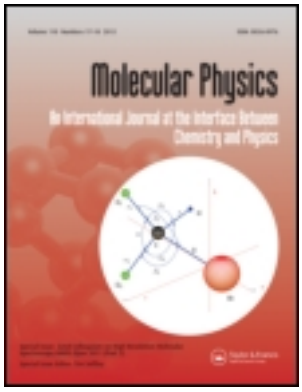

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Forward-backward solution of quantum-classical Liouville equation in the adiabatic mapping basis

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INVITED ARTICLE

Forward–backward solution of quantum-classical Liouville equation in the adiabatic mapping basis

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A forward–backward solution of quantum-classical Liouville equation in the adiabatic mapping basis is constructed. The trajectory dynamics of this solution admits an interpretation that is different from that in the quantum subsystem basis and allows one to establish a connection between mean-field and surface-hopping algorithms within the quantum-classical Liouville equation framework. This adiabatic formulation also suggests hybrid simulation schemes that combine aspects of mean-field and surface-hoping dynamics.

Keywords: Liouville equation; non-adiabatic dynamics; mixed quantum-classical dynamics

1. Introduction

Non-adiabatic dynamics, stemming from the breakdown of the Born–Oppenheimer approximation, play important roles in the description of many chemical and biological processes such as proton and electron transfer reactions, vibrational relaxation, photochemical dynamics, and coherent energy transfer phenomena in biological systems [1]. In all these processes, the non-adiabatic transitions experienced by the quantum system are induced by interactions with the environment in which it resides. To avoid the exponential scaling in computational costs of exact quantum simulations for the composite system, several mixed quantum-classical [2,3] and semi-classical [4,5] schemes have been developed.

In recent work [6,7], we constructed a forward–backward trajectory solution (FBTS) to simulate non-adiabatic dynamics within the quantum-classical Liouville equation (QCLE) formalism. This solution was derived by starting from the formal solution of QCLE in forward–backward form in the subsystem-based mapping approach, which represents the discrete quantum states in terms of positions and momenta of fictitious harmonic oscillators. With this starting point and the introduction of a coherent state basis [8,9] in the mapping space, an approximate solution of the QCLE that involves forward–backward trajectories of the coherent state variables, coupled to the evolution of the bath phase space variables, was derived. The dynamical evolution of the entire system, quantum subsystem plus bath, that is prescribed by the FBTS is described by Newtonian dynamics in the extended phase space comprising coherent state and bath phase space coordinates, providing a simple but approximate simulation algorithm. The earlier surface-hopping-like schemes [10,11] for the solution of the QCLE involve Monte Carlo (MC) sampling of non-adiabatic events, which can lead to instabilities due to accumulations of MC weights unless filtering is applied. The FBTS does not involve such events and is more appealing alternatives in situations where long-time dynamics is of interest.

Comparisons of the FBTS with exact quantum dynamics on a variety of model systems indicate that quantitatively accurate results can be obtained often with small computational cost [7]. In situations where this approximate solution is not quantitatively accurate, its generalisation, termed the jump forward–backward trajectory solution (JFBTS), has been shown to correct deficiencies in the solution. The JFBTS provides a systematic method to numerically recover the exact QCLE results by introducing jumps in the continuous Newtonian trajectories. In the current formulation of the JFBTS, there is no special criterion to determine at which times jumps are inserted; consequently, they are introduced through uniform stochastic sampling. Since the inclusion of jumps in the trajectories adds to the computational cost, it is important to develop better jump sampling strategies for situations where the simple FBTS does not provide sufficient accuracy.

Here, we consider the formulation of the forward–backward solution of the QCLE in the adiabatic mapping representation. In different contexts, the adiabatic mapping representation has been considered in Refs. [12–14]. Several factors suggest this is a worthwhile task. For certain problems, such as proton transfer reactions where the

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time scales of the bath and subsystem are well-separated even during non-adiabatic transitions, adiabatic dynamics can provide qualitatively acceptable results. Therefore, a forward–backward solution of the QCLE in the adiabatic basis will be appropriate for problems of this type. Furthermore, solutions based on the adiabatic basis naturally lead to surface-hopping algorithms [10,11,15]. Consequently, it is interesting to understand how to extract such a surface-hopping dynamics from the FBTS (a mean-field algorithm in the subsystem-based mapping basis), and obtain an alternative approach to inserting jumps to disrupt continuous propagation of trajectories in the mapping space.

The outline of the paper is as follows. In Section 2, we summarise the principal elements of the FBTS. In Section 3, we construct the adiabatic mapping version of the FBTS, present the set of evolution equations that govern the dynamics, and provide an interpretation of the trajectory dynamics in the original FBTS in terms of the adiabatic representation. In this section, we also give a different form of the forward–backward solution that leads to a surface-hopping interpretation of the dynamics. Finally, in Section 4, we comment on the connection between mean-field and surface-hopping algorithms within the QCLE framework and suggest how the formalism might be used to construct hybrid schemes that combine advantageous features of both mean-field and surface-hopping dynamics.

2. Forward–backward solution of the quantum-classical Liouville equation

We consider a quantum subsystem coupled to a bath whose joint dynamics is described by the QCLE. The Hamiltonian has the form,

$$\hat{H}_W(X) = H_b(X) + \hat{h}_s + \hat{V}_c(R) \equiv H_b(X) + \hat{h}(R), \quad (1)$$

where the subscript W refers to a partial Wigner transform over the bath degrees of freedom (DOF). Here, $H_b(X) = P^2/2M + V_b(R)$ is the bath Hamiltonian with $V_b(R)$ the bath potential energy, $\hat{h}_s = \hat{p}^2/2m + \hat{V}_s$ is the subsystem Hamiltonian with $\hat{p}$ and $\hat{V}_s$ the subsystem momentum and potential energy operators, and $\hat{V}_c(R)$ is the coupling potential energy operator. The masses of the subsystem and bath particles are m and M, respectively.

For a partially Wigner transformed operator $\hat{B}_W(X)$, which is a function of the phase space variables $X = (R, P) = (R_1, R_2, \ldots, R_{N_b}, P_1, P_2, \ldots, P_{N_b})$ of the bath, the time evolution is governed by the QCLE,

$$\begin{aligned}\frac{\partial \hat{B}_W(X,t)}{\partial t} &= \frac{i}{\hbar}[\hat{H}_W, \hat{B}_W] \\ &\quad - \frac{1}{2}(\{\hat{H}_W, \hat{B}_W\} - \{\hat{B}_W, \hat{H}_W\}), \\ &= i\hat{\mathcal{L}}\hat{B}_W = \frac{i}{\hbar}(\vec{\mathcal{H}}_\Lambda\ \hat{B}_W - \hat{B}_W\ \overleftarrow{\mathcal{H}}_\Lambda). \quad (2)\end{aligned}$$

For a review with references, see Ref. [3]. In this equation, the square and curly brackets denote the quantum commutator and classical Poisson bracket, respectively. The two kinds of Lie bracket act together as the generator of the mixed quantum-classical dynamics. Due to the fact that $\hat{H}_W(X)$ and $\hat{B}_W(X,t)$ are quantum operators with respect to the subsystem DOF, two differently ordered Poisson brackets are needed to properly account for the mixed dynamics. The last line of the above equation defines the QCL operator $i\mathcal{L}$. The second equality on this line of the equation introduces another equivalent representation of QCL operator in terms of the forward and backward mixed quantum-classical Hamiltonians [16],

$$\vec{\mathcal{H}}_\Lambda = \hat{H}_W\left(1 + \frac{\hbar\Lambda}{2i}\right), \quad \overleftarrow{\mathcal{H}}_\Lambda = \left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{H}_W, \quad (3)$$

where $\Lambda = \overleftarrow{\nabla}_P\vec{\nabla}_R - \overleftarrow{\nabla}_R\vec{\nabla}_P$. The arrow on top of a differential operator indicates the direction in which it acts. The last representation of the QCL operator resembles (formally) the quantum evolution operator, and forms the starting point of the FBTS.

The formally exact solution of the QCLE is given by [15,16]

$$\begin{aligned}\hat{B}_W(X,t) &= e^{i\hat{\mathcal{L}}t}\hat{B}_W(X), \\ &= \mathcal{S}\big(e^{i\vec{\mathcal{H}}_\Lambda t/\hbar}\hat{B}_W(X)e^{-i\overleftarrow{\mathcal{H}}_\Lambda t/\hbar}\big). \quad (4)\end{aligned}$$

The $\mathcal{S}$ operator [6,16] specifies the order in which the forward and backward evolution operators act on $\hat{B}_W(X)$. The ordering of evolution operators is critical because the lack of an underlying Lie algebraic structure of the QCLE.

2.1. *Forward–backward trajectory solution*

We suppose that the time evolution of the quantum subsystem (coupled to the bath) can be accurately described within a Hilbert space of dimension N. Furthermore, the subsystem basis $\{|\lambda\rangle\}$ is chosen for the matrix representations of quantum operators.

In the mapping representation, the state $|\lambda\rangle$ is replaced by $|m_\lambda\rangle$, an eigenfunction of the Hamiltonian for N fictitious harmonic oscillators [5,17], having occupation numbers which are limited to 0 or 1: $|\lambda\rangle \to |m_\lambda\rangle = |0_1, \ldots, 1_\lambda, \ldots 0_N\rangle$. Creation and annihilation operators on these states, $\hat{a}^\dagger_\lambda$ and $\hat{a}_\lambda$, satisfy the commutation relation $[\hat{a}_\lambda, \hat{a}^\dagger_{\lambda'}] = \delta_{\lambda,\lambda'}$. The actions of these operators on the single-excitation mapping states are $\hat{a}^\dagger_\lambda|0\rangle = |m_\lambda\rangle$ and $\hat{a}_\lambda|m_\lambda\rangle = |0\rangle$, where $|0\rangle = |0_1 \ldots 0_N\rangle$ is the ground state of the mapping basis.

We may then define the mapping version of operators, $\hat{B}_m(X)$, given by $\hat{B}_m(X) = B^{\lambda\lambda'}_W(X)\hat{a}^\dagger_\lambda\hat{a}_{\lambda'}$, such that matrix elements of $\hat{B}_W$ in the subsystem basis are equal to the matrix elements of the corresponding mapping

operator: $B_W^{\lambda\lambda'}(X) = \langle\lambda|\hat{B}_W(X)|\lambda'\rangle = \langle m_\lambda|\hat{B}_m(X)|m_{\lambda'}\rangle$. (The Einstein summation convention will be used throughout although sometimes sums will be explicitly written if there is the possibility of confusion.) In particular, the mapped Hamiltonian is

$$\hat{H}_m = H_b(X) + h^{\lambda\lambda'}(R)\hat{a}_\lambda^\dagger\hat{a}_{\lambda'} \equiv H_b(X) + \hat{h}_m, \qquad (5)$$

where we applied the mapping transformation only on the part of the Hamiltonian that involves the subsystem DOF in Equation (5). The mapping Hamiltonian, $\hat{h}_m$, is always a quadratic Hamiltonian with respect to the quantum DOF. The pure bath term, $\hat{H}_b(X)$, acts as an identity operator in the subsystem basis and is mapped onto the identity operator of the mapping space directly. The mapped formal solution in Equation (4) reads

$$\hat{B}_m(X,t) = \mathcal{S}\big(e^{i\overrightarrow{\mathcal{H}}_\Lambda^m t/\hbar}\hat{B}_m(X)e^{-i\overleftarrow{\mathcal{H}}_\Lambda^m t/\hbar}\big), \qquad (6)$$

where $\overrightarrow{\mathcal{H}}_\Lambda^m$ is given by $\overrightarrow{\mathcal{H}}_\Lambda^m = \hat{H}_m(1 + \hbar\Lambda/2i)$, with an analogous definition for $\overleftarrow{\mathcal{H}}_\Lambda^m$.

We now define the coherent states $|z\rangle$ in the mapping space, $\hat{a}_\lambda|z\rangle = z_\lambda|z\rangle$ and $\langle z|\hat{a}_\lambda^\dagger = z_\lambda^*\langle z|$, where $|z\rangle = |z_1, \ldots, z_N\rangle$ and the eigenvalue is $z_\lambda = (q_\lambda + ip_\lambda)/\sqrt{\hbar}$. The variables $q = (q_1, \ldots, q_N)$ and $p = (p_1, \ldots, p_N)$ are mean coordinates and momenta of the harmonic oscillators in the state $|z\rangle$, respectively; i.e., we have $\langle z|\hat{q}_\lambda|z\rangle = q_\lambda$ and $\langle z|\hat{p}_\lambda|z\rangle = p_\lambda$. We note that our coherent state definition differs from those introduced in Refs. [8,9] by a constant factor of $\sqrt{2}$. The coherent states form an overcomplete basis with the inner product between any two such states, $\langle z|z'\rangle = e^{-(|z-z'|^2) - i(z\cdot z'^* - z^*\cdot z')}$. Finally, we remark that the coherent states provide the resolution of identity,

$$1 = \int \frac{d^2z}{\pi^N}|z\rangle\langle z|, \qquad (7)$$

where $d^2z = d(\Re(z))d(\Im(z)) = dqdp/(2\hbar)^N$.

Similar to the path integral approach of solving for the quantum dynamics, we decompose the forward and backward evolution operators in Equation (6) into a concatenation of M short-time evolutions with $\Delta t_i = \Delta t$ and $M\Delta t = t$. In each short-time interval Δt_i, we introduce two sets of coherent states, $|z_i\rangle$ and $|z_i'\rangle$, via Equation (7) to expand the forward and backward time evolution operators, respectively. The time evolution (generated by a quadratic Hamiltonian) of coherent states can be represented by trajectory evolution in the phase space of (q, p). After some algebra, the matrix elements of Equation (6) can be approximated by [6]

$$B_W^{\lambda\lambda'}(X,t) = \sum_{\mu\mu'}\int dxdx'\phi(x)\phi(x') \times \frac{1}{\hbar}(q_\lambda + ip_\lambda)(q'_{\lambda'} - ip'_{\lambda'})B_W^{\mu\mu'}(X_t) \times \frac{1}{\hbar}(q_\mu(t) - ip_\mu(t))(q'_{\mu'}(t) + ip'_{\mu'}(t)), \qquad (8)$$

where $x = (q, p)$ are the real and imaginary parts of z, respectively, $dx = dqdp$, and $\phi(x) = (\hbar)^{-N}e^{-\sum_v(q_v^2+p_v^2)/\hbar}$ is the normalised Gaussian distribution function. In deriving Equation (8), we invoked an 'orthogonality' approximation on the inner product between subsequent coherent state variables, $\langle z_i|e^{\frac{i}{\hbar}\hat{h}_m t}|z_{i+1}\rangle = \langle z_i(t)|z_{i+1}\rangle \approx \pi^N\delta(z_{i+1} - z_i(t_i))$ with i the time step index. This approximation is necessary to obtain a continuous trajectory of $z(t)$. In order to evaluate the integral in Equation (8) via MC, one has to propagate trajectories of $(X(t), z(t), z'(t))$ in the extended phase space of partially Wigner transformed bath DOF and coherent states of the mapped subsystem DOF. In this FBTS solution, the trajectory of the entire system follows Hamiltonian dynamics,

$$\frac{d\mathcal{X}_\mu}{dt} = \frac{\partial H_e(\mathcal{X},\Pi)}{\partial\Pi_\mu}, \qquad \frac{d\Pi_\mu}{dt} = -\frac{\partial H_e(\mathcal{X},\Pi)}{\partial\mathcal{X}_\mu}, \qquad (9)$$

where $H_e(\chi,\pi) = P^2/2M + V_0(R) + \frac{1}{2\hbar}h^{\lambda\lambda'}(R)(q_\lambda q_{\lambda'} + p_\lambda p_{\lambda'} + q'_\lambda q'_{\lambda'} + p'_\lambda p'_{\lambda'})$ with $V_0(R) = V_b(R) - \mathrm{Tr}\hat{h}(R)$, $\mathcal{X} = (R, q, q')$, and $\Pi = (P, p, p')$.

2.2. *Jump forward–backward trajectory solution*

The main approximation introduced in the derivation of the FBTS, Equation (8), is the orthogonality approximation. The simplest improvement to the algorithm is to refrain from applying this approximation at every time step. In Ref. [7], we outlined a practical approach to evaluate the set of selected integrals of z_i and z_i' (which could be evaluated analytically if the orthogonality approximation were applied). We termed this extension of FBTS as the jump FBTS (JFBTS). Since the computational cost grows quickly with respect to the number of jumps inserted, one needs to make a trade-off between numerical efficiency and accuracy.

In the simplest approach, one selects every (M/K) time steps from a total of M steps to fully evaluate the coherent state integrals:

$$B_W^{\lambda\lambda'}(X,t) = \sum_{\mu\mu'}\sum_{\substack{s_0s'_0\ldots\\ s_{K-1}s'_{K-1}}}\int\prod_{v=0}^{K}dxdx'\phi(x_v)\phi(x'_v) \times \frac{1}{\hbar}(q_{0\lambda} + ip_{0\lambda})(q'_{0\lambda'} - ip'_{0\lambda'})B_W^{\mu\mu'}(X_t) \times \frac{1}{\hbar}\left\{\prod_{v=1}^{K}\left(q_{(v-1)s_{v-1}}(\tau_v) - ip_{(v-1)s_{v-1}}(\tau_v)\right)\left(q_{vs_v} + ip_{vs_v}\right)\right\}$$

$$\times \frac{1}{\hbar}\left\{\prod_{v=1}^{K}\left(q'_{(v-1)s_{v-1}}(\tau_v)+ip'_{(v-1)s_{v-1}}(\tau_v)\right)\left(q'_{vs_v}-ip'_{vs_v}\right)\right\}$$
$$\times \frac{1}{\hbar}(q_{K\mu}(\tau_{K+1})-ip_{K\mu}(\tau_{K+1}))(q'_{K\mu'}(\tau_{K+1})$$
$$+ip'_{K\mu'}(\tau_{K+1})), \tag{10}$$

where the subscripts, v and s, refer to the vth time step and the sth component of the q and p vectors, respectively, and $\tau_v = t_{i_v} - t_{i_{v-1}}$ with $t_{i_0} = 0$ and $t_{i_{K+1}} = t$. According to this prescription, the continuous FB trajectories experience K discontinuous jumps in the (x, x') phase space. Between subsequent jumps, the evolution of FB trajectory is governed by Equation (9). Simulations show that with a sufficient number of jumps numerically exact solutions of the QCLE can be obtained [7].

3. Adiabatic forward–backward solution

We now consider an adiabatic version of the FBTS of the QCLE. To this end, we first introduce the adiabatic basis $\{|\alpha; R\rangle\}$ that satisfies

$$\hat{h}(R)\,|\alpha; R\rangle = E_\alpha(R)\,|\alpha; R\rangle\,, \tag{11}$$

where $\hat{h}(R)$ is defined in Equation (1). We choose strictly real-valued adiabatic states for this study, but this restriction is not necessary.

The QCLE, Equation (2), cast in the adiabatic basis, reads [15],

$$\frac{\partial B_W^{\alpha\alpha'}(X,t)}{\partial t} = i\omega_{\alpha\alpha'}(R) + \frac{P}{M}\cdot\frac{\partial B_W^{\alpha\alpha'}}{\partial R} + \frac{P}{M}\cdot\left(d_{\alpha\alpha''}B_W^{\alpha''\alpha'} - B_W^{\alpha\alpha''}d_{\alpha''\alpha'}\right) + \frac{1}{2}\left(F_W^{\alpha\alpha''}\cdot\frac{\partial B_W^{\alpha''\alpha'}}{\partial P} + \frac{\partial B_W^{\alpha\alpha''}}{\partial P}\cdot F_W^{\alpha''\alpha'}\right), \tag{12}$$

where $d_{\alpha\alpha'} = \langle\alpha; R|\,\nabla_R\,|\alpha'; R\rangle$, $\omega_{\alpha\alpha'}(R) = (E_\alpha(R) - E_{\alpha'}(R))/\hbar$ and $F_W^{\alpha\alpha'} = -\langle\alpha; R|\,\frac{\partial(V_b(R)+\hat{V}_c(R))}{\partial R}\,|\alpha'; R\rangle$.

In order to formulate an adiabatic forward–backward representation of QCLE, we explicitly define adiabatic versions of the forward and backward mixed quantum-classical Hamiltonians, $\overrightarrow{\mathcal{H}}^a_\Lambda = |\alpha; R\rangle\,\overrightarrow{\mathcal{H}}^a{}_{\alpha\alpha'}\,\langle\alpha'; R|$, with

$$\overrightarrow{\mathcal{H}}^a_{\alpha\alpha'} \equiv \left(\frac{P^2}{2M} + V_0(R) + E_\alpha(R)\right)\delta_{\alpha\alpha'} + \frac{\hbar}{2i}\left[\frac{P}{M}\cdot\frac{\overrightarrow{\partial}}{\partial R}\delta_{\alpha\alpha'} + 2\frac{P}{M}\cdot d_{\alpha\alpha'} + F_W^{\alpha\alpha'}\cdot\frac{\overrightarrow{\partial}}{\partial P}\right], \tag{13}$$

and $\overleftarrow{\mathcal{H}}^a_\Lambda = |\alpha; R\rangle\,\overleftarrow{\mathcal{H}}^a{}_{\alpha\alpha'}\,\langle\alpha'; R|$, with

$$\overleftarrow{\mathcal{H}}^a_{\alpha\alpha'} \equiv \left(\frac{P^2}{2M} + V_0(R) + E_\alpha(R)\right)\delta_{\alpha\alpha'} - \frac{\hbar}{2i}\left[\frac{P}{M}\cdot\frac{\overleftarrow{\partial}}{\partial R}\delta_{\alpha\alpha'} + 2\frac{P}{M}\cdot d_{\alpha'\alpha} + F_W^{\alpha\alpha'}\cdot\frac{\overleftarrow{\partial}}{\partial P}\right]. \tag{14}$$

We remark that the adiabatic Hamiltonians defined here are different from the basis-independent ones defined in Equation (3). To avoid potential confusion, we add a superscript a to the adiabatic version. The adiabatic evolution operators are also constructed such that the adiabatic matrix elements of the operator equation,

$$\frac{\partial\hat{B}_W(X,t)}{\partial t} = \frac{i}{\hbar}\left(\overrightarrow{\mathcal{H}}^a_\Lambda\;\hat{B}_W(X,t) - \hat{B}_W(X,t)\;\overleftarrow{\mathcal{H}}^a_\Lambda\right), \tag{15}$$

yields the adiabatic representation of the QCLE in the desired form,

$$\frac{\partial B_W^{\alpha\alpha'}(X,t)}{\partial t} = \frac{i}{\hbar}\left(\overrightarrow{\mathcal{H}}^a_{\alpha\alpha''}\;B_W^{\alpha''\alpha'}(X,t) - B_W^{\alpha\alpha''}(X,t)\;\overleftarrow{\mathcal{H}}^a_{\alpha''\alpha'}\right), \tag{16}$$

which can be shown to be identical to Equation (12).

3.1. Forward–backward trajectory solution in the adiabatic representation

The first step in the construction of the forward–backward solution in the adiabatic basis is the introduction of the following mapping transformation:

$$|\alpha; R\rangle\;\overrightarrow{\mathcal{H}}^a_{\alpha\alpha'}\;\langle\alpha; R| \to \overrightarrow{\mathcal{H}}^a_m \equiv \overrightarrow{\mathcal{H}}^a_{\alpha\alpha'}\;\hat{b}^\dagger_\alpha\hat{b}_{\alpha'},$$
$$|\alpha; R\rangle B_W^{\alpha\alpha'}\langle\alpha'; R| \to \hat{B}_m(X) \equiv B_W^{\alpha\alpha'}\hat{b}^\dagger_\alpha\hat{b}_{\alpha'}, \tag{17}$$

where the adiabatic annihilation and creation operators, $\hat{b}_\alpha$ and $\hat{b}^\dagger_\alpha$, respectively, act on the single excitation mapping states, now corresponding the occupancy of the adiabatic states, to give $|0\rangle = \hat{b}_\alpha\,|m_\alpha\rangle$ and $|m_\alpha\rangle = \hat{b}^\dagger_\alpha\,|0\rangle$. The mapping transformation of $\overleftarrow{\mathcal{H}}^a_\Lambda$ is defined in a similar manner. Given these definitions, it is now clear that the mapping matrix elements of the adiabatic mapping operators are identical to the matrix elements of operators in the adiabatic basis. In particular,

$$\langle\alpha; R|\;\overrightarrow{\mathcal{H}}^a_\Lambda\;|\alpha'; R\rangle = \overrightarrow{\mathcal{H}}^a_{\alpha\alpha'} = \langle m_\alpha|\;\overrightarrow{\mathcal{H}}^a_m\;|m_{\alpha'}\rangle. \tag{18}$$

In this adiabatic mapping representation, the time evolution of $\hat{B}_m(X)$ can be decomposed into a concatenation of M

short-time segments such that $\Delta t_j = t_j - t_{j-1} = \Delta t$ for all j with $t_0 = 0$ and $t_M = t$,

$$\begin{aligned}\hat{B}_m(X,t) &= \mathcal{S}\Big[e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m t}\hat{B}_m(X)e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m t}\Big],\\ &= \mathcal{S}\Big[e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t_1}\mathcal{S}\Big[e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t_2}\cdots\\ &\quad\times\mathcal{S}\Big[e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t_M}\hat{B}_m(X)e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m \Delta t_M}\Big]\\ &\quad\times\cdots e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m \Delta t_2}\Big]e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m \Delta t_1}\Big]. \end{aligned} \tag{19}$$

In order to evaluate the short-time propagators, we introduce the coherent states $|y\rangle$ defined such that $\hat{b}_\alpha|y\rangle = y_\alpha|y\rangle$, where $y_\alpha = \frac{1}{\sqrt{\hbar}}(\tilde{q}_\alpha + i\tilde{p}_\alpha)$ and $\tilde{x} = (\tilde{q}, \tilde{p})$. Then, each short-time evolution operator can be factorised via a Trotter decomposition and represented in the coherent state basis labelled by y:

$$\begin{aligned} e^{\frac{i\Delta t}{\hbar}\overrightarrow{\mathcal{H}}^a_m} &= e^{\frac{i\Delta t}{\hbar}\overrightarrow{\mathcal{H}}^a{}_{\alpha\alpha'}\hat{b}^\dagger_\alpha\hat{b}_\alpha}e^{\frac{it}{\hbar}(\frac{P^2}{2M}+V_0(R))}\\ &\approx e^{\frac{\Delta t}{2}[i\overrightarrow{\mathcal{L}}_0+(\delta_{\alpha\alpha'}F^\alpha_W\cdot\frac{\overrightarrow{\partial}}{\partial P}+\Delta E_{\alpha\alpha'}d_{\alpha\alpha'}\cdot\frac{\overrightarrow{\partial}}{\partial P})\hat{b}^\dagger_\alpha\hat{b}_{\alpha'}]}\\ &\quad\times e^{\frac{i\Delta t}{\hbar}(E_\alpha\delta_{\alpha\alpha'}+\frac{\hbar}{i}\frac{P}{M}\cdot d_{\alpha\alpha'})\hat{b}^\dagger_\alpha\hat{b}_{\alpha'}}e^{\frac{it}{\hbar}(\frac{P^2}{2M}+V_0(R))},\\ &\approx \int\frac{d^2y}{\pi^N}|y\rangle\, e^{\frac{\Delta t}{2}i\overrightarrow{\mathcal{L}}_{cl}(X,y)}\,\langle y(\Delta t)|\, e^{\frac{i\Delta t}{\hbar}(\frac{P^2}{2M}+V_0(R))}. \end{aligned} \tag{20}$$

Here, $i\overrightarrow{\mathcal{L}}_0 = P/M\cdot\overrightarrow{\nabla}_R - \nabla_R V_0(R)\cdot\overrightarrow{\nabla}_P$ with

$$i\overrightarrow{\mathcal{L}}_{cl}(X,y) = i\overrightarrow{\mathcal{L}}_0 + F^{\alpha\alpha'}_W\cdot\frac{\overrightarrow{\partial}}{\partial P}y^*_\alpha y_{\alpha'}, \tag{21}$$

$F^{\alpha\alpha'}_W(R) = F^\alpha_W(R) + \Delta E_{\alpha\alpha'}d_{\alpha\alpha'}(R)$, $F^\alpha_W(R) = -\nabla_R E_\alpha(R)$ and $\Delta E_{\alpha\alpha'} = E_\alpha(R) - E_{\alpha'}(R)$. The time-evolved coherent state is given by

$$\langle y(\Delta t)| = \langle y|\, e^{\frac{i\Delta t}{\hbar}(E_\alpha\delta_{\alpha\alpha'}+\frac{\hbar}{i}\frac{P}{M}\cdot d_{\alpha\alpha'})y^*_\alpha y_{\alpha'}}. \tag{22}$$

A similar expression can be derived for $e^{\frac{i\Delta t}{\hbar}\overleftarrow{\mathcal{H}}^a_m}$ in which the coherent states are labelled with a prime, $|y'\rangle$, to denote backward evolution. In Appendix A, we summarise the steps to properly insert the complete set of coherent states into Equation (20).

If one substitutes Equation (20) into Equation (19) and applies the following relation:

$$\begin{aligned}\mathcal{S}\big[e^{i\overrightarrow{\mathcal{L}}_{cl}(X,y)\frac{\Delta t}{2}}\hat{A}(X)e^{i\overleftarrow{\mathcal{L}}_{cl}(X,y')\frac{\Delta t}{2}}\big] &= e^{i\mathcal{L}_e(X,y,y')\Delta t}\hat{A}(X),\\ &= \hat{A}(X_{\Delta t}), \end{aligned} \tag{23}$$

where $i\mathcal{L}_e(X,y,y') = \frac{1}{2}(i\overrightarrow{\mathcal{L}}_{cl}(X,y) + i\overrightarrow{\mathcal{L}}_{cl}(X,y'))$, then one obtains the following expression:

$$\begin{aligned} B^{\alpha\alpha'}_W(X,t) &= \sum_{\beta\beta'}\int\prod_{i=1}^M\frac{d^2y_i}{\pi^N}\frac{d^2y'_i}{\pi^N}\langle m_\alpha|y_1\rangle\langle y'_1|m_{\alpha'}\rangle\\ &\quad e^{i\mathcal{L}_e(X,y_1,y'_1)\Delta t_1}\big(\langle y_1(t_1)|y_2\rangle e^{i\mathcal{L}_e(X,y_2,y'_2)\Delta t_2}\\ &\quad\big(\langle y_2|\cdots B^{\beta\beta'}_W(X)\cdots|y'_2\rangle\big)\langle y'_2|y'_1(t_1)\rangle\big)\\ &= \sum_{\beta\beta'}\int\prod_{i=1}^M\frac{d^2y_i}{\pi^N}\frac{d^2y'_i}{\pi^N}\langle m_\alpha|y_1\rangle\langle y'_1|m_{\alpha'}\rangle\\ &\quad\big(\langle y_1(t_1)|y_2\rangle e^{i\mathcal{L}_e(X_{t_1},y_2,y'_2)\Delta t_2}\\ &\quad\big(\langle y_2|\cdots B^{\beta\beta'}_W(X_{t_1})\cdots|y'_2\rangle\big)\langle y'_2|y'_1(t_1)\rangle\big). \end{aligned} \tag{24}$$

By applying the orthogonality approximation to each of the coherent state inner products, $\langle y_i(t)|y_{i+1}\rangle \approx \pi^N\delta(y_{i+1} - y_i(t))$, all the intermediate integrals can be eliminated. The expression for $B^{\alpha\alpha'}_W(X,t)$ then takes the simpler form,

$$\begin{aligned} B^{\alpha\alpha'}_W(X,t) &= \sum_{\beta\beta'}\int d\tilde{x}d\tilde{x}'\phi(\tilde{x})\phi(\tilde{x}')\\ &\quad\times\frac{1}{\hbar}(\tilde{q}_\alpha + i\tilde{p}_\alpha)(\tilde{q}_{\alpha'} - \tilde{p}_{\alpha'})B^{\beta\beta'}_W(X_t)\\ &\quad\times\frac{1}{\hbar}(\tilde{q}_\beta(t) - i\tilde{p}_\beta(t))(\tilde{q}_{\beta'}(t) + i\tilde{p}_{\beta'}(t)). \end{aligned} \tag{25}$$

The trajectory dynamics in the adiabatic representation is governed by the set of equations of motion,

$$\begin{aligned}\frac{dP}{dt} &= -\frac{\partial V_0}{\partial R} + F^{\alpha\alpha'}_W\frac{1}{2}\left(y_\alpha y^*_{\alpha'} + y'_\alpha y'^*_{\alpha'}\right),\\ \frac{dR}{dt} &= \frac{P}{M},\\ \frac{dy_\alpha}{dt} &= -i\frac{E_\alpha}{\hbar}y_\alpha - \left(d_{\alpha\alpha'}(R)\cdot\frac{P}{M}\right)y_{\alpha'},\\ \frac{dy'_\alpha}{dt} &= -i\frac{E_\alpha}{\hbar}y'_\alpha - \left(d_{\alpha\alpha'}(R)\cdot\frac{P}{M}\right)y'_{\alpha'}. \end{aligned} \tag{26}$$

In contrast to Equations (9), the evolution Equations (26) are not of Hamiltonian form. In this adiabatic representation, the bath momenta evolve under a mean force, $-\nabla_R V_0(R) + F^{\alpha\alpha'}_W\frac{1}{2}\left(y_\alpha y^*_{\alpha'} + y'_\alpha y'^*_{\alpha'}\right)$, which depends on the forward and backward coherent states $|y\rangle$ and $|y'\rangle$. Since

$$\begin{aligned} F^{\alpha\alpha'}_W\left(y_\alpha y^*_{\alpha'} + y'_\alpha y'^*_{\alpha'}\right) &= -\frac{\partial E_\alpha}{\partial R}\left(|y_\alpha|^2 + |y'_\alpha|^2\right)\\ &\quad + \Delta E_{\alpha\alpha'}d_{\alpha\alpha'}(R)\left(y_\alpha y^*_{\alpha'} + y'_\alpha y'^*_{\alpha'}\right), \end{aligned} \tag{27}$$

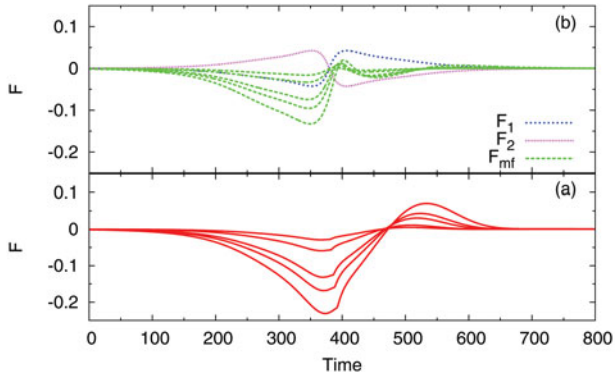

Figure 1. In panel (a), the five curves correspond to the force (27) under different initial conditions. In panel (b), the blue and pink curves are the adiabatic forces associated with the ground (F_1) and the first excited state (F_2), respectively. The five green curves correspond to the averages of Hellmann–Feynman forces, the first part on the right side of Equation (27), under the same set of initial conditions as in panel (a).

this off-diagonal force also accounts for non-adiabatic transitions. Thus, the evolution involves non-adiabatic dynamics on the entire manifold of adiabatic states. In the course of this evolution, the forward and backward quantum coherent state variables evolve by accumulating dynamical phases proportional to the adiabatic energies, accompanied by non-adiabatic effects induced by the term $P/M \cdot d_{\alpha\alpha'}$.

It is interesting to analyse the interplay of the Hellmann–Feynman forces and the non-adiabatic force, the first and second terms on the right side of Equation (27). For this purpose we consider the Tully I avoided crossing model [18], a two-level quantum system coupled to a free particle with momentum $P(t)$. Details of this model as well as the set of parameters used in the present work can be found in Ref. [19]. In particular, the initial momentum, $P = 20$, for the particle is chosen such that the known asymptotic quantum population (after passing the avoided crossing point) is evenly distributed over the two quantum states. In Figure 1, we present forces obtained from a fixed initial condition for the particle and five different initial conditions for the quantum coherent state variables. In panel (a) we plot the full force (27) acting on the particle, while in panel (b) we plot just the average of Hellmann–Feynman (green curves) force contribution. The blue and pink curves represent the adiabatic forces associated with the two states, and the point where the two adiabatic forces cross is the avoided crossing point. These five initial conditions were selected such that the full force is initially a ground adiabatic force, as the quantum system is initialised in the ground state. In this example, where the quantum population should distribute evenly over the two adiabatic states (with exactly opposite energies), the Hellmann–Feynman force becomes relatively negligible around and after the avoided crossing point. Clearly, the non-adiabatic force is the dominant contribution to the trajectory dynamics around the avoided crossing point. This example also demonstrates that the FBTS mean-field force is very different from the Hellmann–Feynman forces.

Finally, we note that if a change of variables is made in Equations (9) that diagonalises the Hamiltonian with matrix elements $h^{\lambda\lambda'}$, the resulting set of equations has the same form as Equations (26). This observation indicates that the FBTS can be implemented in a basis-independent fashion.

3.2. *Surface-hopping description*

We now show that the FBTS can be cast into the form of a surface hopping algorithm. The starting point of the derivation is again Equation (19) but in Equation (20) we factor the short-time evolution operator in a different manner:

$$\begin{aligned}\left(e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t}\right)_{\alpha\beta} \approx & \left(e^{\Delta t \frac{P}{M}\cdot d_{\lambda\lambda'}(1+\frac{1}{2}S_{\lambda\lambda'}\frac{\overrightarrow{\partial}}{\partial P})\hat{b}^\dagger_\lambda \hat{b}_{\lambda'}}\right)_{\alpha\beta} \\ & \times \left(e^{\frac{\Delta t}{2}(i\overrightarrow{\mathcal{L}}_0 + F^\lambda_W \cdot \frac{\overrightarrow{\partial}}{\partial P}\hat{b}^\dagger_\lambda \hat{b}_\lambda)} e^{\frac{i}{\hbar}\Delta t E_\lambda \hat{b}^\dagger_\lambda \hat{b}_\lambda}\right)_{\beta\beta}, \\ & \times e^{\frac{i\Delta t}{\hbar}(\frac{P^2}{2M}+V_0(R))}, \end{aligned} \tag{28}$$

where $S_{\lambda\lambda'} = \Delta E_{\lambda\lambda'} d_{\lambda\lambda'}(R)\left(d_{\lambda\lambda'}\cdot\frac{P}{M}\right)^{-1}$ [15]. Earlier in Equation (20), we factorised the evolution operator by separating terms acting on the subsystem and the bath, respectively. In the present case, we factorise the terms according to their contributions to either adiabatic evolution or non-adiabatic transitions. The present decomposition requires an analysis of the expression $\mathcal{S}[e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t}\hat{A}e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m \Delta t}]$. In Appendix B, we discuss how the operator $\mathcal{S}$, which orders the short-time evolution operators $e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t}$ and $e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m \Delta t}$, can also be factored into two $\mathcal{S}$ operators that separately order the adiabatic and non-adiabatic terms in Equation (28). More precisely, we adopt the following approximation (exact up to order $\mathcal{O}(\Delta t^2)$):

$$\begin{aligned}&\mathcal{S}\left[e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t}\hat{A}e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m \Delta t}\right] \\ &\quad = \mathcal{S}\left[e^{\overrightarrow{\mathcal{J}}_1 \Delta t}\mathcal{S}\left[\left(e^{i\overrightarrow{\mathcal{L}}_{mf}\Delta t}e^{\frac{i}{\hbar}\hat{h}_m \Delta t}\right)\hat{A}\right.\right. \\ &\quad \left.\left.\times\left(e^{i\overleftarrow{\mathcal{L}}_{mf}\Delta t}e^{-\frac{i}{\hbar}\hat{h}_m \Delta t}\right)\right]e^{\overleftarrow{\mathcal{J}}_1 \Delta t}\right], \end{aligned} \tag{29}$$

where $\overrightarrow{\mathcal{J}}_1 = \frac{P}{M}\cdot d_{\lambda\lambda'}(1+\frac{1}{2}S_{\lambda\lambda'}\frac{\overrightarrow{\partial}}{\partial P})\hat{b}^\dagger_\lambda \hat{b}_{\lambda'}$, $i\overrightarrow{\mathcal{L}}_{mf} = \frac{1}{2}(i\overrightarrow{\mathcal{L}}_0 + F^\lambda_W \frac{\overrightarrow{\partial}}{\partial P}\hat{b}^\dagger_\lambda \hat{b}_\lambda)$, and $\hat{h}_m = E_\lambda \hat{b}^\dagger_\lambda \hat{b}_\lambda$. The other left-acting operators can be defined in an analogous manner. In summary, we should replace every instance of $\mathcal{S}[e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}^a_m \Delta t}\cdots e^{-\frac{i}{\hbar}\overleftarrow{\mathcal{H}}^a_m \Delta t}]$ in Equation (19) with an expression like that in Equation (29).

Next, similar to the development given in the previous section, we introduce quantum coherent state variables to represent matrix elements of the adiabatic propagator in Equation (28),

$$\begin{aligned}\left(e^{\frac{i}{\hbar}\overrightarrow{\mathcal{H}}_m^a\Delta t}\right)_{\alpha\beta} &\approx e^{\frac{i\Delta t}{\hbar}\left(\frac{P^2}{2M}+V_0(R)\right)}\\ &\times\left(e^{\Delta t\frac{P}{M}\cdot d_{\lambda\lambda'}(1+\frac{1}{2}S_{\lambda\lambda'}\overrightarrow{\frac{\partial}{\partial P}})\hat{b}_\lambda^\dagger\hat{b}_{\lambda'}}\right)_{\alpha\beta}\\ &\times\int\frac{d^2y}{\pi^N}\langle m_\beta|y\rangle e^{i\overrightarrow{\mathcal{L}}_{cl}(X,y)\frac{\Delta t}{2}}\langle y(\Delta t)|m_\beta\rangle,\end{aligned}\tag{30}$$

where now $\langle y(\Delta t)| = \langle y|\, e^{\frac{i}{\hbar}\Delta t E_\alpha\hat{b}_\alpha^\dagger\hat{b}_\alpha}$ and does not involve non-adiabatic effects.

The next step in the calculation is to substitute Equation (30) and the corresponding equation for $(e^{\frac{i}{\hbar}\overleftarrow{\mathcal{H}}_m^a\Delta t})_{\alpha'\beta'}$ into a properly modified Equation (19), i.e. after applying the approximation (29). By repeatedly applying Equation (23), one may replace $e^{i\overrightarrow{\mathcal{L}}_{mf}(X,y_i)\frac{\Delta t}{2}}$ and $e^{i\overleftarrow{\mathcal{L}}_{mf}(X,y_i')\frac{\Delta t}{2}}$ with $e^{i\mathcal{L}_{eff}(X,y,y')\Delta t} = e^{\frac{i\Delta t}{2}(\mathcal{L}_{mf}(X,y)+\mathcal{L}_{mf}(X,y'))}$ at each time step. Finally, we have to evaluate the matrix elements of non-adiabatic transition terms in Equation (30). To this end, we introduce a super-operator defined by its action on an operator $\hat{A}$,

$$\begin{aligned}&\left(e^{-\mathcal{J}\Delta t}\right)_{\alpha\alpha';\beta\beta'}A_{\beta\beta'}\\ &\quad\equiv\mathcal{S}\Big[\left(e^{\Delta t\frac{P}{M}\cdot d_{\lambda\lambda'}(1+\frac{1}{2}S_{\lambda\lambda'}\overrightarrow{\frac{\partial}{\partial P}})\hat{b}_\lambda^\dagger\hat{b}_{\lambda'}}\right)_{\alpha\beta}A_{\beta\beta'}\\ &\qquad\times\left(e^{\Delta t\frac{P}{M}\cdot d_{\lambda\lambda'}(1+\frac{1}{2}S_{\lambda\lambda'}\overleftarrow{\frac{\partial}{\partial P}})\hat{b}_\lambda^\dagger\hat{b}_{\lambda'}}\right)_{\beta'\alpha'}\Big],\end{aligned}\tag{31}$$

where the super-operator $\mathcal{J}$ can be determined by matching the first-order terms in the Taylor expansions of both sides of the equation,

$$\begin{aligned}\mathcal{J}_{\alpha\alpha';\beta\beta'} = &-(d_{\alpha\beta}\delta_{\alpha'\beta'}+d_{\alpha'\beta'}\delta_{\alpha,\beta})\cdot\frac{P}{M}\\ &-\frac{1}{2}\left(\Delta E_{\alpha\beta}d_{\alpha\beta}\delta_{\alpha'\beta'}+\Delta E_{\alpha'\beta'}d_{\alpha'\beta'}\delta_{\alpha\beta}\right)\cdot\frac{\partial}{\partial P}.\end{aligned}\tag{32}$$

We note that the superoperator $\mathcal{J}$ has appeared in the QCL operator in the adiabatic basis [15], and the propagator $e^{-\mathcal{J}\Delta t}$ can be evaluated using the scheme presented in Ref. [11].

In summary, the modified formal solution in the adiabatic mapping representation reads

$$\begin{aligned}B_W^{\beta\beta'}(X,t) = \sum_{\substack{\alpha_i,\alpha_i'\\(i=1,\ldots,M+1)}}&\int\prod_{i=1}^M d\tilde{x}d\tilde{x}'\phi(\tilde{x}_i)\phi(\tilde{x}_i')\\ &\left\{\prod_{i=1}^M\left(e^{-\mathcal{J}\Delta t_i}\right)_{\alpha_i\alpha_i';\alpha_{i+1}\alpha_{i+1}'}e^{i\mathcal{L}_{eff}(X,y_i,y_i')\Delta t_i}\right.\\ &\left.\times y_{i,\alpha_{i+1}}y_{i,\alpha_{i+1}}^*(\Delta t_i)y_{i,\alpha_{i+1}'}'^*y_{i,\alpha_{i+1}'}'(\Delta t_i)\right\}\\ &\times B_W^{\alpha_{M+1}\alpha_{M+1}'}(X),\end{aligned}\tag{33}$$

where $\alpha_1 = \beta$ and $\alpha_1' = \beta'$, and we substituted the inner product of coherent states and mapping states with its explicit form, $\langle m_\alpha|y\rangle = y_\alpha e^{-|y|^2/2}$.

In this form the adiabatic evolution segments are interspersed with non-adiabatic transitions at every time step. This separation of adiabatic and non-adiabatic events is analogous to that in surface-hopping algorithms [10,11] for the QCLE. Nevertheless, the present formulation is still a mean-field algorithm in practice. In order to simulate the trajectories needed for a MC evaluation of Equation (33), one has to sample values of y_i and y_i' from the Gaussian distributions $\phi(\tilde{x}_i)$ and $\phi(\tilde{x}_i')$, respectively. Thus, both the forward and backward quantum states are superpositions of all possible adiabatic states with weights given by $|y_\alpha|^2$ and $|y_\alpha'|^2$.

In order to extract the zeroth-order adiabatic dynamics from the current formalism, we resort to an approximation termed 'focusing' [20], first proposed by Bonella and Coker. The focusing approximation replaces a normalised Gaussian function with a specific delta function:

$$\begin{aligned}&\int d\,\phi(x)\left(q_\lambda^2+p_\lambda^2\right)f(x)\\ &\quad\approx\int dx\,\delta\left(q_\lambda^2+p_\lambda^2-1\right)\prod_{\mu\neq\lambda}\delta(q_\mu)\delta(p_\mu)\\ &\qquad\times\left(q_\lambda^2+p_\lambda^2\right)f(x).\end{aligned}\tag{34}$$

In Refs. [6,14,21], the effects of the focusing approximation on FBTS and closely related algorithms were analysed in some detail. In general, focusing only provides accurate results for short times or for weak non-adiabatic perturbations. In the present case, we only have to simulate strictly adiabatic dynamics for the trajectories, as the non-adiabatic perturbing terms are separated from the Liouvillian operators in Equation (33). Indeed, one can easily show that the application of the focused condition, $\delta(|y_\alpha|^2-1)\prod_{\beta\neq\alpha}\delta(y_\beta)$, to the coherent state integrals in Equation (33) will result in exact dynamics in the adiabatic state α. Thus, in the adiabatic representation, the focusing approximation can be physically motivated and provides insight into the dynamics.

Finally, we present an approximate expression for Equation (33) that employs focussing:

$$B_W^{\beta\beta'}(X,t) = \sum_{\substack{\alpha_i,\alpha_i' \\ (i=1,\ldots,M+1)}} \left\{ \prod_{i=1}^{M} \left(e^{-\mathcal{J}\Delta t_i}\right)_{\alpha_i\alpha_i';\alpha_{i+1}\alpha_{i+1}'} \times e^{i\mathcal{L}_{\alpha_{i+1}\alpha_{i+1}'}(X)\Delta t_i} e^{\int_{t_i}^{t_{i+1}} d\tau \omega_{\alpha_{i+1}\alpha_{i+1}'}(\tau)} \right\} \times B_W^{\alpha_{M+1}\alpha_{M+1}'}(X), \quad (35)$$

where $i\mathcal{L}_{\alpha_{i+1}\alpha_{i+1}'}(X) = i\mathcal{L}_0 + \frac{1}{2}\left(F_W^{\alpha}(R) + F_W^{\alpha'}(R)\right)\frac{\partial}{\partial P}$. Thus, through the use of the focusing approximation in the adiabatic representation, we obtain a starting point suitable for the construction of a surface-hopping algorithm for QCLE dynamics.

4. Discussion and conclusions

The present work on the adiabatic mapping forward–backward solution for QCLE provides a way to link two different numerical methodologies, mean-field and surface-hopping, for the simulation of QCLE dynamics. The different adiabatic mapping formulations arise from the different decompositions of the forward and backward short-time evolution operators given in Equations (20) and (28). The work also suggests that it may be possible to devise hybrid methodologies that combine the advantages of both mean-field and surface-hopping algorithms. The simplest of such hybrid methodologies would be to evaluate the short-time evolution operator by the surface-hopping approach, Equation (28), in only certain time steps when the non-adiabatic transition probability is high, and treat the short-time evolution operator by the mapping mean-field approach for the rest of the simulation. Such a hybrid scheme might extend the usefulness of surface-hopping algorithms to evolution for long times.

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Appendix A

Here, we summarise the steps involved in the introduction of coherent state variables in Equation (20) [6]. First, we expand the evolution operators up to $\mathcal{O}(\Delta t^2)$. In the zeroth order, we simply apply Equation (7). In the first order, we reverse the normal ordering of $\hat{b}_\alpha^\dagger \hat{b}_{\alpha'} = \hat{b}_{\alpha'}\hat{b}_\alpha^\dagger - \delta_{\alpha\alpha'}$ and insert the resolution of identity of coherent states between the annihilation and creation operators. Because we use the traceless form of the Hamiltonian the Dirac delta term in the above relation can be dropped. Finally, we approximate the evolution operator (in exponential form) using the first two terms to $\mathcal{O}(\Delta t^2)$ that were represented in the coherent state basis. These major steps are summarised as follows:

$$\begin{aligned} & e^{\frac{\Delta t}{2}[i\vec{\mathcal{L}}_0 + F_W^{\alpha\alpha'}\cdot\frac{\vec{\partial}}{\partial P}\hat{b}_\alpha^\dagger\hat{b}_{\alpha'}]} \\ &= \mathcal{I} + \frac{\Delta t}{2}\left[i\,\vec{\mathcal{L}}_0\,\mathcal{I} + F_W^{\alpha\alpha'}\cdot\frac{\vec{\partial}}{\partial P}\hat{b}_{\alpha'}\mathcal{I}\hat{b}_\alpha^\dagger\right] \\ &\quad + \mathcal{O}(\Delta t^2), \\ &= \int \frac{d^2y}{\pi^N}\,|y\rangle\left(1 + \frac{\Delta t}{2}\left[i\,\vec{\mathcal{L}}_0 + F_W^{\alpha\alpha'}\cdot\frac{\vec{\partial}}{\partial P}y_{\alpha'}y_\alpha^*\right]\right)\langle y|\,, \\ &\quad + \mathcal{O}(\Delta t^2), \\ &\approx \int \frac{d^2y}{\pi^N}\,|y\rangle\, e^{i\mathcal{L}_{cl}(\vec{X},y)\frac{\Delta t}{2}}\,\langle y|\,, \end{aligned} \quad (A1)$$

where $\mathcal{I}$ is defined in Equation (7).

Appendix B

In this section, we first prove the claim that

$$\mathcal{S}\Big[e^{i(\vec{\mathcal{A}}+\vec{\mathcal{B}})\Delta t}\,\hat{O}\,e^{i(\overleftarrow{\mathcal{A}'}+\overleftarrow{\mathcal{B}'})\Delta t}\Big] = \mathcal{S}\Big[e^{i\vec{\mathcal{A}}\Delta t}\mathcal{S}\Big[e^{i\vec{\mathcal{B}}\Delta t}\,\hat{O}\,e^{i\overleftarrow{\mathcal{B}'}\Delta t}\Big]e^{i\overleftarrow{\mathcal{A}'}\Delta t}\Big], \tag{B1}$$

whenever $\hat{A}^{(\prime)}$ commutes with $\hat{B}^{(\prime)}$.

According to Ref. [6], the left side of the above equation can be expressed in the following form:

$$\mathcal{S}\Big[e^{i(\vec{\mathcal{A}}+\vec{\mathcal{B}})\Delta t}\,\hat{O}\,e^{i(\overleftarrow{\mathcal{A}'}+\overleftarrow{\mathcal{B}'})\Delta t}\Big] = \sum_{j=0}^{\infty}\frac{(i\,\Delta t)^j}{j!}(\vec{\mathcal{A}}+\vec{\mathcal{B}}+\vec{\mathcal{A}'}+\vec{\mathcal{B}'})^j\,\hat{O}. \tag{B2}$$

Similarly, the right side of the same equation can be written as follows:

$$\begin{aligned}
&\mathcal{S}\Big[e^{i\vec{\mathcal{A}}\Delta t}\mathcal{S}\Big[e^{i\vec{\mathcal{B}}\Delta t}\,\hat{O}\,e^{i\overleftarrow{\mathcal{B}'}\Delta t}\Big]e^{i\overleftarrow{\mathcal{A}'}\Delta t}\Big]\\
&= \sum_{j_A=0}^{\infty}\sum_{j_B=0}^{\infty}\frac{(i\,\Delta t)^{j_A+j_B}}{j_A!\,j_B!}(\vec{\mathcal{A}}+\vec{\mathcal{A}'})^{j_A}(\vec{\mathcal{B}}+\vec{\mathcal{B}'})^{j_B}\,\hat{O},\\
&= \sum_{j=0}^{\infty}\sum_{j_A=j}^{\infty}\frac{(i\,\Delta t)^{j}}{j_A!(j-j_A)!}(\vec{\mathcal{A}}+\vec{\mathcal{A}'})^{j_A}(\vec{\mathcal{B}}+\vec{\mathcal{B}'})^{j-j_A}\,\hat{O},\\
&= \sum_{j=0}^{\infty}\frac{(i\,\Delta t)^{j}}{j!}\sum_{j_A=j}^{\infty}\frac{j!}{j_A!(j-j_A)!}(\vec{\mathcal{A}}+\vec{\mathcal{A}'})^{j_A}\\
&\quad\times(\vec{\mathcal{B}}+\vec{\mathcal{B}'})^{j-j_A}\,\hat{O},\\
&= \sum_{j=0}^{\infty}\frac{(i\,\Delta t)^{j}}{j!}(\vec{\mathcal{A}}+\vec{\mathcal{B}}+\vec{\mathcal{A}'}+\vec{\mathcal{B}'})^{j}\,\hat{O},
\end{aligned} \tag{B3}$$

where $j = j_A + j_B$. To go from the second line to the third line, we re-arranged the sum by ordering $j = j_A + j_B$. To go from the fourth line to the fifth line, we rely on the assumption that $\vec{\mathcal{A}}^{(\prime)}$ and $\vec{\mathcal{B}}^{(\prime)}$ commute.