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Path integrals for nonadiabatically coupled electrons and nuclei in molecules: Force analysis for branching nuclear paths and conservation laws

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Real-time dynamics in electron-nucleus coupled systems in molecules is studied using the path-integral formalism, with a special emphasis on nonadiabatic interactions. We first establish a formal path-integral description of the entire system. Applying the stationary phase approximation, we then derive coupled equations for the mixed quantum-classical treatment of the system: the equations of motion for electron wave-packet dynamics and those for nuclear dynamics driven by what we call the force form. Thus the present theory also serves as a general theory for dynamics in mixed quantum and classical systems. On this theoretical foundation, we analyze two theories of nonadiabatic electron-nucleus coupled systems from the viewpoint of path branching: the semiclassical Ehrenfest theory and the recently developed method of phase-space averaging and natural branching [T. Yonehara, S. Takahashi, and K. Takatsuka, J. Chem. Phys. **130**, 214113 (2009)]. We give a unified account of the essential feature of their physical implications and limitations. Path-integral formalism leads to further refinement of the idea of path branching caused by nonadiabatic coupling, thus giving deeper insight into the nonadiabatic dynamics. Further, we study the conservation laws for energy, linear momentum, and angular momentum in the general mixed quantum-classical representation. We also extend the present path-integral formulation so as to handle nonadiabatic dynamics in laser fields.

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I. INTRODUCTION

In their classic paper [1], Born and Oppenheimer have established the quantum framework of molecular science by decoupling the electronic and nuclear degrees of freedom due to their very large difference in time scales (the so-called adiabatic approximation). This framework then gives the notion of a potential energy hypersurface (PES) produced by electronic energy in a given nuclear configuration, on which the molecular structures and chemical reaction dynamics are well represented. Yet there is a rather ubiquitous situation in which two or more of such PESs come close to one another in the course of chemical rearrangement. In the vicinity of such quasidegeneracy, quantum electronic and nuclear wave packets can be bifurcated by the nuclear kinematic coupling on electrons (the so-called nonadiabatic interaction), which was neglected in the Born-Oppenheimer adiabatic approximation. Many a dramatic change in the electronic states and an interesting chemical conversion are caused by such nonadiabatic interactions.

Many practical theories have been proposed to treat nonadiabatic dynamics (for recent reviews, see Refs. [2–7]). Semiclassical theories like the Landau-Zener classic ansatz have been successfully applied mostly to a one-dimensional slice of the potential functions in the direction perpendicular to the crossing manifold [8–12]. On the contrary, practical techniques such as the surface-hopping [13,14] and spawning methods [15–19] and their variants have been proposed to handle multidimensional nonadiabatic transitions. Nevertheless, we do not follow the notion of stochastic hopping of the nuclear configuration in the present work. Miller and his co-workers have developed a semiclassical theory for nonadiabatic transition that fits in the initial value representation [20,21]. Another kind of nonadiabatic transition is formulated based on electronic wave-packet propagation on smooth "classical" paths. The semiclassical Ehrenfest theory (SET) is a well-known example of this category [22–25]. SET gives an accurate approximation of the coherent evolution of the system. On the contrary, it fails to reproduce appropriate decoherence after the state passes across the crossing region, resulting in unphysical nuclear paths. To overcome this shortcoming of SET, Truhlar and co-workers have devised a method of "natural decoherence" to generate a non-Born-Oppenheimer path that passes through a nonadiabatic region smoothly from one adiabatic potential energy surface to another [26–28].

Yet further sophistication in theory is demanded by the progress in experimental studies such as intense and/or ultrafast pulse lasers and also the interest in many fields of molecular science such as chemical reactions in highly degenerate electronic states, where a clear-cut view of isolated PESs may be missing. Some requirements that should be considered to cope with these situations include (i) multidimensional effects of nonadiabatic interactions like those in conical intersections [6], (ii) an on-the-fly scheme avoiding the generation of global PESs but generating paths even in a nonadiabatic region, (iii) correct and appropriate treatment of wave-packet bifurcation up to the quantum phase, (iv) dynamics of electron wave packets on a time scale shorter than 10 as, and (v) nonadiabatic dynamics in intense laser fields giving rise to induced nonadiabatic interactions.

One of the latest theories of nonadiabatic interaction based on the electronic wave-packet dynamics, trying to satisfy the preceding requirements, is the method of phase-space averaging and natural branching (PSANB) [29]. In this theory, nuclear paths naturally branch simultaneously with electronic

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wavepacket bifurcation in the nonadiabatic region, and each of them eventually runs on one of the adiabatic potential energy surfaces asymptotically. This nuclear dynamics is driven by a generalized classical force in a matrix form [30]. To handle the infinitely many cascades of branching (non-Born-Oppenheimer) paths that are expected as rigorous solutions, an approximation of averaging them in phase space has been proposed. The paths thus generated are smoothly connected throughout the entire space and naturally branch eventually in the asymptotic regions. (See Ref. [29] for illustrative examples of branching and phase-space-averaged paths in the numerical realization of PSANB.) They thereby represent the quantum entanglement between electrons and nuclei in the mixed quantum-classical representation [30]. The entanglement is an essential feature of nonadiabatic transition, which originates from wave-packet bifurcation (see Ref. [31] for direct observation of the wave-packet bifurcation).

It has been numerically verified [29] that PSANB, derived and approximated in the Schrödinger formalism, indeed accurately represents electronic wave-packet bifurcation along smoothly branching paths with and without intense laser fields. Yet there remain some important aspects to be examined. We therefore develop a general path-integral theory of nonadiabatic transition to comprehend the theoretical structure of nonadiabatic dynamics and general mechanics in the mixed quantum-classical representation. Although it looks more complicated, the path integral has an advantage over the Schrödinger dynamics in that the dynamical quantities are all described as the *c* number from the outset in a systematic manner and therefore facilitate extraction of vivid physical insights that appeal to intuition. Nonadiabatic coupling terms arise naturally from the overlap integrals between electronic states of adjacent nuclear positions. Reduction to semiclassical dynamics is clearly formulated by the stationary phase approximation. Pechukas [32,33] and, more recently, Krishna [34] have made full use of the virtue of path-integral formalism to derive formal equations for the time evolution of electron-nucleus coupled systems. We further extend the path-integral formalism so as to analyze practical computational schemes. On the way to such reduction, we clarify the essential features, physical implications, and limitations of the semiclassical Ehrenfest theory and PSANB scheme.

Besides, we show the conservation laws and partial violation of energy, linear momentum, and angular momentum in the SET and PSANB, or, more generally, those in the mixed quantum-classical representation, which have not been explicitly studied before. These provide a critical guiding principle in constructing a general dynamical theory in the mixed quantum and classical systems. Also, we extend the present electron-nucleus path-integral formalism to its nonadiabatic dynamics in a classical vector potential in electromagnetic fields.

This paper is organized as follows. First, in Sec. II, we set up a path-integral formalism for nonadiabatic dynamics in molecules. Then, in Sec. III, we analyze the SET and PSANB from the viewpoint of the path integral and clarify their physical implications. Conservation laws in dynamics in those mixed quantum-classical representations are discussed in Sec. IV. Finally, an extension of the present path integral is made so as to treat nonadiabatic dynamics in laser fields in Sec. V. The paper is concluded in Sec. VI with some remarks.

II. PATH-INTEGRAL FORMULATION

It is Pechukas [32,33] who gave a path-integral description of electron-nucleus coupled systems for the first time. In his formalism, an electronic path integral is performed on fixed nuclear coordinates, which is then followed by a nuclear path integral to recover the nuclear quantum effect. This stepwise integration is theoretically adequate, and on the contrary, the resultant equation to determine the stationary paths turns out to be path dependent, requiring a self-consistent calculation. More recently, Krishna [34] has built a path-integral formalism of nonadiabatic transitions in a different perspective of the Pechukas theory. He has analyzed many important aspects of nonadiabatic dynamics, including the theoretical foundation of the surface hopping model, and so on. We develop here a novel path-integral formalism for nonadiabatic dynamics, which first looks as though it is complementary to Krishna's ansatz but eventually proceeds to totally different representation and analyses of our own issues. In particular, we figure out the split path integration to study in depth the smooth branching of paths as first proposed in PSANB [29], the equations of motion to generate them, the conservation laws, and the nonadiabatic dynamics in laser fields.

A. System studied

The system of our interest is a molecule that contains N_e electrons and N_n nuclei that couple strongly with each other. The Hamiltonian of the system is given as

$$\mathcal{H} = \mathcal{H}^{\text{nuc}} + \mathcal{H}^{\text{el}}, \tag{1}$$

where $\mathcal{H}^{\text{nuc}}$ is the nuclear part

$$\mathcal{H}^{\text{nuc}} = \sum_{j,a} \frac{1}{2M_j}\left(\frac{\hbar}{i}\frac{\partial}{\partial R^{(j,a)}} - \frac{Q_j}{c}A^a\right)^2 + U_{\text{nuc}}, \tag{2}$$

and $\mathcal{H}^{\text{el}}$ is the electronic part, including the electron-nucleus interaction part, such that

$$\mathcal{H}^{\text{el}} = \sum_{j,a} \frac{1}{2m_e}\left(\frac{\hbar}{i}\frac{\partial}{\partial r^{(j,a)}} - \frac{q_e}{c}A^a\right)^2 + V_{\text{el-el}} + V_{\text{nuc-el}}. \tag{3}$$

The indices j are for nuclei or electrons, and a's stand for three-dimensional Cartesian indices (x,y,z). These are also combined in a Greek index as $\mu = (j,a)$. We also use $\mathbf{R}$ to represent the collective vector of all the nuclear positions: $\mathbf{R} = (R^{(1,x)}, R^{(1,y)}, R^{(1,z)}, R^{(2,x)}, \ldots)$. $V_{\text{nuc-el}}$ is the electron-nuclear Coulombic interaction, U_{nuc} is the potential for nuclei as well as the nucleus-nucleus interaction term, and $V_{\text{el-el}}$ is the electron-electron interaction term. M_j, Q_j, m_e, and q_e denote the jth nuclear mass, the jth nuclear charge, the electron mass, and the electron charge, respectively. A^a is an externally applied electromagnetic vector potential. For simplicity, we first consider a field-free case. The effect of a nonzero field is discussed in Sec. V.

Although Eqs. (1)–(3) are formally written in configuration space, we consider electronic degrees of freedom in the Hilbert space of electronic state vectors in the rest of this paper. For a given nuclear configuration $\mathbf{R}$, the electronic Hilbert space is expanded in an $\mathbf{R}$-dependent basis set $\{|\phi_a : \mathbf{R}\rangle\}$, where ϕ_a denotes the ath state. The entire set of indices is denoted $\Lambda_{\mathbf{R}}$. For simplicity, we further assume orthonormality,

$$\langle \phi_a : \mathbf{R} | \phi_b : \mathbf{R} \rangle = \delta_{a,b} \quad \text{for all} \quad a,b \in \Lambda_{\mathbf{R}}. \tag{4}$$

The $\mathbf{R}$-dependent electronic Hamiltonian $\mathcal{H}^{\mathrm{el}}(\mathbf{R})$ is defined as

$$\mathcal{H}^{\mathrm{el}}(\mathbf{R}) = \langle \mathbf{R} | \mathcal{H}^{\mathrm{el}} | \mathbf{R} \rangle, \tag{5}$$

where $|\mathbf{R}\rangle$ is the nuclear "ket," belonging to the nuclear configuration operator $\mathbf{R}$. $\mathcal{H}^{\mathrm{el}}(\mathbf{R})$ is expanded as

$$\mathcal{H}^{\mathrm{el}}(\mathbf{R}) = \sum_{a,b \in \Lambda(\mathbf{R})} |\phi_a : \mathbf{R}\rangle \mathcal{H}^{\mathrm{el}}_{ab}(\mathbf{R}) \langle \phi_b : \mathbf{R}|, \tag{6}$$

with

$$\mathcal{H}^{\mathrm{el}}_{ab}(\mathbf{R}) = \langle \phi_a : \mathbf{R} | \mathcal{H}^{\mathrm{el}}(\mathbf{R}) | \phi_b : \mathbf{R} \rangle. \tag{7}$$

The state of the total system is expanded in a product of the electronic state and nuclear state $|\phi_a : \mathbf{R}\rangle|\mathbf{R}\rangle$. The state of the whole system is characterized as $\{\mathbf{R},\xi(\mathbf{R})\}$, where the nuclear configuration is denoted $\mathbf{R}$ and the electronic state is symbolically denoted $\xi(\mathbf{R})$.

B. Path-integral formulation of electron-nucleus coupled dynamics

1. Integration by step

We consider the transition amplitude of the system from a state $\{\mathbf{R}_i,\xi_i(\mathbf{R}_i)\}$ at time t_i to a state $\{\mathbf{R}_f,\xi_f(\mathbf{R}_f)\}$ at time t_f. We discretize the time interval t_i to t_f into N time slices. Each time interval is $\epsilon = \frac{t_f - t_i}{N}$; $N+1$ time points are denoted $\{t_n\}$, with $t_n = t_i + \epsilon n$. The nuclear coordinate at each time point t_n is denoted $\mathbf{R}_n$, which satisfies, on each boundary, $\mathbf{R}_0 = \mathbf{R}_i$ and $\mathbf{R}_N = \mathbf{R}_f$, respectively. The electronic states are expanded in $\mathbf{R}_n$-dependent bases $|\phi_{a_n} : \mathbf{R}_n\rangle$, which satisfy the orthonormal condition Eq. (4). The whole set of nuclear coordinates is denoted $\{\mathbf{R}\} = \{\mathbf{R}_0,\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N\}$. The propagator for the total system is represented, up to first order in ϵ, as

$$\mathcal{K}(\mathbf{R}_f,\xi_f(\mathbf{R}_f),t_f;\mathbf{R}_i,\xi_i(\mathbf{R}_i),t_i) = \int d\mathbf{R}_{N-1} d\mathbf{R}_{N-2} \cdots d\mathbf{R}_1 \sum_{a_N}\sum_{a_{N-1}} \cdots \sum_{a_1}\sum_{a_0} \langle \xi_f : \mathbf{R}_f | \phi_{a_N} : \mathbf{R}_N \rangle$$
$$\times \prod_{j=0}^{N-1} \langle \mathbf{R}_{j+1} | \langle \phi_{a_{j+1}} : \mathbf{R}_{j+1} | e^{-\frac{i}{\hbar}\epsilon \mathcal{H}} | \phi_{a_j} : \mathbf{R}_j \rangle | \mathbf{R}_j \rangle \langle \phi_{a_0} : \mathbf{R}_0 | \xi_i : \mathbf{R}_i \rangle. \tag{8}$$

This expression is equivalent, in the sense of the path integration, to

$$\mathcal{K}(\mathbf{R}_f,\xi_f(\mathbf{R}_f),t_f;\mathbf{R}_i,\xi_i(\mathbf{R}_i),t_i)$$
$$= \int d\mathbf{R}_{N-1} \cdots d\mathbf{R}_1 \sum_{a_N}\sum_{a_{N-1}} \cdots \sum_{a_1}\sum_{a_0} \langle \xi_f : \mathbf{R}_f | \phi_{a_N} : \mathbf{R}_N \rangle \langle \phi_{a_0} : \mathbf{R}_0 | \xi_i : \mathbf{R}_i \rangle$$
$$\times \prod_{n=0}^{N-1} \left(\exp\left[\frac{i}{\hbar} \left(\sum_j \frac{M_j \left(\mathbf{R}^j_{n+1} - \mathbf{R}^j_n\right)^2}{2\epsilon} - U_{\mathrm{nuc}}(\mathbf{R}_n)\epsilon \right) \right] \langle \phi_{a_{n+1}} : \mathbf{R}_{n+1} | e^{-\frac{i}{\hbar}\epsilon \mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)} | \phi_{a_n} : \mathbf{R}_n \rangle \right), \tag{9}$$

which is further rewritten as

$$\mathcal{K}(\mathbf{R}_f,\xi_f(\mathbf{R}_f),t_f;\mathbf{R}_i,\xi_i(\mathbf{R}_i),t_i)$$
$$= \int \prod_{n=1}^{N-1} d\mathbf{R}_n \exp\left[\frac{i}{\hbar} S_{\mathrm{nuc}}\left(\{\mathbf{R}\}\right) \right.$$
$$\left. + \frac{i}{\hbar} S_{\mathrm{eff}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i) \right], \tag{10}$$

where $\{\mathbf{R}\}$ is, again, the sequence of sliced coordinates adopted in the Trotter decomposition, and the nuclear coordinate integral $\int d\mathbf{R}_{N-1} d\mathbf{R}_{N-2} \cdots d\mathbf{R}_1$ is performed with an appropriate normalization factor in what follows. Details of the Trotter decomposition in Eq. (8) are summarized in Appendix A. The nuclear action $S_{\mathrm{nuc}}\left(\{\mathbf{R}\}\right)$ in Eq. (10) is defined as

$$S_{\mathrm{nuc}}\left(\{\mathbf{R}\}\right) = \sum_n \left(\sum_j \frac{M_j \left(\mathbf{R}^j_{n+1} - \mathbf{R}^j_n\right)^2}{2\epsilon} - U_{\mathrm{nuc}}(\mathbf{R}_n)\epsilon \right). \tag{11}$$

The effective action $S_{\mathrm{eff}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i)$ arising from the electronic part is defined as

$$S_{\mathrm{eff}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i)$$
$$= \frac{\hbar}{i} \ln \mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i), \tag{12}$$

where the electronic propagator $\mathcal{K}^{\mathrm{el}}$ is defined as

$$\mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i)$$
$$= \sum_{a_N}\sum_{a_{N-1}} \cdots \sum_{a_1}\sum_{a_0} \langle \xi_f : \mathbf{R}_f | \phi_{a_N} : \mathbf{R}_N \rangle \langle \phi_{a_0} : \mathbf{R}_0 | \xi_i : \mathbf{R}_i \rangle$$
$$\times \left[\prod_{n=0}^{N-1} \langle \phi_{a_{n+1}} : \mathbf{R}_{n+1} | e^{-\frac{i}{\hbar}\epsilon \mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)} | \phi_{a_n} : \mathbf{R}_n \rangle \right]. \tag{13}$$

2. Evaluation of overlaps

We expand Eq. (13) up to first order in time interval ϵ. Since it includes the electronic matrix elements between the state vectors of two different nuclear configurations $\mathbf{R}$, the overlap product, expanded up to second order in the nuclear coordinate difference $\mathbf{R}_{n+1} - \mathbf{R}_n$, becomes

$$\begin{aligned}\langle \phi_a : \mathbf{R}_{n+1} | \phi_b : \mathbf{R}_n \rangle &= \delta_{a,b} - \sum_{\mu} \left(R^{\mu}_{n+1} - R^{\mu}_{n}\right) X^{\mu}_{ab}(\mathbf{R}_{n+1/2}) \\ &\quad + \frac{1}{2} \sum_{\mu,\nu} \left(R^{\mu}_{n+1} - R^{\mu}_{n}\right)\left(R^{\nu}_{n+1} - R^{\nu}_{n}\right) \mathcal{Y}^{\mu,\nu}_{ab}(\mathbf{R}_{n+1/2}). \qquad (14)\end{aligned}$$

Here we have introduced the first- and second-order derivative coupling matrices X^{μ} and $\mathcal{Y}^{\mu,\nu}$, whose matrix elements are defined as

$$X^{\mu}_{ab}(\mathbf{R}) = \left\langle \phi_a : \mathbf{R} \left| \frac{\partial \phi_b}{\partial R^{\mu}} : \mathbf{R} \right.\right\rangle, \qquad (15)$$

and

$$\begin{aligned}\mathcal{Y}^{\mu,\nu}_{ab}(\mathbf{R}) &= \frac{1}{4}\left(\left\langle \frac{\partial^2 \phi_a}{\partial R^{\mu} \partial R^{\nu}} : \mathbf{R} \right| \phi_b : \mathbf{R} \right\rangle - \left\langle \frac{\partial \phi_a}{\partial R^{\mu}} : \mathbf{R} \left| \frac{\partial \phi_b}{\partial R^{\nu}} : \mathbf{R} \right.\right\rangle \\ &\quad - \left\langle \frac{\partial \phi_a}{\partial R^{\nu}} : \mathbf{R} \left| \frac{\partial \phi_b}{\partial R^{\mu}} : \mathbf{R} \right.\right\rangle + \left\langle \phi_a : \mathbf{R} \left| \frac{\partial^2 \phi_b}{\partial R^{\mu} \partial R^{\nu}} : \mathbf{R} \right.\right\rangle \right). \qquad (16)\end{aligned}$$

We have also introduced the notation $\mathbf{R}_{n+1/2}$ in Eq. (14), which denotes the middle point of $\mathbf{R}_n$ and $\mathbf{R}_{n+1}$, that is, $\mathbf{R}_{n+1/2} = \frac{\mathbf{R}_n + \mathbf{R}_{n+1}}{2}$. Nuclear coordinate derivatives that appear as transition momenta between different nuclear coordinates $\mathbf{R}_{n+1}$and $\mathbf{R}_n$ are to be evaluated at the "midpoint" $\mathbf{R}_{n+1/2}$. This rule is widely referred to as the "midpoint rule," [35] and we adopt it in what follows unless otherwise noted. For notational convenience, we also use three-component (x,y,z) vector notation for X, $\mathbf{X}_{ab}(\mathbf{R}) = \langle \phi_a : \mathbf{R} | \nabla^j | \phi_b : \mathbf{R} \rangle$, and a three-component summed-up form of $\mathcal{Y}$, defined as $\mathcal{Y}^j(\mathbf{R}) = \sum_{a=x,y,z} \mathcal{Y}^{(j,a),(j,a)}(\mathbf{R})$. Symbols with a hat denote the "operator forms" of the corresponding quantities in the manner $\hat{\mathcal{O}}(\mathbf{R}) = \sum_{a,b} |\phi_a : \mathbf{R}\rangle \mathcal{O}_{ab}(\mathbf{R}) \langle \phi_b : \mathbf{R}|$, where $\mathcal{O}$ is either $\mathcal{Y}^{\mu,\nu}, X^{\mu}$, or $\mathcal{Y}^j$. Derivation of Eq. (16) is given in Appendix B.

We then make several assumptions about nuclear paths so that we can identify the terms that contribute to first order in ϵ. (i) In the representation of paths $\{\mathbf{R}\}, |\mathbf{R}_{n+1} - \mathbf{R}_n|$ is an $O(\epsilon)$ quantity, and $|\mathbf{R}_{n+1} + \mathbf{R}_{n-1} - 2\mathbf{R}_n|$ is an $O(\epsilon^2)$ quantity. (ii) Each point $\mathbf{R}_n$ in discretized paths is to be integrated with an appropriate Gaussian kernel. We assume, up to first order in ϵ, that

$$\begin{aligned}\int d\mathbf{R}_{N-1} \cdots d\mathbf{R}_1 e^{\frac{i}{\hbar} S_{\text{nuc}}} \left(R^{(j,a)}_{n+1} - R^{(j,a)}_{n}\right)\left(R^{(k,b)}_{n+1} - R^{(k,b)}_{n}\right) \\ = \delta_{j,k} \delta_{a,b} \frac{i\hbar\epsilon}{M_j} \quad \text{for } \forall\, n. \qquad (17)\end{aligned}$$

Note that the jth nuclear mass M_j and the time interval ϵ are included in S_{nuc} as in Eq. (11). These assumptions are satisfied if the nuclear action of the system is given as Eq. (11). We thus obtain, up to first order in ϵ,

$$\begin{aligned}&\left\langle \phi_{a_{n+1}} : \mathbf{R}_{n+1} \left| e^{-\frac{i}{\hbar}\epsilon \mathcal{H}^{\text{el}}(\mathbf{R}_n)} \right| \phi_{a_n} : \mathbf{R}_n \right\rangle \\ &= \exp\left(-\frac{i}{\hbar} \epsilon \mathcal{H}^{\text{el}}_{a_{n+1},a_n}(\mathbf{R}_n) - \sum_{\mu} \epsilon \dot{R}^{\mu}_{n} X^{\mu}(\mathbf{R}_{n+1/2}) \right. \\ &\quad \left. + \frac{1}{2} \sum_{\mu,\nu} \left(R^{\mu}_{n+1} - R^{\mu}_{n}\right)\left(R^{\nu}_{n+1} - R^{\nu}_{n}\right) \mathcal{Y}^{\mu,\nu}(\mathbf{R}_{n+1/2}) \right), \qquad (18)\end{aligned}$$

where

$$\dot{R}^{\mu}_{n} \epsilon = R^{\mu}_{n+1} - R^{\mu}_{n}. \qquad (19)$$

3. *Path integral for electronic degrees of freedom*

To implement the path integral of electronic degrees of freedom, we expand the electronic states in a complete basis set. Although the path integral allows for an arbitrary choice of basis, we use a set of configuration state functions (CSFs) as the basis, which are symmetry-adapted linear combinations of the Slater determinants that are eigenstates of spin and orbital angular momenta. In numerical calculation, CSFs are calculated using the graphical unitary group approach [36,37]. The ith CSF at $\mathbf{R}$ is denoted $|I : \mathbf{R}\rangle$, which satisfies the orthonormal condition

$$\langle I : \mathbf{R} | J : \mathbf{R} \rangle = \delta_{I,J}. \qquad (20)$$

The closure is expressed by the c-number integral over CSF coefficients in the manner of coherent state representation [40,41] as follows: Define an "unnormalized" electronic state vector $|c : \mathbf{R}\rangle \equiv \sum_I \tilde{c}^I |I : \mathbf{R}\rangle$, which has a closure relation

$$\int d[c,c^*] |c : \mathbf{R}\rangle \langle c : \mathbf{R}| \exp\left[-\sum_I |\tilde{c}^I|^2 \right] = 1 \qquad (21)$$

as in the generalized coherent state representation. To save the spacing, we further define "normalized" coefficients c^I in such a way that

$$c^I \equiv \frac{\tilde{c}^I}{\sqrt{\sum_J |\tilde{c}^J|^2}}. \qquad (22)$$

All c^I's in the following action integrals are to be understood as "normalized" coefficients. Details of the notation we adopted here are summarized in Appendix C. With this set of bases, the electronic propagator becomes

$$\begin{aligned}&\mathcal{K}^{\text{el}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f), t_f; \xi_i(\mathbf{R}_i), t_i) \\ &= \int d[c_N, c_N^*] \langle \xi_f : \mathbf{R}_f | c_N : \mathbf{R}_f \rangle d[c_0, c_0^*] \langle c_0 : \mathbf{R}_i | \xi_i : \mathbf{R}_i \rangle \\ &\quad \times \prod_{n=1}^{N-1} d[c_n, c_n^*] \langle c_{n+1} : \mathbf{R}_{n+1} | e^{-\frac{i}{\hbar}\epsilon \mathcal{H}^{\text{el}}(\mathbf{R}_n)} | c_n : \mathbf{R}_n \rangle. \qquad (23)\end{aligned}$$

Applying the same procedure that we used to derive Eq. (18), we obtain

$$\begin{aligned}
&\mathcal{K}^{el}\boldsymbol{(}\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i\boldsymbol{)}\\
&\simeq \int (d[c_N,c_N^*]\langle\xi_f|c_N\rangle)\,(d[c_0,c_0^*]\langle c_0|\xi_i\rangle)\\
&\quad\times\prod_{n=1}^{N-1} d[c_n,c_n^*]\exp\Bigg(\frac{i}{\hbar}\sum_{I,J} c_{n+1}^{*I}\Bigg(i\hbar\big(c_{n+1}^I - c_n^I\big)\delta_{IJ}\\
&\quad-(\mathcal{H}^{\text{el}}(\mathbf{R}_n)_{IJ}\epsilon - i\hbar\dot{\mathbf{R}}_n\cdot\mathbf{X}_{IJ}\epsilon)\\
&\quad-\frac{i\hbar}{2}\sum_{\mu,\nu}\big(R_{n+1}^{\mu}-R_n^{\mu}\big)\big(R_{n+1}^{\nu}-R_n^{\nu}\big)\mathcal{Y}_{IJ}^{\mu,\nu}\Bigg)c_n^J\Bigg).
\end{aligned}\tag{24}$$

C. Evaluation of path integrals

The formal expression of the electronic kernel formulated thus far is not necessarily practically useful. As a standard technique, we also apply the stationary phase approximation to proceed further. The stationary phase conditions for nuclear and electronic paths give rise to coupled equations of motion for both degrees of freedom. Then the approximate time evolution of the system is numerically realized by integration of the coupled equations of motion.

1. Path integral for nuclear degrees of freedom

We seek, for the stationary phase condition with respect to R_n^{μ},

$$\begin{aligned}
&\frac{\partial}{\partial R_n^{\mu}}(S_{\text{nuc}}[\{\mathbf{R}\}]+S_{\text{eff}}[\{\mathbf{R}\}])\\
&= -M\ddot{R}_n^{\mu}\epsilon\\
&\quad-\frac{\partial}{\partial R_n^{\mu}}\left(U_{\text{nuc}}\epsilon - \frac{\hbar}{i}\ln\mathcal{K}^{\text{el}}\boldsymbol{(}\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i\boldsymbol{)}\right)\\
&= 0,
\end{aligned}\tag{25}$$

where

$$\ddot{R}_n^{\mu}\epsilon^2 = R_{n+1}^{\mu} + R_{n-1}^{\mu} - 2R_n^{\mu}.\tag{26}$$

Thus we obtain the "equation of motion" for nuclei:

$$M_j\ddot{R}_n^{(j,a)} = -\frac{\partial}{\partial R_n^{\mu}}U_{\text{nuc}} + \mathcal{F}_n^{(j,a)}\Big|_{[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]}.\tag{27}$$

The quantity $\mathcal{F}$ in this expression is defined as

$$\begin{aligned}
&\mathcal{F}_n^{\mu}\Big|_{[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]}\\
&= -\frac{\partial}{\partial R_n^{\mu}}\left(-\frac{\hbar}{i\epsilon}\ln\mathcal{K}^{\text{el}}\boldsymbol{(}\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i\boldsymbol{)}\right)\\
&= \overline{\langle c_{n+1} : \mathbf{R}_{n+1}|\hat{\mathcal{F}}_n^{\mu}|c_n : \mathbf{R}_n\rangle}_{[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]},
\end{aligned}\tag{28}$$

where the operator $\hat{\mathcal{F}}_n^{\mu}$ is defined as

$$\begin{aligned}
\hat{\mathcal{F}}_n^{\mu} &= \mathcal{H}^{\text{el}}(\mathbf{R}_n)\hat{X}^{\mu} - \hat{X}^{\mu}\mathcal{H}^{\text{el}}(\mathbf{R}_n)\\
&\quad-\sum_{I,J}|I : \mathbf{R}_n\rangle\frac{\partial}{\partial R_n^{\mu}}\langle I : \mathbf{R}_n|\mathcal{H}^{\text{el}}(\mathbf{R}_n)|J : \mathbf{R}_n\rangle\langle J : \mathbf{R}_n|\\
&\quad+i\hbar\dot{R}_n^{\nu}(\hat{X}^{\mu}\hat{X}^{\nu} - \hat{X}^{\nu}\hat{X}^{\mu}) + \boldsymbol{(}\dot{\mathbf{R}}_n\times(\nabla\times i\hbar\hat{\mathbf{X}})\boldsymbol{)}^{\mu}.
\end{aligned}\tag{29}$$

The symbol $\overline{\cdots}_{[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]}$ in Eq. (28) is defined such that, for an arbitrary electronic operator $\hat{A}$,

$$\begin{aligned}
&\overline{A}_{n\ [\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]}\\
&= \frac{1}{\mathcal{K}^{el}\boldsymbol{(}\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i\boldsymbol{)}}\\
&\quad\times\int d[c_N,c_N^*]\langle\xi_f : \mathbf{R}_f|c_N : \mathbf{R}_N\rangle\\
&\quad\times\prod_{\ell=n+1}^{N-1}\left\{d[c_\ell,c_\ell^*]\langle c_{\ell+1} : \mathbf{R}_{\ell+1}|e^{-\frac{i}{\hbar}\epsilon\mathcal{H}^{\text{el}}(\mathbf{R}_\ell)}|c_\ell : \mathbf{R}_\ell\rangle\right\}\\
&\quad\times d[c_n,c_n^*]\langle c_{n+1} : \mathbf{R}_{n+1}|e^{-\frac{i}{\hbar}\epsilon\mathcal{H}^{\text{el}}(\mathbf{R}_n)}\hat{A}|c_n : \mathbf{R}_n\rangle\\
&\quad\times\prod_{\ell=0}^{n-1}\left\{d[c_\ell,c_\ell^*]\langle c_{\ell+1} : \mathbf{R}_{\ell+1}|e^{-\frac{i}{\hbar}\epsilon\mathcal{H}^{\text{el}}(\mathbf{R}_\ell)}|c_\ell : \mathbf{R}_\ell\rangle\right\}\\
&\quad\times\langle c_0 : \mathbf{R}_0|\xi_i : \mathbf{R}_i\rangle,
\end{aligned}\tag{30}$$

which recalls that the electronic matrix elements are to be evaluated by path integration in the electronic degrees of freedom along the series of nuclear coordinates (path). We further note that $\mathcal{Y}$-related terms become first order in nuclear displacement and do not appear in the stationary phase condition.

The operator $\hat{\mathcal{F}}$ is referred to as the "force matrix" in what follows. It is equivalent to the operator form of the force matrix formerly defined in Eq. (28) of Ref. [29]. The quantity $\mathcal{F}^{\mu}$ in Eq. (29) is called the "force form," which is a c-number quantity that depends on the double-ended boundary of the kernel $[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]$, corresponding to an evaluation of the force matrix along a "path" in $[\{\mathbf{R}\};\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]$. Therefore, naively, the force and a resultant path, if any, should be determined in a self-consistent manner as in the original Pechukas procedure [32,33] (recall that the force matrix is defined locally and does not depend on the boundary conditions). We return to this aspect later. Among the terms on the right-hand side of Eq. (29), the first to third terms are the derivatives of the electronic Hamiltonian. In fact, as pointed out in Ref. [23], when the basis set $\{|I : \mathbf{R}\rangle\}$ is complete, $-\langle I : \mathbf{R}|\mathcal{H}^{\text{el}}(\mathbf{R}_n)X^{\mu} - X^{\mu}\mathcal{H}^{\text{el}}(\mathbf{R}_n)|J : \mathbf{R}\rangle$ and $-\frac{\partial}{\partial R_n^{\mu}}\langle I : \mathbf{R}|\mathcal{H}^{\text{el}}(\mathbf{R}_n)|J : \mathbf{R}\rangle$ are combined to give the "Hellman-Feynman force": $-\langle I : \mathbf{R}|\frac{\partial}{\partial R^{\mu}}\mathcal{H}^{\text{el}}(\mathbf{R}_n)|J : \mathbf{R}\rangle$. The fourth to sixth terms originate from the derivatives of the X matrices. The fourth and fifth terms arise if X matrices are mutually incommutable. The sixth term is analogous to the Lorentz force in the electromagnetic dynamics. This kind of force is discussed in detail in Ref. [30].

2. Path integral for electronic degrees of freedom

Next we derive the stationary phase condition for electronic degrees of freedom. Differentiation of Eq. (24) with respect to c_{n+1}^{*I} gives the stationary phase condition for the electronic state as

$$\begin{aligned}
i\hbar\dot{c}_n^I = \sum_J\Bigg(&\mathcal{H}^{\text{el}}(\mathbf{R}_n)_{IJ} - i\hbar\dot{\mathbf{R}}_n\cdot\mathbf{X}_{IJ}\\
&+\frac{i\hbar}{2}\sum_{\mu,\nu}\big(R_{n+1}^{\mu}-R_n^{\mu}\big)\big(R_{n+1}^{\nu}-R_n^{\nu}\big)\mathcal{Y}_{IJ}^{\mu,\nu}\Bigg)c_n^J,
\end{aligned}\tag{31}$$

with $\dot{c}_n^I \epsilon = c_{n+1}^I - c_n^I$ in discretized notation. The last term in Eq. (31) has a subtle effect as shown later. Although it is of second order in nuclear displacement, if we perform the path integral of the nuclear coordinates, or apply the steepest descent method, it yields a contribution of order $O(\epsilon)$ as in Eq. (17). The physical origin of this $O(\epsilon)$ contribution is the quantal fluctuation of nuclear coordinates. If we apply the stationary phase approximation for the nuclear degrees of freedom at the same level of approximation, the last term in Eq. (31), that is, $\frac{i\hbar}{2}\sum_{\mu,\nu}(R_{n+1}^{\mu} - R_n^{\mu})(R_{n+1}^{\nu} - R_n^{\nu})\mathcal{Y}_{IJ}^{\mu,\nu}$ is replaced with $\sum_j \frac{\hbar^2}{2M_j}\mathcal{Y}_{IJ}^j$, and thus we obtain

$$i\hbar\dot{c}_n^I = \sum_J \left(\mathcal{H}^{\rm el}(\mathbf{R}_n)_{IJ} - i\hbar\dot{\mathbf{R}}_n \cdot \mathbf{X}_{IJ} - \sum_j \frac{\hbar^2}{2M_j}\mathcal{Y}_{IJ}^j\right)c_n^J. \tag{32}$$

Note that the term $\mathcal{Y}_{IJ}^j$ in Eq. (32), defined in Eq. (16), is manifestly Hermitian, provided that the the derivative coupling is evaluated at the midpoint $\mathbf{R}_{n+1/2}$. A less symmetric expression is obtained through the "end-point" derivative as

$$i\hbar\dot{c}_n^I = \sum_J \left(\mathcal{H}^{\rm el}(\mathbf{R}_n)_{IJ} - i\hbar\dot{\mathbf{R}}_n \cdot \mathbf{X}_{IJ} - \sum_j \frac{\hbar^2}{2M_j}Y_{IJ}^j\right)c_n^J, \tag{33}$$

with

$$Y_{ab}^j = \left\langle \phi_a : \mathbf{R} \middle| \sum_a \frac{\partial^2 \phi_b}{\partial R^{(j,a)2}} : \mathbf{R} \right\rangle. \tag{34}$$

The last term in Eq. (33) is the same as the second-order derivative coupling Y_{IJ}^k in Eq. (8) of Ref. [30]. (More precisely, our Y_{IJ}^j corresponds to the sum of Y_{IJ}^k in Ref. [30] over all the coordinate indices k that belong to the jth nucleus.) The diagonal elements of Y^j are known as an energy correction arising from the non-Born-Oppenheimer effect [42].

Note that in our formulation, the path integrations over the nuclear coordinates have to be performed after the electronic path integrals. Thus, strictly speaking, the replacement of $\frac{i\hbar}{2}\sum_{\mu,\nu}(R_{n+1}^{\mu} - R_n^{\mu})(R_{n+1}^{\nu} - R_n^{\nu})\mathcal{Y}_{IJ}^{\mu,\nu}$ with $\sum_j \frac{\hbar^2}{2M_j}\mathcal{Y}_{IJ}^j$ effectively violates the order. Nevertheless, we adopt this approximation on the grounds that it gives physically reasonable equations of motion.

III. STUDY OF PATH BRANCHING IN TERMS OF SPLIT PATH INTEGRATIONS

The equations of motion for nuclei, Eq. (27), and for electrons, Eq. (32), should be solved simultaneously. However, as noted earlier, Eq. (27) implicitly depends on the resultant nuclear path to be solved, if any, and should be solved in a recursive manner, which is practically prohibitive. Therefore we next study a methodology to resolve this problem on a practical level.

A. Split path integral and branching

Before proceeding, we introduce a general transformation to the electronic part of the path integrals in Eq. (9). Consider an identical transformation of path integral by inserting the identity operator $1 = \sum_{p\in\Lambda}|\lambda_p\rangle\langle\lambda_p|$ at some fixed time t_S,[1] where t_S lies in between t_i and t_f ($t_i \leqslant t_S \leqslant t_f$), and $\{\lambda_p\}_{p\in\Lambda}$ is a complete basis set that satisfies the orthonormal relation, $\langle\lambda_{p'}|\lambda_p\rangle = \delta_{p',p}$. The choice of $\{\lambda_p\}_{p\in\Lambda}$ is otherwise arbitrary, and we specify it later to our convenience on a physical ground. We obtain, as an identical transformation of Eq. (9),

$$\begin{aligned}
&\mathcal{K}(\mathbf{R}_f,\xi_f(\mathbf{R}_f),t_f;\mathbf{R}_i,\xi_i(\mathbf{R}_i),t_i)\\
&\quad = \int d\mathbf{R}_{N-1}\cdots d\mathbf{R}_1 e^{\frac{i}{\hbar}S_{\rm nuc}(\{\mathbf{R}_n\})}\\
&\qquad \times \sum_p \mathcal{K}^{\rm el}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\lambda_p,t_S)\\
&\qquad \times \mathcal{K}^{\rm el}(\{\mathbf{R}\} : \lambda_p,t_S;\xi_i(\mathbf{R}_i),t_i)\\
&\quad = \sum_p \int d\mathbf{R}_{N-1}\cdots d\mathbf{R}_1 e^{\frac{i}{\hbar}S_{\rm nuc}[\{\mathbf{R}_n\}]}\\
&\qquad \times \mathcal{K}^{\rm el}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\lambda_p,t_S)\mathcal{K}^{\rm el}(\{\mathbf{R}\} : \lambda_p,t_S;\xi_i(\mathbf{R}_i),t_i)\\
&\quad = \sum_p \int d\mathbf{R}_{N-1}\cdots d\mathbf{R}_1 \exp\left(\frac{i}{\hbar}S_{\rm nuc}\left(\{\mathbf{R}\}\right)\right)\\
&\qquad \times \exp\left(\frac{i}{\hbar}S_{\rm eff}^{(\xi_f;\lambda_p)}\left(\{\mathbf{R}\}\right) + \frac{i}{\hbar}S_{\rm eff}^{(\lambda_p;\xi_i)}\left(\{\mathbf{R}\}\right)\right).
\end{aligned} \tag{35}$$

As shown in Eq. (35), the propagator is split, and each propagator has a state projection $|\lambda_p\rangle\langle\lambda_p|$ at the time point t_S. The effective action $S_{\rm eff}^{(\xi_f;\lambda_p)}\left(\{\mathbf{R}\}\right)$ in this expression is defined as

$$S_{\rm eff}^{(\xi_f;\lambda_p)}\left(\{\mathbf{R}\}\right) = \frac{\hbar}{i}\ln[\mathcal{K}^{\rm el}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\lambda_p,t_S)]. \tag{36}$$

Equation (35) is merely an identical transformation, provided that the integrations are performed exactly. However, it makes it possible to introduce a new approximation by imposing multiple stationary phase conditions on the nuclear path integrations, as we see later.

We can further insert the electronic state projections $|\lambda_p\rangle\langle\lambda_p|$ at time points $t_{S_1},t_{S_2},\ldots,t_{S_{M-1}}$, to obtain

$$\begin{aligned}
\mathcal{K}(\mathbf{R}_f,\xi_f(\mathbf{R}_f),t_f;\mathbf{R}_i,\xi_i(\mathbf{R}_i),t_i) = {}& \sum_{p_{M-1}}\sum_{p_{M-2}}\cdots\sum_{p_1}\int d\mathbf{R}_{N-1}\cdots d\mathbf{R}_1 \exp\left(\frac{i}{\hbar}S_{\rm nuc}\left(\{\mathbf{R}\}\right)\right)\mathcal{K}^{\rm el}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f),t_f;\lambda_{p_{M-1}},t_{S_{M-1}})\\
&\times \left\{\prod_{k=1}^{M-2}\mathcal{K}^{\rm el}(\{\mathbf{R}\} : \lambda_{p_{k+1}},t_{S_{k+1}};\lambda_{p_k},t_{S_k})\right\}\mathcal{K}^{\rm el}(\{\mathbf{R}\} : \lambda_{p_1},t_{S_1};\xi_i(\mathbf{R}_i),t_i)
\end{aligned}$$

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[1] Here we do not specify the nuclear coordinate $\mathbf{R}$. When we perform the electronic path integral, we fix the nuclear position $\mathbf{R}$ at time points $\{t_n\}$, thus if t_S coincides with one of the t_n values, the nuclear coordinate is $\mathbf{R}_n$; otherwise, the nuclear coordinate takes some intermediate value.

$$= \sum_{p_{M-1}} \sum_{p_{M-2}} \cdots \sum_{p_1} \int d\mathbf{R}_{N-1} \cdots d\mathbf{R}_1 \exp\left(\frac{i}{\hbar} S_{\text{nuc}}(\{\mathbf{R}\})\right) \times \left\{ \prod_{k=0}^{M-1} \mathcal{K}^{\text{el}}\boldsymbol{(}\{\mathbf{R}\} : \lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k}\boldsymbol{)} \right\}$$

$$= \sum_{p_{M-1}} \sum_{p_{M-2}} \cdots \sum_{p_1} \int d\mathbf{R}_{N-1} \cdots d\mathbf{R}_1 \exp\left(\frac{i}{\hbar} S_{\text{nuc}}(\{\mathbf{R}\})\right) \exp\left(\frac{i}{\hbar} \sum_{k=0}^{M-1} S_{\text{eff}}^{(\lambda_{p_{k+1}};\lambda_{p_k})}(\{\mathbf{R}\})\right), \tag{37}$$

where, for notational convenience, we denote $t_{S_M} = t_f$, $t_{S_0} = t_i$, $\lambda_{p_M} = \xi_f$, and $\lambda_{p_0} = \xi_0$.

We then apply the stationary phase approximation for the nuclear coordinate $\mathbf{R}_n$, to obtain

$$M \ddot{R}_n^{\mu\,(\lambda_{p_{a+1}},\lambda_{p_a})} = -\frac{\partial}{\partial R_n^\mu} U_{\text{nuc}} + \mathcal{F}_n^{\mu\,(\lambda_{p_{a+1}},\lambda_{p_a})}\Big|_{[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]}, \tag{38}$$

where p_{a+1} and p_a are chosen so that $t_{p_a} \leqslant t_n \leqslant t_{p_{a+1}}$, and the force form in Eq. (38) is

$$\mathcal{F}_n^{\mu\,(\lambda_{p_{a+1}},\lambda_{p_a})}\Big|_{[\{\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]}$$
$$= -\frac{\partial}{\partial R_n^\mu}\left(-\frac{\hbar}{i\epsilon} \ln \left\{ \prod_{k=0}^{M-1} \mathcal{K}^{\text{el}}(\{\mathbf{R}\} : \lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k}) \right\}\right)$$
$$= \frac{\hbar}{i\epsilon} \frac{\partial_{R_n^\mu} \mathcal{K}^{\text{el}}(\{\mathbf{R}\} : \lambda_{p_{a+1}}, t_{p_{a+1}}; \lambda_{p_a}, t_{p_a})}{\mathcal{K}^{\text{el}}(\{\mathbf{R}\} : \lambda_{p_{a+1}}, t_{p_{a+1}}; \lambda_{p_a}, t_{p_a})}. \tag{39}$$

The stationary phase condition, or the equation of motion, Eq. (38), is valid for the time interval $t_{p_a} \leqslant t \leqslant t_{p_{a+1}}$, and the solution is dependent on the state projection $(\lambda_{p_{a+1}},\lambda_{p_a})$. Thus the displacements in nuclear coordinates and momentum in the time interval t_n to t_{n+1} driven by the force $\mathcal{F}_n^{(\lambda_{p_{a+1}},\lambda_{p_a})}$ are state dependent and hence denoted $\Delta R_n^{\mu\,(\lambda_{p_{a+1}},\lambda_{p_a})}$ and $\Delta P_n^{\mu\,(\lambda_{p_{a+1}},\lambda_{p_a})}$, respectively.[2] On the other hand, the stationary phase condition for the electron system is

$$i\hbar \dot{c}_n^I = \sum_J \left(\mathcal{H}^{\text{el}}(\mathbf{R}_n)_{IJ} - i\hbar \dot{\mathbf{R}}_n \cdot \mathbf{X}_{IJ} - \sum_j \frac{\hbar^2}{2M_j} \mathcal{Y}_{IJ}^j \right) c_n^J, \tag{40}$$

with an additional constraint at time t_{S_a}, $c^I(t = t_{S_a}) = \lambda_{p_a}^I$, where $\lambda_{p_a}^I$ are the expansion coefficients of state $|\lambda_{p_a}\rangle$ in such a manner that $|\lambda_{p_a}\rangle = \sum_I \lambda_{p_a}^I |I\rangle$. Although Eq. (40) has the same form as Eq. (32), all the nuclear-coordinate-dependent quantities $\mathcal{H}^{\text{el}}(\mathbf{R}), X(\mathbf{R})$, and state vectors $\{|I : \mathbf{R}\rangle\}$ are to be evaluated along the state-dependent path.

The nature of the split path integral is further clarified by the following consideration. We note that the original approximation for the path integrals (i.e., the stationary phase approximation without path splitting) are reproduced from Eq. (37) by taking summation over all the electronic state projections before applying the stationary phase approximation, which inevitably imposes that all the stationary displacements $\{\Delta\mathbf{R}_n^{(\lambda_{p_{k+1}},\lambda_{p_k})}\}$ should be the same irrespective of the state projections; that is, $\Delta\mathbf{R}_n^{(\lambda_{p_{k+1}},\lambda_{p_k})} = \widetilde{\Delta\mathbf{R}}_n$ for all k and n. Taking summation before the stationary phase approximation, on the contrary, the effective action becomes

$$S_{\text{eff}} = \frac{\hbar}{i} \ln \left(\sum_{p_{M-1}} \sum_{p_{M-2}} \cdots \sum_{p_1} \left\{ \prod_{k=0}^{M-1} \mathcal{K}^{\text{el}}(\{\mathbf{R}\} : \lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k}) \right\} \right), \tag{41}$$

and $\mathcal{F}_n^\mu|_{[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]}$ looks like

$$\mathcal{F}_n^\mu\Big|_{[\xi_f(\mathbf{R}_f),t_f;\xi_i(\mathbf{R}_i),t_i]} = -\frac{\partial}{\partial R_n^\mu}\left(-\frac{\hbar}{i\epsilon} \ln \left(\sum_{p_{M-1}} \sum_{p_{M-2}} \cdots \sum_{p_1} \left\{ \prod_{k=0}^{M-1} \mathcal{K}^{\text{el}}(\lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k}) \right\} \right) \right)$$
$$= \frac{\hbar}{i\epsilon} \frac{\sum_{p_{M-1}} \sum_{p_{M-2}} \cdots \sum_{p_1} \partial_{R_n^\mu} \mathcal{K}^{\text{el}}(\lambda_{p_{a+1}}, t_{S_{a+1}}; \lambda_{p_a}, t_{S_a}) \left\{ \prod_{k=0}^{\prime\, M-1} \mathcal{K}^{\text{el}}(\lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k}) \right\}}{\sum_{p_{M-1}} \sum_{p_{M-2}} \cdots \sum_{p_1} \left\{ \prod_{k=0}^{M-1} \mathcal{K}^{\text{el}}(\lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k}) \right\}}, \tag{42}$$

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[2] In fact, from the classical nature of the (approximate) time evolution of nuclear coordinates, the nuclear coordinates and the momenta are dependent on *all* state projections in the past, as $\mathcal{R}_{n+1}^{\lambda_{p_{a+1}},\lambda_{p_a},\cdots,\lambda_{p_0}}$ and $\mathcal{P}_{n+1}^{\lambda_{p_{a+1}},\lambda_{p_a},\cdots,\lambda_{p_0}}$, respectively. Thus, for coordinates, even the *displacements* in the time interval t_n to t_{n+1} have an implicit dependence on state projections in the past, as $\Delta\mathcal{R}_n^{(j,a)\,(\lambda_{p_{a+1}},\lambda_{p_a},\cdots,\lambda_{p_0})} = \frac{1}{M_j}(\mathcal{F}_n^{(j,a)\,(\lambda_{p_{a+1}},\lambda_{p_a})}\frac{\epsilon^2}{2} + \mathcal{P}_{n-1}^{\lambda_{p_a},\lambda_{p_{a-1}},\cdots,\lambda_{p_0}}\epsilon)$.

where the product with prime $\prod_{k=0}^{\prime\, M-1}$ is to be taken without the $k = a$ contribution. The nuclear coordinate displacement $\widetilde{\Delta \mathbf{R}}_n$ is driven by the force of Eq. (42), which is "averaged" over the electronic states (effectively, the electronic states involved in the wave packet) with a weight

$$\frac{\prod_{k=0}^{\prime\, M-1} \mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k})}{\sum_{p_{M-1}} \sum_{p_{M-2}} \cdots \sum_{p_1} \left\{ \prod_{k=0}^{M-1} \mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \lambda_{p_{k+1}}, t_{S_{k+1}}; \lambda_{p_k}, t_{S_k}) \right\}}. \tag{43}$$

However, if we use the split path integral, the force form is not "averaged" as in Eq. (39), and approximately the same factor appears as the weight of the probability amplitude (propagator) in Eq. (37). In short, the difference between these two arises from the difference in the order of path summation and the stationary phase approximation.

It is crucial to note that the splitting path integral by electronic state projections, followed by application of the stationary phase approximation for each state-projected effective action, gives the "branching" force form. On the contrary, summation over the electronic state projection *before* the stationary phase approximation, which inevitably restricts the stationary nuclear path to be a single path, gives the "state-averaged" force form. As is intuitively expected, the stationary phase solution for each electronic state gives a correct result in the adiabatic limit, which is formally stated in Appendix D. We next study the notion of path branching due to the "branching" force form in a greater detail.

B. Semiclassical Ehrenfest theory

We first revisit the SET from the view point of path branching. In the present formalism, SET is derived as a combination of the stationary phase equations, Eqs. (27) and (32), together with the assumption of a single nuclear path. SET implicitly assumes the existence of a single nuclear path in the simultaneous equations of the force form in Eq. (27) and the electronic equation of motion Eq. (32) that gives the coefficients c_n^I of the electronic basis. (Recall that the equation of motion for electrons, Eq. (32), is the same as that for the slightly generalized SET [23].) As a prescription to remove the dependence of the force form on the final state, which is designated as a boundary condition for the path integration, we have to make a rather particular assumption:

$$|\xi_f : \mathbf{R}_f\rangle|\mathbf{R}_f\rangle = \exp\left[-\frac{i}{\hbar}\mathcal{H}(t_f - t_i)\right]|\xi_i : \mathbf{R}_i\rangle|\mathbf{R}_i\rangle, \tag{44}$$

which simplifies the force form at time point t_n to

$$\begin{aligned}
&\mathcal{F}_n^{\mu}\big|_{[\xi_f(\mathbf{R}_f), t_f; \xi_i(\mathbf{R}_i), t_i]} \\
&= \sum_{I,J} \frac{\mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f), t_f; I, t_n)\mathcal{F}_{IJ}^{\mu}\mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : J, t_n; \xi_i(\mathbf{R}_i), t_i)}{\mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f), t_f; \xi_i(\mathbf{R}_i), t_i)} \\
&= \sum_{I,J} \frac{\langle \xi_i : \mathbf{R}_i | e^{\frac{i}{\hbar}\mathcal{H}(t_f - t_n)} | I : \mathbf{R}_n\rangle \mathcal{F}_{IJ}^{\mu} \langle J : \mathbf{R}_n | e^{-\frac{i}{\hbar}\mathcal{H}(t_n - t_i)} | \xi_i : \mathbf{R}_i\rangle}{1} \\
&= \sum_{I,J} c_n^{I*} \mathcal{F}_{IJ}^{\mu} c_n^{J}.
\end{aligned} \tag{45}$$

Substituting Eq. (45) into Eq. (27) yields the nuclear equation of motion of SET [23]. Note that the assumption in Eq. (44) that $\mathbf{R}_i$ is to be shifted to $\mathbf{R}_f$ by the action of the total Hamiltonian, thereby forming a single path, is particularly wrong in a nonadiabatic region.

As confirmed in Eq. (45), the force form is averaged over all the electronic states that consist in the wave packet $\sum_I c_n^I |I : \mathbf{R}_n\rangle$ at a given time t_n and at a nuclear coordinate $\mathbf{R}$. It is numerically verified that the electronic transition probability estimated with SET is quite accurate [29]. In addition, SET conserves constants of motion such as total energy, momentum, and angular momenta, as we show later. However, the assumption of a single nuclear path should *not* be valid except in dynamics on a single potential surface with no nonadiabatic coupling. The single path picture after the transition is totally wrong, giving rise to an unphysical nuclear path.

C. Method of phase-space averaging and natural branching

1. *Smooth and continuous path branching by nonadiabatic coupling*

Next we consider path branching to represent both the electronic and the nuclear wave-packet bifurcations, which was first studied in the PSANB scheme based on the variational principle in the Schrödinger wave mechanics [29]. The main idea of PSANB is to diagonalize the force matrix. We revisit it here from the viewpoint of the split path integration of Eq. (37).

Let $|\lambda_p\rangle$ be an eigenvector of the force matrix along the moving direction $\hat{\mathcal{F}} = \sum_\mu \frac{\dot{R}^\mu}{|\dot{\mathbf{R}}|}\hat{\mathcal{F}}^\mu$. The eigenvector $|\lambda_{p_n} : \mathbf{R}_n\rangle$ satisfies

$$\hat{\mathcal{F}}_n |\lambda_{p_n} : \mathbf{R}_n\rangle = f_{p_n} |\lambda_{p_n} : \mathbf{R}_n\rangle, \tag{46}$$

where f_{p_n} is the p_nth eigenvalue of the force matrix $\hat{\mathcal{F}}_n$. We can insert closure $1 = \sum_{p_n} |\lambda_{p_n} : \mathbf{R}_n\rangle\langle\lambda_{p_n} : \mathbf{R}_n|$ at time $t_S = t_n$ and nuclear configuration $\mathbf{R}_n$ for all $0 \leqslant n \leqslant N-1$. We consider only finite basis expansion and the number of eigenstates is limited to some large number N_b. Consider the stationary phase condition, Eq. (38), for the nuclear coordinate small time interval ϵ after t_n. Since $\mathcal{K}^{\mathrm{el}}$ has the form

$$\begin{aligned}
&\mathcal{K}(\{\mathbf{R}\} : \mathbf{R}_f, \xi_f(\mathbf{R}_f), t_f; \mathbf{R}_i, \xi_i(\mathbf{R}_i), t_i) \\
&= \sum_{p_{N-1}} \sum_{p_{N-2}} \cdots \sum_{p_0} \int d\mathbf{R}_{N-1} \cdots d\mathbf{R}_1 \exp\left[\frac{i}{\hbar} S_{\mathrm{nuc}}[\{\mathbf{R}\}]\right] \\
&\quad \times \int \prod_n d[c_n, c_n^*] \langle \xi_f : \mathbf{R}_f | c_N : \mathbf{R}_N\rangle \\
&\quad \times \left\{ \prod_{n=0}^{N-1} \langle c_{n+1} : \mathbf{R}_{n+1} | e^{-\frac{i}{\hbar}\mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)} | \lambda_{p_n} : \mathbf{R}_n\rangle \langle \lambda_{p_n} : \mathbf{R}_n | c_n : \mathbf{R}_n\rangle \right\} \\
&\quad \times \langle c_0 : \mathbf{R}_0 | \xi_i : \mathbf{R}_i\rangle
\end{aligned} \tag{47}$$

for each electronic propagator, the force form, Eq. (39), projected onto the moving direction gives rise to

$$\mathcal{F}_n^{(\lambda_{p_{n+1}},\lambda_{p_n})} = \frac{\int d[c_{n+1},c_{n+1}^*]\langle\lambda_{p_{n+1}} : \mathbf{R}_{n+1}|c_{n+1} : \mathbf{R}_{n+1}\rangle\langle c_{n+1} : \mathbf{R}_{n+1}|e^{-\frac{i}{\hbar}\epsilon\mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)}\hat{\mathcal{F}}|\lambda_{p_n} : \mathbf{R}_n\rangle}{\mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \lambda_{p_{n+1}},t_{n+1};\lambda_{p_n},t_n)} = f_{p_n}. \tag{48}$$

We note that with this choice of basis, $\mathcal{F}_n^{(\lambda_{p_{n+1}},\lambda_{p_n})}$ is actually independent of the electronic state projection at time t_{n+1}, which means that the eigenforce acting on the nuclei does not induce electronic state mixing. Thus $\mathcal{F}_n^{(\lambda_{p_n})}$ is responsible only for path generation, resulting in a small increment $\Delta\mathbf{R}^{(\lambda_{p_n})}$ for a short time. Thus, at time $t_n + \epsilon$ we have N_b different stationary nuclear paths, each emanating from a single point $\mathbf{R}_n$ under force f_{p_n} and having a probability amplitude proportional to $\mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \lambda_{p_n},t_n;\lambda_{p_{n-1}},t_{n-1})$. However, since these eigenstates $\{|\lambda_{p_n} : \mathbf{R}_n\rangle\}$ are not the eigenstates of $\mathcal{H}^{\mathrm{el}}$, the force-matrix eigenstates at time t_n no longer satisfy Eq. (46) in the next step, $t_n + \epsilon$. Therefore at each end point $\mathbf{R}_n + \Delta\mathbf{R}^{(\lambda_{p_n})}$ thus produced, the similar diagonalization procedure should apply and generate further N_b paths. This gives rise to a cascade of branching paths, which constitutes the heart of the PSANB scheme.

2. *Phase-space averaging of to-be-branched paths*

The preceding branching procedure leading to an infinite sequence of branching cascades indeed reflects the real physics of nonadiabatic interactions in the mixed quantum-classical representation. It is also a manifestation of the electronic and nuclear entanglement in this representation. However, it is still impossible to treat the infinite cascade of branching practically. Therefore the PSANB scheme proposes the following approximation as a tractable strategy, which is summarized as follows [29]. First, we divide the system evolution into the following three stages in terms of the relative strength of nonadiabatic coupling terms: (i) an asymptotic adiabatic region before nonadiabatic interaction, where nonadiabatic couplings among electronic states are weak enough for the system to remain as the initial electronic state; (ii) a strongly interacting region, where nonadiabatic coupling is strong for the avoid-crossing and conical intersection, and the system evolves into a superposition of different electronic states; and (iii) an asymptotic adiabatic region after nonadiabatic coupling, where the nonadiabatic interaction becomes weak again, and each adiabatic electronic state well approximates the true eigenstate. Each electronic state evolves independently to a product state.

In stage (i), branching is negligible, since the major nonadiabatic contribution $\mathcal{H}^{\mathrm{el}}(\mathbf{R})\hat{X} - \hat{X}\mathcal{H}^{\mathrm{el}}(\mathbf{R})$ is small enough relative to $\frac{\partial\mathcal{E}_I}{\partial\mathbf{R}}$, where $\mathcal{E}_I(\mathbf{R})$ is the Ith eigenvalue of the electronic Hamiltonian $\mathcal{H}^{\mathrm{el}}(\mathbf{R})$. The eigenstates of the force matrix coincide with the adiabatic states.

In stage (ii), the strong nonadiabatic coupling makes series of branchings as stated previously. To avoid an infinite number of branchings as well as allowing interaction among states, the PSANB scheme resorts to a strategy of taking an averaged nuclear displacement $\overline{\Delta\mathbf{R}}$ and averaged associated momentum $\overline{\Delta\mathbf{P}}$ (average in phase space) as follows:

$$\overline{\Delta\mathbf{R}} = \sum_{\lambda_p} |\langle\lambda_p|\xi : \mathbf{R}_n\rangle|^2 \Delta\mathbf{R}^{(\lambda_p)}, \tag{49}$$

$$\overline{\Delta\mathbf{P}} = \sum_{\lambda_p} |\langle\lambda_p|\xi : \mathbf{R}_n\rangle|^2 \Delta\mathbf{P}^{(\lambda_p)}, \tag{50}$$

where $\Delta\mathbf{R}$ and $\Delta\mathbf{P}$ are nuclear coordinate and momentum displacement, and $|\xi : \mathbf{R}_n\rangle$ is the electronic wave-packet vector at time t_n, whose initial state at t_i is $|\xi_i : \mathbf{R}_i\rangle$. $\Delta\mathbf{R}^{(\lambda_p)}$ and $\Delta\mathbf{P}^{(\lambda_p)}$ denote the coordinate and momentum displacements dependent on the effective action $S_{\mathrm{eff}}^{(\lambda_{p'},\lambda_p)}$. Then $\mathbf{R}_{n+1} = \mathbf{R}_n + \overline{\Delta\mathbf{R}}$, along with $\mathbf{P}_{n+1} = \mathbf{P}_n + \overline{\Delta\mathbf{P}}$, is a point where we repeat the process of Eq. (46). The averaging may continue until the resultant path gets out of the strong interaction region. Or one may let an averaged path branch several times before getting out of the nonadiabatic region. In the latter case, a single path may give birth to a large but finite number of non-Born-Oppenheimer paths.

We note that this averaging procedure is merely an approximation (or strategy), although the numerical tests have supported very affirmatively that PSANB is a highly accurate yet tractable approximation [29]. Nevertheless, there is no unique theoretical route found through which the averaging procedure comes about mathematically from the original Schrödinger equation. Nevertheless, the same expression for the averaged nuclear position $\overline{\mathbf{R}}$ is obtained from the path-integral formulation as follows. Let us consider a wave packet $\xi(\mathbf{R})$ at time t_n and estimate the averaged nuclear position $\mathbf{R}'$ after just a short time, $t = t_n + \Delta t$. Here we assume that the nuclear displacement is obtained as $\Delta\mathbf{R}^{(\lambda_p)}$ for each state projection. Let $\xi'(\mathbf{R}')$ be the electronic state at time t and $\chi(\mathbf{R}',\xi'(\mathbf{R}'),t)$ be the associated nuclear wave function. Then we observe

$$\begin{aligned}\overline{\mathbf{R}}|_{\xi'(\mathbf{R}')} &= \int d\mathbf{R}'\,\mathbf{R}'|\chi(\mathbf{R}',\xi'(\mathbf{R}'),t)|^2 = \int d\mathbf{R}'\,\mathbf{R}'\left|\int d\mathbf{R}\mathcal{K}(\mathbf{R}',\xi'(\mathbf{R}'),t;\mathbf{R},\xi(\mathbf{R}),t_n)\chi(\mathbf{R},\xi(\mathbf{R}),t_n)\right|^2\\ &= \int d\mathbf{R}'\,\mathbf{R}'\left|\sum_{\lambda_{p'}}\sum_{\lambda_p}\int d\mathbf{R}\langle\xi' : \mathbf{R}'|\lambda_{p'} : \mathbf{R}'\rangle\mathcal{K}(\mathbf{R}',\lambda_{p'}(\mathbf{R}'),t;\mathbf{R},\lambda_p(\mathbf{R}),t_n)\langle\lambda_p : \mathbf{R}|\xi : \mathbf{R}\rangle\chi(\mathbf{R},\lambda_p(\mathbf{R}),t_n)\right|^2\\ &= \int d\mathbf{R}'\,\mathbf{R}'\left|\sum_{\lambda_{p'}}\sum_{\lambda_p}\int d\mathbf{R}\int d\mathbf{R}_{N-1}\cdots d\mathbf{R}_1 e^{\frac{i}{\hbar}S_{\mathrm{nuc}}[\{\mathbf{R}_n\}]}\langle\xi' : \mathbf{R}'|\lambda_{p'} : \mathbf{R}'\rangle\mathcal{K}^{\mathrm{el}}(\lambda_{p'},t;\lambda_p,t_n)\langle\lambda_p : \mathbf{R}|\xi : \mathbf{R}\rangle\chi(\mathbf{R},\lambda_p(\mathbf{R}),t_n)\right|^2.\end{aligned} \tag{51}$$

We then apply the stationary phase approximation and replace the nuclear coordinate integrals with the stationary phase solution, which is $\delta(\mathbf{R}'-\mathbf{R}-\Delta\mathbf{R}^{(\lambda_p)})$ by assumption. We also approximate the nuclear wave function $\chi(\mathbf{R},\lambda_p(\mathbf{R}),t_n)$ as a pointlike function centered at $\mathbf{R}_n$, which is $\delta(\mathbf{R}-\mathbf{R}_n)$. Then we obtain

$$\begin{aligned}\overline{\mathbf{R}}|_{\xi'(\mathbf{R}')} &\approx \int d\mathbf{R}'\mathbf{R}'\Bigg|\sum_{\lambda_{p'}}\sum_{\lambda_p}\int d\mathbf{R}\langle\xi':\mathbf{R}'|\lambda_{p'}:\mathbf{R}'\rangle\delta_{\lambda_{p'}\lambda_p}\\ &\qquad\times\delta(\mathbf{R}'-\mathbf{R}-\Delta\mathbf{R}^{(\lambda_p)})\langle\lambda_p:\mathbf{R}|\xi:\mathbf{R}\rangle\delta(\mathbf{R}-\mathbf{R}_n)\Bigg|^2\\ &=\sum_{\lambda_p}(\mathbf{R}_n+\Delta\mathbf{R}^{(\lambda_p)})|\langle\xi':\mathbf{R}'|\lambda_p:\mathbf{R}'\rangle\langle\lambda_p:\mathbf{R}_n|\xi:\mathbf{R}_n\rangle|^2.\end{aligned}\tag{52}$$

Therefore it is understood that the "state-averaged nuclear coordinate" becomes

$$\sum_{\xi'(\mathbf{R}')}\overline{\mathbf{R}}|_{\xi'(\mathbf{R}')}=\sum_{\lambda_p}(\mathbf{R}_n+\Delta\mathbf{R}^{(\lambda_p)})|\langle\lambda_p:\mathbf{R}|\xi:\mathbf{R}_n\rangle|^2,\tag{53}$$

where summation over states is to be made so that $\sum_{\xi'(\mathbf{R}')}|\langle\xi'(\mathbf{R}')|\lambda_p\rangle|^2=1$ for any λ_p. Thus the path-integral formulation verifies the state-averaged nuclear position in Eq. (49) under several approximations, but it does not necessarily mean that the method of averaging itself is unique. In fact, one may introduce as many branchings as desired into the averaging procedures. We have not yet found a unique condition or threshold to fix those places and frequencies of branching.

In stage (iii), nonadiabatic coupling becomes weak, and at the place where it exits the coupling region, each path undergoes its final branching. PSANB stops averaging at the point where the nonadiabatic coupling term $\mathbf{X}\cdot\dot{\mathbf{R}}$ becomes smaller than some predetermined threshold value [29].

The key idea of PSANB has been formulated beginning with the full quantum wave-packet description in the Schrödinger picture, but to move to the mixed quantum-classical representation, the quantum nuclear momentum operators are replaced with the classical counterparts. Being correct intuitively, this replacement is not totally clear and should need to be verified. It is therefore meaningful for the present path-integral formulation starting with all the c-numbers to have reached the essential feature of PSANB. However, the path integrals could neither claim clear-cut theoretical support about the averaging procedure nor say anything mathematical about a reasonable choice of "branching point," the point where we stop averaging. These aspects are left for further study.

IV. CONSERVATION LAWS

We show here the validity of the action in Eq. (24) by examining the conservation laws explicitly for three quantities: total energy, linear momentum, and angular momentum. We also examine whether the SET and PSANB conserve these quantities. In what follows, we consider only the continuous limit for simplicity, although all the results hold in the discretized form if we replace the time derivative with the finite difference.

A. Infinitesimal transformations in electron nuclear dynamics

Let us begin with a Lagrangian of the form

$$\mathcal{L}_{\text{tot}}(\mathbf{R},\mathbf{V},\xi,\eta)=\mathcal{L}^{(1)}(\mathbf{R},\mathbf{V},\xi,\eta)+\mathcal{L}^{(2)}(\mathbf{R},\mathbf{V}),\tag{54}$$

where ξ and $\eta=\dot{\xi}$ denote the electronic degrees of freedom, while $\mathbf{R}$ and $\mathbf{V}=\dot{\mathbf{R}}$ represent the nuclear degrees of freedom. A dot over a symbol means the time derivative as $\dot{\mathbf{R}}=\frac{d\mathbf{R}}{dt}$. Variation of the total Lagrangian yields

$$\delta\mathcal{L}=\delta\mathcal{L}^{(1)}+\delta\mathcal{L}^{(2)}.\tag{55}$$

We first consider the first term, namely, the electronic part, and obtain

$$\begin{aligned}\delta\mathcal{L}^{(1)}&=\partial_\xi\mathcal{L}^{(1)}\delta\xi+\partial_\eta\mathcal{L}^{(1)}\delta\eta+\partial_{\mathbf{R}}\mathcal{L}^{(1)}\delta\mathbf{R}+\partial_{\mathbf{V}}\mathcal{L}^{(1)}\delta\mathbf{V}\\ &=\frac{d}{dt}(\partial_\eta\mathcal{L}^{(1)}\delta\xi+\partial_{\mathbf{V}}\mathcal{L}^{(1)}\delta\mathbf{R})+\left\{\partial_\xi\mathcal{L}^{(1)}-\frac{d}{dt}(\partial_\eta\mathcal{L}^{(1)})\right\}\delta\xi\\ &\quad+\left\{\partial_{\mathbf{R}}\mathcal{L}^{(1)}-\frac{d}{dt}(\partial_{\mathbf{V}}\mathcal{L}^{(1)})\right\}\delta\mathbf{R}.\end{aligned}\tag{56}$$

If the electronic variables ξ and η satisfy the Euler-Lagrange equation, the first curly bracket vanishes, and hence we obtain

$$\begin{aligned}&\frac{d}{dt}(\partial_\eta\mathcal{L}^{(1)}\delta\xi+\partial_{\mathbf{V}}\mathcal{L}^{(1)}\delta\mathbf{R})-\delta\mathcal{L}^{(1)}\\ &\quad=-\left\{\partial_{\mathbf{R}}\mathcal{L}^{(1)}-\frac{d}{dt}(\partial_{\mathbf{V}}\mathcal{L}^{(1)})\right\}\delta\mathbf{R}.\end{aligned}\tag{57}$$

Variation of $\mathcal{L}^{(2)}$ gives

$$\begin{aligned}\delta\mathcal{L}^{(2)}&=\partial_{\mathbf{R}}\mathcal{L}^{(2)}\delta\mathbf{R}+\partial_{\mathbf{V}}\mathcal{L}^{(2)}\delta\mathbf{V}\\ &=\frac{d}{dt}(\partial_{\mathbf{V}}\mathcal{L}^{(2)}\delta\mathbf{R})+\left\{\partial_{\mathbf{R}}\mathcal{L}^{(2)}-\frac{d}{dt}(\partial_{\mathbf{V}}\mathcal{L}^{(2)})\right\}\delta\mathbf{R},\end{aligned}\tag{58}$$

and therefore,

$$\frac{d}{dt}(\partial_{\mathbf{R}}\mathcal{L}^{(2)}\delta\mathbf{R})-\delta\mathcal{L}^{(2)}=-\left\{\partial_{\mathbf{R}}\mathcal{L}^{(2)}-\frac{d}{dt}(\partial_{\mathbf{V}}\mathcal{L}^{(2)})\right\}\delta\mathbf{R}.\tag{59}$$

The sum of these two yields

$$\begin{aligned}&\frac{d}{dt}\boldsymbol{(}\partial_\eta\mathcal{L}^{(1)}\delta\xi+\partial_{\mathbf{R}}(\mathcal{L}^{(1)}+\mathcal{L}^{(2)})\delta\mathbf{R}\boldsymbol{)}-\delta\mathcal{L}^{(1)}-\delta\mathcal{L}^{(2)}\\ &\quad=-\left\{\partial_{\mathbf{R}}\mathcal{L}^{(1)}+\partial_{\mathbf{R}}\mathcal{L}^{(2)}-\frac{d}{dt}\boldsymbol{(}\partial_{\mathbf{V}}(\mathcal{L}^{(1)}+\mathcal{L}^{(2)})\boldsymbol{)}\right\}\delta\mathbf{R},\end{aligned}\tag{60}$$

the right-hand side of which vanishes if the $\mathbf{R}$ and $\mathbf{V}$ satisfy the equation of motion,

$$\frac{d}{dt}\boldsymbol{(}\partial_{\mathbf{V}}(\mathcal{L}^{(1)}+\mathcal{L}^{(2)})\boldsymbol{)}+\partial_{\mathbf{R}}(\mathcal{L}^{(1)}+\mathcal{L}^{(2)})=0.\tag{61}$$

This leads to the conservation laws of the system, as we see later.

We then consider the following set of Lagrangians. For electronic degrees of freedom,

$$\begin{aligned}\mathcal{L}^{(1)}=\sum_{I,J}c_I^*\Bigg(&i\hbar\partial_t-\mathcal{H}^{\text{el}}_{IJ}(\mathbf{R})+i\hbar\mathbf{X}_{IJ}(\mathbf{R})\cdot\dot{\mathbf{R}}\\ &+\sum_j\frac{\hbar^2}{2M_j}Y^j_{IJ}(\mathbf{R})\Bigg)c_J,\end{aligned}\tag{62}$$

which is the continuous limit of the Lagrangian that appears in the path integrals of Eq. (24). For nuclear degrees of freedom, we have

$$\mathcal{L}^{(2)} = \sum_j \frac{M_j \dot{\mathbf{R}}_j^2}{2} - U_{\text{nuc}}(\mathbf{R}), \tag{63}$$

which yields the continuous limit of the nuclear action S_{nuc} in Eq. (11). The Euler-Lagrange equation for electronic degrees of freedom is

$$i\hbar \dot{c}_I = \sum_J \left(\mathcal{H}^{\text{el}}_{IJ}(\mathbf{R}) - i\hbar \dot{\mathbf{R}} \cdot \mathbf{X}_{IJ}(\mathbf{R}) - \sum_j \frac{\hbar^2}{2M_j} Y^j_{IJ}(\mathbf{R}) \right) c_J, \tag{64}$$

which is the continuous limit of Eq. (32). On the contrary, the Euler-Lagrange equation for the nuclear degree of freedom is

$$M_j \ddot{\mathbf{R}}^{(j,a)} = -\frac{\partial}{\partial R^{(j,a)}} U_{\text{nuc}}(\mathbf{R}) + \sum_{I,J} c_I^* \mathcal{F}^{(j,a)}_{IJ} c_J, \tag{65}$$

which differs from Eq. (27) in that the force form is replaced with $\sum_{I,J} c_I^* \mathcal{F}^{(j,a)}_{IJ} c_J$. This force form is the continuous limit of Eq. (45), which is adopted in SET. There are three symmetries in these Lagrangians.

1. Time translation symmetry: Since each of these Lagrangians does not have an explicit dependence on time, each should have time-translation symmetry. This invariance is materialized by setting

$$\delta \mathbf{R} = \dot{\mathbf{R}} \epsilon, \tag{66}$$

$$\delta c_I = \dot{c}_I \epsilon, \tag{67}$$

where ϵ is an infinitesimal variation of time.

2. Spatial translation symmetry: The total Lagrangian $\mathcal{L}^{(1)} + \mathcal{L}^{(2)}$ has translational symmetry. In fact, the symmetry holds separately on each Lagrangian since the interaction term in $\mathcal{L}^{(2)}$ is invariant with respect to the total space translation. We then set

$$\delta R^{(j,a)} = \varepsilon^a, \tag{68}$$

$$\delta c_I = \sum_a \varepsilon^a \left[\sum_J \left(\frac{i}{\hbar} \mathcal{P}^a_{IJ} + \sum_j X^{(j,a)}_{IJ}(\mathbf{R}) \right) c_J \right], \tag{69}$$

where ε^a is an infinitesimal variation of spatial coordinates. $\mathcal{P}^a$ is the total momentum operator of the electronic system. Note that although c_I and $\mathbf{R}$ values are distinct dynamical variables, the basis set of c_I values changes due to the translation of $\mathbf{R}$.

3. Spatial rotation symmetry: The total Lagrangian $\mathcal{L}^{(1)} + \mathcal{L}^{(2)}$ has rotational symmetry about the center of mass of the molecule. Again, the symmetry holds separately on each Lagrangian. The infinitesimal translation on each degree of freedom should be taken as

$$\delta \mathbf{R}^j = \boldsymbol{\varepsilon} \times \mathbf{R}^j, \tag{70}$$

$$\delta c_I = \boldsymbol{\varepsilon} \left(\sum_J \left(\frac{i}{\hbar} (\mathbf{J}^{\text{el}})_{IJ} + \sum_j \mathbf{R}^j \times \mathbf{X}^j_{IJ}(\mathbf{R}) \right) c_J \right), \tag{71}$$

where $\boldsymbol{\varepsilon} = \epsilon \mathbf{n}$ and denotes a rotation of infinitesimal angle ϵ around a unit vector $\mathbf{n}$. The operator $\mathbf{J}^{\text{el}}$ is the total angular momentum operator of the electronic system.

B. Conservation laws

1. Energy

We substitute the displacement vectors of Eq. (66) into Eq. (57) and see

$$\begin{aligned}
&\frac{d}{dt}\left[\sum_I i\hbar c_I^* \dot{c}_I - \mathcal{L}^{(1)} + \sum_{I,J} c_I^* i\hbar \mathbf{X}_{IJ}(\mathbf{R}) c_J \right] \\
&= \sum_{I,J} c_I^* \Bigg[(-\dot{\mathbf{R}}^j \cdot \mathbf{X}^j(\mathbf{R})) \left(-\mathcal{H}^{\text{el}}(\mathbf{R}) + i\hbar \dot{\mathbf{R}} \cdot \mathbf{X}(\mathbf{R}) + \sum_j \frac{\hbar^2}{2M_j} Y^j(\mathbf{R}) \right) \\
&\quad + \left(-\mathcal{H}^{\text{el}}(\mathbf{R}) + i\hbar \dot{\mathbf{R}} \cdot \mathbf{X}(\mathbf{R}) + \sum_j \frac{\hbar^2}{2M_j} Y^j(\mathbf{R}) \right) (\dot{\mathbf{R}} \cdot \mathbf{X}(\mathbf{R})) \Bigg]_{IJ} c_J \\
&\quad + \sum_{I,J} c_I^* \left[-\sum_{(j,a)} \partial_{R^{(j,a)}} \mathcal{H}^{\text{el}}_{IJ}(\mathbf{R}) + \partial_{R^{(j,a)}} (i\hbar \dot{\mathbf{R}} \cdot \mathbf{X}_{IJ}(\mathbf{R})) + \frac{d}{dt} (i\hbar \mathbf{X}^{(j,a)}_{IJ}(\mathbf{R})) \right] c_J \dot{R}^{(j,a)}.
\end{aligned} \tag{72}$$

Thus we obtain

$$\begin{aligned}
&-\frac{d}{dt}\left(\sum_{I,J} c_I^* \left(\mathcal{H}^{\text{el}}_{IJ}(\mathbf{R}) - \sum_j \frac{\hbar^2}{2M_j} Y^j_{IJ}(\mathbf{R}) \right) c_J \right) \\
&= \sum_{I,J} \sum_\mu c_I^* \mathcal{F}^\mu_{IJ} c_J \dot{R}^\mu,
\end{aligned} \tag{73}$$

which simply states that the energy gain in electron system is provided by the work through the force matrix of the nuclear system. We have neglected the commutator of Y and X in the same approximation that we made in the derivation of the force form. Equation (73) holds if the electronic system satisfies the equation of motion, Eq. (32). Note that the first-order derivative coupling term in the Lagrangian $\dot{\mathbf{R}} \cdot \mathbf{X}$ is canceled out, while the second-order derivative coupling term Y is added to the total energy. The conservation law for the total system then becomes

$$\frac{d}{dt}\left(\sum_{I,J} c_I^*\left(\mathcal{H}^{\mathrm{el}}_{IJ}(\mathbf{R}) - \sum_j \frac{\hbar^2}{2M_j} Y^j_{IJ}(\mathbf{R})\right)c_J + \sum_j \frac{M_j \dot{\mathbf{R}}_j^2}{2} + U(\mathbf{R})\right) = 0, \tag{74}$$

which holds if the nuclear coordinates satisfy the equation of motion, Eq. (65).

2. *Linear momentum*

Substitute the displacement vectors of Eq. (68) into Eq. (57), leading to the relation

$$-\frac{d}{dt}\left(\sum_{I,J} c_I^* \mathcal{P}^a_{IJ} c_J\right) = \sum_{I,J} c_I^* \sum_j \mathcal{F}^{(j,a)}_{IJ} c_J, \tag{75}$$

which indicates that the momentum change of the electronic subsystem is compensated by those of the nuclear subsystems. The total conservation law becomes

$$\frac{d}{dt}\left(\sum_{I,J} c_I^* \mathcal{P}^a_{IJ} c_J + \sum_j M_j \dot{R}^{(j,a)}\right) = 0. \tag{76}$$

3. *Angular momentum*

Substitution of the quantities of Eq. (70) into Eq. (57) gives the relation

$$-\frac{d}{dt}\left(\sum_{I,J} c_I^* \mathbf{J}^{\mathrm{el}}_{IJ} c_J\right) = \mathbf{R} \times \sum_{I,J} c_I^* \boldsymbol{\mathcal{F}}_{IJ} c_J, \tag{77}$$

which indicates that the angular momentum change in the electronic subsystem is provided by the torque from the nuclear subsystem. The total conservation law then becomes

$$\frac{d}{dt}\left(\sum_{I,J} c_I^* \mathbf{J}^{\mathrm{el}}_{IJ} c_J + \sum_j \mathbf{R}_j \times \mathbf{P}_j\right) = 0. \tag{78}$$

The conservation laws of Eqs. (73), (75), and (77) hold subject to the condition that the electronic subsystem satisfies the equation of motion, Eq. (64). Those equations illustrate the fact that energy, momentum, and angular momentum are exchanged between the quantal (electronic) part and the classical (nuclear) part through work, force, and torque, respectively, expressed in terms of force form. This fact in turn confirms the validity of the force form or force matrix as the analog of the classical force. On the contrary, the conservation laws Eqs. (74), (76), and (78) rest on more special conditions; both Eq. (64) and Eq. (65) should be satisfied.

C. Conservation laws in phase-space averaging and natural branching and semiclassical Ehrenfest theory

Next we examine practical methods of SET and PSANB. We first note that the conservation laws of Eqs. (73), (75), and (77) hold in both of these methods, since they satisfy the electronic equation of motion, Eq. (64). As for the conservation laws, Eqs. (74), (76), and (78), we can see that all three laws hold in SET since it uses the Euler-Lagrange equation, Eqs. (64) and (65). PSANB, on the contrary, uses a different scheme for nuclear propagation. However, it still conserves energy and momentum in its direction of movement as follows. PSANB decomposes the electronic state vector at $t_n, c_n(\mathbf{R}_n)$ to force matrix eigenvectors $\lambda_{p_n}(\mathbf{R}_n)$,

$$|c_n(\mathbf{R}_n)\rangle = \sum_{p_n} a_{p_n} \big|\lambda_{p_n}(\mathbf{R}_n)\big\rangle, \tag{79}$$

where a_{p_n} is the coefficient for the p_nth eigenvector $a_{p_n} = \langle \lambda_{p_n} : \mathbf{R}_n | c_n : \mathbf{R}_n \rangle$. According to Eq. (49), the nuclear kinetic energy changes as

$$\begin{aligned}
\delta&\left(\sum_j \frac{M_j \dot{\mathbf{R}}_j^2}{2}\right) \\
&= \sum_j M_j \dot{\mathbf{R}}_j \cdot \delta \dot{\mathbf{R}}_j \\
&= \sum_j \dot{\mathbf{R}}_j \cdot M_j \sum_{p_n} \delta \dot{\mathbf{R}}_j^{(p_n)} |a_{p_n}|^2 \\
&= |\dot{\mathbf{R}}| \sum_{p_n} \epsilon \left(f_{p_n} - \sum_j \frac{\dot{\mathbf{R}}_j}{|\dot{\mathbf{R}}|} \cdot \partial_{\mathbf{R}^j} U(\mathbf{R}) \right) |a_{p_n}|^2 \\
&= |\dot{\mathbf{R}}| \epsilon \sum_{p_n} f_{p_n} |a_{p_n}|^2 - \sum_j \dot{\mathbf{R}}_j \cdot \partial_{\mathbf{R}^j} U(\mathbf{R}),
\end{aligned} \tag{80}$$

while the electronic energy change is derived from the right-hand side of Eq. (73) as

$$\begin{aligned}
&\sum_{I,J} \sum_j \epsilon c^{I*}(t) \big(\dot{\mathbf{R}}_j \cdot \boldsymbol{\mathcal{F}}^j_{IJ}\big) c^J(t) \\
&\quad = \sum_{p_n} \sum_{I,J} \sum_j \epsilon a^*_{p_n} \lambda^{I*}_{p_n} \big(\dot{\mathbf{R}}_j \cdot \boldsymbol{\mathcal{F}}^j_{IJ}\big) a_{p'_n} \lambda^J_{p'_n} \\
&\quad = \sum_{p_n} \epsilon |a_{p_n}|^2 f_{p_n} |\dot{\mathbf{R}}|,
\end{aligned} \tag{81}$$

where we have used the fact that $\{\lambda_p\}$ are eigenvectors of the force matrix in the direction of movement. Thus the electronic energy change balances that of the nuclear energy, leading to the (averaged) energy conservation.

V. ELECTRON-NUCLEUS COUPLED DYNAMICS IN ELECTROMAGNETIC VECTOR POTENTIALS

So far, we have considered the dynamics without an external field applied. We now extend the present theory so that we can study (both intrinsic and induced) nonadiabatic dynamics in a laser field. This extension is quite important in view of the recent great progress in laser technology. (See Refs. [38] and [39] for the important roles of nonadiabatic couplings in electron wave-packet dynamics in laser fields.) A great advantage of the path-integral formalism is that such an extension is rather straightforward and transparent due to its c-number algebra. The total propagator is simply modified as

$$\begin{aligned}
\mathcal{K}\big(\mathbf{R}_f, \xi_f(\mathbf{R}_f), t_f; \mathbf{R}_i, \xi_i(\mathbf{R}_i), t_i\big) &= \int d\mathbf{R}_{N-1} d\mathbf{R}_{N-2} \cdots d\mathbf{R}_1 \\
&\times \exp\left(\frac{i}{\hbar} S_{\mathrm{nuc}}[\{\mathbf{R}\}] + \frac{i}{\hbar} S_{\mathrm{eff}}[\{\mathbf{R}\} : \xi_f(\mathbf{R}_f), t_f; \xi_i(\mathbf{R}_i), t_i]\right),
\end{aligned} \tag{82}$$

with the nuclear action

$$S_{\mathrm{nuc}}[\{\mathbf{R}\}] = \sum_n \left(\sum_j \frac{M_j \left(\mathbf{R}^j_{n+1} - \mathbf{R}^j_n\right)^2}{2\epsilon} - U_{\mathrm{nuc}}(\mathbf{R}_n)\epsilon + \sum_j \frac{Q_j}{c} \dot{\mathbf{R}}^j_n \cdot \mathbf{A}\left(\mathbf{R}^j_{n+1/2}\right)\epsilon \right), \tag{83}$$

where $\mathbf{R}^j_{n+1/2}$ is again the "midpoint" we introduced in Sec. II B2. The effective action S_{eff} is related to the electronic propagator $\mathcal{K}^{\mathrm{el}}$ by $S_{\mathrm{eff}} = \frac{\hbar}{i} \ln \mathcal{K}^{\mathrm{el}}$. The electronic propagator $\mathcal{K}^{\mathrm{el}}$ under an external field is

$$\begin{aligned} \mathcal{K}^{\mathrm{el}}(\{\mathbf{R}\} : \xi', t' : \xi, t; R) = \int (d[c_N, c_N^*]\langle \xi_f | c_N \rangle)\,(d[c_0, c_0^*]\langle c_0 | \xi_i \rangle) \prod_n d[c_n, c_n^*] \\ \times \exp\left[\frac{i}{\hbar} \sum_{I,J} c^{*I}_{n+1} \left(i\hbar\left(c^I_{n+1} - c^I_n\right)\delta_{IJ} - \left(\epsilon \mathcal{H}^{\mathrm{el}}_{IJ}(\mathbf{R}_n) - i\hbar\epsilon \dot{\mathbf{R}}_n \cdot \mathbf{X}_{IJ} - \sum_j \frac{\hbar^2}{2M_j} \epsilon \mathcal{Y}^j_{IJ} \right) c^J_n \right) \right]. \end{aligned} \tag{84}$$

Here the external field is included in the Hamiltonian $\mathcal{H}^{\mathrm{el}}$. The nuclear equation of motion turns out to be

$$\begin{aligned} M_j \ddot{R}^{(j,a)}_n = -\frac{\partial}{\partial R^{(j,a)}} U^{\mathrm{nuc}}(\mathbf{R}_n) + \mathcal{F}^{(j,a)}_n \Big|_{[\{\mathbf{R}_\ell\}, \xi_f(\mathbf{R}_f), t_f; \xi_i(\mathbf{R}_i), t_i]} \\ + Q_j \left(\mathbf{E} + \dot{\mathbf{R}}^j_n \times \mathbf{B}\right)^{(a)}, \end{aligned} \tag{85}$$

where **E** and **B** are the externally applied electric field and magnetic field, respectively. The last term in Eq. (85) denotes the Lorentz force. The force form $\mathcal{F}$ in Eq. (85) has the same form as Eq. (29), but it now includes the external field since the corresponding force matrix is of the form

$$\begin{aligned} \hat{\mathcal{F}}_n{}^{\mu} = {} & \mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)\hat{X}^{\mu} - \hat{X}^{\mu}\mathcal{H}^{\mathrm{el}}(\mathbf{R}_n) \\ & - \sum_{I,J} |I : \mathbf{R}_n\rangle \frac{\partial}{\partial R^{\mu}_n} \langle I : \mathbf{R}_n | \mathcal{H}^{\mathrm{el}}(\mathbf{R}_n) | J : \mathbf{R}_n \rangle \langle J : \mathbf{R}_n | \\ & + i\hbar \dot{R}^{\nu}_n (\hat{X}^{\mu}\hat{X}^{\nu} - \hat{X}^{\nu}\hat{X}^{\mu}) + (\dot{\mathbf{R}}_n \times (\nabla \times i\hbar\hat{\mathbf{X}}))^{\mu}, \end{aligned} \tag{86}$$

where we should note that $\mathcal{H}^{\mathrm{el}}$ now includes the external field. Here we have presented just a formal extension of the present path integrals. More about the coupling between the nonadiabatic interaction and the electromagnetic fields will be discussed elsewhere, along with numerical results.

VI. CONCLUDING REMARKS

We have studied the theoretical structure of nonadiabatic dynamics of electrons and nuclei in a molecule through path-integral formalism. Coupled equations of motion have been derived for bifurcating electron wave packets within an on-the-fly scheme, whose nuclear nonclassical paths have also been derived through the stationary phase approximation of the path integrations. These dynamical equations serve as a general theory for the mixed quantum-classical representation, where classical force is replaced by the force form. The validity of the force form has been further confirmed by the conservation laws, in which we have seen that the force form exchanges the energy, linear momentum, and angular momentum between quantum and classical subsystems.

It was clarified that the derivative coupling terms arise from the overlap product of adjacent nuclear positions, and the midpoint rule leads the second-order derivative coupling term $\mathcal{Y}$ to a Hermitian form.

The present path-integral formalism has made it possible to clearly analyze the notion of path branching induced by nonadiabatic dynamics. Such path branching is a manifestation of electronic and nuclear wave-packet bifurcations and their mutual quantum entanglement in the mixed representation, which is the most essential feature of nonadiabatic dynamics. Furthermore, it has been shown in terms of the split path-integral technique that the force form is naturally responsible for such path branching and is closely related to the force matrix, which was derived before in the Schrödinger picture. From the viewpoint of path branching, we have analyzed the method of PSANB as well as the SET in great detail through the present formalism. The conservation laws in these methods are also discussed. Some technical matters in PSANB, such as the choice of the points of path branching and the length of phase-space averaging, are left for further study, since no mathematically unique condition to determine these is found even in the path-integral formalism. However, further study is worth performing to improve the PSANB method, which is indeed a promising theory both theoretically and practically.

Finally, the present path integral is extended so as to handle nonadiabatic dynamics in laser fields. This may provide a guiding principle in our future study of laser control of the electronic states in molecules.

The present paper is devoted only to mathematical analyses of nonadiabatic electron wave-packet dynamics on the fly. The derived equations of motion for both electronic and nuclear dynamics are already implemented in the ab initio quantum mechanical framework. We shall report the physical and chemical aspects of these dynamics in the near future.

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APPENDIX A: DETAILS OF THE TROTTER DECOMPOSITION

Here we prove the validity of the Trotter decomposition in Eq. (8). We first decompose the total Hamiltonian into nuclear position diagonal terms and off-diagonal terms,

$$\mathcal{H} = \mathcal{T}_{\mathrm{nuc}} + U_{\mathrm{nuc}} + \mathcal{H}^{\mathrm{el}}, \tag{A1}$$

where $\mathcal{T}_{\mathrm{nuc}}$, U_{nuc}, and $\mathcal{H}^{\mathrm{el}}$ are the nuclear kinetic energy terms, nuclear Coulombic interaction, and electronic Hamiltonian, respectively. Thus the infinitesimal propagator turns out, up to first order in ϵ, to be

$$\begin{aligned}
&\boldsymbol{\langle}\mathbf{R}_{n+1}\boldsymbol{|}\langle\phi_{a_{n+1}} : \mathbf{R}_{n+1}|e^{-\frac{i}{\hbar}\epsilon\mathcal{T}_{\mathrm{nuc}}}e^{-\frac{i}{\hbar}\epsilon(U_{\mathrm{nuc}}+\mathcal{H}^{\mathrm{el}})}|\phi_{a_n} : \mathbf{R}_n\rangle\boldsymbol{|}\mathbf{R}_n\boldsymbol{\rangle}\\
&= \boldsymbol{\langle}\mathbf{R}_{n+1}\boldsymbol{|}\big\langle\phi_{a_{n+1}} : \mathbf{R}_{n+1}\big|\sum_{\alpha}|\alpha\rangle\langle\alpha|\int d\mathbf{P}\boldsymbol{|}\mathbf{P}\boldsymbol{\rangle}\boldsymbol{\langle}\mathbf{P}\boldsymbol{|}\exp\left[-\frac{i}{\hbar}\epsilon\mathcal{T}_{\mathrm{nuc}}\right]\exp\left[-\frac{i}{\hbar}\epsilon\big(U_{\mathrm{nuc}}(\mathbf{R}_n)+\mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)\big)\right]|\phi_{a_n} : \mathbf{R}_n\rangle\boldsymbol{|}\mathbf{R}_n\boldsymbol{\rangle}\\
&= \int d\mathbf{P}\boldsymbol{\langle}\mathbf{R}_{n+1}\boldsymbol{|}\mathbf{P}\boldsymbol{\rangle}\exp\left[-\frac{i}{\hbar}\epsilon\sum_j\frac{\mathbf{P}_j^2}{2M_j}\right]\boldsymbol{\langle}\mathbf{P}\boldsymbol{|}\mathbf{R}_n\boldsymbol{\rangle}\exp\left[-\frac{i}{\hbar}\epsilon U_{\mathrm{nuc}}(\mathbf{R}_n)\right]\sum_{\alpha}\langle\phi_{a_{n+1}} : \mathbf{R}_{n+1}|\alpha\rangle\langle\alpha|e^{-\frac{i}{\hbar}\epsilon\mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)}|\phi_{a_n} : \mathbf{R}_n\rangle\\
&= \int d\mathbf{P}\exp\left[\frac{i}{\hbar}\mathbf{P}\cdot(\mathbf{R}_{n+1}-\mathbf{R}_n)-\frac{i}{\hbar}\epsilon\sum_j\frac{\mathbf{P}_j^2}{2M_j}-\frac{i}{\hbar}\epsilon U_{\mathrm{nuc}}(\mathbf{R}_n)\right]\sum_{\alpha}\langle\phi_{a_{n+1}} : \mathbf{R}_{n+1}|\alpha\rangle\langle\alpha|e^{-\frac{i}{\hbar}\epsilon\mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)}|\phi_{a_n} : \mathbf{R}_n\rangle\\
&= \exp\left[\frac{i}{\hbar}\left(\sum_j\frac{M_j\big(\mathbf{R}_{n+1}^j-\mathbf{R}_n^j\big)^2}{2\epsilon}-U_{\mathrm{nuc}}(\mathbf{R}_n)\epsilon\right)\right]\langle\phi_{a_{n+1}} : \mathbf{R}_{n+1}|e^{-\frac{i}{\hbar}\epsilon\mathcal{H}^{\mathrm{el}}(\mathbf{R}_n)}|\phi_{a_n} : \mathbf{R}_n\rangle.
\end{aligned} \tag{A2}$$

Here $|\mathbf{P}\rangle$ is the momentum eigenstate of the nuclei system, and $\int d\mathbf{P} = \int\prod_j\frac{d^3\mathbf{P}_j}{(2\pi\hbar)^3}$ is the momentum integral. $\{|\alpha\rangle\}$ is a complete set of electronic basis that is independent of nuclear position.

APPENDIX B: DERIVATION OF THE OVERLAP PRODUCT

We here derive Eq. (16). We evaluate the overlap product of state vectors of different nuclear positions, $\langle\phi_a : \mathbf{R}_{n+1}|\phi_b : \mathbf{R}_n\rangle$. The "ket" vector $|\phi_b : \mathbf{R}_n\rangle$ is expanded around $\mathbf{R}_{n+1/2}$ up to second order in the coordinate difference $\mathbf{R}_{n+1}-\mathbf{R}_n$ as

$$\begin{aligned}
|\phi_b : \mathbf{R}_n\rangle &= |\phi_b : \mathbf{R}_{n+1/2}\rangle - \sum_{\mu}\frac{\big(R_{n+1}^{\mu}-R_n^{\mu}\big)}{2}\partial_{\mu}|\phi_b : \mathbf{R}_{n+1/2}\rangle\\
&\quad + \frac{1}{2}\sum_{\mu}\sum_{\nu}\frac{\big(R_{n+1}^{\mu}-R_n^{\mu}\big)}{2}\frac{\big(R_{n+1}^{\nu}-R_n^{\nu}\big)}{2}\partial_{\mu}\partial_{\nu}|\phi_b : \mathbf{R}_{n+1/2}\rangle\\
&\quad + O(|\mathbf{R}_{n+1}-\mathbf{R}_n|^3),
\end{aligned} \tag{B1}$$

where ∂_{μ} indicates $\frac{\partial}{\partial R^{\mu}}$. The "bra" vector $\langle\phi_a : \mathbf{R}_{n+1}|$ is also expanded in a similar manner. Hence the product becomes

$$\begin{aligned}
&\langle\phi_a : \mathbf{R}_{n+1}|\phi_b : \mathbf{R}_n\rangle\\
&\quad= \delta_{a,b} - \sum_{\mu}\big(R_{n+1}^{\mu}-R_n^{\mu}\big)X_{ab}^{\mu}(\mathbf{R}_{n+1/2})\\
&\qquad + \frac{1}{2}(R_{n+1}-R_n)^{\mu}(R_{n+1}-R_n)^{\nu}\sum_{\mu}\sum_{\nu}\mathcal{Y}_{ab}^{\mu,\nu}.
\end{aligned} \tag{B2}$$

In the first line, we used the relation

$$\langle\phi_a : \mathbf{R}|\partial_{\mu}\phi_b : \mathbf{R}\rangle + \langle\partial_{\mu}\phi_a : \mathbf{R}|\phi_b : \mathbf{R}\rangle = 0, \tag{B3}$$

which is obtained by differentiating the orthonormal relation Eq. (4). Thus we obtain Eq. (16). Yet a different expression is obtained if we evaluate the derivative at the end point as follows:

$$\begin{aligned}
\langle\phi_a : \mathbf{R}_{n+1}|\phi_b : \mathbf{R}_n\rangle &= \delta_{a,b} - \sum_{\mu}\big(R_{n+1}^{\mu}-R_n^{\mu}\big)\left(X_{ab}^{\mu}(\mathbf{R}_n) + \sum_{\nu}\frac{\big(R_{n+1}^{\nu}-R_n^{\nu}\big)}{2}\partial_{\nu}X_{ab}^{\mu}(\mathbf{R}_n)\right)\\
&\quad + \frac{1}{2}(R_{n+1}-R_n)^{\mu}(R_{n+1}-R_n)^{\nu}\sum_{\mu}\sum_{\nu}\mathcal{Y}_{ab}^{\mu,\nu}(\mathbf{R}_{n+1/2})\\
&= \delta_{a,b} - \sum_{\mu}\big(R_{n+1}^{\mu}-R_n^{\mu}\big)X_{ab}^{\mu}(\mathbf{R}_n) + \frac{1}{2}\sum_{\mu}\sum_{\nu}(R_{n+1}-R_n)^{\mu}(R_{n+1}-R_n)^{\nu}\langle\phi_a : \mathbf{R}_n|\partial_{\mu}\partial_{\nu}\phi_b : \mathbf{R}_n\rangle.
\end{aligned} \tag{B4}$$

Here terms of third order or higher in $\mathbf{R}_{n+1} - \mathbf{R}_n$ have been neglected, because they vanish or give $O(\epsilon^2)$ contribution to the path integral after the Gaussian integration. We have also used the following relation obtained by the second derivative of Eq. (4):

$$\begin{aligned}\langle \partial_\mu \partial_\nu \phi_a : \mathbf{R} | \phi_b : \mathbf{R} \rangle &+ \langle \partial_\mu \phi_a : \mathbf{R} | \partial_\nu \phi_b : \mathbf{R} \rangle \\ &+ \langle \partial_\nu \phi_a : \mathbf{R} | \partial_\mu \phi_b : \mathbf{R} \rangle + \langle \phi_a : \mathbf{R} | \partial_\mu \partial_\nu \phi_b : \mathbf{R} \rangle = 0. \qquad \text{(B5)}\end{aligned}$$

APPENDIX C: DETAILS OF INTEGRATION OVER ELECTRONIC STATE VECTORS

We define the integral over the CSF coefficients as in Eq. (21). As in the standard manner for coherent state representation [40,41], the integrals are performed over the real part and the imaginary part of all components c^I values as follows:

$$\begin{aligned}\int d[c,c^*] f(c,c^*) = \prod_I \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{da^I db^I}{2\pi} \\ \times f\left(\frac{1}{\sqrt{2}}(a+ib), \frac{1}{\sqrt{2}}(a-ib)\right),\end{aligned} \qquad \text{(C1)}$$

where a^I and b^I are real and imaginary degrees of freedom of c^I:

$$a^I = \frac{1}{\sqrt{2}}(\tilde{c}^I + \tilde{c}^{*I}), \qquad \text{(C2)}$$

$$b^I = \frac{1}{i\sqrt{2}}(\tilde{c}^I - \tilde{c}^{*I}). \qquad \text{(C3)}$$

APPENDIX D: ADIABATIC LIMIT AND PATH SPLITTING

It is shown that the stationary phase approximation of the "split path integral," with correct choice of the projection basis, leads to a correct result in the adiabatic limit. On the contrary, straightforward application of the stationary phase approximation to the original form of the path integral does not. Here adiabatic means the limit $||\hbar \dot{\mathbf{R}} \cdot \mathbf{X}||/\Delta E \ll 1$, where ΔE is the typical energy level difference between the adjacent electronic states, and $||\dot{\mathbf{R}} \cdot \mathbf{X}||$ is the maximum matrix element of the nonadiabatic coupling term in Eq. (3). It means that nuclear motion is "slow" compared to that of electrons, while the motion itself is not limited. In such a limit, by the adiabatic theorem, each electronic state does not change its quantum number. We here choose the expansion basis $\{|\phi_\alpha : \mathbf{R}\rangle\}$ as the adiabatic states of nuclear position $\mathbf{R}$,

$$\mathcal{H}^{(\mathrm{el})}(\mathbf{R}) |\phi_\alpha : \mathbf{R}\rangle = E_\alpha(\mathbf{R}) |\phi_\alpha : \mathbf{R}\rangle. \qquad \text{(D1)}$$

The electronic propagator becomes

$$\begin{aligned}&\mathcal{K}^{\mathrm{el}}\big(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f), t_f; \xi_i(\mathbf{R}_i), t_i\big) \\ &\quad = \sum_\alpha \langle \xi_f : \mathbf{R}_f | \phi_\alpha : \mathbf{R}_f \rangle \mathcal{K}^{\mathrm{el}}\big(\{\mathbf{R}\} : \phi_\alpha(\mathbf{R}_f), t_f; \phi_\alpha(\mathbf{R}_i), t_i\big) \\ &\qquad \times \langle \phi_\alpha : \mathbf{R}_i | \xi_i : \mathbf{R}_i \rangle,\end{aligned} \qquad \text{(D2)}$$

where $\mathcal{K}^{\mathrm{el}}\big(\{\mathbf{R}\} : \phi_\alpha(\mathbf{R}_f), t_f; \phi_\alpha(\mathbf{R}_i), t_i\big)$ is the electronic propagator of adiabatic state α:

$$\mathcal{K}^{\mathrm{el}}\big(\{\mathbf{R}\} : \phi_\alpha(\mathbf{R}_f), t_f; \phi_\alpha(\mathbf{R}_i), t_i\big) = \prod_{n=0}^{N-1} e^{-\frac{i}{\hbar}\epsilon E_\alpha(\mathbf{R}_n)}. \qquad \text{(D3)}$$

The total propagator then becomes

$$\begin{aligned}&\mathcal{K}\big(\mathbf{R}_f, \xi_f(\mathbf{R}_f), t_f : \mathbf{R}_i, \xi_i(\mathbf{R}_i), t_i\big) \\ &\quad = \int d\mathbf{R}_{N-1} \cdots d\mathbf{R}_1 e^{\frac{i}{\hbar} S_{\mathrm{nuc}}[\{\mathbf{R}\}]} \sum_\alpha \langle \xi_f : \mathbf{R}_f | \phi_\alpha : \mathbf{R}_f \rangle \\ &\qquad \times \mathcal{K}^{\mathrm{el}}\big(\{\mathbf{R}\} : \phi_\alpha(\mathbf{R}_f), t_f; \phi_\alpha(\mathbf{R}_i), t_i\big) \langle \phi_\alpha : \mathbf{R}_i | \xi_i : \mathbf{R}_i \rangle.\end{aligned} \qquad \text{(D4)}$$

Thus the stationary phase approximation for each state-projected effective action gives

$$M \ddot{R}^\mu = -\frac{\partial}{\partial R_n^\mu} \big(U_{\mathrm{nuc}} + E_\alpha(\mathbf{R})\big), \qquad \text{(D5)}$$

which is a correct nuclear equation of motion in the adiabatic limit. On the contrary, summation before the stationary phase approximation gives the equation of motion with the state-averaged force form as

$$M \ddot{R}^\mu = -\frac{\partial}{\partial R_n^\mu} U_{\mathrm{nuc}} - \sum_\alpha \frac{\langle \xi_f : \mathbf{R}_f | \phi_\alpha : \mathbf{R}_f \rangle \langle \phi_\alpha : \mathbf{R}_i | \xi_i : \mathbf{R}_i \rangle \frac{\partial E_\alpha(\mathbf{R}_n)}{\partial R_n^\mu} \exp\big[-\frac{i}{\hbar} \sum_\ell E_\alpha(\mathbf{R}_\ell)\big]}{\mathcal{K}^{\mathrm{el}}\big(\{\mathbf{R}\} : \xi_f(\mathbf{R}_f), t_f; \xi_i(\mathbf{R}_i), t_i\big)} \qquad \text{(D6)}$$

and does not reproduce the adiabatic limit of Eq. (D5).

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