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ABSTRACT

Although the quantum classical Liouville equation (QCLE) arises by cutting off the exact equation of motion for a coupled nuclear-electronic system at order 1 ($1 = \hbar^0$), we show that the QCLE does include Berry's phase effects and Berry's forces (which are proportional to a higher order, $\hbar = \hbar^1$). Thus, the fundamental equation underlying mixed quantum-classical dynamics does not need a correction for Berry's phase effects and is valid for the case of complex (i.e., not just real) Hamiltonians, where exotic features can arise in the course of electronic relaxation. Furthermore, we also show that, even though Tully's surface hopping model ignores Berry's phase, Berry's phase effects are included automatically within Ehrenfest dynamics. These findings should be of great importance if we seek to model coupled nuclear-electronic dynamics for systems with odd numbers of electrons and spin-orbit coupling, where the complex nature of the Hamiltonian is paramount.

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I. INTRODUCTION

Nonadiabatic dynamics are a continuous source of interest and intrigue in the chemical physics community. On the one hand, the fast exchange of energy between nuclear and electronic degrees of freedom violates the Born Oppenheimer (BO) approximation, the bedrock of modern chemistry.[1] When one violates the BO approximation even moderately, one can find many unexpected effects, the most famous being Berry's phase effects.[2] On the other hand, because quantum mechanics is so expensive to propagate, there is a strong impetus to understand nonadiabatic dynamics in a semiclassical fashion,[3–7] focusing on quantum electrons and classical nuclei. Thus, for many researchers, the nature of nonadiabatic effects becomes entangled with semiclassical approximations, which leads to only more questions about the fundamental nature of nonadiabatic dynamics.

In this paper, we want to directly address one such fundamental question in nonadiabatic dynamics: the connection between Berry's phase[2] and the quantum classical Liouville equation (QCLE).[8,9] A few words are now appropriate regarding Berry's phase, both in the context of real and complex Hamiltonians. In general, Berry's phase effects are usually derived by considering the phase of an electronic wavefunction in the limit of a very slowly evolving potential that mixes together different adiabatic states, and the presence of Berry's phase can lead to interference effects around degeneracies and conical intersections (e.g., the Aharanov-Bohm effect[10,11] and tunneling suppression[12]). When the Hamiltonian is real, Berry's phase is effectively a generalization of the Longuet-Higgins phase,[13–15] and there is an enormous literature in the chemical physics literature regarding the role of Berry's phase effects around conical intersections.[16,17] Of note, however, is that for a complex Hamiltonian, Berry's phase can yield real effects even without a relevant intersection point; the Berry curvature [see Eq. (6)] will be nonzero.[18,19] Although this case is not usually addressed in the chemical physics literature (where we usually assume that the molecular Hamiltonian is real), the question of curve crossings with complex Hamiltonians

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has been investigated previously,[20–23] and Takatsuka and Yonehara have written extensively about Berry's "Lorentz-like" forces in the context of semiclassical, path branching dynamics.[24,25]

Let us now turn to the QCLE.[8,9] The QCLE represents the simplest means to rigorously take the semiclassical limit of coupled nuclear-electronic systems, treating nuclei classically and electrons quantum mechanically. The basic premise is to take a partial Wigner transform over a set of nuclear degrees of freedom and then expand the total equation of motion in units of $\hbar$. The QCLE includes only terms on the order of $\hbar^{-1}$ and $\hbar^0 = 1$; all terms on the order of $\hbar$, $\hbar^2$, ..., etc. are ignored. Formally, the resulting dynamics have some failures—there is no Jacobi identity and correlation functions will not be invariant to time translation.[26] Nevertheless, the dynamics are generally considered to be very accurate. In the context of the spin-boson model, the QCLE is exact. In this spirit, the QCLE is the underlying phase space equation against which one would like to compare all other semiclassical approaches. In almost all cases,[27–33] however, the QCLE has been applied to situations where the Hamiltonian is real, i.e., the imaginary number i never appears in any electronic Hamiltonian.

With this background in mind, recent work has identified a subtle question with regards to nonadiabatic dynamics, namely: Does the QCLE correctly incorporate Berry's phase effects in the case of a complex Hamiltonian (as would be relevant for an odd number of electrons with spin)?[20] On the one hand, one might assume that Berry's phase and Berry's curvature—both proportional to $\hbar$—can arise only if it goes beyond the QCLE to include all $\hbar^1$ terms in the expansion. Beside this $\hbar$ expansion argument, note also that Berry's forces are usually derived by considering the Berry potential (or Berry connection) $\tilde{A} \equiv i\hbar\langle\Phi|\nabla\Phi\rangle$ for a nearly adiabatic state $|\Phi\rangle$ and, through a gauge transformation acting on the nuclear space, converting the Berry potential to a magnetic force[19] (just as one changes from the vector potential A to the magnetic field B in electrodynamics[34]). Because gauge transformations of the classical degrees of freedom are not preserved in a quantum-classical treatment, one might assume that Berry's forces cannot be derived by the QCLE.

On the other hand, recent work by Dou *et al.* derived the electronic friction tensor starting from the QCLE[35] and found the same friction tensor as calculated by a Berry's phase calculation with a complex density matrix[36,37]—suggesting that Berry's phase should be derivable from the QCLE. Furthermore, Berry's phase effects have already been isolated and studied within the QCLE for *real*, spin-boson Hamiltonians[38] (where the QCLE is exact). Thus, in this paper, we seek to tease out the answer to the following question: Are *all* of Berry's phase effects captured by the QCLE, especially for the case of a *complex* Hamiltonian? Below, we will show clearly that, yes, Berry's phase is derivable from the QCLE through a simple change of representation, as appropriate in the limit of nearly adiabatic dynamics. We will also show that, while such Berry's phase effects are not captured by surface hopping dynamics, they are captured (at least partially) by Ehrenfest dynamics.

Our conclusions are important for three reasons. First, because the QCLE has traditionally been regarded as the benchmark for all semiclassical algorithms, the present findings are very reassuring: we may continue to use the QCLE as the gold standard—with real or complex Hamiltonians. There is no need to improve upon the QCLE in the presence of complex Hamiltonians, and in particular, we may rest assure that the electronic friction tensor as developed in Ref. 35 already includes all appropriate Berry's phase effects. Second, our results should be extremely helpful for understanding and improving upon mixed quantum classical trajectory techniques.[39] Recent work has clearly shown that Tully's fewest switches surface hopping (FSSH) algorithm does not include Berry's forces[40] for the case of imaginary Hamiltonians (although some Berry's phase effects can be captured with FSSH for real Hamiltonians with real conical intersections[41]). Even though FSSH is already a partial solution to the QCLE,[27,28] the failure of surface hopping to recover complex Berry phase effects sheds light on the approximations made in Refs. 27 and 28 and thus justifies modifying FSSH to better reproduce the QCLE and treat the case of complex Hamiltonians.[40] At the same time, we can also infer that all approximations to the QCLE based around Ehrenfest trajectories[42–47] already include Berry phase effects and need no such modification. Third and finally, the present results highlight just how the Berry phase arises for nuclear motion in the adiabatic limit, starting from a very general nonadiabatic approach but without needing to discuss closed loops in any parameter or function space.[48,49] Our findings confirm that, at least semiclassically, Berry's phase effects can be understood in terms of well-understood equations of motion already present in the chemical physics literature and within all regimes—from the highly nonadiabatic to the highly adiabatic. With that in mind, we should also be able to learn exactly when Berry's phase is appropriate—what terms must be small in order to take the semiclassical adiabatic limit?

For convenience below, we will use Einstein summation notation. Electronic states are indexed by 1, 2 and nuclear degrees of freedom are indexed by Greek letters (α, β, γ).

II. THEORY

Without loss of generality, consider the case of two electronic states 1 and 2. According to the quantum classical Liouville equation (QCLE),[8] to first order in the electron-nucleus mass ratio $(m/M)^{1/2}$, the equations of motion for the partial Wigner transformed density operator in an adiabatic basis A^W_{ij} are (for the diagonal and off-diagonal components)

$$\frac{\partial}{\partial t}A^W_{11}(R,P,t) = \frac{2P^\alpha}{M^\alpha}\mathrm{Re}\left(A^W_{12}d^\alpha_{21}\right) - \frac{P^\alpha}{M^\alpha}\frac{\partial A^W_{11}}{\partial R^\alpha} - F^\alpha_{11}\frac{\partial A^W_{11}}{\partial P^\alpha} - \mathrm{Re}\left(\frac{\partial A^W_{12}}{\partial P^\alpha}F^\alpha_{21}\right) \tag{1}$$

and

$$\frac{\partial}{\partial t}A^W_{12}(R,P,t) = \frac{-i}{\hbar}(V_{11}-V_{22})A^W_{12} - \frac{P^\alpha}{M^\alpha}d^\alpha_{12}\left(A^W_{22}-A^W_{11}\right) - \frac{P^\alpha}{M^\alpha}\frac{\partial A^W_{12}}{\partial R^\alpha} - \frac{1}{2}\left(F^\alpha_{11}+F^\alpha_{22}\right)\frac{\partial A^W_{12}}{\partial P^\alpha} - \frac{1}{2}F^\alpha_{12}\left(\frac{\partial A^W_{11}}{\partial P^\alpha}+\frac{\partial A^W_{22}}{\partial P^\alpha}\right). \tag{2}$$

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A similar equation holds for A^W_{22}. Here, $V_{ii}(\vec{R})$ are the adiabatic potential energy surfaces and $\{F_{ij}(\vec{R})\}$ are the set of forces, $F^\alpha_{ij}(\vec{R}) \equiv -\langle\Phi_i(\vec{R})|\frac{\partial V}{\partial R^\alpha}|\Phi_j(\vec{R})\rangle$. $\{|\Phi_i(\vec{R})\rangle\}$ are an adiabatic basis set of electronic states, and $d^\alpha_{ij}(\vec{R})$ are the derivative couplings, $d^\alpha_{ij}(\vec{R}) \equiv F^\alpha_{ij}(\vec{R})/\big(V_{ii}(\vec{R}) - V_{jj}(\vec{R})\big)$. We note that $d_{ij} = -d^*_{ji}$.

At this point, we assume that all dynamics are being propagated near the adiabatic limit, with the population of state 1 close to unity (and only barely changing in time). Thus, the coherences are nearly stationary and (hopefully) not evolving much as well. In such a case, we can identify the steady state equation of motion for the coherences in Eq. (2) by ignoring any evolution of the coherences,[35]

$$\frac{-i}{\hbar}(V_{11}-V_{22})A^W_{12} - \frac{P^\alpha}{M^\alpha}d^\alpha_{12}\big(A^W_{22}-A^W_{11}\big) - \frac{1}{2}F^\alpha_{12}\left(\frac{\partial A^W_{11}}{\partial P^\alpha}+\frac{\partial A^W_{22}}{\partial P^\alpha}\right) = 0, \tag{3}$$

which has the solution $A^W_{12} = \zeta$, where

$$\zeta \equiv \frac{i\hbar\frac{P^y}{M^y}d^y_{12}\big(A^W_{22}-A^W_{11}\big)}{V_{11}-V_{22}} + \frac{i\hbar}{2}d^\alpha_{12}\left(\frac{\partial A^W_{11}}{\partial P^\alpha}+\frac{\partial A^W_{22}}{\partial P^\alpha}\right). \tag{4}$$

Thereafter, we change variables from A^W_{12} to $B^W_{12} \equiv A^W_{12} - \zeta$. The equations of motion for the populations are modified as follows:

$$\begin{aligned}\frac{\partial}{\partial t}A^W_{11}(R,P,t) &= \frac{2P^\alpha}{M^\alpha}\mathrm{Re}\big(\big(B^W_{12}+\zeta\big)d^\alpha_{21}\big) - \frac{P^\alpha}{M^\alpha}\frac{\partial A^W_{11}}{\partial R^\alpha} \\ &\quad - F^\alpha_{11}\frac{\partial A^W_{11}}{\partial P^\alpha} - \mathrm{Re}\left(\frac{\partial\big(B^W_{12}+\zeta\big)}{\partial P^\alpha}F^\alpha_{21}\right) \\ &= \frac{2P^\alpha}{M^\alpha}\mathrm{Re}\big(B^W_{12}d^\alpha_{21}\big) - \frac{P^\alpha}{M^\alpha}\frac{\partial A^W_{11}}{\partial R^\alpha} - F^\alpha_{11}\frac{\partial A^W_{11}}{\partial P^\alpha} \\ &\quad - \mathrm{Re}\left(\frac{\partial B^W_{12}}{\partial P^\alpha}F^\alpha_{21}\right) + 2\hbar\mathrm{Im}\left(d^\beta_{21}\frac{P^\alpha}{M^\alpha}d^\alpha_{12}\right)\frac{\partial A^W_{11}}{\partial P^\beta}.\end{aligned} \tag{5}$$

The equations of motion for the coherences are more involved and given in the Appendix. If we assume that we are in the adiabatic limit moving along adiabat 1, noting B^W_{12} vanishes in the adiabatic limit, Eq. (5) simplifies to

$$\frac{\partial}{\partial t}A^W_{11}(R,P,t) = -\frac{P^\alpha}{M^\alpha}\frac{\partial A^W_{11}}{\partial R^\alpha} - F^\alpha_{11}\frac{\partial A^W_{11}}{\partial P^\alpha} + 2\hbar\mathrm{Im}\left(d^\beta_{21}\frac{P^\alpha}{M^\alpha}d^\alpha_{12}\right)\frac{\partial A^W_{11}}{\partial P^\beta}.$$

The total effective force is the usual adiabatic force $\vec{F}_{11}$ plus the Berry magnetic force $\vec{F}^B_{11}$,

$$\vec{F}^B_{11} = -2\hbar\mathrm{Im}\left(\vec{d}_{21}\frac{P^\alpha}{M^\alpha}d^\alpha_{12}\right) = 2\hbar\mathrm{Im}\left(\vec{d}_{12}\frac{P^\alpha}{M^\alpha}d^\alpha_{21}\right). \tag{6}$$

Historically, Eq. (6) was derived only indirectly: one takes the curl of the Berry connection ($\vec{A} \equiv i\hbar\langle\Phi|\nabla\Phi\rangle$) and thereafter finds an effective magnetic force, leading to Eq. (6) through the Lorentz force law. Yet, clearly, the QCLE includes such Berry force whenever the Hamiltonian is complex.

III. DISCUSSION: IMPLICATIONS FOR SEMICLASSICAL DYNAMICS

Having successfully isolated Berry's phase within the QCLE, let us now discuss the implications of our findings for mixed quantum classical methods. After all, one can view semiclassical nonadiabatic dynamics methods as approximations to the QCLE, and so one must wonder: Do the standard semiclassical approaches (surface hopping and Ehrenfest dynamics) also account for Berry's phase?

Consider the Hamiltonian that was introduced in Ref. 40,

$$H = A\begin{bmatrix} -\cos\theta & \sin\theta e^{i\phi} \\ \sin\theta e^{-i\phi} & \cos\theta \end{bmatrix}, \tag{7}$$

where $\theta(x) \equiv \frac{\pi}{2}(\mathrm{erf}(Bx)+1)$, and $\phi(y) \equiv Wy$.

The Hamiltonian in Eq. (7) represents an avoided crossing between two diabatic states whose energies change (and cross) as a function of x; the diabatic coupling between the diabats changes in magnitude as a function of x and by a phase as a function of y. For this Hamiltonian, the adiabatic surfaces are completely flat with energies $\pm A$; we choose this model so that we can cleanly disentangle how wavepackets move nonadiabatically between different surfaces without any complications from branching and/or decoherence onto different surfaces (as would be caused by different forces on different adiabatic surfaces).

For an incoming wavepacket on surface 2 beginning at $x = -\infty$ and traveling in the $+x$ direction, the Born-Oppenheimer approximation would predict that motion remains completely unchanged in the x-direction, but the exact solution predicts that the wavepacket should bend upwards. If W is small enough, the asymptotic momentum of the transmitted wavepacket should be W. This behavior follows by considering Berry's force. For the Hamiltonian in Eq. (7), the Berry force is $\vec{F}^B_2 = 2\hbar\mathrm{Im}\left[\vec{d}_{21}\left(\frac{\vec{P}}{M}\cdot\vec{d}_{12}\right)\right] = \frac{\hbar W}{2}\partial_x\theta\sin\theta\left(-\frac{P^y}{M},\frac{P^x}{M}\right)$. When W is small enough, we can assume that P^x is roughly constant, and so we may calculate the final y-direction momentum (at the end of a scattering event) by integrating the y-component of the Berry force,

$$p^y = \int_0^\infty \frac{\hbar W}{2}\partial_x\theta\sin\theta\frac{P^x}{M}dt = \hbar W. \tag{8}$$

Of course, if W is not small, the result above is invalid; instead, the wavepacket can actually split apart and a portion of the wavepacket will reflect —even though the adiabats are completely flat.

Now, the example above makes very clear (as shown in Ref. 40) that the FSSH algorithm does not capture Berry's phase effects in the case of a *complex* Hamiltonian.[38] FSSH dictates motion along adiabats and the algorithm will not predict any bending or reflection; for this reason, in Ref. 40, we have recommended augmenting FSSH dynamics with the Berry force $\vec{F}_B$ [in Eq. (6)] in order to better agree with the QCLE and capture the correct quantum dynamics. Clearly, further benchmarking of such a corrected FSSH approach will be necessary.

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At this point, it is worthwhile to consider the natural alternative to FSSH dynamics, namely, Ehrenfest dynamics. Does Ehrenfest dynamics correctly account for Berry's phase or does it also require a Berry phase correction? We will now argue (analytically and numerically) that Ehrenfest dynamics *do already include* Berry's phase; for the Hamiltonian in Eq. (7), in the limit of nearly adiabatic dynamics, Ehrenfest trajectories will bend the correct amount. Thus, despite the many failures of Ehrenfest dynamics (i.e., a lack of branching,[3] a lack of detailed balance,[50,51] and a lack of decoherence[52–56]), a correction for Berry's phase effects is not needed.

To prove this point, consider the propagation of the wavefunction during an Ehrenfest trajectory for the Hamiltonian in Eq. (7),

$$\begin{aligned}\dot{c}_1 &= -\frac{iE_1}{\hbar}c_1 - \frac{\vec{P}}{M}\cdot\vec{d}_{12}c_2,\\ \dot{c}_2 &= -\frac{iE_2}{\hbar}c_2 - \frac{\vec{P}}{M}\cdot\vec{d}_{21}c_1.\end{aligned} \tag{9}$$

The time evolution of density matrix element ($\rho_{jk} \equiv c_j c_k^*$) is

$$\dot{\rho_{21}} = i\omega_{12}\rho_{21} + \left(\frac{\vec{P}}{M}\cdot\vec{d}_{21}\right)(\rho_{22}-\rho_{11}) \approx i\omega_{12}\rho_{21} + \left(\frac{\vec{P}}{M}\cdot\vec{d}_{21}\right). \tag{10}$$

Here, $\omega_{12} \equiv (E_1 - E_2)/\hbar$ and the adiabatic limit has been invoked such that trajectories are moving along surface 2 at all times ($\rho_{22} \approx 1$). Solving the above ordinary differential equation [Eq. (10)] with initial condition $\rho_{21}(0) = 0$, we find

$$\rho_{21}(t) = e^{i\omega_{12}t}\int_0^t\left(\frac{\vec{P}}{M}\cdot\vec{d}_{21}\right)e^{-i\omega_{12}\tau}d\tau. \tag{11}$$

For the Hamiltonian in Eq. (7), one can compute $\vec{d}_{21} = \frac{1}{2}(-\partial_x\theta, iW\sin\theta)$. Thus, for the small W case where P^x is constant and $P^y \approx 0$, we can integrate $\rho_{21}(t)$ by parts (with the fact that $\left.\frac{\partial^k\theta}{\partial t^k}\right|_{t=0} = 0$ for any order of k assuming that we initially start far away from the crossing),

$$\begin{aligned}\rho_{21}(t) &= -\frac{1}{2}e^{i\omega_{12}t}\int_0^t\frac{\partial\theta}{\partial\tau}e^{-i\omega_{12}\tau}d\tau\\ &= -\frac{1}{2}e^{i\omega_{12}t}\left(-\frac{1}{i\omega_{12}}e^{-i\omega_{12}\tau}\frac{\partial\theta(\tau)}{\partial\tau}\Big|_0^t + \frac{1}{i\omega_{12}}\int_0^t\frac{\partial^2\theta(\tau)}{\partial\tau^2}e^{-i\omega_{12}\tau}d\tau\right)\\ &= \frac{1}{2}\sum_{k=1}^{\infty}\frac{1}{(i\omega_{12})^k}\frac{\partial^k\theta}{\partial t^k}.\end{aligned} \tag{12}$$

To approximate the above series, we use the definition of θ in Eq. (7). For the term associated with $\frac{\partial^k\theta}{\partial t^k}$, one can show that the order of magnitude is $\left(\frac{BP^x}{\omega_{12}M}\right)^k$. Thus, if $\frac{BP^x}{\omega_{12}M}$ is small, the first term will dominate the series, and the average force (as well as the final momentum) can be calculated as

$$\langle F^y\rangle(t) = 2\mathrm{Re}\left(F^y_{12}\rho_{21}(t)\right) = \frac{\hbar W}{2}\sin\theta(t)\frac{\partial\theta}{\partial t}, \tag{13}$$

$$p^y = \int_0^{\infty}\langle F^y\rangle(t)dt = \hbar W. \tag{14}$$

From this argument, it is clear that the Berry phase effects are already included in Ehrenfest dynamics (unlike FSSH) and there is no need for any additional corrections.

Finally, in order to numerically assess the relative value of Berry-corrected FSSH and Ehrenfest dynamics, in Fig. 1 we plot the transmitted y momentum as a function of incoming momentum in both the adiabatic and diabatic regimes for the Hamiltonian in Eq. (7). For this dataset, we set $W = 5$, $M = 1000$, and $B = 3.0$, and as far as the FSSH is concerned, we rescale all velocities in the x-direction whenever a hop occurs. We imagine a particle coming on adiabat 2 from the left. For comparison, besides Ehrenfest and FSSH, we also plot results for exact dynamics as well as classical adiabatic dynamics with Berry's forces. Reflection is rare and not important here. As shown in Fig. 1, Ehrenfest outperforms Berry-corrected FSSH in both the diabatic and adiabatic regimes as far as the

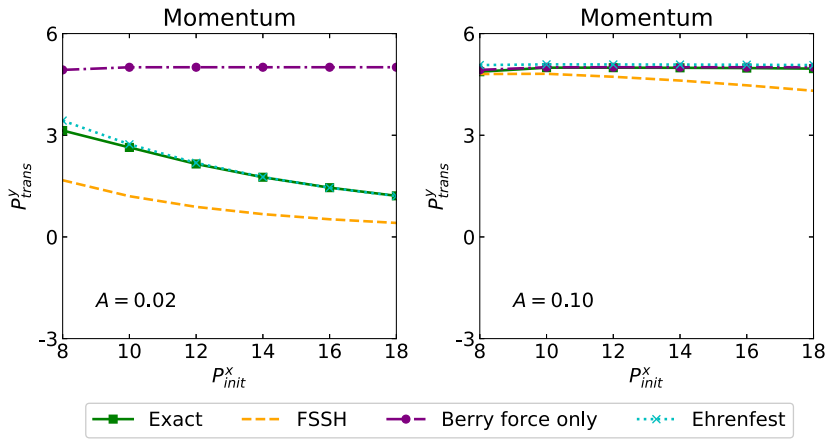


FIG. 1. Transmitted and average y-momentum as a function of initial momentum P^x_{init}. Left: $A = 0.02$, corresponding to the diabatic regime; right: $A = 0.10$, corresponding to the adiabatic regime. $P^y_{init} = 0$. Little reflection is observed for both cases. While FSSH (with an imposed Berry force) captures the correct trend, it is numerically outperformed by Ehrenfest dynamics (which naturally accounts for Berry's phase). Adiabatic dynamics with a Berry force works only in the adiabatic regime, $A = 0.1$.

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average momentum, indicating that Ehrenfest dynamics work better than FSSH even after a Berry-phase correction. Clearly, despite its many failures,[3,50–56] Ehrenfest dynamics incorporate Berry's forces naturally and work very well for this problem of flat adiabatic surfaces; FSSH captures the correct trends but has a relatively larger error.

Finally, using a Berry force and running purely adiabatic dynamics can be very accurate in the adiabatic regime, i.e., $A = 0.10$. That being said, running adiabatic dynamics with a Berry force is awful in the diabatic regime, i.e., $A = 0.02$.

IV. CONCLUSIONS

In this paper, we have demonstrated that, even though the QCLE arises from a cutoff in $\hbar$ at order 0 from the Wigner distribution equation of motion, QCLE dynamics *do* include Berry's phase effects (which are of order $\hbar$) which are amplified for a complex Hamiltonian. As such, even though Berry's phase effects are not usually studied explicitly with the QCLE,[31–33,38] if classical nuclei are sufficient, one can safely study many physical problems with complex Hamiltonians and geometric phase using the well-established QCLE and approximations thereof; of course, the bigger problem remains how to solve the QCLE in practice. Here, we have shown that Tully's surface hopping approximation to the QCLE does not include Berry's phase effects (when the Hamiltonian is complex) and we have recently made the sensible suggestion to simply add in the Berry force [Eq. (6)].[40] At the same time, we have also shown that Ehrenfest dynamics do contain Berry's phase and, as such, no extra force is required.

Looking forward, the keen reader should observe that our model problem here [Eq. (7)] is an extremely unphysical example whereby one can easily isolate Berry's phase effects. For most problems with avoided crossings and conical intersections,[57] the adiabatic force difference will not be constant and surface hopping is usually expected to be a better approximation than Ehrenfest dynamics at recovering long time dynamics (e.g., populations during electron transfer dynamics[58]). Further research will need to assess whether FSSH can still be improved and how to incorporate decoherence[59–71] within a Berry-force modified algorithm. Another important question is how to choose a momentum rescaling direction for surface hopping; here, for the Hamiltonian in Eq. (7), we simply chose x as the rescaling direction but for a more general Hamiltonian, a better ansatz is needed. Unfortunately, preliminary evidence suggests that the algorithms in Ref. 40 are not yet optimal; perhaps the different form of the QCLE [as present in Eqs. (5) and (A1)] will be useful for future derivations. At the very least, the equations should yield insight into exactly when one can make the adiabatic approximation and ignore B_{12}.

Finally and most importantly, now that we know that Berry's phase dynamical effects are already included within the QCLE, this paper raises the distinct possibility of using the QCLE (and approximations thereof) to study coupled nuclear-electronic motion on the surfaces of topological materials, where the electronic Hamiltonian is complex and electronic Berry's phase effects are already known to be of crucial importance.[72] One must wonder if one will learn something new about nonadiabatic dynamics in such a context.

SUPPLEMENTARY MATERIAL

See supplementary material for the detailed derivations of $\frac{\partial A_{11}^W}{\partial t}$ [Eq. (5)] and $\frac{\partial B_{12}^W}{\partial t}$ [Eq. (A1)].

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APPENDIX: EXPRESSION FOR $\frac{\partial B_{12}^W}{\partial t}$

After a great deal of algebra (see the supplementary material), the equation of motion for B_{12}^W can be shown to be

$$\begin{aligned}\frac{\partial}{\partial t}B_{12}^W(R,P,t) = {}& \frac{-i}{\hbar}(V_{11}-V_{22})B_{12}^W - \frac{P^\alpha}{M^\alpha}\frac{\partial B_{12}^W}{\partial R^\alpha} - \frac{1}{2}\left(F_{11}^\alpha + F_{22}^\alpha\right)\frac{\partial B_{12}^W}{\partial P^\alpha} \\ & - i\hbar\frac{P^\alpha}{M^\alpha}\frac{\partial d_{12}^\gamma}{\partial R^\alpha}\frac{P^\gamma}{M^\gamma}\frac{\left(A_{22}^W - A_{11}^W\right)}{(V_{11}-V_{22})} - i\hbar\frac{P^\alpha}{M^\alpha}\frac{d_{12}^\gamma P^\gamma}{M^\gamma}\frac{\left(A_{22}^W - A_{11}^W\right)}{(V_{11}-V_{22})^2}\left(F_{11}^\alpha - F_{22}^\alpha\right) - \frac{i\hbar P^\alpha}{2M^\alpha}\frac{\partial d_{12}^\gamma}{\partial R^\alpha}\left(\frac{\partial A_{11}^W}{\partial P^\gamma} + \frac{\partial A_{22}^W}{\partial P^\gamma}\right) \\ & - \frac{i\hbar}{2}\left(F_{11}^\alpha + F_{22}^\alpha\right)\frac{d_{12}^\alpha\left(A_{22}^W - A_{11}^W\right)}{M^\alpha(V_{11}-V_{22})} + \frac{i\hbar}{4}d_{12}^\gamma\left(\left(F_{22}^\alpha - F_{11}^\alpha\right)\left(\frac{\partial^2 A_{22}^W}{\partial P^\alpha\partial P^\gamma} - \frac{\partial^2 A_{11}^W}{\partial P^\alpha\partial P^\gamma}\right)\right) \\ & + \frac{i\hbar P^\gamma d_{12}^\gamma}{M^\gamma(V_{11}-V_{22})}\left(\frac{4P^\alpha}{M^\alpha}\mathrm{Re}\left(B_{12}^W d_{21}^\alpha\right) + \frac{1}{2}\left(F_{22}^\alpha - F_{11}^\alpha\right)\left(\frac{\partial A_{22}^W}{\partial P^\alpha} - \frac{\partial A_{11}^W}{\partial P^\alpha}\right)\right) + \frac{i\hbar}{2}\frac{d_{12}^\alpha}{M^\alpha}\left(\frac{\partial A_{11}^W}{\partial R^\alpha} + \frac{\partial A_{22}^W}{\partial R^\alpha}\right) \end{aligned} \tag{A1}$$

$$\begin{aligned} & + i\hbar d_{12}^\gamma\mathrm{Re}\left(\frac{\partial^2 B_{12}^W}{\partial P^\alpha\partial P^\gamma}F_{21}^\alpha\right) + \frac{i\hbar P^\gamma d_{12}^\gamma}{M^\gamma(V_{11}-V_{22})}\left[2\hbar\mathrm{Im}\left(d_{21}^\alpha\frac{P^\beta}{M^\beta}d_{12}^\beta\right)\left(\frac{\partial A_{11}^W}{\partial P^\alpha} + \frac{\partial A_{22}^W}{\partial P^\alpha}\right)\right] \\ & - i\hbar d_{12}^\gamma\left[\hbar\mathrm{Im}\left(\frac{d_{12}^\alpha d_{21}^\gamma}{M^\gamma}\right)\left(\frac{\partial A_{22}^W}{\partial P^\alpha} - \frac{\partial A_{11}^W}{\partial P^\alpha}\right)\right] - i\hbar d_{12}^\gamma\left[\hbar\mathrm{Im}\left(d_{12}^\alpha\frac{P^\beta}{M^\beta}d_{21}^\beta\right)\left(\frac{\partial^2 A_{22}^W}{\partial P^\alpha\partial P^\gamma} - \frac{\partial^2 A_{11}^W}{\partial P^\alpha\partial P^\gamma}\right)\right]. \end{aligned} \tag{A2}$$

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