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ABSTRACT

We show that standard Ehrenfest dynamics does not conserve linear and angular momentum when using a basis of truncated adiabatic states. However, we also show that previously proposed effective Ehrenfest equations of motion [M. Amano and K. Takatsuka, "Quantum fluctuation of electronic wave-packet dynamics coupled with classical nuclear motions," J. Chem. Phys. **122**, 084113 (2005) and V. Krishna, "Path integral formulation for quantum nonadiabatic dynamics and the mixed quantum classical limit," J. Chem. Phys. **126**, 134107 (2007)] involving the non-Abelian Berry force do maintain momentum conservation. As a numerical example, we investigate the Kramers doublet of the methoxy radical using generalized Hartree–Fock with spin–orbit coupling and confirm that angular momentum is conserved with the proper equations of motion. Our work makes clear some of the limitations of the Born–Oppenheimer approximation when using *ab initio* electronic structure theory to treat systems with unpaired electronic spin degrees of freedom, and we demonstrate that Ehrenfest dynamics can offer much improved, qualitatively correct results.

I. INTRODUCTION

Given the speed and power of modern computational supercomputers, nonadiabatic dynamics is widely used at present to study ultrafast photochemical and charge-transfer dynamics (as probed by state-of-the-art experiments).[3] When connecting with experiments, however, in practice, nonadiabatic simulations must almost always make a quantum–classical approximation[4–9] in order to be computationally feasible. The fundamental assumption of propagating nuclei classically and the electrons quantum mechanically inevitably raises the issue of how to correctly incorporate the feedback between the quantum and the classical subsystems. One of the most popular choices at present is the surface hopping approach,[10–13] whereby a swarm of trajectories move along a single adiabatic surface and stochastically hop between surfaces to account for nonadiabatic effects. As we have recently documented,[14] the surface-hopping algorithm faces difficulties in the presence of spin–orbit coupling (SOC), which we will address in a separate paper. A second approach, orthogonal to the surface-hopping ansatz, is to include the interaction between the quantum and classical subsystems in a mean-field way, which gives rise to the standard Ehrenfest approach[15–18]—an approach that is always well-defined (with or without SOC).

The pros and cons of Ehrenfest dynamics are well-known within the community.[19–26] Ehrenfest is most advantageous if there are frequent transitions between nearly parallel states, and one can work with either a handful or a dense manifold[27] of such states. However, the mean-field approximation between the quantum and classical subsystems can break down when there is a strong coupling between the two subsystems (e.g., when two potential energy surfaces are much displaced from each other); in such a case, methods such as multi-configurational Ehrenfest have been developed.[28,29] Standard Ehrenfest also cannot account for decoherence nor achieve a detailed balance,[21,22] which are important when studying systems in the condensed phase; various correction schemes have been proposed to address these deficiencies as well.[24–26,30–32] As a side note, we mention that, in this paper, we will concern ourselves strictly with what is known as "linear-response" Ehrenfest, where the electronic wavefunction is expanded in a basis of adiabatic/diabatic states; we will not concern ourselves with real-time Ehrenfest dynamics,[18,33] whereby the electronic wavefunction is propagated directly in the original atomic orbital basis.

As a practical matter, there are several means by which one can judge the value of any dynamical approach. Almost always, the very first constraint on any good dynamics algorithm is energy conservation; in fact, checking for energy conservation is usually the very first means of making sure one's code is free of bugs.[34] Beyond energy conservation, in the absence of an external torque on the system, a second constraint is that the total angular momentum is also conserved. Interestingly, as opposed to energy conservation, angular momentum conservation is rarely emphasized in the context of nonadiabatic dynamics (though see below). Consider the most standard class of molecular dynamics, namely single-state dynamics within the Born–Oppenheimer (BO) approximation. For such dynamics, the electronic linear and angular momentum are usually neglected (or more formally folded into the nuclear degrees of freedom),[35] and the *nuclear* linear and angular momentum are conserved due to translational symmetry and isotropy of space. However, as we have recently shown,[36] if one runs BO dynamics (without Berry force) along one of the degenerate doublet surfaces (in the presence of spin–orbit coupling) and keeps track of the fluctuating electronic angular momentum, one will inevitably compute a total angular momentum that fluctuates (i.e., one will predict a violation of angular momentum conservation).

Now, one means to resolve this paradox is not to use BO theory at all, but rather exact factorization,[37–39] where angular momentum exchange has recently been explored.[40] As pointed out in Ref. 36, however, an even simpler resolution to this paradox is that, within BO theory, one must include a Berry force (see below) acting on the nuclear motion. More precisely, for nonadiabatic systems with odd numbers of electrons plus SOC, the on-diagonal derivative coupling $\boldsymbol{d}$ is not zero, so the nuclear kinetic momentum $\boldsymbol{\pi}_{\mathrm{n}}$ is not equivalent to the canonical momentum $\boldsymbol{P}_{\mathrm{n}}$ (recall that $\boldsymbol{\pi}_{\mathrm{n}} = \boldsymbol{P}_{\mathrm{n}} - i\hbar\boldsymbol{d}$). In order to minimize gauge problems, the usual approach is then to pick one adiabat from the Kramers pair to run along (say, j, which is computed from some approximate electronic structure techniques) and then to propagate the nuclear kinetic momentum $\boldsymbol{\pi}_{\mathrm{n}}$; the latter step inevitably introduces the Abelian Berry force in the equation of motion for $\boldsymbol{\pi}_{\mathrm{n}}$, $\boldsymbol{F}_j^{\mathrm{Berry}} = i\hbar(\nabla_{\mathrm{n}} \times \boldsymbol{d}_{jj}) \cdot \frac{\boldsymbol{\pi}_{\mathrm{n}}}{M}$. As shown in Ref. 36, including the pseudo-magnetic Berry force allows for a full exchange of angular momentum between electronic, nuclear, and spin degrees of freedom. Of course, there is still no guarantee that the dynamics are correct (i.e., following one adiabat of a pair), but at least the resulting dynamics are guaranteed to conserve the total angular momentum.

The above background raises crucial questions for the field of nonadiabatic dynamics. If one needs to go beyond BO dynamics, one can ask: do nonadiabatic dynamics algorithms conserve the total (electronic plus nuclear) momentum? In a recent paper, Shu *et al.*[41] showed that the nuclear angular momentum is not conserved within an *ab initio* Ehrenfest scheme propagated in an adiabatic basis. In Ref. 41, the authors addressed this issue by projecting out the translational and rotational components of the derivative coupling that enters the force; see Eq. (18). While this scheme offers a practical way to conserve nuclear angular momentum, we will show below that the problems arising in Ref. 41 are at bottom created by using a truncated adiabatic basis, for which there is a rigorous (not *ad hoc*) solution. Deriving and understanding such a solution is the main focus of the present paper, but in a nutshell, if BO dynamics require the Abelian Berry curvature in order to maintain momentum conservation, nonadiabatic Ehrenfest dynamics in a truncated basis require the non-Abelian Berry curvature[42] in order to achieve the same feat.

Finally, before concluding this section, a few words are appropriate regarding spin. The most obvious cases where we expect angular momentum conservation to be interesting are systems with a flow of angular momentum between different degrees of freedom (including nuclear, electronic, and spin degrees of freedom). For organic systems, the spin degree of freedom often operates on a much longer time scale than the electronic degree of freedom and sometimes even longer than the nuclear motion. In such cases, the validity of the BO approximation is dubious. Indeed, in this paper, we will show that a simple rotation of the methoxy radical breaks the BO approximation because, within the BO approximation, the total spin vector rotates with the molecule instantaneously (which is incorrect). One would hope that the Ehrenfest equations of motion would perform far better, and, indeed, Ehrenfest does (correctly) slow down the spin change with the nuclear motion.

This paper is organized as follows. In Sec. II, we begin by demonstrating momentum conservation for Ehrenfest dynamics propagated over a complete electronic Hilbert space; this conclusion holds whether one performs the dynamics in a diabatic or adiabatic basis, and by comparing the calculations in two different basis sets, one inevitably learns about the non-Abelian Berry curvature. In Sec. III, we then remove the assumption of a complete set of states and show that, according to standard Ehrenfest dynamics, neither linear nor angular momentum is conserved in a truncated set of states. To restore momentum conservation in the presence of a truncated basis, we show that the equations of motion must include the non-Abelian Berry curvature and we present the relevant Hamiltonian from which Hamilton's equations can be derived (where the final form agrees with the derivations in Refs. 1 and 2). In Sec. VI, in order to demonstrate the importance of momentum conservation, we perform two *ab initio* Ehrenfest calculations of the methoxy radical in the Kramers pair basis. We study both excitation of a vibration and excitation of angular momentum. These two cases make clear that including the non-Abelian Berry curvature can have a strong impact on the resulting spin dynamics and that, more generally, the BO approximation can badly break down in the presence of unpaired electrons. In Sec. VIII, we conclude and discuss future possible *ab initio* directions.

II. THEORY: DYNAMICS WITHIN A COMPLETE (UNTRUNCATED) ELECTRONIC HILBERT SPACE

We begin our analysis by assuming that we are working in a complete (untruncated) electronic vector space with zero curvature. This scenario represents a very ideal condition because the electronic Hilbert space is immense—requiring an enormous number (infinite) of one-particle electronic basis functions and then an even larger number (infinite) of many-body electronic wavefunctions (and just about any finite basis will exhibit a nonzero Berry curvature[42]). Nevertheless, the analysis below will still be useful insofar as teaching us how to understand how the Ehrenfest equations can take different forms in different representations.

A. A strictly diabatic representation

To begin our discussion, let us imagine that we are given an electronic Hamiltonian expressed in a strictly diabatic basis; in other words, the electronic basis does not depend at all on nuclear position. The Hamiltonian ($\tilde{\boldsymbol{H}}$) and the energy ($\tilde{E}$) are postulated to be of the form

$$\tilde{\boldsymbol{H}} = \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I^2}}{2M_I} + \tilde{\boldsymbol{V}}, \tag{1}$$

$$\tilde{E} = \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I^2}}{2M_I} + \mathrm{Tr}\big(\tilde{\boldsymbol{\sigma}}\tilde{\boldsymbol{V}}\big), \tag{2}$$

where we denote the classical nuclear position $\boldsymbol{R}_{\mathrm{n}}$ and nuclear momentum $\boldsymbol{P}_{\mathrm{n}}$. Here and below, we use the indices IJ for nuclei and $\alpha\beta\gamma$ for the Cartesian indices xyz. The potential operator $\tilde{\boldsymbol{V}} = \tilde{\boldsymbol{T}}_{\mathrm{e}} + \tilde{\boldsymbol{V}}_{\mathrm{ee}} + \tilde{\boldsymbol{V}}_{\mathrm{en}} + \tilde{\boldsymbol{V}}_{\mathrm{nn}}$ includes the electronic kinetic energy, electron–electron interaction, electron–nuclear Coulomb interaction, and nuclear–nuclear repulsion terms, respectively. We use the notation "~" to indicate operators in a diabatic basis. For the energy expression, the first term is the nuclear kinetic energy and the second term is the potential energy term that one computes by integrating over the electronic degree of freedom with the electronic density operator $\tilde{\boldsymbol{\sigma}}$ in a diabatic basis.

According to Hamilton's equations, the equations of motions for nuclear position and momentum are

$$\dot{R}_{\mathrm{n}}^{I\alpha} = \frac{\partial \tilde{E}}{\partial P_{\mathrm{n}}^{I\alpha}} = \frac{P_{\mathrm{n}}^{I\alpha}}{M_I}, \tag{3}$$

$$\dot{P}_{\mathrm{n}}^{I\alpha} = -\frac{\partial \tilde{E}}{\partial R_{\mathrm{n}}^{I\alpha}} = -\mathrm{Tr}\left(\tilde{\boldsymbol{\sigma}}\frac{\partial \tilde{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}}\right). \tag{4}$$

The associated density matrix operator evolves according to the quantum Liouville equation,

$$\dot{\tilde{\boldsymbol{\sigma}}} = -\frac{i}{\hbar}\big[\tilde{\boldsymbol{V}}, \tilde{\boldsymbol{\sigma}}\big]. \tag{5}$$

Using Eqs. (3) and (4), it is straightforward to show that the total energy in the diabatic representation [Eq. (2)] is conserved $\frac{d\tilde{E}}{dt} = 0$.

At this point, it will be helpful to define the nuclear angular momentum,

$$J_{\mathrm{n}}^{\alpha} \equiv \sum_{I\beta\gamma} \varepsilon_{\alpha\beta\gamma} R_{\mathrm{n}}^{I\beta} M_I \dot{R}_{\mathrm{n}}^{I\gamma}, \tag{6}$$

where $\varepsilon_{\alpha\beta\gamma}$ is the Levi–Civita symbol. Using Eq. (3), it follows that we can also write

$$J_{\mathrm{n}}^{\alpha} = \sum_{I\beta\gamma} \varepsilon_{\alpha\beta\gamma} R_{\mathrm{n}}^{I\beta} P_{\mathrm{n}}^{I\gamma}, \tag{7}$$

$$\dot{J}_{\mathrm{n}}^{\alpha} = \sum_{I\beta\gamma} \varepsilon_{\alpha\beta\gamma} R_{\mathrm{n}}^{I\beta} \dot{P}_{\mathrm{n}}^{I\gamma}. \tag{8}$$

Using Eqs. (4) and (5), we can now evaluate the time derivative of the total linear and angular momentum,

$$\begin{aligned}\dot{P}_{\mathrm{tot}}^{\alpha} &= \dot{P}_{\mathrm{n}}^{\alpha} + \mathrm{Tr}\big(\dot{\tilde{\boldsymbol{\sigma}}}\tilde{\boldsymbol{P}}_{\mathrm{e}}^{\alpha}\big)\\ &= -\sum_I \mathrm{Tr}\left(\tilde{\boldsymbol{\sigma}}\frac{\partial \tilde{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}}\right) - \frac{i}{\hbar}\mathrm{Tr}\big(\tilde{\boldsymbol{\sigma}}[\tilde{\boldsymbol{P}}_{\mathrm{e}}^{\alpha}, \tilde{\boldsymbol{V}}]\big),\end{aligned} \tag{9}$$

$$\begin{aligned}\dot{J}_{\mathrm{tot}}^{\alpha} &= \dot{J}_{\mathrm{n}}^{\alpha} + \mathrm{Tr}\big(\dot{\tilde{\boldsymbol{\sigma}}}\tilde{\boldsymbol{J}}_{\mathrm{e}}^{\alpha}\big)\\ &= \sum_{I\beta\gamma} \varepsilon_{\alpha\beta\gamma} R_{\mathrm{n}}^{I\beta}\dot{P}_{\mathrm{n}}^{I\gamma} - \frac{i}{\hbar}\mathrm{Tr}\big(\tilde{\boldsymbol{\sigma}}[\tilde{\boldsymbol{J}}_{\mathrm{e}}^{\alpha}, \tilde{\boldsymbol{V}}]\big).\end{aligned} \tag{10}$$

Finally, *because we have assumed a complete electronic Hilbert space*, for a finite system in real space, the translational symmetry and the isotropy of space imply the following identities:

$$\big[\tilde{\boldsymbol{P}}_{\mathrm{n}} + \tilde{\boldsymbol{P}}_{\mathrm{e}}, \tilde{\boldsymbol{V}}\big] = 0, \tag{11}$$

$$\big[\tilde{\boldsymbol{J}}_{\mathrm{n}} + \tilde{\boldsymbol{J}}_{\mathrm{e}}, \tilde{\boldsymbol{V}}\big] = 0. \tag{12}$$

These equations lead to the following further identities:

$$-\frac{i}{\hbar}[\tilde{\boldsymbol{P}}_{\mathrm{e}}^{\alpha}, \tilde{\boldsymbol{V}}] = \frac{i}{\hbar}[\tilde{P}_{\mathrm{n}}^{\alpha}, \tilde{\boldsymbol{V}}] = \frac{\partial \tilde{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{\alpha}}, \tag{13}$$

$$-\frac{i}{\hbar}[\tilde{\boldsymbol{J}}_{\mathrm{e}}^{\alpha}, \tilde{\boldsymbol{V}}] = \frac{i}{\hbar}[\tilde{J}_{\mathrm{n}}^{\alpha}, \tilde{\boldsymbol{V}}] = \sum_{I\beta\gamma} \varepsilon_{\alpha\beta\gamma} R_{\mathrm{n}}^{I\beta}\frac{\partial \tilde{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\gamma}}. \tag{14}$$

If we plug the above commutators into Eqs. (9) and (10), we find momentum conservation $\dot{P}_{\mathrm{tot}}^{\alpha} = \dot{J}_{\mathrm{tot}}^{\alpha} = 0$.

B. Adiabatic representation

The above-mentioned equations of motion for Ehrenfest dynamics can be transformed into an adiabatic basis as well with the same conclusions, though we will find that the existence of a complete electronic basis is expressed differently than what we found in Eqs. (11) and (12). To proceed, let us define a unitary matrix that transforms the diabatic basis (with indices *abcd*) to adiabatic basis (with indices *ijkl*): $|\psi_k\rangle = \sum_a |\phi_a\rangle U_{ak}$. The density and potential operators in the adiabatic basis obtained after the diabatic-to-adiabatic transformation are

$$\hat{\boldsymbol{\sigma}} = \boldsymbol{U}^{\dagger}\tilde{\boldsymbol{\sigma}}\boldsymbol{U}, \tag{15}$$

$$\hat{\boldsymbol{V}} = \boldsymbol{U}^{\dagger}\tilde{\boldsymbol{V}}\boldsymbol{U}. \tag{16}$$

To transform the equations of motions in the diabatic basis [Eqs. (3)–(5)] to the adiabatic basis, let us write the equations of motion in terms of $\hat{\boldsymbol{\sigma}}$ and $\hat{\boldsymbol{V}}$. Specifically,

$$\dot{R}_{\mathrm{n}}^{I\alpha} = \frac{P_{\mathrm{n}}^{I\alpha}}{M_I}, \tag{17}$$

$$\begin{aligned}\dot{P}_{\mathrm{n}}^{I\alpha} &= -\operatorname{Tr}\left(\boldsymbol{U}^{\dagger}\tilde{\boldsymbol{\sigma}}\boldsymbol{U}\boldsymbol{U}^{\dagger}\frac{\partial\tilde{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}}\boldsymbol{U}\right)\\ &= -\operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\partial\hat{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}}\right) + \frac{i}{\hbar}\operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\left[\boldsymbol{A}^{I\alpha}, \hat{\boldsymbol{V}}\right]\right),\end{aligned} \tag{18}$$

$$\dot{\hat{\boldsymbol{\sigma}}} = \frac{d}{dt}\left(\boldsymbol{U}^{\dagger}\tilde{\boldsymbol{\sigma}}\boldsymbol{U}\right) = -\frac{i}{\hbar}\left[\hat{\boldsymbol{V}} - \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I}\cdot\boldsymbol{A}^{I}}{M_I}, \hat{\boldsymbol{\sigma}}\right]. \tag{19}$$

Here, we have defined

$$A_{jk}^{I\alpha} = i\hbar\sum_a U_{ja}^{\dagger}\frac{\partial U_{ak}}{\partial R_{\mathrm{n}}^{I\alpha}} = i\hbar\left\langle\psi_j\middle|\frac{\partial\psi_k}{\partial R_{\mathrm{n}}^{I\alpha}}\right\rangle, \tag{20}$$

which is commonly known as the nonadiabatic coupling term or the Berry connection. It is also the negative of the nuclear momentum operator,

$$A_{jk}^{I\alpha} = -\langle\psi_j|\hat{P}_{\mathrm{n}}^{I\alpha}|\psi_k\rangle. \tag{21}$$

Equations (17)–(19) are often considered the standard Ehrenfest equations of motion in an adiabatic basis.[7,43]

To demonstrate momentum conservation within this adiabatic representation, we again evaluate the time derivative of the total linear and angular momentum,

$$\dot{P}_{\mathrm{tot}}^{\alpha} = \sum_I \dot{P}_{\mathrm{n}}^{I\alpha} + \operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{P}}_{\mathrm{e}}^{\alpha} + \dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{P}_{\mathrm{e}}^{\alpha}\right), \tag{22}$$

$$\dot{J}_{\mathrm{tot}}^{\alpha} = \sum_I \dot{J}_{\mathrm{n}}^{I\alpha} + \operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{J}}_{\mathrm{e}}^{\alpha} + \dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{J}_{\mathrm{e}}^{\alpha}\right). \tag{23}$$

Note that when propagating the equations of motion in the adiabatic basis, one can choose an arbitrary phase of the adiabatic state as long as it is smooth in the configuration space. For instance, let us assume that, in the vicinity of configuration $\boldsymbol{R}_0$, the electronic state is chosen as

$$\psi_k(\boldsymbol{r};\boldsymbol{R}_{\mathrm{n}}) = \phi_k(\boldsymbol{r} - \boldsymbol{R}_{\mathrm{n}})e^{\frac{i}{\hbar}\zeta_k(\boldsymbol{R}_{\mathrm{n}} - \boldsymbol{R}_0)}. \tag{24}$$

In such a case, one finds the following relations:

$$\left(\sum_I \hat{P}_{\mathrm{n}}^{I\alpha} + \hat{P}_{\mathrm{e}}^{\alpha}\right)|\psi_k\rangle = \sum_I \xi_k^{I\alpha}(\boldsymbol{R}_{\mathrm{n}})|\psi_k\rangle, \tag{25}$$

$$\left(\sum_I \hat{J}_{\mathrm{n}}^{I\alpha} + \hat{J}_{\mathrm{e}}^{\alpha}\right)|\psi_k\rangle = \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma}R_{\mathrm{n}}^{I\eta}\xi_k^{I\gamma}(\boldsymbol{R}_{\mathrm{n}})|\psi_k\rangle, \tag{26}$$

where $\xi_k^{I\alpha}(\boldsymbol{R}_{\mathrm{n}}) = \nabla_{I\alpha}\zeta_k(\boldsymbol{R}_{\mathrm{n}})$.

Thereafter, one can arrive at the following identities for the matrix elements of electronic momentum and angular momentum operators:

$$\begin{aligned}\langle\psi_j|\hat{P}_{\mathrm{e}}^{\alpha}|\psi_k\rangle &= -\sum_I \langle\psi_j|\hat{P}_{\mathrm{n}}^{I\alpha}|\psi_k\rangle + \sum_I \xi_k^{I\alpha}\delta_{jk}\\ &= \sum_I A_{jk}^{I\alpha} + \xi_k^{I\alpha}\delta_{jk},\end{aligned} \tag{27}$$

$$\begin{aligned}\langle\psi_j|\hat{J}_{\mathrm{e}}^{\alpha}|\psi_k\rangle &= -\sum_I \langle\psi_j|\hat{J}_{\mathrm{n}}^{I\alpha}|\psi_k\rangle + \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma}R_{\mathrm{n}}^{I\eta}\xi_k^{I\gamma}\delta_{jk}\\ &= \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma}R_{\mathrm{n}}^{I\eta}(A_{jk}^{I\gamma} + \xi_k^{I\gamma}\delta_{jk}).\end{aligned} \tag{28}$$

If we differentiate the above-mentioned matrix elements with respect to time, we find

$$\begin{aligned}\dot{P}_{\mathrm{e},jk}^{\alpha} &= \sum_I \dot{A}_{jk}^{I\alpha} + \dot{\xi}_k^{I\alpha}\delta_{jk}\\ &= \sum_{IJ\beta} \dot{R}_{\mathrm{n}}^{J\beta}\left(\frac{\partial A_{jk}^{I\alpha}}{\partial R_{\mathrm{n}}^{J\beta}} + \xi_k^{J\beta,I\alpha}\delta_{jk}\right),\end{aligned} \tag{29}$$

$$\begin{aligned}\dot{J}_{\mathrm{e},jk}^{\alpha} &= \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma}\dot{R}_{\mathrm{n}}^{I\eta}(A_{jk}^{I\gamma} + \xi_k^{I\gamma}\delta_{jk})\\ &\quad + \sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma}R_{\mathrm{n}}^{I\eta}\dot{R}_{\mathrm{n}}^{J\beta}\left(\frac{\partial A_{jk}^{I\gamma}}{\partial R_{\mathrm{n}}^{J\beta}} + \xi_k^{J\beta,I\gamma}\delta_{jk}\right).\end{aligned} \tag{30}$$

Here, we introduce the notation $\xi_k^{J\beta,I\alpha}(\boldsymbol{R}_{\mathrm{n}}) = \nabla_{J\beta}\xi_k^{I\alpha}(\boldsymbol{R}_{\mathrm{n}})$.

1. Linear momentum conservation

To demonstrate the conservation of linear momentum, let us now evaluate all terms in Eq. (22).

- From Eq. (18), the first term in Eq. (22) ($\sum_I \dot{P}_{\mathrm{n}}^{I\alpha}$) is

$$\begin{aligned}\sum_I \dot{P}_{\mathrm{n}}^{I\alpha} &= \sum_I -\operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\partial\hat{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}}\right) + \frac{i}{\hbar}\operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\left[\boldsymbol{A}^{I\alpha}, \hat{\boldsymbol{V}}\right]\right)\\ &= \frac{i}{\hbar}\sum_I \operatorname{Tr}\left(\left[\hat{\boldsymbol{V}}, \hat{\boldsymbol{\sigma}}\right]\boldsymbol{A}^{I\alpha}\right),\end{aligned} \tag{31}$$

  where the first term vanishes since we assume a translationally invariant potential energy surface.
- From Eq. (29), the second term in Eq. (22) $[\operatorname{Tr}(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{P}}_{\mathrm{e}}^{\alpha})]$ is

$$\operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{P}}_{\mathrm{e}}^{\alpha}\right) = \sum_{IJ\beta jk} \hat{\sigma}_{kj}\dot{R}_{\mathrm{n}}^{J\beta}\left(\frac{\partial A_{jk}^{I\alpha}}{\partial R_{\mathrm{n}}^{J\beta}} + \xi_k^{J\beta,I\alpha}\delta_{jk}\right). \tag{32}$$

- Using Eq. (27) to express $\boldsymbol{P}_{\mathrm{e}}^{\alpha}$ in terms of $\boldsymbol{A}^{I\alpha}$, the last term $[\operatorname{Tr}(\dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{P}_{\mathrm{e}}^{\alpha})]$ in Eq. (22) becomes

$$\operatorname{Tr}\left(\dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{P}_{\mathrm{e}}^{\alpha}\right) = \sum_{Ijk} \dot{\hat{\sigma}}_{kj}\left(A_{jk}^{I\alpha} + \xi_k^{I\alpha}\delta_{jk}\right). \tag{33}$$

If we plug Eq. (19) into Eq. (33), the second term in Eq. (33) becomes

$$\sum_{Ijk} \dot{\hat{\sigma}}_{kj}\xi_k^{I\alpha}\delta_{jk} = -\frac{i}{\hbar}\sum_{Ijk} \xi_k^{I\alpha}\left(\hat{V}_{kk}\hat{\sigma}_{kj} - \hat{\sigma}_{kj}\hat{V}_{jj}\right)\delta_{jk} + \frac{i}{\hbar}\sum_{IJ\beta jk} \dot{R}_{\mathrm{n}}^{J\beta}\hat{\sigma}_{kj}(\xi_j^{I\alpha} - \xi_k^{I\alpha})A_{jk}^{J\beta} \tag{34}$$

$$= -\frac{i}{\hbar}\sum_{IJ\beta jk} \dot{R}_{\mathrm{n}}^{J\beta}\hat{\sigma}_{kj}(\xi_k^{I\alpha} - \xi_j^{I\alpha})A_{jk}^{J\beta}. \tag{35}$$

If we plug Eqs. (19) and (35) into Eq. (33), we can then simplify the total expression in Eq. (33),

$$\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\boldsymbol{P}_{\mathrm{e}}^{\alpha}\right) = -\frac{i}{\hbar}\sum_{I} \mathrm{Tr}\left(\left[\hat{\boldsymbol{V}},\hat{\boldsymbol{\sigma}}\right]\boldsymbol{A}^{I\alpha}\right) + \frac{i}{\hbar}\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\sum_{IJ\beta}\dot{R}_{\mathrm{n}}^{J\beta}\left[\boldsymbol{A}^{I\alpha},\boldsymbol{A}^{J\beta}\right]\right) - \frac{i}{\hbar}\sum_{IJ\beta jk} \dot{R}_{\mathrm{n}}^{J\beta}\hat{\sigma}_{kj}(\xi_k^{I\alpha} - \xi_j^{I\alpha})A_{jk}^{J\beta}. \tag{36}$$

Using Eqs. (31), (32), and (36), we can finally evaluate the time dependence of the total linear momentum in Eq. (22). We notice that Eq. (31) cancels with the first term in Eq. (36), and we are left with

$$\dot{P}_{\mathrm{tot}}^{\alpha} = \sum_{IJ\beta} \mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{R}_{\mathrm{n}}^{J\beta}\left(\frac{\partial \boldsymbol{A}^{I\alpha}}{\partial R_{\mathrm{n}}^{J\beta}} + \frac{i}{\hbar}\left[\boldsymbol{A}^{I\alpha},\boldsymbol{A}^{J\beta}\right]\right)\right) + \sum_{IJ\beta jk} \hat{\sigma}_{kj}\dot{R}_{\mathrm{n}}^{J\beta}\left[\xi_k^{J\beta,I\alpha}\delta_{jk} - \frac{i}{\hbar}(\xi_k^{I\alpha} - \xi_j^{I\alpha})A_{jk}^{J\beta}\right] \tag{37}$$

$$= \sum_{IJ\beta} \mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{R}_{\mathrm{n}}^{J\beta}\left(-\frac{\partial \boldsymbol{A}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}} + \frac{\partial \boldsymbol{A}^{I\alpha}}{\partial R_{\mathrm{n}}^{J\beta}} + \frac{i}{\hbar}\left[\boldsymbol{A}^{I\alpha},\boldsymbol{A}^{J\beta}\right]\right)\right) \tag{38}$$

$$= -\sum_{IJ\beta} \mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{R}_{\mathrm{n}}^{J\beta}\boldsymbol{\Omega}^{I\alpha J\beta}\right). \tag{39}$$

Note that to go from Eq. (37) to Eq. (38), we used the following relation, which is proven in Sec. S1 of the supplementary material:

$$\sum_{I} \frac{\partial A_{jk}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}} = -\sum_{I} \xi_k^{J\beta,I\alpha}\delta_{jk} + \frac{i}{\hbar}\sum_{I} (\xi_k^{I\alpha} - \xi_j^{I\alpha})A_{jk}^{J\beta}. \tag{40}$$

The above-mentioned analysis leads us to consider the famous non-Abelian Berry curvature $\boldsymbol{\Omega}^{I\alpha J\beta}$,[42,44] which is defined as

$$\boldsymbol{\Omega}^{I\alpha J\beta} = \frac{\partial \boldsymbol{A}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}} - \frac{\partial \boldsymbol{A}^{I\alpha}}{\partial R_{\mathrm{n}}^{J\beta}} - \frac{i}{\hbar}\left[\boldsymbol{A}^{I\alpha},\boldsymbol{A}^{J\beta}\right]. \tag{41}$$

As is well-known, the non-Abelian Berry curvature vanishes in the limit of a complete basis, as one can readily demonstrate by inserting a resolution of identity, $\sum_l |\psi_l\rangle\langle\psi_l|$,

$$\frac{\partial A_{jk}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}} - \frac{\partial A_{jk}^{I\alpha}}{\partial R_{\mathrm{n}}^{J\beta}} = \frac{i}{\hbar}\sum_{l} \left(A_{jl}^{I\alpha}A_{lk}^{J\beta} - A_{jl}^{J\beta}A_{lk}^{I\alpha}\right). \tag{42}$$

To repeat, the total linear momentum is conserved when we perform the calculation with a complete electronic basis, and in an adiabatic representation, this conservation becomes clear because the non-Abelian Berry curvature vanishes.

2. Angular momentum conservation

Next, let us demonstrate the same conclusion for angular momentum conservation. We must evaluate all the terms in Eq. (23).

- From the expression for $\dot{J}_{\mathrm{n}}^{\alpha}$ in Eq. (8) and the expression for $\dot{P}_{\mathrm{n}}^{I\gamma}$ in Eq. (18), we can write out the first term in Eq. (23),

$$\sum_{I} \dot{J}_{\mathrm{n}}^{I\alpha} = \sum_{I\beta\gamma} \varepsilon_{\alpha\beta\gamma}R_{\mathrm{n}}^{I\beta}\,\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\left(-\frac{\partial \hat{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\gamma}} + \frac{i}{\hbar}\left[\boldsymbol{A}^{I\gamma},\hat{\boldsymbol{V}}\right]\right)\right) = \frac{i}{\hbar}\sum_{I\beta\gamma} \varepsilon_{\alpha\beta\gamma}R_{\mathrm{n}}^{I\beta}\,\mathrm{Tr}\left(\left[\hat{\boldsymbol{V}},\hat{\boldsymbol{\sigma}}\right]\boldsymbol{A}^{I\gamma}\right). \tag{43}$$

  In the above-mentioned equation, the first term vanishes because we assume that space is isotropic.
- To write down the expression for the second term $\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{J}}_{\mathrm{e}}^{\alpha}\right)$ in Eq. (23), let us simplify the expression for $\dot{\boldsymbol{J}}_{\mathrm{e}}^{\alpha}$ in Eq. (30). Specifically, we will use the following relation, which is proved in Sec. S1 of the supplementary material:

$$\sum_{\gamma} \varepsilon_{\alpha\eta\gamma}(A_{jk}^{I\gamma} + \xi_k^{I\gamma}\delta_{jk}) = \sum_{J\beta\gamma} \varepsilon_{\alpha\beta\gamma}R_{\mathrm{n}}^{J\beta}\left[-\frac{\partial A_{jk}^{I\eta}}{\partial R_{\mathrm{n}}^{J\gamma}} + \frac{i}{\hbar}(\xi_k^{J\gamma} - \xi_j^{J\gamma})A_{jk}^{I\eta} - \delta_{jk}\xi_k^{I\eta,J\gamma}\right]. \tag{44}$$

  If we substitute Eq. (44) into Eq. (30) and change dummy index labels, we recover

$$\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{J}}_{\mathrm{e}}^{\alpha}\right) = \sum_{IJ\eta\beta\gamma jk} \hat{\sigma}_{kj}\varepsilon_{\alpha\eta\gamma}R_{\mathrm{n}}^{I\eta}\dot{R}_{\mathrm{n}}^{J\beta}\left[\frac{\partial A_{jk}^{I\gamma}}{\partial R_{\mathrm{n}}^{J\beta}} - \frac{\partial A_{jk}^{J\beta}}{\partial R_{\mathrm{n}}^{I\gamma}} + \frac{i}{\hbar}(\xi_k^{I\gamma} - \xi_j^{I\gamma})A_{jk}^{J\beta}\right]. \tag{45}$$

- Using Eq. (28), the last term $\mathrm{Tr}\left(\dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{J}_{\mathrm{e}}^{\alpha}\right)$ in Eq. (23) becomes

$$\mathrm{Tr}\left(\dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{J}_{\mathrm{e}}^{\alpha}\right) = \sum_{I\eta\gamma jk} \varepsilon_{\alpha\eta\gamma}R_{\mathrm{n}}^{I\eta}\dot{\hat{\sigma}}_{kj}(A_{jk}^{I\gamma} + \xi_k^{I\gamma}\delta_{jk}). \tag{46}$$

We begin by evaluating and plugging Eq. (35) into the second term of Eq. (46),

$$\sum_{I\eta\gamma jk} \varepsilon_{\alpha\eta\gamma} R_{\mathrm{n}}^{I\eta} \dot{\hat{\sigma}}_{kj} \xi_k^{I\gamma} \delta_{jk} = -\frac{i}{\hbar} \sum_{IJjk\beta\gamma\eta} \varepsilon_{\alpha\eta\gamma} R_{\mathrm{n}}^{I\eta} \dot{R}_{\mathrm{n}}^{J\beta} \times \hat{\sigma}_{kj} (\xi_k^{I\gamma} - \xi_j^{I\gamma}) A_{jk}^{J\beta}. \tag{47}$$

If we then plug Eqs. (19) and (47) into Eq. (46) and simplify, we find

$$\begin{aligned} \mathrm{Tr}\Big(\dot{\hat{\boldsymbol{\sigma}}} \boldsymbol{J}_{\mathrm{e}}^{\alpha}\Big) = \sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma} R_{\mathrm{n}}^{I\eta} \bigg(& -\frac{i}{\hbar} \mathrm{Tr}\Big(\big[\hat{\boldsymbol{V}}, \hat{\boldsymbol{\sigma}}\big] \boldsymbol{A}^{I\gamma}\Big) \\ & + \frac{i}{\hbar} \dot{R}_{\mathrm{n}}^{J\beta} \mathrm{Tr}\Big(\hat{\boldsymbol{\sigma}} [\boldsymbol{A}^{I\gamma}, \boldsymbol{A}^{J\beta}]\Big) \\ & - \frac{i}{\hbar} \dot{R}_{\mathrm{n}}^{J\beta} \hat{\sigma}_{kj} (\xi_k^{I\gamma} - \xi_j^{I\gamma}) A_{jk}^{J\beta} \bigg). \end{aligned} \tag{48}$$

From Eqs. (43), (45), and (48), we can evaluate the time derivative of angular momentum in Eq. (23). Specifically, we see that Eq. (43) cancels with the first term in Eq. (48) and the phase-dependent terms (depending on ξ) in Eqs. (45) and (48) cancel as well. The remaining terms are

$$\begin{aligned} \dot{j}_{\mathrm{tot}}^{\alpha} &= \sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma} \mathrm{Tr}\left(\hat{\boldsymbol{\sigma}} R_{\mathrm{n}}^{I\eta} \dot{R}_{\mathrm{n}}^{J\beta} \left(\frac{\partial \boldsymbol{A}^{I\gamma}}{\partial R_{\mathrm{n}}^{J\beta}} - \frac{\partial \boldsymbol{A}^{J\beta}}{\partial R_{\mathrm{n}}^{I\gamma}} + \frac{i}{\hbar} \Big[\boldsymbol{A}^{I\gamma}, \boldsymbol{A}^{J\beta} \Big] \right) \right) \\ &= -\sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma} \mathrm{Tr}\Big(\hat{\boldsymbol{\sigma}} R_{\mathrm{n}}^{I\eta} \dot{R}_{\mathrm{n}}^{J\beta} \boldsymbol{\Omega}^{I\gamma J\beta} \Big). \end{aligned} \tag{49}$$

As above, the non-Abelian Berry curvature appears, and in this case, the conservation of angular momentum is implied by the fact that the non-Abelian Berry curvature vanishes in the limit of a complete set of adiabatic states.

C. Independence of choice of gauge

Before concluding this section, it is crucial to emphasize that the above results do not depend in any way on the gauge ξ in Eqs. (25) and (26). To the seasoned practitioner of Ehrenfest (or Ehrenfest based) dynamics,[45] this may not be surprising because Eqs. (17)–(19) hold in any basis whatsoever. At the risk of redundancy, for the sake of completeness, let us show this result explicitly by imagining that we rotate our old set of basis states to a new set of basis states with a unitary matrix $\left|\psi_{\bar{j}}\right\rangle = \sum_k |\psi_k\rangle \overline{U}_{k\bar{j}}$. In the new basis, the density matrix, the electronic Hamiltonian, and the Berry connection take the following forms:

$$\overline{\boldsymbol{\sigma}} = \overline{\boldsymbol{U}}^{\dagger} \hat{\boldsymbol{\sigma}} \overline{\boldsymbol{U}}, \tag{50}$$

$$\overline{\boldsymbol{V}} = \overline{\boldsymbol{U}}^{\dagger} \hat{\boldsymbol{V}} \overline{\boldsymbol{U}}, \tag{51}$$

$$\overline{\boldsymbol{A}} = \overline{\boldsymbol{U}}^{\dagger} \boldsymbol{A} \overline{\boldsymbol{U}} + i\hbar \overline{\boldsymbol{U}}^{\dagger} \nabla_{\mathrm{n}} \overline{\boldsymbol{U}}. \tag{52}$$

Using Eqs. (50)–(52) in Eq. (18), we can readily show that the equation of motion for the nuclear momentum is unchanged,

$$\begin{aligned} \dot{P}_{\mathrm{n}}^{I\alpha} &= -\mathrm{Tr}\left(\overline{\boldsymbol{U}}^{\dagger} \hat{\boldsymbol{\sigma}} \overline{\boldsymbol{U}} \frac{\partial \hat{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}} \overline{\boldsymbol{U}} \right) + \frac{i}{\hbar} \mathrm{Tr}\Big(\overline{\boldsymbol{\sigma}} \Big[\overline{\boldsymbol{U}}^{\dagger} \boldsymbol{A}^{I\alpha} \overline{\boldsymbol{U}}, \overline{\boldsymbol{V}} \Big] \Big) & (53) \\ &= -\mathrm{Tr}\left(\overline{\boldsymbol{\sigma}} \frac{\partial \overline{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}} \right) + \frac{i}{\hbar} \mathrm{Tr}\Big(\overline{\boldsymbol{\sigma}} \big[\overline{\boldsymbol{A}}^{I\alpha}, \overline{\boldsymbol{V}} \big] \Big). & (54) \end{aligned}$$

Here, we used the following relationship:

$$\nabla_{\mathrm{n}} \overline{\boldsymbol{V}} = \overline{\boldsymbol{U}}^{\dagger} \nabla_{\mathrm{n}} \hat{\boldsymbol{V}} \overline{\boldsymbol{U}} - \Big[\overline{\boldsymbol{U}}^{\dagger} \nabla_{\mathrm{n}} \overline{\boldsymbol{U}}, \overline{\boldsymbol{V}} \Big]. \tag{55}$$

Next, we can show that the equation of motion for the electronic density matrix propagation is also independent of basis. By definition,

$$\begin{aligned} \dot{\overline{\boldsymbol{\sigma}}} &= \overline{\boldsymbol{U}}^{\dagger} \dot{\hat{\boldsymbol{\sigma}}} \overline{\boldsymbol{U}} + \dot{\boldsymbol{R}}_{\mathrm{n}} \Big(\nabla_{\mathrm{n}} \overline{\boldsymbol{U}}^{\dagger} \hat{\boldsymbol{\sigma}} \overline{\boldsymbol{U}} + \overline{\boldsymbol{U}}^{\dagger} \hat{\boldsymbol{\sigma}} \nabla_{\mathrm{n}} \overline{\boldsymbol{U}} \Big) & (56) \\ &= \overline{\boldsymbol{U}}^{\dagger} \dot{\hat{\boldsymbol{\sigma}}} \overline{\boldsymbol{U}} - \left[\sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^I}{M_I} \cdot \overline{\boldsymbol{U}}^{\dagger} \nabla_{\mathrm{I}} \overline{\boldsymbol{U}}, \overline{\boldsymbol{\sigma}} \right]. & (57) \end{aligned}$$

Now, using Eqs. (50)–(52) together with Eq. (19), it follows that

$$\begin{aligned} \overline{\boldsymbol{U}}^{\dagger} \dot{\hat{\boldsymbol{\sigma}}} \overline{\boldsymbol{U}} &= -\frac{i}{\hbar} \left[\overline{\boldsymbol{V}} - \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^I}{M_I} \cdot \overline{\boldsymbol{U}}^{\dagger} \boldsymbol{A}^I \overline{\boldsymbol{U}}, \overline{\boldsymbol{\sigma}} \right] & (58) \\ &= -\frac{i}{\hbar} \left[\overline{\boldsymbol{V}} - \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^I}{M_I} \cdot \overline{\boldsymbol{A}}^I, \overline{\boldsymbol{\sigma}} \right] + \left[\sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^I}{M_I} \cdot \overline{\boldsymbol{U}}^{\dagger} \nabla_{\mathrm{I}} \overline{\boldsymbol{U}}, \overline{\boldsymbol{\sigma}} \right]. & (59) \end{aligned}$$

Thus, if we plug Eq. (59) into Eq. (57), we find the desired result,

$$\dot{\overline{\boldsymbol{\sigma}}} = -\frac{i}{\hbar} \left[\overline{\boldsymbol{V}} - \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^I}{M_I} \cdot \overline{\boldsymbol{A}}^I, \overline{\boldsymbol{\sigma}} \right]. \tag{60}$$

III. A REALISTIC WINDOW WITH A TRUNCATED NUMBER OF ADIABATIC BASIS FUNCTIONS

In Sec. II, we showed that both linear momentum and angular momentum are conserved for the Ehrenfest equations of motion [Eqs. (3)–(5)] postulated in a complete electronic Hilbert space. In practice, however, a strictly diabatic basis[46–48] and a complete set of adiabatic states are generally not available; one almost always works in a truncated basis of adiabatic electronic states. In such a case, when studying chemical systems using the above formalism, one might suppose that the linear and angular momentum will not be conserved according to Eqs. (39) and (49), and thus, one might inevitably question the accuracy of such dynamics.

Now, in order to conserve momentum, it is fairly straightforward to guess a solution. Namely, the culprit that has appeared above is the non-Abelian Berry curvature, and given Eq. (39), it is fairly straightforward to guess that we ought to damp the nuclear equation of motion by the non-Abelian Berry curvature,

$$\ddot{R}_{\mathrm{n}}^{\alpha} \to \ddot{R}_{\mathrm{n}}^{\alpha} + \sum_{IJ\beta} \mathrm{Tr}\Big(\hat{\boldsymbol{\sigma}} \dot{R}_{\mathrm{n}}^{J\beta} \boldsymbol{\Omega}^{I\alpha J\beta} \Big), \tag{61}$$

or some variation thereof. Indeed, such equations have been derived by a Lagrangian formulation[1] and a path integral formulation.[2] The interested reader can find a proper derivation therein, but for our purposes, the correct Ehrenfest equations of motion can be heuristically derived from the following effective (non-linear) Hamiltonian $\hat{\boldsymbol{H}}$ in the adiabatic representation:

$$\begin{aligned}\hat{\boldsymbol{H}} =&\sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I\,2}}{2M_I} - \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I}\cdot\boldsymbol{A}^{I}}{M_I} + \sum_I \mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\boldsymbol{A}^{I}\big)\cdot\frac{\boldsymbol{A}^{I}}{M_I}\\ &-\sum_I \frac{1}{2M_I}\big[\mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\boldsymbol{A}^{I}\big)\big]^2 + \hat{\boldsymbol{V}}.\end{aligned} \tag{62}$$

The corresponding expectation value of the energy E is

$$E = \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I\,2}}{2M_I} + \mathrm{Tr}\left[\hat{\boldsymbol{\sigma}}\left(\hat{\boldsymbol{V}} - \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I}\cdot\boldsymbol{A}^{I}}{M_I}\right)\right] + \sum_I \frac{1}{2M_I}\big[\mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\boldsymbol{A}^{I}\big)\big]^2. \tag{63}$$

The equations of motion for $(\boldsymbol{R}_{\mathrm{n}}, \boldsymbol{P}_{\mathrm{n}})$ are

$$\dot{\hat{\boldsymbol{\sigma}}} = -\frac{i}{\hbar}\left[\hat{\boldsymbol{V}} - \sum_I \frac{\boldsymbol{P}_{\mathrm{n}}^{I}\cdot\boldsymbol{A}^{I}}{M_I} + \sum_I \mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\boldsymbol{A}^{I}\big)\cdot\frac{\boldsymbol{A}^{I}}{M_I}, \hat{\boldsymbol{\sigma}}\right], \tag{64}$$

$$\dot{R}_{\mathrm{n}}^{I\alpha} = \frac{\partial E}{\partial P_{\mathrm{n}}^{I\alpha}} = \frac{P_{\mathrm{n}}^{I\alpha}}{M_I} - \mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\boldsymbol{A}^{I\alpha}}{M_I}\right), \tag{65}$$

$$\begin{aligned}\dot{P}_{\mathrm{n}}^{I\alpha} &= -\frac{\partial E}{\partial R_{\mathrm{n}}^{I\alpha}}\\ &= -\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\left(\frac{\partial\hat{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}} - \sum_{J\beta}\frac{\big[P_{\mathrm{n}}^{J\beta} - \mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\boldsymbol{A}^{J\beta}\big)\big]}{M_J}\frac{\partial\boldsymbol{A}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}}\right)\right).\end{aligned} \tag{66}$$

According to Eq. (65), we find a difference between the kinetic and canonical momentum. If we now change variables from the canonical to the kinetic momentum,[49]

$$\pi_{\mathrm{n}}^{I\alpha} = P_{\mathrm{n}}^{I\alpha} - \mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\boldsymbol{A}^{I\alpha}\big), \tag{67}$$

we can rewrite the equations of motion in terms of $(\boldsymbol{R}_{\mathrm{n}}, \boldsymbol{\pi}_{\mathrm{n}})$,

$$\dot{\hat{\boldsymbol{\sigma}}} = \frac{-i}{\hbar}\left[\hat{\boldsymbol{V}} - \sum_{I\alpha}\frac{\boldsymbol{\pi}_{\mathrm{n}}^{I\alpha}}{M_I}\cdot\boldsymbol{A}^{I\alpha}, \hat{\boldsymbol{\sigma}}\right], \tag{68}$$

$$\dot{R}_{\mathrm{n}}^{I\alpha} = \frac{\pi_{\mathrm{n}}^{I\alpha}}{M_I}, \tag{69}$$

$$\dot{\pi}_{\mathrm{n}}^{I\alpha} = \dot{P}_{\mathrm{n}}^{I\alpha} - \mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{A}}^{I\alpha}\big) - \mathrm{Tr}\big(\dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{A}^{I\alpha}\big) \tag{70}$$

$$\begin{aligned}&= -\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\partial\hat{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}}\right) + \sum_{J\beta}\frac{\pi_{\mathrm{n}}^{J\beta}}{M_J}\mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\boldsymbol{\Omega}^{I\alpha J\beta}\big)\\ &\quad + \frac{i}{\hbar}\mathrm{Tr}\big(\big[\hat{\boldsymbol{V}}, \hat{\boldsymbol{\sigma}}\big]\boldsymbol{A}^{I\alpha}\big).\end{aligned} \tag{71}$$

These are the equations of motion derived properly in Refs. 1 and 2. Compared to the standard adiabatic Ehrenfest equations in Eqs. (17)–(19), the equation of motion for the kinetic momentum $\pi_{\mathrm{n}}^{I\alpha}$ takes on an additional term that depends on the non-Abelian Berry curvature [in analogy to what was guessed in Eq. (61)]. Of course, in the limit of a complete set of states, the non-Abelian Berry curvature goes to zero and Eqs. (68)–(71) reduce to the standard adiabatic Ehrenfest equations in Eqs. (17)–(19). For the sake of completeness (and at the slight risk of redundancy), let us now demonstrate that Eqs. (68)–(71) formally obey linear and angular momentum conservation.

A. Linear momentum conservation

We first examine the linear momentum conservation. Based on the expression for $\dot{\pi}_{\mathrm{n}}^{I\alpha}$ in Eq. (70),

$$\dot{P}_{\mathrm{tot}}^{\alpha} = \sum_I \dot{\pi}_{\mathrm{n}}^{I\alpha} + \mathrm{Tr}\big(\dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{P}_{\mathrm{e}}^{\alpha}\big) + \mathrm{Tr}\big(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{P}}_{\mathrm{e}}^{\alpha}\big) \tag{72}$$

$$\begin{aligned}&= \sum_I \dot{P}_{\mathrm{n}}^{I\alpha} + \mathrm{Tr}\left[\dot{\hat{\boldsymbol{\sigma}}}\left(\boldsymbol{P}_{\mathrm{e}}^{\alpha} - \sum_I \boldsymbol{A}^{I\alpha}\right)\right]\\ &\quad + \mathrm{Tr}\left[\hat{\boldsymbol{\sigma}}\left(\dot{\boldsymbol{P}}_{\mathrm{e}}^{\alpha} - \sum_I \dot{\boldsymbol{A}}^{I\alpha}\right)\right].\end{aligned} \tag{73}$$

Now, evaluate each term in Eq. (73).

- From Eq. (66), the first term in Eq. (73) is

$$\begin{aligned}\sum_I \dot{P}_{\mathrm{n}}^{I\alpha} &= -\sum_I \mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\partial\hat{\boldsymbol{V}}}{\partial R_{\mathrm{n}}^{I\alpha}}\right) + \sum_{IJ\beta}\frac{\pi_{\mathrm{n}}^{J\beta}}{M_J}\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\partial\boldsymbol{A}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}}\right)\\ &= \sum_{IJ\beta}\dot{R}_{n}^{J\beta}\,\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\partial\boldsymbol{A}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}}\right)\end{aligned} \tag{74}$$

  for a translationally invariant potential energy surface.
- Rearranging Eq. (27) and using Eq. (35), the second term in Eq. (73) is

$$\begin{aligned}\mathrm{Tr}\left[\dot{\hat{\boldsymbol{\sigma}}}\left(\boldsymbol{P}_{\mathrm{e}}^{\alpha} - \sum_I \boldsymbol{A}^{I\alpha}\right)\right] &= \sum_{Ijk}\dot{\hat{\sigma}}_{kj}\xi_k^{I\alpha}\delta_{jk}\\ &= -\frac{i}{\hbar}\sum_{IJ\beta jk}\hat{\sigma}_{kj}\dot{R}_{\mathrm{n}}^{J\beta}\big(\xi_k^{I\alpha} - \xi_j^{I\alpha}\big)A_{jk}^{J\beta}.\end{aligned} \tag{75}$$

- Rearranging Eq. (29), the third term in Eq. (73) is

$$\begin{aligned}\mathrm{Tr}\left[\hat{\boldsymbol{\sigma}}\left(\dot{\boldsymbol{P}}_{\mathrm{e}}^{\alpha} - \sum_I \dot{\boldsymbol{A}}^{I\alpha}\right)\right] &= \sum_{Ijk}\hat{\sigma}_{kj}\dot{\xi}_k^{I\alpha}\delta_{jk}\\ &= \sum_{IJ\beta jk}\hat{\sigma}_{kj}\dot{R}_{\mathrm{n}}^{J\beta}\xi_k^{J\beta,I\alpha}\delta_{jk}.\end{aligned} \tag{76}$$

  If we add Eqs. (74)–(76) together, the time dependence of the total linear momentum in Eq. (73) becomes

$$\begin{aligned}\dot{P}_{\mathrm{tot}}^{\alpha} &= \sum_{IJ\beta}\dot{R}_{n}^{J\beta}\,\mathrm{Tr}\left(\hat{\boldsymbol{\sigma}}\frac{\partial\boldsymbol{A}^{J\beta}}{\partial R_{\mathrm{n}}^{I\alpha}}\right) + \sum_{IJ\beta jk}\hat{\sigma}_{kj}\dot{R}_{\mathrm{n}}^{J\beta}\\ &\quad\times\left(\xi_k^{J\beta,I\alpha}\delta_{jk} - \frac{i}{\hbar}\big(\xi_k^{I\alpha} - \xi_j^{I\alpha}\big)A_{jk}^{J\beta}\right) = 0.\end{aligned} \tag{77}$$

Here, we have used the relation in Eq. (40). In the end, the proposed equations of motion [Eqs. (68)–(71)] strictly conserve linear momentum within a truncated space of adiabatic states.

B. Angular momentum conservation

To investigate angular momentum conservation, we must be very careful now to use Eq. (6) instead of Eq. (7) for the nuclear angular momentum, as the two definitions are no longer equivalent. The derivative of the total angular momentum is now

$$\dot{\boldsymbol{J}}^{\alpha}_{\text{tot}} = \sum_{\eta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{\pi}^{I\gamma}_{\text{n}} + \text{Tr}\left(\hat{\boldsymbol{\sigma}}\dot{\boldsymbol{J}}^{\alpha}_{\text{e}} + \dot{\hat{\boldsymbol{\sigma}}}\boldsymbol{J}^{\alpha}_{\text{e}}\right) \tag{78}$$

$$\begin{aligned} &= \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{P}^{I\gamma}_{\text{n}} + \text{Tr}\left[\hat{\boldsymbol{\sigma}}\left(\dot{\boldsymbol{J}}^{\alpha}_{\text{e}} - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{\boldsymbol{A}}^{I\gamma}\right)\right] \\ &\quad + \text{Tr}\left[\dot{\hat{\boldsymbol{\sigma}}}\left(\boldsymbol{J}^{\alpha}_{\text{e}} - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \boldsymbol{A}^{I\gamma}\right)\right]. \end{aligned} \tag{79}$$

As mentioned above, we must evaluate each term in Eq. (79).

- From Eq. (66), the first term in Eq. (79) can be written as

  $$\sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{P}^{I\gamma}_{\text{n}} = \sum_{IJjk\eta\beta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{R}^{J\beta}_{\text{n}} \hat{\sigma}_{kj} \frac{\partial A^{J\beta}_{jk}}{\partial R^{I\gamma}_{\text{n}}}. \tag{80}$$

  Here, we recognize $-\sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} \text{Tr}\left(\hat{\boldsymbol{\sigma}} R^{I\eta}_{\text{n}} \frac{\partial \hat{\boldsymbol{V}}}{\partial R^{I\gamma}_{\text{n}}}\right) = 0$ due to the isotropy of space.
- Rearranging Eq. (45), we recover for the second term in Eq. (79)

  $$\begin{aligned} \text{Tr}\left[\hat{\boldsymbol{\sigma}}\left(\dot{\boldsymbol{J}}^{\alpha}_{\text{e}} - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{\boldsymbol{A}}^{I\gamma}\right)\right] &= \sum_{IJjk\eta\beta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{R}^{J\beta}_{\text{n}} \hat{\sigma}_{kj} \\ &\quad \times \left[-\frac{\partial A^{J\beta}_{jk}}{\partial R^{I\gamma}_{\text{n}}} + \frac{i}{\hbar}(\xi^{I\gamma}_{k} - \xi^{I\gamma}_{j}) A^{J\beta}_{jk}\right]. \end{aligned} \tag{81}$$

- According to Eqs. (46) and (47), the third term in Eq. (79) becomes

  $$\begin{aligned} &\text{Tr}\left[\dot{\hat{\boldsymbol{\sigma}}}\left(\boldsymbol{J}^{\alpha}_{\text{e}} - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \boldsymbol{A}^{I\gamma}\right)\right] \\ &\quad = -\frac{i}{\hbar} \sum_{IJ\eta\gamma\beta jk} \varepsilon_{\alpha\eta\gamma} R^{I\eta}_{\text{n}} \dot{R}^{J\beta}_{\text{n}} \hat{\sigma}_{kj} (\xi^{I\gamma}_{k} - \xi^{I\gamma}_{j}) A^{J\beta}_{jk}. \end{aligned} \tag{82}$$

Comparing Eqs. (80)–(82), we find that when adding them together, the first term of Eq. (81) cancels with Eq. (80). The second term of Eq. (81) cancels with Eq. (82), and hence, $\dot{J}^{\alpha}_{\text{tot}} = 0$. In the end, with translation symmetry and isotropy of space, propagating the equations of motion in Eqs. (68)–(71) conserves both linear and angular momentum—even for a truncated set of states.

C. Choice of gauge and basis

As we found when running Ehrenfest dynamics with a complete set of basis states, the above result holds for any choice of gauge in Eqs. (25) and (26); and, more generally, if one considers Eqs. (68)–(71), one finds that these equations are completely unchanged if one rotates the adiabatic states into some other basis set [just as was found for Eqs. (17)–(19)]. The same proof is appropriate, noting only that when we change basis, the non-Abelian Berry curvature has the remarkable property (as shown in Sec. S2 of the supplementary material) that

$$\bar{\boldsymbol{\Omega}}^{I\alpha J\beta} = \bar{\boldsymbol{U}}^{\dagger} \boldsymbol{\Omega}^{I\alpha J\beta} \bar{\boldsymbol{U}}. \tag{83}$$

The above-mentioned Ehrenfest theory depends only on the window of electronic states chosen (but not on the choice of basis states within that window).

IV. A DIFFERENT EHRENFEST APPROXIMATION

Before studying several applications of the theory above, it is worth emphasizing that Eqs. (68)–(71) are not the only possible Ehrenfest approximations. In fact, in Eqs. (S30)–(S34) of the supplementary material, we study a different flavor of Ehrenfest approximations,[50–52] where the electronic Hamiltonian and the semiclassical energies in Eqs. (62) and (63) are replaced with

$$\hat{\boldsymbol{H}} = \sum_{I} \frac{\boldsymbol{P}^{I\,2}_{\text{n}}}{2M_I} - \sum_{I} \frac{\boldsymbol{P}^{I}_{\text{n}} \cdot \boldsymbol{A}^{I}}{M_I} + \sum_{I} \frac{\boldsymbol{A}^{I^2}}{2M_I} + \hat{\boldsymbol{V}}, \tag{84}$$

$$E = \sum_{I} \frac{\boldsymbol{P}^{I^2}_{\text{n}}}{2M_I} + \text{Tr}\left[\hat{\boldsymbol{\sigma}}\left(\sum_{I} \frac{-2\boldsymbol{P}^{I}_{\text{n}} \cdot \boldsymbol{A}^{I} + \boldsymbol{A}^{I^2}}{2M_I} + \hat{\boldsymbol{V}}\right)\right]. \tag{85}$$

In the supplementary material, we show that the resulting equations still conserve the total linear and angular momentum—*but only with the choice of gauge* $\xi = 0$ *in Eqs. (25) and (26)*. Note that the resulting dynamics are also *not* invariant to changing the adiabatic basis by a unitary transformation. More discussion regarding the crucial choice of gauge and its implication for *ab initio* on-the-fly dynamics are given in Sec. VII A.

V. A TRAVELING HYDROGEN ATOM

In Sec. VI, we will present an *ab initio* calculation exploring momentum conservation numerically. Before presenting such data, however, it is conceptually helpful to first treat the simplest, analytical example of Ehrenfest theory: the example of a hydrogen atom traveling at a constant velocity. For such a system, $\hat{\boldsymbol{V}}$ and $\boldsymbol{A}$ are constants, and neither the electronic state nor the momentum should change as a function of time. Thus, as far as the electronic system is concerned, we must find $\dot{\hat{\boldsymbol{\sigma}}} = 0$, which implies that [according to Eq. (19)] the electronic wavefunction must be an eigenvector of $\hat{\boldsymbol{V}} - \sum_\alpha \dot{R}_{\rm n}^\alpha \cdot \boldsymbol{A}^\alpha$. Mathematically, we, therefore, conclude

$$\left[\hat{\boldsymbol{V}}, \hat{\boldsymbol{\sigma}}\right] = \left[\sum_\alpha \dot{R}_{\rm n}^\alpha \cdot \boldsymbol{A}^\alpha, \hat{\boldsymbol{\sigma}}\right] \tag{86}$$

so that the electronic population in Eq. (19) does not change with the translation of the hydrogen atom.

Let us now examine how momentum changes with time according to the dynamics in Eq. (18). The first term $-\operatorname{Tr}\left(\hat{\boldsymbol{\sigma}} \frac{\partial \hat{\boldsymbol{V}}}{\partial R_{\rm n}^\alpha}\right)$ in Eq. (18) is zero due to the translation-invariant potential. For the remaining term in Eq. (18), $\frac{i}{\hbar} \operatorname{Tr}\left(\left[\hat{\boldsymbol{V}}, \hat{\boldsymbol{\sigma}}\right] \boldsymbol{A}^\alpha\right)$, we plug in Eq. (86), and Eq. (18) then becomes

$$\dot{\boldsymbol{P}}_{\rm n}^\alpha = \frac{i}{\hbar} \operatorname{Tr}\left(\left[\hat{\boldsymbol{V}}, \hat{\boldsymbol{\sigma}}\right] \boldsymbol{A}^\alpha\right) \tag{87}$$

$$= \frac{i}{\hbar} \sum_\beta \dot{R}_{\rm n}^\beta \operatorname{Tr}\left(\hat{\boldsymbol{\sigma}}\left[\boldsymbol{A}^\alpha, \boldsymbol{A}^\beta\right]\right). \tag{88}$$

As the derivative couplings between certain eigenstates of the hydrogen atom are non-zero (i.e., $1s$ and $3p_x$), Eq. (88) is non-zero. Therefore, using the standard Ehrenfest approach in Eqs. (17)–(19) cannot capture a translating hydrogen atom in a truncated basis: an isolated hydrogen atom changes its momentum during translation.

Now, there are two ways to resolve this issue: (i) One way is to apply electron-translation factor corrections,[53,54] which effectively allows us to replace the Berry connection by zero, $\boldsymbol{A} \to 0$ in Eqs. (18) and (19), so that the wavefunction $\phi(r,t) = \phi_{1s}(r - R(t))$ becomes a stationary state (though admittedly without any electronic momentum),[55,56] and (ii) the other alternative way is to use the effective Ehrenfest equations in Eqs. (68)–(71), according to which the kinetic momentum feels a force from the non-Abelian Berry curvature [Eq. (41)], so that the second term of Eq. (71) becomes

$$\sum_\beta \frac{\pi_{\rm n}^\beta}{M} \operatorname{Tr}\left(\hat{\boldsymbol{\sigma}} \boldsymbol{\Omega}^{\alpha\beta}\right) = \sum_\beta \frac{\pi_{\rm n}^\beta}{M} \operatorname{Tr}\left\{\hat{\boldsymbol{\sigma}}\left(\frac{\partial \boldsymbol{A}^\beta}{\partial R_{\rm n}^\alpha} - \frac{\partial \boldsymbol{A}^\alpha}{\partial R_{\rm n}^\beta} - \frac{i}{\hbar}\left[\boldsymbol{A}^\alpha, \boldsymbol{A}^\beta\right]\right)\right\}. \tag{89}$$

Moreover, for a hydrogen atom, $\boldsymbol{A}$ does not depend on $\boldsymbol{R}_{\rm n}$ so that

$$\sum_\beta \frac{\pi_{\rm n}^\beta}{M} \operatorname{Tr}\left(\hat{\boldsymbol{\sigma}} \boldsymbol{\Omega}^{\alpha\beta}\right) = -\frac{i}{\hbar} \sum_\beta \frac{\pi_{\rm n}^\beta}{M} \operatorname{Tr}\left\{\hat{\boldsymbol{\sigma}}\left(\left[\boldsymbol{A}^\alpha, \boldsymbol{A}^\beta\right]\right)\right\}. \tag{90}$$

The first term on the right-hand side of Eq. (71) is still zero, and thus, using Eqs. (88) and (90), the right-hand side of Eq. (71) is entirely zero. In other words, in order for Ehrenfest dynamics to properly capture a traveling hydrogen atom, one requires inserting the non-Abelian curvature in the equation of motion for the momentum. Presumably, this non-Abelian Berry curvature is not needed in the limit of a complete electronic basis.

VI. RESULTS

To verify and further investigate angular momentum conservation, we have performed Ehrenfest dynamics with [Eqs. (68)–(71)] and without the Berry force [Eqs. (17)–(19)] for the methoxy radical, a doublet that exhibits a Kramers degeneracy. The initial geometry was optimized with the hydrogens on the carbon at the unrestricted Hartree–Fock level of theory. We calculated the relevant ground state using generalized Hartree–Fock (GHF) theory, i.e., we assume a HF ansatz where each orbital can be a linear combination of a spin-up and spin-down spatial orbital so that S_z is no longer a good quantum number. We used the 6-31G basis set, and we included SOC.[57,58] GHF is the HF equivalent of non-collinear density-functional theory.[59] Note that the GHF ansatz converges to one state of the doublet (hereafter denoted $|GHF\rangle$); the other state was generated by applying a time reversal symmetry operator (hereafter denoted $|TGHF\rangle$). Note also that because the energies of the Kramers doublet ground states are degenerate, the last term in Eq. (71) is zero. The initial velocity was set to be the direction corresponding to the lowest vibrational mode with an initial kinetic energy of 0.005 a.u. (≈1491 K); see Fig. 1(a). The dynamics were performed with a step size of 5 a.u. (0.121 fs). The initial amplitude was fixed as $\boldsymbol{c} = (\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}})$ in the GHF/TGHF basis, which gives an initial density matrix $\boldsymbol{\sigma} = \boldsymbol{c}\boldsymbol{c}^\dagger = \begin{pmatrix} \frac{1}{2}, -\frac{i}{2} \\ \frac{i}{2}, \frac{1}{2} \end{pmatrix}$. The non-Abelian Berry curvature in Eq. (71) was computed by a finite difference approach. The calculations were performed in a local branch of Q-Chem 6.0.[60]

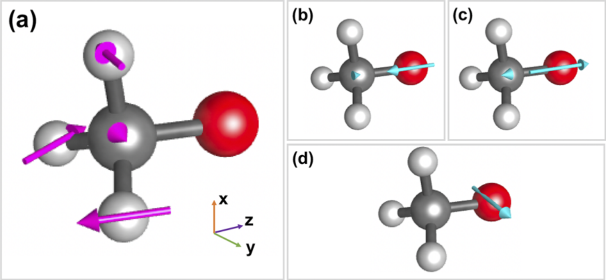

FIG. 1. (a) (Magenta) The displacements of the first vibrational mode along which we propagate dynamics. In (b), we plot (cyan) the atom-based spin magnetic moments for a single GHF+SOC solution, and in (c), we plot the corresponding moments for its degenerate time-reversed solution. (d) The weighted spin magnetic moments on each atom using the initial amplitude $\boldsymbol{c} = (\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}})$.

In Figs. 1(b) and 1(c), using cyan arrows, we plot the spin magnetic moments on each atom according to a Mulliken-like scheme[61] at time zero for each of the two double states: one doublet state is plotted in (b), and the time reversed state is plotted in (c) (which is, of course, in the exact opposite direction). In Fig. 1(d), we plot the weighted spin magnetic moments on each atom using the initial amplitude, $\boldsymbol{c} = (\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}})$. In Fig. S1, we plot the change in the amplitudes and the population during dynamics. The Ehrenfest average of the atom-based spin magnetic moments rotates in the xy plane, as also shown in Fig. S1 of the supplementary material.

In Fig. 2, we plot the change in the angular momentum and linear momentum during the trajectory. To begin our discussion, consider first the case where the Berry force is not included [Figs. 2(a), 2(c), and 2(e)]. When the Berry force is not included, the nuclear angular momentum is calculated from the canonical momentum $\boldsymbol{P}_{\rm n}$, and there is no change in the nuclear momentum (red solid line).

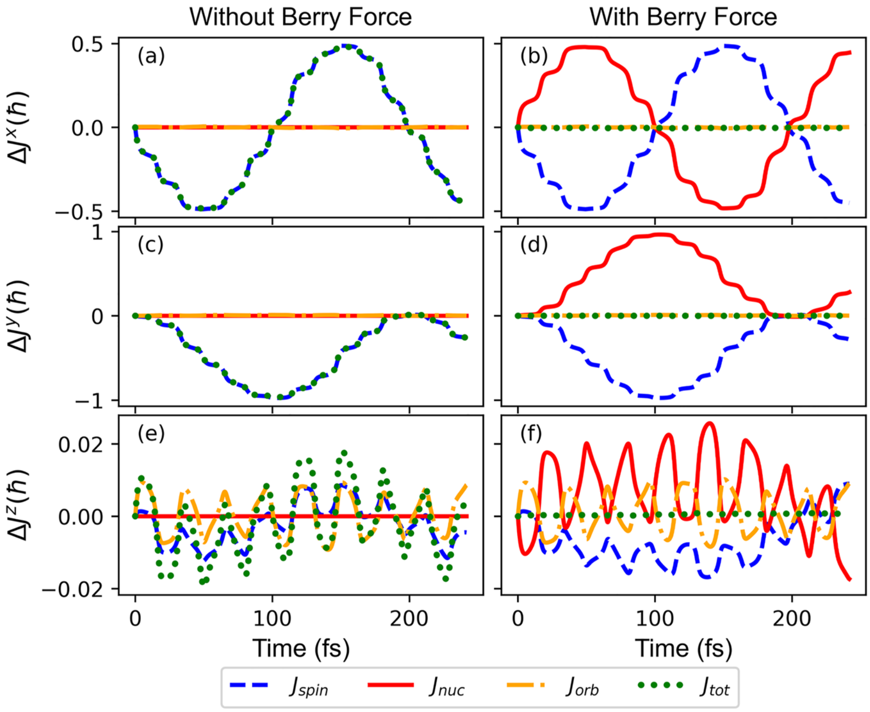

FIG. 2. Change in the real-time angular momentum $\Delta J^{\alpha}(t) = J^{\alpha}(t) - J^{\alpha}(0)$ (relative to time zero) according to an Ehrenfest trajectory simulating methoxy radical moving along its lowest normal mode vibration. The nonzero initial values of components of the angular momentum are listed: $J^{y}_{\text{spin}} = 0.4811\ \hbar$, $J^{y}_{\text{orb}} = -0.0054\ \hbar$, $J^{x}_{\text{nuc}} = 0.0075\ \hbar$, and $J^{z}_{\text{nuc}} = -0.0048\ \hbar$. The three panels (a), (c), and (e) on the left exclude the non-Abelian Berry force and correspond to the Cartesian coordinates *x*, *y*, and *z* shown in Fig. 1 [and the same for (b), (d), and (f) but now including the Berry force]. Without a Berry force, the total angular momentum is not conserved; with a Berry force, the total angular momentum is conserved. In (b) and (d), when we correctly include the Berry force, we find that the nuclear and spin degrees of freedom transfer angular momentum between each other. In (f), the nuclear, spin, and electronic orbital degrees of freedom all exchange angular momentum. Comparing (e) and (f), we observe that the electronic spin changes differently with or without a Berry force; this change arises because adding the Berry force can change the nuclear motion and yield a reasonably different trajectory.

Note that the canonical momentum is conserved in this example because the two basis states are degenerate. In the more general case, with multiple non-degenerate states, the canonical momentum would not be conserved, as previously shown in Ref. 41. In blue, we plot the electronic spin angular momentum; in orange, we plot the electronic orbital angular momentum. In Figs. 2(a) and 2(c), the electronic spin angular momentum changes tracks exactly with the total angular momentum (i.e., the electronic orbital angular momentum is effectively constant). In Fig. 2(e), both the electronic orbital and spin angular momentum fluctuate, and the total angular momentum appears more chaotic.

Next, consider Figs. 2(b), 2(d), and 2(f) where the Berry force is included. Here, we see that the nuclear angular momentum [as calculated from the kinetic momentum $\boldsymbol{\pi}_{\text{n}}$ in Eq. (71)] changes with time, and the Berry force captures the angular momentum transfer from the electronic spin/orbital angular momentum to the nuclear angular momentum. As must be true, the total angular momentum is constant and conserved. (In Fig. S2, we also show numerically that the total linear momentum is conserved when the Berry force is included.) Of most importance, when comparing Figs. 2(e) and 2(f), we observe that the electronic spin changes noticeably depending on whether or not a Berry force is included, clearly emphasizing the importance of going beyond standard BO dynamics (and including Berry forces) in the presence of non-trivial spin degrees of freedom.

VII. DISCUSSION

A. Choice of phase/gauge ζ

At this point, it is essential for us to discuss our choice of phase. For the case of a real Hamiltonian, one can choose the Hamiltonian eigenfunctions to be real as well (in a smooth fashion), and thus, one can ignore the gauge choice ξ in Eqs. (25) and (26). However, in the case of a complex-valued Hamiltonian, the choice of phase is far more complicated. Obviously, Berry phases can appear (which should not be ignored) if one moves around in a closed loop.[62] Even more importantly, for our semiclassical purposes, the choice of phase will always be somewhat uncontrollable for *ab initio* on-the-fly dynamics because one must pick the phase of the resulting wavefunction at each step with very limited information: one does not have the capacity to make sure that the phases of wavefunctions are matched for similar nuclear configurations and one cannot easily attach different phase factors for translational, rotational, and internal motions. Thus, at the end of the day, for the most part,

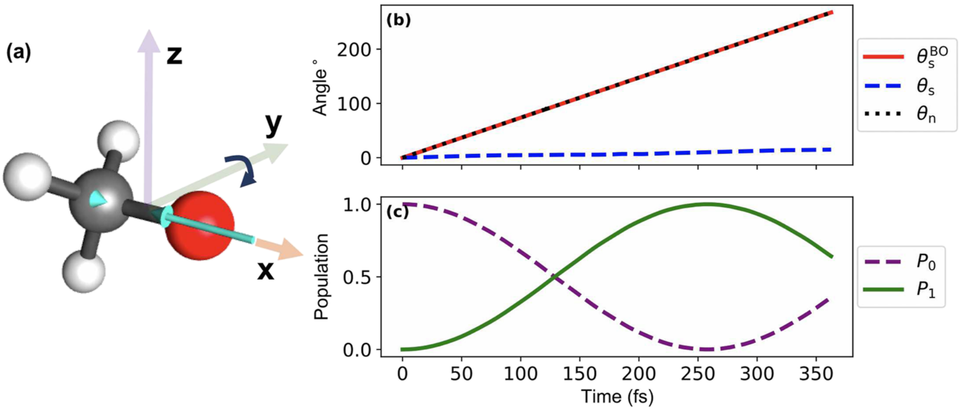

FIG. 3. (a) The orientation of the methoxy radical molecule, the rotation direction, and atom-based spin magnetic moments (cyan arrows) at the initial step. (b) The rotational angles of the molecule (black dotted line), the (completely unphysical) total spin vector as predicted by BO dynamics (red solid line), and the (more physical) total spin vector as calculated by Ehrenfest dynamics (blue dashed line). (c) The populations for the Kramers doublet states (P_0 and P_1) with time from the Ehrenfest dynamics.

the usual approach is simply to align the phases of nuclear wavefunctions at two slightly different geometries (separated by one time step) using a parallel transport. Parallel transport does not satisfy $\xi = 0$ in Eqs. (25) and (26). Therefore, when running semiclassical dynamics, one seeks equations of motion that are insensitive to the gauge and to that end, as a practical matter, the Ehrenfest equations in Eqs. (68)–(71) have a huge advantage over those in Eqs. (84) and (85).

B. Ehrenfest vs BO dynamics

Finally, before concluding, in order to numerically emphasize the need to go beyond the BO approximation when treating spin degrees of freedom, we will report one more simulation. Let us orient the methoxy radical molecule with the CO bond aligned along the x axis; within such a frame, a GHF calculation with SOC reveals that all spin magnetic moments point along the x axis [Fig. 3(a)]. Let us now apply a rotational force around the y axis, with the initial nuclear angular momentum $\boldsymbol{J}_{\text{nuc}} = (0.0, 39.28\hbar, 0.0)$, and propagate the resulting dynamics with both BO and Ehrenfest. For both sets of dynamics, we include the corresponding Berry force (the on-diagonal Berry force for BO dynamics[36,58] and the non-Abelian Berry force[1,2] for Ehrenfest dynamics) so that both trajectories conserve the total angular momentum. For additional trajectory data, and in particular for the time-dependent state populations and an analysis of the spin angular momentum in terms of relevant $|GHF\rangle$ and $|TGHF\rangle$ wavefunctions, see the supplementary material.

In Fig. 3(b), as a function of time, we plot the rotational angle for the molecule as well as the total expectation values for the spin vectors according to both BO and Ehrenfest dynamics. As one might expect, within the BO approximation (as calculated along a continuous GHF+SOC state), the total spin vector $\mathbf{S}_{\text{BO}}$ rotates with the molecule (red line). This prediction is of course completely unphysical. In reality, the spin direction does not change instantaneously with the molecular frame but rather changes depending on the spin–orbit coupling. This slow change of direction is correctly captured by the Ehrenfest dynamics (blue dashed line). Finally, this BO failure can be verified in Fig. 3(c), where we plot population as a function of time and show that, by the time the molecule has rotated 180° (244 fs), the populated Kramers doublet has effectively switched, which represents a complete breakdown of the BO approximation.

VIII. CONCLUSIONS

In this paper, we have demonstrated that, in order for Ehrenfest dynamics to conserve the linear or angular momentum in a truncated basis, the nuclei must experience a force arising from the non-Abelian curvature $\boldsymbol{\Omega}$ [as presented in Eqs. (68)–(71)]. This result is independent of the choice of gauge for the electronic states in Eqs. (25) and (26) or any basis transformation. As examples, we have studied both the traveling hydrogen atom (analytically) and the methoxy radical (numerically). Both examples make clear that the non-Abelian curvature term is needed, and, in the case of the methoxy radical, our data also highlight that the evolution of the spin degrees of freedom can be different as a result. Looking forward, the present results should have an immediate impact in a variety of fields where nuclear, electronic, and spin motions are all entangled, perhaps especially for systems displaying chiral-induced spin selectivity.[63,64]

SUPPLEMENTARY MATERIAL

In the supplementary material, we include a proof of Eqs. (40) and (44), a proof of the gauge covariance of the non-Abelian Berry curvature [Eq. (83)], a detailed discussion of the alternative Ehrenfest scheme in Eqs. (84) and (85) vis-a-vis momentum conservation, and more details of the methoxy radical dynamics.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Zhen Tao: Data curation (lead); Methodology (equal); Software (lead); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Xuezhi Bian**: Methodology (equal); Validation (equal); Writing – review & editing (supporting). **Yanze Wu**: Validation (supporting); Writing – review & editing (supporting). **Jonathan Rawlinson**: Conceptualization (supporting); Validation (supporting); Writing – review & editing (supporting). **Robert G. Littlejohn**: Conceptualization (supporting); Validation (supporting); Writing – review & editing (supporting). **Joseph E. Subotnik**: Conceptualization (lead); Methodology (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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