

Total Angular Momentum Conservation in Ehrenfest Dynamics with a Truncated Basis of Adiabatic States

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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^{1,2} 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 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 today 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 documented recently,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 which 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 manifold²⁷ 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 very 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

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 sidenote, 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.

Now, 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 recently showed,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 Born-Oppenheimer at all, but rather exact factorization,^{37–39} where angular momentum exchange was recently explored.⁴⁰ As pointed out in Ref. 36, however, an even simpler resolution to this paradox is that, within BO theory, one must in-

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clude 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 d is not zero, and so the nuclear kinetic momentum π_n is not equivalent to the canonical momentum P_n (recall that $\pi_n = P_n - i\hbar d$). 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 technique) and then to propagate the nuclear kinetic momentum π_n ; the latter step inevitably introduces the Abelian Berry force in the equation of motion for π_n , $F_j^{\text{Berry},I} = i\hbar(\nabla_n \times d_{jj}) \cdot \frac{\pi_n}{M_I}$. 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 background above 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. al⁴¹ have recently shown 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 curvature⁴² 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) slows down the spin change with the nuclear motion.

This paper is organized as follows. In Section 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 the 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 and angular momentum are 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 curvature⁴²). Nevertheless, the analysis below will still be useful insofar as teaching us how to understand how the Ehrenfest equations can take different form 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{H}) and the energy (\tilde{E}) are postulated to be of the form:

$$\tilde{H} = \sum_I \frac{\mathbf{P}_n^{I^2}}{2M_I} + \tilde{V} \quad (1)$$

$$\tilde{E} = \sum_I \frac{\mathbf{P}_n^{I^2}}{2M_I} + \text{Tr}(\tilde{\sigma} \tilde{V}) \quad (2)$$

where we denote the classical nuclear position \mathbf{R}_n and nuclear momentum \mathbf{P}_n . Here and below we use the indices IJ for nuclei and $\alpha\beta\gamma$ for the Cartesian indices xyz . The potential operator $\tilde{V} = \tilde{T}_e + \tilde{V}_{ee} + \tilde{V}_{en} + \tilde{V}_{nn}$ includes the electronic kinetic

energy, electron-electron interaction, and the electron-nuclear Coulomb interaction, and nuclear-nuclear repulsion term, respectively. We use the notation " \sim " 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 $\tilde{\sigma}$ in a diabatic basis.

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

$$\dot{R}_n^{I\alpha} = \frac{\partial \tilde{E}}{\partial P_n^{I\alpha}} = \frac{P_n^{I\alpha}}{M_I} \quad (3)$$

$$\dot{P}_n^{I\alpha} = -\frac{\partial \tilde{E}}{\partial R_n^{I\alpha}} = -\text{Tr} \left(\tilde{\sigma} \frac{\partial \tilde{V}}{\partial R_n^{I\alpha}} \right) \quad (4)$$

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

$$\dot{\tilde{\sigma}} = -\frac{i}{\hbar} [\tilde{V}, \tilde{\sigma}] \quad (5)$$

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

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

$$J_n^\alpha \equiv \sum_{I\beta\gamma} \epsilon_{\alpha\beta\gamma} R_n^{I\beta} M_I \dot{R}_n^{I\gamma} \quad (6)$$

Here $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol. Using Eq. 3 above, it follows that we can also write:

$$J_n^\alpha = \sum_{I\beta\gamma} \epsilon_{\alpha\beta\gamma} R_n^{I\beta} P_n^{I\gamma} \quad (7)$$

$$J_n^\alpha = \sum_{I\beta\gamma} \epsilon_{\alpha\beta\gamma} R_n^{I\beta} P_n^{I\gamma} \quad (8)$$

With Eq.4 and Eq.5, we can now evaluate the time-derivative of the total linear and angular momentum

$$\begin{aligned} \dot{P}_{\text{tot}}^\alpha &= \dot{P}_n^\alpha + \text{Tr} (\tilde{\sigma} \tilde{P}_e^\alpha) \\ &= -\sum_I \text{Tr} \left(\tilde{\sigma} \frac{\partial \tilde{V}}{\partial R_n^{I\alpha}} \right) - \frac{i}{\hbar} \text{Tr} (\tilde{\sigma} [\tilde{P}_e^\alpha, \tilde{V}]) \end{aligned} \quad (9)$$

$$\begin{aligned} \dot{J}_{\text{tot}}^\alpha &= J_n^\alpha + \text{Tr} (\tilde{\sigma} \tilde{J}_e^\alpha) \\ &= \sum_{I\beta\gamma} \epsilon_{\alpha\beta\gamma} R_n^{I\beta} \dot{P}_n^{I\gamma} - \frac{i}{\hbar} \text{Tr} (\tilde{\sigma} [\tilde{J}_e^\alpha, \tilde{V}]) \end{aligned} \quad (10)$$

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

$$[\tilde{P}_n + \tilde{P}_e, \tilde{V}] = 0 \quad (11)$$

$$[\tilde{J}_n + \tilde{J}_e, \tilde{V}] = 0 \quad (12)$$

These equations lead to the following further identities:

$$-\frac{i}{\hbar} [\tilde{P}_e^\alpha, \tilde{V}] = \frac{i}{\hbar} [\tilde{P}_n^\alpha, \tilde{V}] = \frac{\partial \tilde{V}}{\partial R_n^\alpha} \quad (13)$$

$$-\frac{i}{\hbar} [\tilde{J}_e^\alpha, \tilde{V}] = \frac{i}{\hbar} [\tilde{J}_n^\alpha, \tilde{V}] = \sum_{I\beta\gamma} \epsilon_{\alpha\beta\gamma} R_n^{I\beta} \frac{\partial \tilde{V}}{\partial R_n^{I\gamma}} \quad (14)$$

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

B. Adiabatic Representation

The above 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. 11-12. 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,

$$\hat{\sigma} = U^\dagger \tilde{\sigma} U \quad (15)$$

$$\hat{V} = U^\dagger \tilde{V} U \quad (16)$$

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

$$\dot{R}_n^{I\alpha} = \frac{P_n^{I\alpha}}{M_I} \quad (17)$$

$$\begin{aligned} \dot{P}_n^{I\alpha} &= -\text{Tr} \left(U^\dagger \tilde{\sigma} U U^\dagger \frac{\partial \tilde{V}}{\partial R_n^{I\alpha}} U \right) \\ &= -\text{Tr} \left(\hat{\sigma} \frac{\partial \hat{V}}{\partial R_n^{I\alpha}} \right) + \frac{i}{\hbar} \text{Tr} (\hat{\sigma} [A^{I\alpha}, \hat{V}]) \end{aligned} \quad (18)$$

$$\dot{\hat{\sigma}} = \frac{d}{dt} (U^\dagger \tilde{\sigma} U) = -\frac{i}{\hbar} \left[\hat{V} - \sum_I \frac{P_n^I \cdot A^I}{M_I}, \hat{\sigma} \right] \quad (19)$$

Here we have defined

$$A_{jk}^{I\alpha} = i\hbar \sum_a U_{ja}^\dagger \frac{\partial U_{ak}}{\partial R_n^{I\alpha}} = i\hbar \left\langle \psi_j \left| \frac{\partial \psi_k}{\partial R_n^{I\alpha}} \right. \right\rangle, \quad (20)$$

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

$$A_{jk}^{I\alpha} = -\langle \psi_j | \hat{P}_n^{I\alpha} | \psi_k \rangle \quad (21)$$

Eqs.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.

$$\dot{P}_{\text{tot}}^\alpha = \sum_I \dot{P}_n^{I\alpha} + \text{Tr} (\hat{\sigma} \hat{P}_e^\alpha + \dot{\hat{\sigma}} \hat{P}_e^\alpha) \quad (22)$$

$$\dot{J}_{\text{tot}}^\alpha = \sum_I \dot{J}_n^{I\alpha} + \text{Tr} (\hat{\sigma} \hat{J}_e^\alpha + \dot{\hat{\sigma}} \hat{J}_e^\alpha) \quad (23)$$

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 \mathbf{R}_0 , the electronic state is chosen as

$$\psi_k(\mathbf{r}; \mathbf{R}_n) = \phi_k(\mathbf{r} - \mathbf{R}_n) e^{\frac{i}{\hbar} \zeta_k(\mathbf{R}_n - \mathbf{R}_0)} \quad (24)$$

In such a case, one finds the relations below:

$$\left(\sum_I \hat{P}_n^{I\alpha} + \hat{P}_e^\alpha \right) |\psi_k\rangle = \sum_I \xi_k^{I\alpha}(\mathbf{R}_n) |\psi_k\rangle \quad (25)$$

$$\left(\sum_I \hat{J}_n^{I\alpha} + \hat{J}_e^\alpha \right) |\psi_k\rangle = \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \xi_k^{I\gamma}(\mathbf{R}_n) |\psi_k\rangle \quad (26)$$

where $\xi_k^{I\alpha}(\mathbf{R}_n) = \nabla_{I\alpha} \zeta_k(\mathbf{R}_n)$.

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

$$\begin{aligned} \langle \psi_j | \hat{P}_e^\alpha | \psi_k \rangle &= - \sum_I \langle \psi_j | \hat{P}_n^{I\alpha} | \psi_k \rangle + \sum_I \xi_k^{I\alpha} \delta_{jk} \\ &= \sum_I A_{jk}^{I\alpha} + \xi_k^{I\alpha} \delta_{jk} \end{aligned} \quad (27)$$

$$\begin{aligned} \langle \psi_j | \hat{J}_e^\alpha | \psi_k \rangle &= - \sum_I \langle \psi_j | \hat{J}_n^{I\alpha} | \psi_k \rangle + \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \xi_k^{I\gamma} \delta_{jk} \\ &= \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} (A_{jk}^{I\gamma} + \xi_k^{I\gamma} \delta_{jk}) \end{aligned} \quad (28)$$

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

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

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

Here we introduce the notation $\xi_k^{J\beta,I\alpha}(\mathbf{R}_n) = \nabla_{J\beta} \xi_k^{I\alpha}(\mathbf{R}_n)$.

1. Linear Momentum Conservation

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

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

$$\begin{aligned} \sum_I \dot{P}_n^{I\alpha} &= \sum_I -\text{Tr} \left(\hat{\sigma} \frac{\partial \hat{V}}{\partial R_n^{I\alpha}} \right) + \frac{i}{\hbar} \text{Tr} (\hat{\sigma} [\mathbf{A}^{I\alpha}, \hat{V}]) \\ &= \frac{i}{\hbar} \sum_I \text{Tr} ([\hat{V}, \hat{\sigma}] \mathbf{A}^{I\alpha}), \end{aligned} \quad (31)$$

where the first term above vanishes since we assume a translationally invariant potential energy surface.

- From Eq. 29, the second term in Eq. 22 [$\text{Tr} (\hat{\sigma} \dot{P}_e^\alpha)$] is

$$\text{Tr} (\hat{\sigma} \dot{P}_e^\alpha) = \sum_{IJ\beta jk} \hat{\sigma}_{kj} \dot{R}_n^{J\beta} \left(\frac{\partial A_{jk}^{I\alpha}}{\partial R_n^{J\beta}} + \xi_k^{J\beta,I\alpha} \delta_{jk} \right) \quad (32)$$

- Using Eq. 27 to express \mathbf{P}_e^α in terms of $\mathbf{A}^{I\alpha}$, the last term [$\text{Tr} (\hat{\sigma} \mathbf{P}_e^\alpha)$] in Eq. 22 becomes

$$\text{Tr} (\hat{\sigma} \mathbf{P}_e^\alpha) = \sum_{Ijk} \hat{\sigma}_{kj} \left(A_{jk}^{I\alpha} + \xi_k^{I\alpha} \delta_{jk} \right) \quad (33)$$

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

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

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

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

$$\begin{aligned} \text{Tr} (\hat{\sigma} \mathbf{P}_e^\alpha) &= - \frac{i}{\hbar} \sum_I \text{Tr} ([\hat{V}, \hat{\sigma}] \mathbf{A}^{I\alpha}) \\ &\quad + \frac{i}{\hbar} \text{Tr} \left(\hat{\sigma} \sum_{IJ\beta} \dot{R}_n^{J\beta} [\mathbf{A}^{I\alpha}, \mathbf{A}^{J\beta}] \right) \\ &\quad - \frac{i}{\hbar} \sum_{IJ\beta jk} \dot{R}_n^{J\beta} \hat{\sigma}_{kj} (\xi_k^{I\alpha} - \xi_j^{I\alpha}) A_{jk}^{J\beta} \end{aligned} \quad (36)$$

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

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

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

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

Note that to go from Eq. 37 to Eq. 38, we used the following relation, which is proven in Sec. S1 of the SI,

$$\sum_I \frac{\partial A_{jk}^{J\beta}}{\partial R_{\text{n}}^{I\alpha}} = - \sum_I \xi_k^{J\beta, I\alpha} \delta_{jk} + \frac{i}{\hbar} \sum_I (\xi_k^{I\alpha} - \xi_j^{I\alpha}) A_{jk}^{J\beta} \quad (40)$$

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

$$\Omega^{I\alpha J\beta} = \frac{\partial \mathbf{A}^{J\beta}}{\partial R_{\text{n}}^{I\alpha}} - \frac{\partial \mathbf{A}^{I\alpha}}{\partial R_{\text{n}}^{J\beta}} - \frac{i}{\hbar} [\mathbf{A}^{I\alpha}, \mathbf{A}^{J\beta}] \quad (41)$$

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: $\sum_l |\psi_l\rangle \langle \psi_l|$,

$$\frac{\partial A_{jk}^{J\beta}}{\partial R_{\text{n}}^{I\alpha}} - \frac{\partial A_{jk}^{I\alpha}}{\partial R_{\text{n}}^{J\beta}} = \frac{i}{\hbar} \sum_l (A_{jl}^{I\alpha} A_{lk}^{J\beta} - A_{jl}^{J\beta} A_{lk}^{I\alpha}) \quad (42)$$

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.

$$\text{Tr} (\hat{\sigma} \dot{\mathbf{J}}_{\text{e}}^{\alpha}) = \sum_{IJ\eta\beta\gamma jk} \hat{\sigma}_{kj} \epsilon_{\alpha\eta\gamma} R_{\text{n}}^{I\eta} \dot{R}_{\text{n}}^{J\beta} \left[\frac{\partial A_{jk}^{I\gamma}}{\partial R_{\text{n}}^{J\beta}} - \frac{\partial A_{jk}^{J\beta}}{\partial R_{\text{n}}^{I\gamma}} + \frac{i}{\hbar} (\xi_k^{I\gamma} - \xi_j^{I\gamma}) A_{jk}^{J\beta} - \delta_{jk} \xi_k^{I\eta, J\gamma} \right] \quad (45)$$

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

$$\text{Tr} (\hat{\sigma} \dot{\mathbf{J}}_{\text{e}}^{\alpha}) = \sum_{I\eta\gamma jk} \epsilon_{\alpha\eta\gamma} R_{\text{n}}^{I\eta} \dot{\sigma}_{kj} (A_{jk}^{I\gamma} + \xi_k^{I\gamma} \delta_{jk}) \quad (46)$$

2. Angular Momentum Conservation

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

- From the expression for J_{n}^{α} in Eq. 8 and the expression for $\dot{P}_{\text{n}}^{I\gamma}$ in Eq. 18, we can write out the first term in Eq. 23,

$$\begin{aligned} \sum_I J_{\text{n}}^{I\alpha} &= \sum_{I\beta\gamma} \epsilon_{\alpha\beta\gamma} R_{\text{n}}^{I\beta} \text{Tr} \left(\hat{\sigma} \left(-\frac{\partial \hat{V}}{\partial R_{\text{n}}^{I\gamma}} + \frac{i}{\hbar} [\mathbf{A}^{I\gamma}, \hat{V}] \right) \right) \\ &= \frac{i}{\hbar} \sum_{I\beta\gamma} \epsilon_{\alpha\beta\gamma} R_{\text{n}}^{I\beta} \text{Tr} ([\hat{V}, \hat{\sigma}] \mathbf{A}^{I\gamma}), \end{aligned} \quad (43)$$

Above, the first term vanishes because we assume that space is isotropic.

- Before writing down the expression for the second term $\text{Tr} (\hat{\sigma} \dot{\mathbf{J}}_{\text{e}}^{\alpha})$ in Eq. 23, let us simplify the expression for $\dot{\mathbf{J}}_{\text{e}}^{\alpha}$ in Eq. 30. Specifically, we used the following the relation, which is proved in the section S1 of the Supporting Information,

$$\begin{aligned} &\sum_{\gamma} \epsilon_{\alpha\eta\gamma} (A_{jk}^{I\gamma} + \xi_k^{I\gamma} \delta_{jk}) \\ &= \sum_{J\beta\gamma} \epsilon_{\alpha\beta\gamma} R_{\text{n}}^{J\beta} \left[-\frac{\partial A_{jk}^{I\gamma}}{\partial R_{\text{n}}^{J\gamma}} + \frac{i}{\hbar} (\xi_k^{J\gamma} - \xi_j^{J\gamma}) A_{jk}^{I\eta} - \delta_{jk} \xi_k^{I\eta, J\gamma} \right] \end{aligned} \quad (44)$$

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

We begin by evaluating plugging Eq. 35 into the second

term of Eq.46,

$$\begin{aligned} & \sum_{I\eta\gamma jk} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \hat{\sigma}_{kj} \xi_k^{I\gamma} \delta_{jk} \\ &= -\frac{i}{\hbar} \sum_{Jjk\beta\gamma\eta} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} R_n^{J\beta} \hat{\sigma}_{kj} (\xi_k^{I\gamma} - \xi_j^{I\gamma}) A_{jk}^{J\beta} \quad (47) \end{aligned}$$

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

$$\text{Tr}(\dot{\sigma} J_e^\alpha) = \sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \left(-\frac{i}{\hbar} \text{Tr}([\hat{V}, \hat{\sigma}] A^{I\gamma}) + \frac{i}{\hbar} \dot{R}_n^{J\beta} \text{Tr}(\hat{\sigma} [A^{I\gamma}, A^{J\beta}]) - \frac{i}{\hbar} \dot{R}_n^{J\beta} \hat{\sigma}_{kj} (\xi_k^{I\gamma} - \xi_j^{I\gamma}) A_{jk}^{J\beta} \right) \quad (48)$$

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 Eq.45 and Eq. 48 cancel as well. The remaining terms are

$$\begin{aligned} J_{\text{tot}}^\alpha &= \sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma} \text{Tr} \left(\hat{\sigma} R_n^{I\eta} \dot{R}_n^{J\beta} \left(\frac{\partial A^{I\gamma}}{\partial R_n^{J\beta}} - \frac{\partial A^{J\beta}}{\partial R_n^{I\gamma}} + \frac{i}{\hbar} [A^{I\gamma}, A^{J\beta}] \right) \right) \\ &= - \sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma} \text{Tr} \left(\hat{\sigma} R_n^{I\eta} R_n^{J\beta} \Omega^{I\gamma J\beta} \right) \end{aligned} \quad (49)$$

As above, the non-Abelian Berry curvature appears and in this case, 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 results above do not depend in any way on the gauge ξ in Eqs. 25-26. To the seasoned practitioner of Ehrenfest (or Ehrenfest based) dynamics⁴⁵, 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 $|\psi_j\rangle = \sum_k |\psi_k\rangle \overline{U}_{kj}$. In the new basis, the density matrix, the electronic Hamiltonian, and the Berry connection take the form:

$$\bar{\sigma} = \overline{U}^\dagger \hat{\sigma} \overline{U} \quad (50)$$

$$\bar{V} = \overline{U}^\dagger \hat{V} \overline{U} \quad (51)$$

$$\bar{A} = \overline{U}^\dagger A \overline{U} + i\hbar \overline{U}^\dagger \nabla_n \overline{U} \quad (52)$$

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

$$\begin{aligned} \dot{P}_n^{I\alpha} &= -\text{Tr} \left(\overline{U}^\dagger \hat{\sigma} \overline{U} \frac{\partial \hat{V}}{\partial R_n^{I\alpha}} \overline{U} \right) \\ &+ \frac{i}{\hbar} \text{Tr} \left(\bar{\sigma} [\overline{U}^\dagger A^{I\alpha} \overline{U}, \bar{V}] \right) \end{aligned} \quad (53)$$

$$= -\text{Tr} \left(\bar{\sigma} \frac{\partial \bar{V}}{\partial R_n^{I\alpha}} \right) + \frac{i}{\hbar} \text{Tr} \left(\bar{\sigma} [A^{I\alpha}, \bar{V}] \right) \quad (54)$$

Here, we used the relationship:

$$\nabla_n \bar{V} = \overline{U}^\dagger \nabla_n \hat{V} \overline{U} - [\overline{U}^\dagger \nabla_n \overline{U}, \bar{V}] \quad (55)$$

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

$$\dot{\bar{\sigma}} = \overline{U}^\dagger \dot{\hat{\sigma}} \overline{U} + \dot{R}_n \left(\nabla_n \overline{U}^\dagger \hat{\sigma} \overline{U} + \overline{U}^\dagger \hat{\sigma} \nabla_n \overline{U} \right) \quad (56)$$

$$= \overline{U}^\dagger \dot{\hat{\sigma}} \overline{U} - \left[\sum_I \frac{P_n^I}{M_I} \cdot \overline{U}^\dagger \nabla_I \overline{U}, \bar{\sigma} \right] \quad (57)$$

Now, using Eqs. 50-52 together with Eq. 19, it follows that:

$$\bar{U}^\dagger \hat{\sigma} \bar{U} = -\frac{i}{\hbar} \left[\bar{V} - \sum_I \frac{\mathbf{P}_n^I}{M_I} \cdot \bar{U}^\dagger \mathbf{A}^I \bar{U}, \bar{\sigma} \right] \quad (58)$$

$$\begin{aligned} &= -\frac{i}{\hbar} \left[\bar{V} - \sum_I \frac{\mathbf{P}_n^I}{M_I} \cdot \bar{\mathbf{A}}^I, \bar{\sigma} \right] \\ &\quad + \left[\sum_I \frac{\mathbf{P}_n^I}{M_I} \cdot \bar{U}^\dagger \nabla_I \bar{U}, \bar{\sigma} \right] \end{aligned} \quad (59)$$

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

$$\bar{\sigma} = -\frac{i}{\hbar} \left[\bar{V} - \sum_I \frac{\mathbf{P}_n^I}{M_I} \cdot \bar{\mathbf{A}}^I, \bar{\sigma} \right] \quad (60)$$

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

In the previous section, we showed that both linear 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 basis⁴⁶⁻⁴⁸ and a complete set of adiabatic states is 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 formalism above, 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:

$$\dot{R}_n^\alpha \rightarrow \dot{R}_n^\alpha + \sum_{IJ\beta} \text{Tr}(\hat{\sigma} R_n^{J\beta} \Omega^{I\alpha J\beta}) \quad (61)$$

or some variation thereof. Indeed, such equations have been derived by a Lagrangian formulation¹ and a path integral formulation². 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{H} in the adiabatic representation,

$$\begin{aligned} \hat{H} = & \sum_I \frac{\mathbf{P}_n^I}{2M_I} - \sum_I \frac{\mathbf{P}_n^I \cdot \mathbf{A}^I}{M_I} + \sum_I \text{Tr}(\hat{\sigma} \mathbf{A}^I) \cdot \frac{\mathbf{A}^I}{M_I} \\ & - \sum_I \frac{1}{2M_I} [\text{Tr}(\hat{\sigma} \mathbf{A}^I)]^2 + \hat{V} \end{aligned} \quad (62)$$

The corresponding expectation value of the energy E is

$$E = \sum_I \frac{\mathbf{P}_n^I}{2M_I} + \text{Tr} \left[\hat{\sigma} \left(\hat{V} - \sum_I \frac{\mathbf{P}_n^I \cdot \mathbf{A}^I}{M_I} \right) \right] + \sum_I \frac{1}{2M_I} [\text{Tr}(\hat{\sigma} \mathbf{A}^I)]^2 \quad (63)$$

The equations of motion for $(\mathbf{R}_n, \mathbf{P}_n)$ are:

$$\dot{\sigma} = -\frac{i}{\hbar} \left[\hat{V} - \sum_I \frac{\mathbf{P}_n^I \cdot \mathbf{A}^I}{M_I} + \sum_I \text{Tr}(\hat{\sigma} \mathbf{A}^I) \cdot \frac{\mathbf{A}^I}{M_I}, \hat{\sigma} \right] \quad (64)$$

$$\dot{R}_n^{I\alpha} = \frac{\partial E}{\partial P_n^{I\alpha}} = \frac{P_n^{I\alpha}}{M_I} - \text{Tr} \left(\hat{\sigma} \frac{\mathbf{A}^{I\alpha}}{M_I} \right) \quad (65)$$

$$\dot{P}_n^{I\alpha} = -\frac{\partial E}{\partial R_n^{I\alpha}} \quad (66)$$

$$= -\text{Tr} \left(\hat{\sigma} \left(\frac{\partial \hat{V}}{\partial R_n^{I\alpha}} - \sum_{J\beta} \frac{[P_n^{J\beta} + \text{Tr}(\hat{\sigma} \mathbf{A}^{J\beta})]}{M_J} \frac{\partial \mathbf{A}^{J\beta}}{\partial R_n^{I\alpha}} \right) \right)$$

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

$$\pi_n^{I\alpha} = P_n^{I\alpha} - \text{Tr}(\hat{\sigma} \mathbf{A}^{I\alpha}), \quad (67)$$

we can rewrite the equations of motion in terms of (\mathbf{R}_n, π_n) :

$$\dot{\sigma} = -\frac{i}{\hbar} \left[\hat{V} - \sum_{I\alpha} \frac{\pi_n^{I\alpha}}{M_I} \cdot \mathbf{A}^{I\alpha}, \hat{\sigma} \right] \quad (68)$$

$$\dot{R}_n^{I\alpha} = \frac{\pi_n^{I\alpha}}{M_I} \quad (69)$$

$$\dot{\pi}_n^{I\alpha} = \dot{P}_n^{I\alpha} - \text{Tr}(\hat{\sigma} \dot{\mathbf{A}}^{I\alpha}) - \text{Tr}(\hat{\sigma} \mathbf{A}^{I\alpha}) \quad (70)$$

$$\begin{aligned} &= -\text{Tr} \left(\hat{\sigma} \frac{\partial \hat{V}}{\partial R_n^{I\alpha}} \right) + \sum_{J\beta} \frac{\pi_n^{J\beta}}{M_J} \text{Tr}(\hat{\sigma} \Omega^{I\alpha J\beta}) \\ &\quad + \frac{i}{\hbar} \text{Tr}([\hat{V}, \hat{\sigma}] \mathbf{A}^{I\alpha}) \end{aligned} \quad (71)$$

These are the equations of motion derived properly in Refs. 1,2. Compared against the standard adiabatic Ehrenfest equations in Eqs. 17-19, the equation of motion for the kinetic momentum $\pi_n^{I\alpha}$ 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 $\dot{\pi}_n^{I\alpha}$ in Eq. 70,

$$\dot{P}_{\text{tot}}^\alpha = \sum_I \dot{P}_n^{I\alpha} + \text{Tr}(\hat{\sigma} \dot{P}_e^\alpha) + \text{Tr}(\hat{\sigma} \dot{P}_e^\alpha) \quad (72)$$

$$\begin{aligned} &= \sum_I \dot{P}_n^{I\alpha} + \text{Tr} \left[\hat{\sigma} (P_e^\alpha - \sum_I A^{I\alpha}) \right] \\ &\quad + \text{Tr} \left[\hat{\sigma} (\dot{P}_e^\alpha - \sum_I \dot{A}^{I\alpha}) \right] \end{aligned} \quad (73)$$

Now evaluate each term in Eq. 73.

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

$$\begin{aligned}\sum_I \dot{P}_n^{I\alpha} &= -\sum_I \text{Tr} \left(\hat{\sigma} \frac{\partial \hat{V}}{\partial R_n^{I\alpha}} \right) + \sum_{IJ\beta} \frac{\pi_n^{J\beta}}{M_J} \text{Tr} \left(\hat{\sigma} \frac{\partial \mathbf{A}^{J\beta}}{\partial R_n^{I\alpha}} \right) \\ &= \sum_{IJ\beta} \dot{R}_n^{J\beta} \text{Tr} \left(\hat{\sigma} \frac{\partial \mathbf{A}^{J\beta}}{\partial R_n^{I\alpha}} \right)\end{aligned}\quad (74)$$

for a translationally invariant potential energy surface.

- Rearranging Eq. 27 and using Eq. 35, the second term

in Eq. 73 is

$$\begin{aligned}\text{Tr} \left[\hat{\sigma} \left(\mathbf{P}_e^\alpha - \sum_I \mathbf{A}^{I\alpha} \right) \right] &= \sum_{Ijk} \hat{\sigma}_{kj} \xi_k^{I\alpha} \delta_{jk} \\ &= -\frac{i}{\hbar} \sum_{IJ\beta jk} \hat{\sigma}_{kj} \dot{R}_n^{J\beta} (\xi_k^{I\alpha} - \xi_j^{I\alpha}) A_{jk}^{J\beta}\end{aligned}\quad (75)$$

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

$$\begin{aligned}\text{Tr} \left[\hat{\sigma} \left(\dot{\mathbf{P}}_e^\alpha - \sum_I \dot{\mathbf{A}}^{I\alpha} \right) \right] &= \sum_{Ijk} \hat{\sigma}_{kj} \dot{\xi}_k^{I\alpha} \delta_{jk} \\ &= \sum_{IJ\beta jk} \hat{\sigma}_{kj} \dot{R}_n^{J\beta} \xi_k^{J\beta, I\alpha} \delta_{jk}\end{aligned}\quad (76)$$

If we add Eq. 74, Eq. 75, and Eq. 76 together, the time-dependence of the total linear momentum in Eq. 73 becomes

$$\sum_I \dot{P}_{\text{tot}}^{I\alpha} = \sum_{IJ\beta} \dot{R}_n^{J\beta} \text{Tr} \left(\hat{\sigma} \frac{\partial \mathbf{A}^{J\beta}}{\partial R_n^{I\alpha}} \right) + \sum_{IJ\beta jk} \hat{\sigma}_{kj} \dot{R}_n^{J\beta} \left(\xi_k^{J\beta, I\alpha} \delta_{jk} - \frac{i}{\hbar} (\xi_k^{I\alpha} - \xi_j^{I\alpha}) A_{jk}^{J\beta} \right) = 0 \quad (77)$$

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:

$$\dot{\mathbf{J}}_{\text{tot}}^\alpha = \sum_{\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \dot{\pi}_n^{I\gamma} + \text{Tr} \left(\hat{\sigma} \dot{\mathbf{J}}_e^\alpha + \dot{\sigma} \mathbf{J}_e^\alpha \right) \quad (78)$$

$$\begin{aligned}&= \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \dot{P}_n^{I\gamma} + \text{Tr} \left[\hat{\sigma} \left(\mathbf{J}_e^\alpha - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \dot{\mathbf{A}}^{I\gamma} \right) \right] \\ &\quad + \text{Tr} \left[\dot{\sigma} \left(\mathbf{J}_e^\alpha - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \mathbf{A}^{I\gamma} \right) \right]\end{aligned}\quad (79)$$

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

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

$$\sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \dot{P}_n^{I\gamma} = \sum_{IJk\eta\beta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \dot{R}_n^{J\beta} \hat{\sigma}_{kj} \frac{\partial A_{jk}^{J\beta}}{\partial R_n^{I\gamma}} \quad (80)$$

Here we recognize $-\sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} \text{Tr} \left(\hat{\sigma} R_n^{I\eta} \frac{\partial \hat{V}}{\partial R_n^{I\gamma}} \right) = 0$ due to the isotropy of space.

- Rearranging Eq. 45, we recover for the second term in Eq. 79

$$\begin{aligned}\text{Tr} \left[\hat{\sigma} \left(\mathbf{J}_e^\alpha - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \dot{\mathbf{A}}^{I\gamma} \right) \right] &= \sum_{IJk\eta\beta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \dot{R}_n^{J\beta} \hat{\sigma}_{kj} \left[-\frac{\partial A_{jk}^{J\beta}}{\partial R_n^{I\gamma}} + \frac{i}{\hbar} (\xi_k^{I\gamma} - \xi_j^{I\gamma}) A_{jk}^{J\beta} \right]\end{aligned}\quad (81)$$

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

$$\begin{aligned}\text{Tr} \left[\dot{\sigma} \left(\mathbf{J}_e^\alpha - \sum_{I\eta\gamma} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} \mathbf{A}^{I\gamma} \right) \right] &= -\frac{i}{\hbar} \sum_{IJ\eta\gamma\beta} \varepsilon_{\alpha\eta\gamma} R_n^{I\eta} R_n^{J\beta} \hat{\sigma}_{kj} (\xi_k^{I\gamma} - \xi_j^{I\gamma}) A_{jk}^{J\beta}\end{aligned}\quad (82)$$

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 $\sum_I \dot{J}_{\text{tot}}^{I\alpha} = 0$. 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 result above holds for any choice

of gauge in Eqs. 25-26; 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 section S2 in the SI) that

$$\bar{\Omega}^{I\alpha J\beta} = \bar{U}^\dagger \Omega^{I\alpha J\beta} \bar{U} \quad (83)$$

The Ehrenfest theory above 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 the Eqs. 68-71 are not the only possible Ehrenfest approximations. In fact, in the SI, Eqs. S24-S28, we study a different flavor of Ehrenfest approximations⁵⁰⁻⁵² where the electronic Hamiltonian and the semiclassical energies in Eqs. 62-63 are replaced with

$$\hat{H} = \sum_I \frac{\mathbf{P}_n^I{}^2}{2M_I} - \sum_I \frac{\mathbf{P}_n^I \cdot \mathbf{A}^I}{M_I} + \sum_I \frac{\mathbf{A}^I{}^2}{2M_I} + \hat{V} \quad (84)$$

$$E = \sum_I \frac{\mathbf{P}_n^I{}^2}{2M_I} + \text{Tr} \left[\hat{\sigma} \left(\sum_I \frac{-2\mathbf{P}_n^I \cdot \mathbf{A}^I + \mathbf{A}^I{}^2}{2M_I} + \hat{V} \right) \right] \quad (85)$$

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

V. A TRAVELING HYDROGEN ATOM

In Sec. VI below, we will present an *ab initio* calculation exploring momentum conservation numerically. Before presenting such data, however, it is helpful conceptually to first treat the simplest, analytical example of Ehrenfest theory: the example of a hydrogen atom traveling at constant velocity. For such a system, \hat{V} and \mathbf{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 $\hat{\sigma} = 0$, which implies that (according to Eq. 19) the electronic wavefunction must be an eigenvector of: $\hat{V} - \sum_\alpha \dot{R}_n^\alpha \cdot \mathbf{A}^\alpha$. Mathematically, we therefore conclude:

$$[\hat{V}, \hat{\sigma}] = \left[\sum_\alpha \dot{R}_n^\alpha \cdot \mathbf{A}^\alpha, \hat{\sigma} \right] \quad (86)$$

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 Eq. 18. The first term $-\text{Tr} \left(\hat{\sigma} \frac{\partial \hat{V}}{\partial R_n^\alpha} \right)$ in Eq. 18 is zero due to translation-invariant potential. For the remaining term in Eq. 18, $\frac{i}{\hbar} \text{Tr} \left([\hat{V}, \hat{\sigma}] \mathbf{A}^\alpha \right)$, we plug in Eq. 86, and Eq. 18 then becomes

$$\dot{P}_n^\alpha = \frac{i}{\hbar} \text{Tr} \left([\hat{V}, \hat{\sigma}] \mathbf{A}^\alpha \right) \quad (87)$$

$$= \frac{i}{\hbar} \sum_\beta \dot{R}_n^\beta \text{Tr} \left(\hat{\sigma} [\mathbf{A}^\alpha, \mathbf{A}^\beta] \right) \quad (88)$$

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, $\mathbf{A} \rightarrow 0$ in Eqs. 18-19, so that the wavefunction $\phi(r, t) = \phi_{1s}(r - R(t))$ becomes a stationary state (though admittedly without any electronic momentum).^{55,56} Alternatively, (ii) a second approach 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

$$\begin{aligned} & \sum_\beta \frac{\pi_n^\beta}{M} \text{Tr} \left(\hat{\sigma} \Omega^{\alpha\beta} \right) \\ &= \sum_\beta \frac{\pi_n^\beta}{M} \text{Tr} \left\{ \hat{\sigma} \left(\frac{\partial \mathbf{A}^\beta}{\partial R_n^\alpha} - \frac{\partial \mathbf{A}^\alpha}{\partial R_n^\beta} - \frac{i}{\hbar} [\mathbf{A}^\alpha, \mathbf{A}^\beta] \right) \right\} \quad (89) \end{aligned}$$

Moreover, for a hydrogen atom, \mathbf{A} does not depend on R_n so that

$$\sum_\beta \frac{\pi_n^\beta}{M} \text{Tr} \left(\hat{\sigma} \Omega^{\alpha\beta} \right) = -\frac{i}{\hbar} \sum_\beta \frac{\pi_n^\beta}{M} \text{Tr} \left\{ \hat{\sigma} ([\mathbf{A}^\alpha, \mathbf{A}^\beta]) \right\} \quad (90)$$

The first term on the right-hand side of Eq. 71 is still zero, and thus using Eq. 88 and Eq. 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 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. ($\approx 1491K$); 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 $c = (\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}})$ in the GHF/TGHF basis, which gives an initial density matrix $\sigma = cc^T = \begin{pmatrix} \frac{1}{2}, \frac{i}{2} \\ -\frac{i}{2}, \frac{1}{2} \end{pmatrix}$. The non-Abelian Berry curvature in Eq. 71 was computed by finite-difference. The calculations were performed in a local branch of Q-Chem 6.0.⁶⁰

In Fig. 1(b) and (c), using cyan arrows, we plot the spin magnetic moments on each atom according to a Mulliken-like scheme⁶¹ at time zero for each of the two doublets; 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, $c = (\frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}})$. 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 rotate in the xy plane, as also shown in Fig. S1 in the Supporting Information.

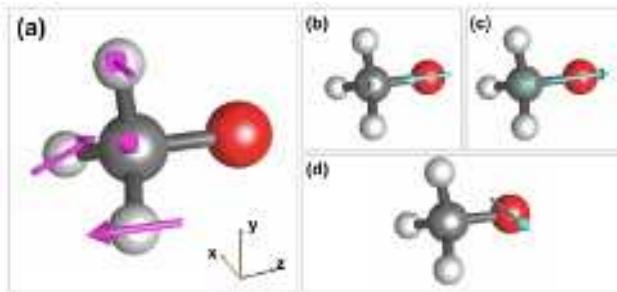


FIG. 1. (a) [Magenta] The displacements of the first vibrational mode along which we propagate dynamics. In (b), we plot [cyan] the atom-based spin magnetic moments for a single GHF+SOC solution, and in (c) we plot the corresponding moments for its degenerate time-reversed solution. (d) The weighted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

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 Berry force is not included (Fig. 2(a)(c)(e)). When the Berry force is not included, the nuclear angular momentum is calculated from the canonical momentum P_n , which is conserved for a translationally invariant surface, and hence there is no change in the nuclear

momentum (red solid line). 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 shown previously in Ref.⁴¹. In blue, we plot the electronic spin angular momentum; in orange, we plot the electronic orbital angular momentum. In Fig. 2(a) and (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 Fig. 2(b)(d)(f) where the Berry force is included. Here, we see the nuclear angular momentum (as calculated from the kinetic momentum π_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 a Berry force is included.) Of most importance, when comparing Figs. 2(e) and (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 ξ

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. 25-26. 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 loop⁶². 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 motion. Thus, at the end of the day, for the most part, the usual approach is simply to align the phases of nuclear wavefunctions at two slightly different geometries (separated by one time step) using parallel transport. Parallel transport does not satisfy $\xi = 0$ in Eqs. 25-26. 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. 84-85.

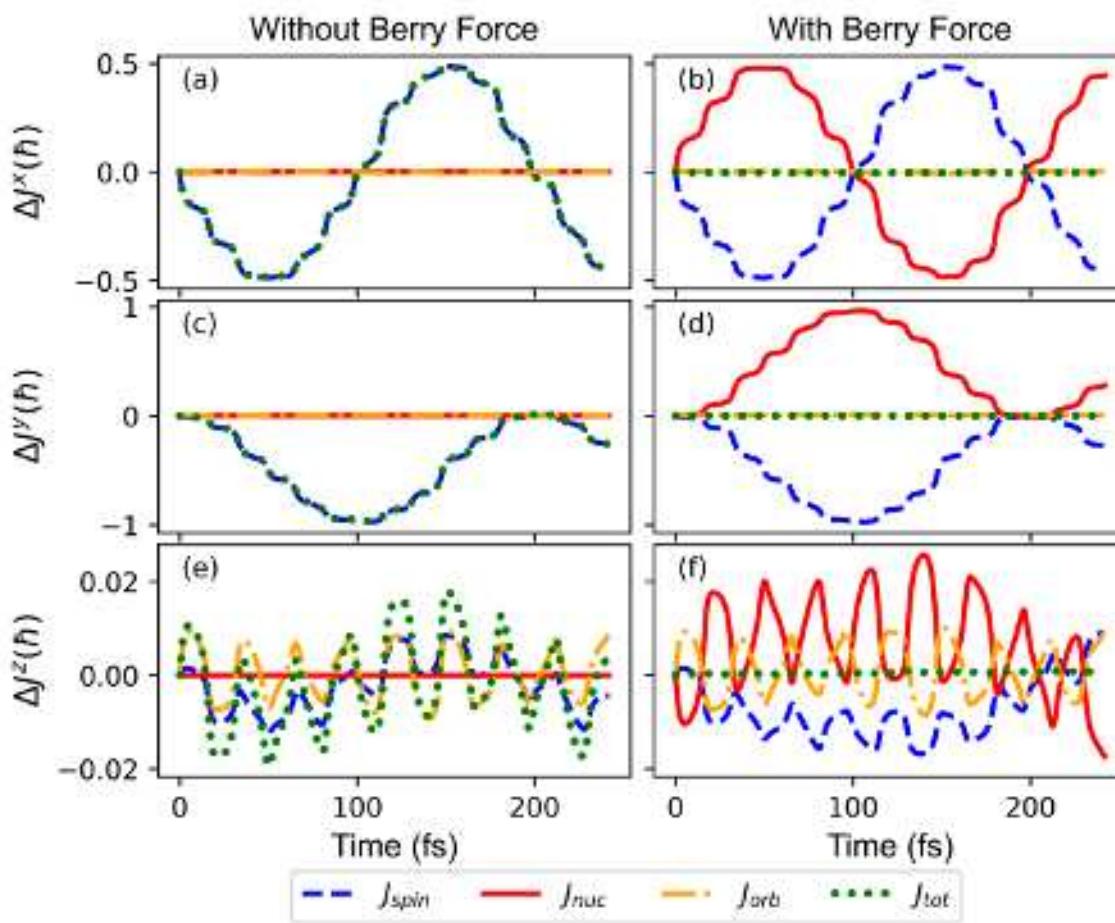


FIG. 2. The change in the real-time angular momentum $\Delta J^\alpha(t) = J^\alpha(t) - J^\alpha(0)$ (relative to time zero) according to an Ehrenfest trajectory simulating methoxy radical moving along its lowest normal mode vibration. The nonzero initial values of components of the angular momentum are listed: $J_{\text{spin}}^y = 0.4811\hbar$, $J_{\text{orb}}^y = -0.0054\hbar$, $J_{\text{nuc}}^x = 0.0075\hbar$, and $J_{\text{nuc}}^z = -0.0048\hbar$. The three panels (a),(c),(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 Figs.(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 Figs.(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 Figs (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 changes the nuclear motion and yields a reasonably different trajectory.

B. Ehrenfest vs BO Dynamics

Lastly, before concluding, in order to numerically emphasize the need to go beyond the BO approximation when treating spin 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 $J_{\text{nuc}} = (0.0, 39.28\hbar, 0.0)$, 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 addi-

tional trajectory data, and in particular for the time-dependent state populations and an analysis of the spin angular momentum in terms of the relevant $|\text{GHF}\rangle$ and $|\text{TGHF}\rangle$ wavefunctions, see the SI. In Fig. 3(b), as a function of time, we plot the rotation 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}_{BO} rotates with the molecule (red line). This prediction is of course unphysical, however; the spin direction does not change instantaneously with molecular frame but rather changes depending on the spin-orbit coupling. This slow change of direction is correctly captured by Ehrenfest dynamics (blue dashed lines). Lastly, this BO failure can be verified in 3(c), where we plot population as a function of time and show, the time the molecule has rotated 180 degrees (244

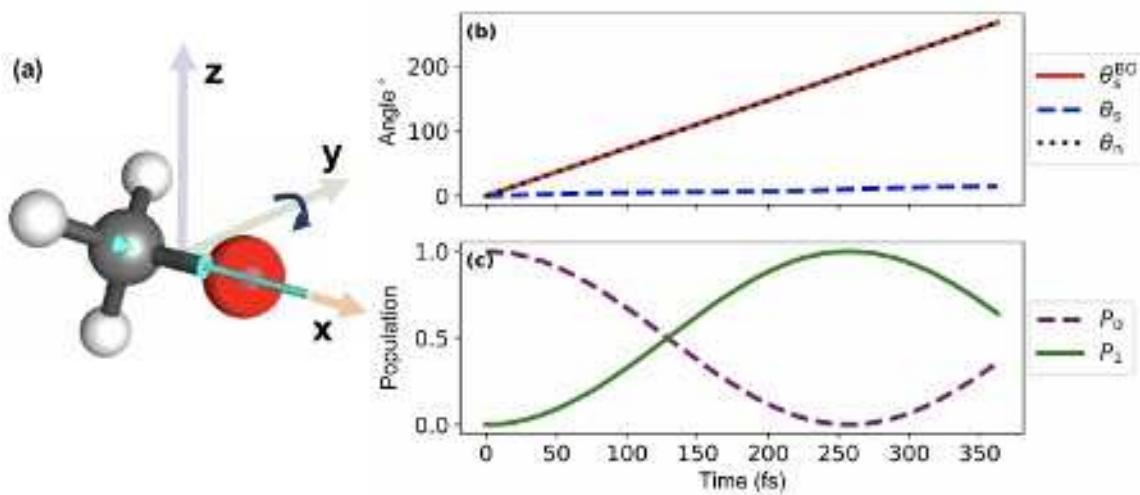


FIG. 3. (a) The orientation of the methoxy radical molecule, the rotation direction, and atom-based spin magnetic moments (cyan arrows) at the initial step. (b) The rotation angles of the molecule (black dotted line), the total spin vector from the BO dynamics (red solid line), and from the Ehrenfest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

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 Ω (as present in Eqs. 68–71). This result is independent of the choice of gauge for the electronic states in Eqs. 25–26. As examples, we have studied both the traveling hydrogen atom (analytically) as well as 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 highlights that the evolution of the spin degrees of freedom can be different as a result. Looking forward, the present results should have immediate impact in a variety of fields where nuclear, electronic and spin motion are all entangled perhaps especially for systems displaying chiral-induced spin selectivity^{63,64}.

IX. SUPPLEMENTARY MATERIAL

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

X. ACKNOWLEDGMENT

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