta(\overline{R}_k)+\nabla\theta_{\beta'}(\overline{R}_k)}{2}\right]\Delta\overline{R}_k}\\&\times e^{\frac{i}{\hbar}\Theta_{0\alpha}G_0r_{0\alpha}}e^{\frac{i}{\hbar}\tau\sum_{k=1}^{N}(\theta_\beta(\overline{R}_k)-\theta_{\beta'}(\overline{R}_k))r_{t\beta}\left(\left\{\overline{R}_k+\frac{\Delta R_k}{2}\right\}\right)}\\&\times\langle\alpha|\hat{\rho}w(\overline{R}_0,\overline{P}_1)|\alpha'\rangle e^{-\frac{i}{\hbar}\Theta'_{0\alpha'}G'_0r'_{0\alpha'}r'_{t\beta'}\left(\left\{\overline{R}_k-\frac{\Delta R_k}{2}\right\}\right)}.\end{aligned} \tag{32}$$

Assuming that the functions $r_{t\beta}$ and $r'_{t\beta'}$ vary slowly with the difference variables compared to the phase factor $e^{\frac{i}{\hbar}\tau\sum_{k=1}^{N}(\theta_{t\beta}(\overline{R}_k)-\theta_{t\beta'}(\overline{R}_k))}$ and can therefore be evaluated as functions of the path of mean variables only, the integrals over the difference variables ΔR_k can now be performed. These integrals are in fact representations of delta functions and the equation above can also be written as

$$\begin{aligned}\left\langle\overline{R}_N+\frac{\Delta R_N}{2},\beta|\hat{\rho}(t)|\overline{R}_N-\frac{\Delta R_N}{2},\beta'\right\rangle&=\sum_{\alpha,\alpha'}\int d\overline{R}_0\int\prod_{k=1}^{N-1}d\overline{R}_k\frac{d\overline{P}_k}{2\pi\hbar}\frac{d\overline{P}_N}{2\pi\hbar}\\&\times\prod_{k=1}^{N}\delta\left[\tau\frac{\overline{P}_k}{M}-(\overline{R}_k-\overline{R}_{k-1})\right]\int dq_0dp_0\int dq'_0dp'_0e^{\frac{i}{\hbar}\overline{P}_N\Delta R_N}\\&\times\prod_{k=1}^{N-1}\delta[\overline{P}_{k+1}-\overline{P}_k-\tau F(\overline{R}_k,\beta,\beta')]e^{\frac{i}{\hbar}\Theta_{0\alpha}}G_0r_{0\alpha}e^{\frac{i}{\hbar}\tau\sum_{k=1}^{N}(\theta_\beta(\overline{R}_k)-\theta_{\beta'}(\overline{R}_k))}\\&\times r_{t\beta}(\{\overline{R}_k\})\langle\alpha|\hat{\rho}w(\overline{R}_0,\overline{P}_1)|\alpha'\rangle e^{-\frac{i}{\hbar}\Theta'_{0\alpha'}}G_{0'}r'_{0\alpha'}r'_{t\beta'}(\{\overline{R}_k\}).\end{aligned} \tag{33}$$

The argument of the delta functions in the expression above determines a propagation scheme for the path of mean variables: the mean coordinates are advanced from step $k-1$ to step k based on the usual 'Newtonian' prescription $\overline{R}_{k-1}=\overline{R}_k+\tau\frac{\overline{P}_k}{M}$, while the mean momenta are advanced from step k to step $k+1$ as $\overline{P}_{k+1}=\overline{P}_k+\tau F(\overline{R}_k,\beta,\beta')$. Note that, although this expression may also appear of classical form, the 'force' $F(\overline{R}_k,\beta,\beta')$, is, in general, non-Hamiltonian and given by

$$\begin{aligned}F(\overline{R}_k,\beta,\beta')=&-\frac{1}{2}\{\nabla_{\overline{R}_k}h_{\beta,\beta}(\overline{R}_k)+\nabla_{\overline{R}_k}h_{\beta',\beta'}(\overline{R}_k)\}\\&-\frac{1}{2}\sum_{\lambda\neq\beta}\nabla_{\overline{R}_k}h_{\beta,\lambda}(\overline{R}_k)\left\{\frac{(p_{\beta k}p_{\lambda k}+q_{\beta k}q_{\lambda k})}{(p^2_{\beta k}+q^2_{\beta k})}\right\}\\&-\frac{1}{2}\sum_{\lambda\neq\beta'}\nabla_{\overline{R}_k}h_{\beta',\lambda}(\overline{R}_k)\left\{\frac{(p'_{\beta'k}p'_{\lambda k}+q'_{\beta'k}q'_{\lambda k})}{(p'^2_{\beta'k}+q'^2_{\beta'k})}\right\}.\end{aligned} \tag{34}$$

This expression for the force accounts for the effect of non-adiabatic transitions among the electronic states on the nuclear dynamics and it is typical of the LAND-Map method. In spite of this unusual force term, however, the linearization approximation reduces, via the presence of the delta functions, all propagations necessary to compute the matrix element of the density operator to a time-stepping prescription whose numerical complexity is similar to that of classical mechanics as stated in 2.

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