10196 *J. Phys. Chem. A* **2007,** *111,* 10196−10204

Generalization of Classical Mechanics for Nuclear Motions on Nonadiabatically Coupled Potential Energy Surfaces in Chemical Reactions†

Kazuo Takatsuka

Department of Basic Science, The University of Tokyo, Komaba, 153-8902 Tokyo, Japan

Received: March 21, 2007; In Final Form: June 19, 2007

Classical trajectory study of nuclear motion on the Born−Oppenheimer potential energy surfaces is now one of the standard methods of chemical dynamics. In particular, this approach is inevitable in the studies of large molecular systems. However, as soon as more than a single potential energy surface is involved due to nonadiabatic coupling, such a naive application of classical mechanics loses its theoretical foundation. This is a classic and fundamental issue in the foundation of chemistry. To cope with this problem, we propose a generalization of classical mechanics that provides a path even in cases where multiple potential energy surfaces are involved in a single event and the Born−Oppenheimer approximation breaks down. This generalization is made by diagonalization of the matrix representation of nuclear forces in nonadiabatic dynamics, which is derived from a mixed quantum-classical representation of the electron−nucleus entangled Hamiltonian [Takatsuka, K. *J. Chem. Phys.* **2006**, *124*, 064111]. A manifestation of quantum fluctuation on a classical subsystem that directly contacts with a quantum subsystem is discussed. We also show that the Hamiltonian thus represented gives a theoretical foundation to examine the validity of the so-called semiclassical Ehrenfest theory (or mean-field theory) for electron quantum wavepacket dynamics, and indeed, it is pointed out that the electronic Hamiltonian to be used in this theory should be slightly modified.

I. Introduction

Since the inception of the field of quantum nuclear wavepacket dynamics some 30 years ago,[1−3] chemical reaction dynamics and studies of intramolecular vibrational energy redistribution have been extensively developed. Indeed, it is now widely known that a variety of ultrafast laser experimental techniques make it possible to map the real-time *wavepacket positions* at a femtosecond time scale (see for instance, refs 4−6 for reviews). For example, our theoretical studies have shown that pump−probe photoelectron spectroscopy provides a quite powerful means for this purpose,[7] including the detections of the instant of wavepacket bifurcation due to nonadiabatic transition (or electron−nucleus quantum entanglement) of Na I,[8] real time dynamics of proton transfer in the electronic ground state of chloromalonaldehyde,[9,10] and rapid passage of a wavepacket across the conical intersection in NO_2 molecule.[11] On the other hand, ultrafast chemical dynamics is now entering the stage of the attosecond time scale,[12−15] where the dynamics of electron wavepackets should be one of the most interesting objectives. Despite a large difference in the general time scales of electronic and nuclear motions, electronic wavepackets quite often couple with the dynamics of nuclear motion.[16,17] The appropriate treatment of electron−nucleus dynamical coupling is crucial also for a molecule placed in an extremely intense laser field,[18] where the vector potential can be as strong as the Coulombic interaction between the particles within a molecule.[19]

The electron dynamics is usually determined quantum mechanically (quantum chemically),[20,21] but the nuclear motions are often treated within the framework of classical mechanics driven by the electronic energy as a potential, because the wave lengths of the nuclei are generally much shorter than those of electrons. However, this framework loses theoretical consistency when more than two electronic states are closely involved and the Born−Oppenheimer approximation breaks down. (See ref 22 for the validity and error estimate of the Born−Oppenheimer approximation.) This is simply because the bifurcation and merging of a nuclear wavepacket at the so-called avoided crossing region does not have a classical counterpart. Thus, use of the classical path concept becomes invalid as soon as the state passes through a region where the nonadiabatic coupling is to some extent large, a ubiquitous situation in chemical systems. This has long been a fundamental issue in theoretical chemistry. In particular, the work of the groups of Rossky[23,24] and Truhlar[25−28] should be noted. They have explicitly (or artificially) introduced a dephasing interaction among the coupled electronic states (due to the bath modes in the study of Rossky), which is used to determine non-Born−Oppenheimer paths. The present paper is also devoted to a resolution of the present fundamental issue from a viewpoint that has not yet been formulated.

To specify the mathematical framework of the problem, we will outline in this section some very basic material about nonadiabatic interactions featuring the semiclassical Ehrenfest theory that is dedicated to a description of electron wavepacket dynamics coupled with the nuclear “classical motions”. Those familiar with this material may skip to section II. With this background, we then reformulate a Hamiltonian in section II, in which the electronic and nuclear parts are described in the Hilbert space and ordinary configuration space, respectively. This Hamiltonian is readily transformed to an approximate form of a mixed quantum electronic and classical nuclear representation. With this mixed representation of the Hamiltonian, we derive in section III the correct form of the semiclassical Ehrenfest theory, which is usually written down intuitively without an explicit derivation. This treatment shows that a term

---

† Part of the special issue “Robert E. Wyatt Festschrift”.

10.1021/jp072233j CCC: $37.00

is missing in the standard Ehrenfest theory. In section IV, which lies at the heart of this paper, we uncover a natural extension of classical mechanics: the forces acting on nuclei are represented in a matrix form, whose suffixes specify the electronic states mutually coupled through the nonadiabatic couplings. By diagonalizing this force matrix, we obtain eigenforces that determine non-Born−Oppenheimer paths. These paths are naturally reduced to the ordinary Born−Oppenheimer classical trajectories when only a single adiabatic potential energy surface is involved. In section V, we explore how the present non-Born−Oppenheimer paths can be applied to calculate a nonadiabatic transition probability and discuss how entanglement between “classical” nuclear motion and electronic quantum wavepacket dynamics arises. This paper concludes in section VI with some remarks.

A. Newtonian Paths on an Adiabatic Potential Energy Surface and Its Conceptual Breakdown. *1. Coupled Nuclear Wavepacket Dynamics in the Nonadiabatic Problem.* We first review one of the aspects of nonadiabatic dynamics that is necessary to formulate the path concept in nonadiabatic dynamics.[29−32] The total Schrödinger equation of our problem is

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = \left[-\frac{\hbar^2}{2}\sum_{\mathrm{A}}\nabla_{\mathrm{A}}{}^2 + H^{\mathrm{el}}(\mathbf{r},\mathbf{R})\right]\Psi(\mathbf{r},\mathbf{R},t) \quad (1)$$

where $\mathbf{r}$ and $\mathbf{R}$ represent the electronic and nuclear coordinates, respectively, and $\nabla_{\mathrm{A}}{}^2$ is the Laplacian for a nucleus A. Throughout this paper we adopt the mass-weighted coordinates for $\mathbf{R}$, so that all the nuclear masses are set to unity. The electronic Hamiltonian $H^{\mathrm{el}}(\mathbf{r},\mathbf{R})$ is

$$H^{\mathrm{el}}(\mathbf{r},\mathbf{R}) = -\frac{\hbar^2}{2m_{\mathrm{e}}}\sum_a\nabla_a{}^2 + \sum_{a<b}\frac{e^2}{|\mathbf{r}_a-\mathbf{r}_b|} - \sum_{a,\mathrm{A}}\frac{Z_{\mathrm{A}}e^2}{|\mathbf{r}_a-\mathbf{R}_{\mathrm{A}}|} + \sum_{\mathrm{A}<\mathrm{B}}\frac{Z_{\mathrm{A}}Z_{\mathrm{B}}e^2}{|\mathbf{R}_{\mathrm{A}}-\mathbf{R}_{\mathrm{B}}|} \quad (2)$$

in standard notation. One generally uses an electronic basis to expand the total wavefunction as

$$\Psi(\mathbf{r},\mathbf{R},t) = \sum_I \chi_I(\mathbf{R},t)\,\Phi_I(\mathbf{r};\mathbf{R}) \quad (3)$$

where χ_I and Φ_I stand for nuclear and electronic wavefunctions, respectively, and the total Schrödinger equation is projected onto coupled equations of motion for the nuclear wavepackets such that

$$i\hbar\frac{\partial}{\partial t}\chi_I(\mathbf{R},t) = \frac{1}{2}\sum_k\hat{P}_k{}^2\chi_I(\mathbf{R},t) + \sum_J H^{\mathrm{el}}_{IJ}(\mathbf{R})\,\chi_J(\mathbf{R},t) - i\hbar\sum_k\sum_J X^k_{IJ}(\mathbf{R})\,\hat{P}_k\chi_J(\mathbf{R},t) - \frac{\hbar^2}{2}\sum_k\sum_J Y^k_{IJ}(\mathbf{R})\,\chi_J(\mathbf{R},t) \quad (4)$$

where, and in what follows, k indicates a component of the entire list of the nuclear coordinates, and $\hat{P}_k$ is the nuclear momentum operator in the kth coordinate. We consistently assume orthonormality of the electronic basis functions

$$\langle\Phi_I(\mathbf{R})|\Phi_J(\mathbf{R})\rangle|_{\mathbf{R}=\mathbf{R}(t)} = \delta_{IJ} \quad (5)$$

and $H^{\mathrm{el}}_{IJ}(\mathbf{R})$ is defined as

$$H^{\mathrm{el}}_{IJ}(\mathbf{R}) = \langle\Phi_I(\mathbf{R})|H^{\mathrm{el}}(\mathbf{R})|\Phi_J(\mathbf{R})\rangle \quad (6)$$

where these integrals represented with the bra−ket inner products are to be performed over the electronic coordinates. The nonadiabatic coupling elements X^k_{IJ} and Y^k_{IJ} are defined as

$$X^k_{IJ}(\mathbf{R}) = \left\langle\Phi_I(\mathbf{R})\left|\frac{\partial\Phi_J(\mathbf{R})}{\partial R^k}\right.\right\rangle = -\left\langle\left.\frac{\partial\Phi_I(\mathbf{R})}{\partial R^k}\right|\Phi_J(\mathbf{R})\right\rangle \quad (7)$$

and

$$Y^k_{IJ}(\mathbf{R}) = \left\langle\Phi_I(\mathbf{R})\left|\frac{\partial^2\Phi_J(\mathbf{R})}{\partial R^{k2}}\right.\right\rangle \quad (8)$$

where R^k is the kth component of $\mathbf{R}$. This result is sometimes rewritten using the vector potential expression[31,32] as

$$i\hbar\frac{\partial}{\partial t}\chi_I(\mathbf{R},t) = \sum_J\left[\frac{1}{2}\sum_k(\delta_{IJ}\hat{P}_k - i\hbar X^k_{IJ})^2 + H^{\mathrm{el}}_{IJ}(\mathbf{R})\right]\chi_J(\mathbf{R},t) \quad (9)$$

in which $Y^k_{IJ}(\mathbf{R})$ does not appear explicitly. These coupled equations of motion provide the theoretical foundation of nonadiabatic dynamics from the viewpoint of nuclear wavepacket.

2. Born−Oppenheimer Approximation and Classical Trajectories. In cases where the coupling between the electronic states is small, using the eigenfunction of the electronic Hamiltonian at each nuclear configuration

$$H^{\mathrm{el}}(\mathbf{r};\mathbf{R})\;\Phi^{\mathrm{ad}}_I(\mathbf{r};\mathbf{R}) = V_I(\mathbf{R})\;\Phi^{\mathrm{ad}}_I(\mathbf{r};\mathbf{R}) \quad (10)$$

one can decouple eq 4 to obtain functions as

$$i\hbar\frac{\partial}{\partial t}\chi_I(\mathbf{R},t) = \left[\frac{1}{2}\sum_k\hat{P}_k{}^2 + V_I(\mathbf{R})\right]\chi_I(\mathbf{R},t) \quad (11)$$

As a consequence of quantum-classical correspondence (an approximation, of course), it is not difficult to “classicalize” this Schrödinger equation, leading to the Newtonian equations

$$\ddot{\mathbf{R}}^k = -\frac{\partial V_I(\mathbf{R})}{\partial R^k} \quad (12)$$

This is the theoretical foundation of the ordinary molecular dynamics.

3. Path Concepts in Nonadiabatic Dynamics. As seen above, in a crossing region between two (or more) potential surfaces, either in an adiabatic or in a diabatic representation, a quantum wavepacket for the nuclear motion should branch into two pieces (for the real-time observation of this bifurcation, see ref 8). However, any ray (trajectory-like) solution that is generated from ordinary differential equations, e.g., a classical trajectory, cannot have a branching in phase space, as long as the relevant differential equations are a well-posed initial value problem. Here appears an explicit discrepancy in the correspondence between quantum and classical mechanics. Several elegant theories for treating the nonadiabatic transitions that retain the concept of nuclear paths have been proposed; among others, the methods due to Pechukas[33] and Miller and George[34] should be noted. Unfortunately, these are severely limited in practical use, for instance, the Miller−George theory requires finding paths in the complex **R**-plane that pass across a branch-cut between two analytically continued adiabatic potential energy surfaces.

At the opposite extreme, the Tully surface hopping model[35,36] and its extensions[37−40] provide the most practical approaches. However, its theoretical foundation is rather intuitive. In these theories, a trajectory running on an adiabatic potential energy surface is designed to remain on it or to hop to another at some **R** in the crossing region with a probability which is to be provided by another theoretical framework such as the Landau−Zener[41] and Zhu−Nakamura theories.[30,42,43] Blais and Truhlar's later reformulation allows for surface hopping based on the magnitude of the coefficients given in the semiclassical Ehrenfest scheme.[44]

B. Fundamental Difficulty in Electronic Wavepacket Approach with the Semiclassical Ehrenfest Theory. Nonadiabatic theory from the viewpoint of electronic wavepacket dynamics is also attractive, particularly in the realm of attosecond dynamics. A typical theory is the so-called semiclassical Ehrenfest method.[31,45−47] Consider the dynamics of an electronic wavepacket $\Phi(\mathbf{r},t;\mathbf{R}(t))$ that is to be propagated along time-evolving nuclear coordinates $\mathbf{R}(t)$. In view of eq 10, where $H^{\mathrm{el}}(\mathbf{r};\mathbf{R})$ is the electronic Hamiltonian for a static **R**, it seems natural that the straightforward generalization of this electronic Schrödinger equation for the dynamical $\mathbf{R}(t)$ should be

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\Phi(\mathbf{r},t;\mathbf{R}(t)) = H^{\mathrm{el}}(\mathbf{r};\mathbf{R}(t))\ \Phi(\mathbf{r},t;\mathbf{R}(t)) \tag{13}$$

where $H^{\mathrm{el}}(\mathbf{r};\mathbf{R}(t))$ is an obvious modification of the electronic Hamiltonian of eq 2. Equation 13 is solved with an expansion

$$\Phi(\mathbf{r},t;\mathbf{R}(t)) = \sum C_I(t)\ \Phi_I(\mathbf{r};\mathbf{R})|_{\mathbf{R}=\mathbf{R}(t)} \tag{14}$$

along with the associated Newtonian equations

$$\begin{aligned}\ddot{\mathbf{R}}_k &= -\langle\Phi(t;\mathbf{R}(t))|(\partial_k H^{\mathrm{el}})|\Phi(t;\mathrm{R}(t))\rangle\\ &= -\sum_{I,J} C_I^*\langle\Phi_I|(\partial_k H^{\mathrm{el}})|\Phi_J\rangle C_J\end{aligned} \tag{15}$$

where $\partial_k H^{\mathrm{el}} = \partial H^{\mathrm{el}}/\partial R^k$. Some more details will be described in section III.

Although this theory seems quite natural and its validity seems robust, there are two intrinsic problems: (i) The use of these eqs 13 and 15, along with eq 28 to be described later as a matrix representation of eq 13, in trajectory-based simulations cannot be rigorously derived from a fully quantum mechanical treatment. Because eq 13 is not an axiom, but rather because we implicitly regard eqs 13−15 as a semiclassical projection of the total Schrödinger eq 1 onto the electronic space along a nuclear classical path, we would like to see how it is derived. Without such a derivation, there is no way to specify the "classical" dynamics of $\mathbf{R}(t)$ and even to justify the validity of eq 15. (ii) Indeed, the classical path passing across the avoided crossing determined by eq 15 is forced to run on a potential energy that is averaged over the comprising adiabatic potential surfaces responsible for the avoided crossing. Therefore once a path passes through the crossing region, it becomes incompatible with the standard view of a "classical trajectory running on an adiabatic surface". This constitutes a fundamental difficulty in the theoretical framework of molecular science.

In resolving this second problem, Truhlar and his co-workers[25−28] conceived that running on the averaged potential as in eq 15 should be a reflection of the biased quantum coherence between two states that have branched by passing across the avoided crossing. To overcome this difficulty, they actually have introduced "decoherence" so that the path eventually falls onto one of the adiabatic potential surfaces. The idea of decoherence was first introduced by Bittner and Rossky and their co-workers in the study of nonadiabatic dynamics in the condensed phase, where the decoherence arises physically from the fluctuation of solvent modes.[23,24] We do not consider such external source of fluctuation in the present paper.

C. Difficulty in the Quantum-Classical Mixed Representation. So far, the nonadiabatic dynamics has been considered for fast electrons and slow nuclei. The similar representation for a weakly coupled dynamics between fast and slow parts within the nuclear dynamics alone is often adopted. For instance, in studying proton dynamics, the proton motions may be treated quantum mechanically, and the other atoms constituting skeletons may be approximated with classical mechanics. This is the so-called mixed quantum-classical representation,[48−52] in which the above semiclassical Ehrenfest theory or its variants are usually applied. Hence, the problem of a path running on an average potential energy arises again.

II. Hamiltonian for Electron−Nucleus Entangled States

To retain the (classical) path concept in nonadiabatic dynamics, we generalize classical mechanics subject to a condition that it should naturally reduce to eq 12 in the limit of vanishing nonadiabatic coupling elements. We resume our study by representing the Hamiltonian of eq 2 in such a way to expose the entanglement between the nuclear and electronic motions more explicitly.[53]

A. Total Hamiltonian. First we rewrite the ansatz (4) to represent the total Hamiltonian in the Hilbert space for electrons and the configuration space (**R**-space) for nuclei, that is $\{|\Phi_I(\mathbf{R})\rangle|\mathbf{R}\rangle\}$, such that[54]

$$\begin{aligned}\hat{H}(\mathbf{R},e) = \frac{1}{2}\sum_k(\hat{P}_k - i\hbar\sum_{I,J}|\Phi_I(\mathbf{R})(X^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|)^2 +\\ \sum_{I,J}|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\end{aligned} \tag{16}$$

where the electronic state vectors are defined at each nuclear coordinates **R**, and "e" in $\hat{H}(\mathbf{R},e)$ is designated to remind of the electronic state representation. This Hamiltonian is expanded as

$$\begin{aligned}\hat{H}(\mathbf{R},e) = \frac{1}{2}\sum_k \hat{P}_k^{\,2} + \sum_{I,J}|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})| -\\ i\hbar\sum_k\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\hat{P}_k -\\ \frac{\hbar^2}{2}\sum_k\sum_{I,J}|\Phi_I(\mathbf{R})\rangle Y^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\end{aligned} \tag{17}$$

as was proven in ref 53. One can readily recover eq 4 as

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\chi_I(\mathbf{R},t) &= \sum_J \langle \Phi_I(\mathbf{R})|(\hat{H}(\mathbf{R},e)\,\chi_J(\mathbf{R},t))\Phi_J(\mathbf{R})\rangle \\
&= \frac{1}{2}\sum_k (\hat{P}_k{}^2\chi_I(\mathbf{R},t)) + \sum_J H^{\mathrm{el}}_{IJ}(\mathbf{R})\,\chi_J(\boldsymbol{R},t) - \\
&\qquad i\hbar\sum_k\sum_J X^k_{IJ}(\mathbf{R})(\hat{P}_k\chi_J(\mathbf{R},t)) - \\
&\qquad \frac{\hbar^2}{2}\sum_k\sum_J Y^k_{IJ}(\mathbf{R})\,\chi_J(\mathbf{R},t)
\end{aligned}
\tag{18}
$$

where $\langle \Phi_I(\mathbf{R})|(\hat{H}(\mathbf{R},e)\,\chi_J(\mathbf{R},t))\Phi_J(\mathbf{R})\rangle$ indicates that (i) $\hat{H}(\mathbf{R},e)$ should operate on $\chi_J(\mathbf{R},t)$ first and (ii) at each $\mathbf{R}$ the matrix element over the electronic states $\langle \Phi_I(\mathbf{R})|*|\Phi_J(\mathbf{R})\rangle$ is evaluated. $\hat{P}_k$ is not to operate on $\Phi_J(\mathbf{R})$ at this stage and is supposed to operate only on the nuclear wavepackets. Equation 18 confirms the validity of the representation in eq 16.

B. Classical Nuclear Variables and Electronic State Vectors. We *define* the quantum-classical mixed version of $\hat{H}$ by simply replacing the quantum momentum operator $\hat{P}_k$ with a scalar classical momentum P_k such that[55]

$$
\begin{aligned}
H(\mathbf{R},\mathbf{P},e) &= \frac{1}{2}\sum_k \Big(P_k - i\hbar\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\Big)^2 + \\
&\qquad \sum_{I,J}|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})| \\
&= \frac{1}{2}\sum_k P_k{}^2 + \sum_{I,J}|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})| - \\
&\qquad i\hbar\sum_k\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|P_k - \\
&\qquad \frac{\hbar^2}{2}\sum_k\sum_{I,J}|\Phi_I(\mathbf{R})\rangle Y^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|
\end{aligned}
\tag{19}
$$

Then, the following argument can proceed in a parallel manner to that of classical electromagnetic theory.[56] Regarding

$$
\mathbf{A}^k(\mathbf{R}) = i\hbar\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})| \tag{20}
$$

as a vector potential, we can generate the "canonical" equations of motion for nuclei with the usual prescription as

$$
\frac{\mathrm{d}}{\mathrm{d}t}R_k = \frac{\partial\hat{H}}{\partial P_k} = P_k - i\hbar\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^k_{IJ}\,(\mathbf{R})\langle\Phi_J(\mathbf{R})| \tag{21}
$$

and

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}P_k &= -\frac{\partial\hat{H}}{\partial R_k} \\
&= i\hbar\sum_l \Big(P_k - i\hbar\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^l_{IJ}(\boldsymbol{R})\langle\Phi_J(\mathbf{R})|\Big) \\
&\qquad \left(\frac{\partial}{\partial R^k}\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^l_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})\right|\Bigg) \\
&\qquad - \frac{\partial}{\partial R^k}\Big(\sum_{I,J}|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\Big)
\end{aligned}
\tag{22}
$$

A major difference from the purely classical electromagnetic field theory is that the present equations of motion include the bra–ket vectors for electronic states. Therefore, $\dot{R}^k$ and $\dot{P}_k$ are not simple scalars but "operators" that are to be represented in terms of the electronic bra–ket vectors. Hence they can be numerically determined only when the relevant electronic states are specified. To remind one that $\dot{R}^k$ and $\ddot{\mathrm{R}}^k$ function as operators in electronic Hilbert space, they are denoted as $\dot{\mathscr{R}}^k$ and $\dot{\mathscr{R}}^k$, respectively. For instance, by sandwiching eq 21 with $\langle\Phi(\mathbf{R},t)|$ and $|\Phi(\mathbf{R},t)\rangle$ we obtain a simple relation

$$
\begin{aligned}
\langle\Phi(\mathbf{R},t)|\dot{\mathscr{R}}^k|\Phi(\mathbf{R},t)\rangle = \dot{R}^k &= P_k\langle\Phi(\mathbf{R},t)|\Phi(\mathbf{R},t)\rangle - \\
&\qquad i\hbar\left\langle\Phi(\mathbf{R},t)\left|\frac{\partial}{\partial R^k}\right|\Phi(\mathbf{R},t)\right\rangle \\
&= P_k
\end{aligned}
\tag{23}
$$

Thus $\dot{R}^k$ can be replaced with P_k subject to this condition. Otherwise, they are not generally identical.[57]

We now examine whether these canonical equations of motion reproduce the Newton-type equation. To this end we consider the acceleration $\ddot{\mathscr{R}}^k$ by taking a derivative of eq 21, which formally results in

$$
\begin{aligned}
\frac{\mathrm{d}^2}{\mathrm{d}t^2}\mathscr{R}^k &= -\frac{\partial}{\partial R^k}\Big(\sum_{I,J}|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\Big) - \\
&\qquad \frac{\partial}{\partial t}\Big(i\hbar\sum_{I,J}|\Phi_I(\mathbf{R})\rangle X^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\Big) + [\mathbf{v}\times(\nabla\times\mathbf{A})]_k
\end{aligned}
\tag{24}
$$

As is well-known, the vector field defined in eq 20 generates a "magnetic field", which gives rises to the "Lorentzian force". Hence the electron–nuclear coupling generates a force that is perpendicular to the velocity vector $\mathbf{v} = \{\dot{R}^k\}$. (Recall that for an electromagnetic Hamiltonian with a vector field $\mathbf{A}$

$$
H = \frac{1}{2m}\Big(\mathbf{p} - \frac{e}{c}\mathbf{A}\Big)^2 \tag{25}
$$

the classical force $\mathbf{F}$ on a particle placed in this field is

$$
\mathbf{F} = -\frac{e}{c}\frac{\partial\mathbf{A}}{\partial t} + \frac{e}{c}[\mathbf{v}\times(\nabla\times\mathbf{A})] \tag{26}
$$

(see Schatz and Ratner[56]). With some manipulations, and noting that the second term in the right-hand side of eq 24 is zero, we obtain

$$
\begin{aligned}
\ddot{\mathscr{R}}^k &= \frac{\mathrm{d}^2}{\mathrm{d}t^2}\mathscr{R}^k \\
&= -\sum_{I,J}\frac{\partial}{\partial R^k}\big(|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\big) + \\
&\qquad i\hbar\sum_{I,J}\sum_l \dot{R}_l\Bigg[\frac{\partial}{\partial R^k}\big(|\Phi_I(\mathbf{R})(X^l_{IJ}(\mathbf{R})\rangle\Phi_J(\mathbf{R})|\big) - \\
&\qquad \frac{\partial}{\partial R^l}\big(|\Phi_I(\mathbf{R})\rangle X^k_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|\big)\Bigg]
\end{aligned}
\tag{27}
$$

We will return to this point in section IV.

III. Physical Meaning of the Semiclassical Ehrenfest Theory: Need for a Correction Term

In this section we examine the validity of the semiclassical Ehrenfest theory from the view point of the mixed quantum-classical representation of the Hamiltonian equtiaon (19) and also clarify how the average potential energy arises. We then show how this theory should be modified to be more consistent theoretically.

A. Standard Semiclassical Ehrenfest Theory. With finite basis expansions, eqs 13 and 14 lead to the coupled equations

$$\mathrm{i}\hbar\frac{\partial}{\partial t}C_I(t) = \sum_J [H^{\mathrm{el}}_{IJ}(\mathbf{R}(t)) - \mathrm{i}\hbar\sum_k \dot{R}^k(t)X^k_{IJ}]C_J \qquad (28)$$

and[16]

$$\ddot{R}^k = -\sum_{I,J,K}[C_I^* X^k_{IK}(\mathbf{R})\, H^{\mathrm{el}}_{KJ}(\mathbf{R})C_J - C_I^* H^{\mathrm{el}}_{IK}(\mathbf{R})\, X^k_{KJ}(\mathbf{R})C_J + C_I^*(\partial_k H^{\mathrm{el}}_{IJ}(\mathbf{R}))C_J\delta_{JK}] + \mathrm{i}\hbar\sum_{I,J}\sum_l \dot{R}^l C_I^*[\partial_k X^l_{IJ}(\mathbf{R}) - \partial_l X^k_{IJ}(\mathbf{R})]C_J \qquad (29)$$

The summation over I and J in the above expression reduces the velocity ($\dot{R}_l$) dependent terms to zero,[58] and therefore this force turns out to be

$$\ddot{R}^k = -\sum_{I,J}C_I^*(\partial_k H^{\mathrm{el}}_{IJ}(\mathbf{R}))C_J - \sum_{I,J,K}C_I^*[X^k_{IK}(\mathbf{R})\, H^{\mathrm{el}}_{KJ}(\mathbf{R}) - H^{\mathrm{el}}_{IK}(\mathbf{R})\, X^k_{KJ}(\mathbf{R})]C_J \qquad (30)$$

Furthermore, if a complete set of the adiabatic eigenfunctions satisfying eq 10 were available, eq 30 would be equivalent to the well-known compact form[27,59]

$$\ddot{R}^k = -\sum_I |C_I|^2(\partial_k V_I(\mathbf{R})) - \sum_{I,J}C_I^* C_J X^k_{IJ}[V_J(\mathbf{R}) - V_I(\mathbf{R})] \qquad (31)$$

This expression can in turn be reexpressed with use of the Hellmann−Feynman force as

$$\ddot{\mathbf{R}}^k = -\sum_{I,J}C_I^*\langle\Phi_I|(\partial_k H^{\mathrm{el}})|\Phi_J\rangle C_J \qquad (32)$$

which brings us back to eq 15.

B. How Does the Averaged Potential Energy Arise? Let us examine the acceleration term of eq 27 to see the origin of the averaged potential. Consider the electronic wavepacket average of $\ddot{\mathscr{R}}^k$ of eq 27, which gives rise to

$$\langle\Phi(\mathbf{R},t)|\ddot{\mathscr{R}}^k|\Phi(\mathbf{R},t)\rangle = -\sum_{I,J,K}[C_I^* X^k_{IK}(\mathbf{R})\, H^{\mathrm{el}}_{KJ}(\mathbf{R})C_J - C_I^* H^{\mathrm{el}}_{IK}(\mathbf{R})\, X^k_{KJ}(\mathbf{R})C_J + C_I^*(\partial_k H^{\mathrm{el}}_{IJ}(\mathbf{R}))C_J\delta_{JK}] + \mathrm{i}\hbar\sum_{I,J}\sum_l \dot{R}^l C_I^*[\partial_k X^l_{IJ}(\mathbf{R}) - \partial_l X^k_{IJ}(\mathbf{R})]C_J \qquad (33)$$

Comparison of this expression with eq 29 shows immediately that $\ddot{\mathbf{R}}^k$ in the Ehrenfest theory, which is represented in a variety of the forms as eqs 29 and 30, should itself be interpreted as $\langle\Phi(\mathbf{R},t)|\dot{\mathscr{R}}^k|\Phi(\mathbf{R},t)\rangle$. *Hence, the trajectories in the semiclassical Ehrenfest theory are forced to run on an averaged potential (a mean field), simply because one takes the wavepacket average in* eq *33*. This is not surprising if we recall the property of the original Ehrenfest theorem.[60] However, what is much more significant in this study is that there are other ways of using $\dot{\mathscr{R}}^k$ of eq 27 than taking the wavepacket average. We explore this in the next section.

C. Correction to the Semiclassical Ehrenfest Theory. On the basis of the above description of the mixed quantum-classical Hamiltonian, we try to derive the semiclassical Ehrenfest expressions. For classical nuclear motion, the Euler−Lagrange variational principle gives rise to Lagrangian dynamics, which is eventually transformed into Hamilton's canonical equations of motion. This procedure is actually what we have adopted in the preceding section. To recover the quantum dynamics of the electronic part from the Hamiltonian in eq 29, we accordingly resort to the time-dependent variational principle[61,62]

$$\delta\int \mathrm{d}t\left\langle\Phi(\mathbf{R},t)\left|\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - H(\mathbf{R},\mathbf{P},e)\right)\right|\Phi(\mathbf{R},t)\right\rangle = 0 \qquad (34)$$

Because ${P_k}^2$ is a scalar here, we have

$$\delta\int \mathrm{d}t\,\langle\Phi(\mathbf{R},t)|{P_k}^2|\Phi(\mathbf{R},t)\rangle = {P_k}^2\delta\int \mathrm{d}t\,\langle\Phi(\mathbf{R},t)|\Phi(\mathbf{R},t)\rangle = 0 \qquad (35)$$

With an operator

$$F(\mathbf{R},\mathbf{P},e) = H(\mathbf{R},\mathbf{P},e) - \frac{1}{2}\sum_k {P_k}^2 \qquad (36)$$

Equation 34 is readily reduced to

$$\mathrm{i}\hbar\frac{\partial}{\partial t}C_I(t) \equiv \sum_J\langle\Phi_I(R)|F(\mathbf{R},\mathbf{P},e)|\Phi_J(\mathbf{R})\rangle C_J(t) \qquad (37)$$

with

$$\langle\Phi_I(\mathbf{R})|F(\mathbf{R},\mathbf{P},e)|\Phi_J(\mathbf{R})\rangle = H^{\mathrm{el}}_{IJ}(\mathbf{R}) - \mathrm{i}\hbar\sum_k P_k X^k_{IJ}(\mathbf{R}) - \frac{\hbar^2}{2}\sum_k Y^k_{IJ}(\mathbf{R}) \qquad (38)$$

which is given by eq 19. Thus we finally have

$$\mathrm{i}\hbar\frac{\partial}{\partial t}C_I(t) = \sum_J\left[H^{\mathrm{el}}_{IJ}(\mathbf{R}) - \mathrm{i}\hbar\sum_k P_k X^k_{IJ}(\mathbf{R}) - \frac{\hbar^2}{2}\sum_k Y^k_{IJ}(\mathbf{R})\right]C_J(t) \qquad (39)$$

With use of eq 23, this equation is rewritten as

$$\mathrm{i}\hbar\frac{\partial}{\partial t}C_I(t) = \sum_J\left[H^{\mathrm{el}}_{IJ}(\mathbf{R}) - \mathrm{i}\hbar\sum_k \dot{R}_k X^k_{IJ}(\mathbf{R}) - \frac{\hbar^2}{2}\sum_k Y^k_{IJ}(\mathbf{R})\right]C_J(t) \qquad (40)$$

Therefore it turns out that eq 28, or the more fundamental looking eq 13, misses the last term of eq 40 and should be accordingly corrected.

There is no mathematical mechanism to make it possible for the terms $-\hbar^2/2\sum_k Y^k_{IJ}(\mathbf{R})$ to arise from eq 13, but on the other hand their presence in eq 39 is quite acceptable if we compare the operators in eq 39 with those in eq 4. In this regard, it is worthwhile to reconfirm that our starting equation is not eq 13 but the total Schrödinger equation for the study of electron wavepacket dynamnics coupled with nuclear motion. Though it is usual practice to neglect the correction terms $-\hbar^2/2\sum_k Y^k_{IJ}(\mathbf{R})$ for the reason that they are of order $\hbar^2$ and can be expected to be small, this correction term should not be forgotten from a conceptual point of view. This is an independent issue from numerical accuracy. In particular, the diagonal terms $Y^k_{II}(\mathbf{R})$ are not zero, in marked contrast to the identity $X^k_{II}(\mathbf{R}) = 0$, and therefore the individual diagonal energies $H^{\mathrm{el}}_{II}(\mathbf{R})$ should be so modified in the electron dynamics. This should cause a dynamical effect in the phase part of $C_I(t)$ in addition to the mixing of the electronic states induced by the off-diagonal terms

$X^k_{IJ}(\mathbf{R})$ and $Y^k_{IJ}(\mathbf{R})$. The $C_I(t)$ thus modified may result in the modification of the nuclear dynamics.

IV. Generalization of Classical Mechanics in the Presence of Nonadiabatic Coupling

The Newtonian-like equations of motion of eq 27 suggest that they can be solved only when the electronic basis functions are available to specify the projection of $\dot{\mathscr{R}}$ onto a proper subspace of the electronic states. We now explore how to do this.

A. Matrix Form of the Newtonian Equations. Instead of taking the wavepacket average of $\dot{\mathscr{R}}^k$ in eq 27, we consider the following matrix elements

$$\begin{aligned}\ddot{\mathscr{R}}^k_{IJ} &= \langle \Phi_I(\mathbf{R})|\ddot{\mathscr{R}}^k|\Phi_J(\mathbf{R})\rangle \\ &= -\sum_K [X^k_{IK}(\mathbf{R})\, H^{\rm el}_{KJ}(\mathbf{R}) - H^{\rm el}_{IK}(\mathbf{R})\, X^k_{KJ}(\mathbf{R}) + \\ &\qquad (\partial_k H^{\rm el}_{IJ}(\mathbf{R}))] + i\hbar \sum_{l(\neq k)} \dot{R}^l [\partial_k X^l_{IJ}(\mathbf{R}) - \partial_l X^k_{IJ}(\mathbf{R})] \end{aligned} \tag{41}$$

The velocity dependent term in this expression is rewritten as

$$\begin{aligned} i\hbar\sum_l \dot{R}^l[\partial_k X^l_{IJ}(\mathbf{R}) - \partial_l X^k_{IJ}(\mathbf{R})] &= \\ i\hbar\sum_l \dot{R}^l [\langle \partial_k \Phi_I(\mathbf{R})|\partial_l \Phi_J(\mathbf{R})\rangle &- \langle \partial_l \Phi_I(\mathbf{R})|\partial_k \Phi_J(\mathbf{R})\rangle] \end{aligned} \tag{42}$$

and may be approximately evaluated as

$$i\hbar\sum_l \dot{R}^l \sum_K [-X^k_{IK}(\mathbf{R})\, X^l_{KJ}(\mathbf{R}) + X^l_{IK}(\mathbf{R})\, X^k_{KJ}(\mathbf{R})] \tag{43}$$

Note that these velocity-dependent terms vanish in the averaging process of the semiclassical Ehrenfest theory, but this is not the case in these matrix elements. It should be also noted that the velocity-dependent factor identically vanishes in one-dimensional systems and thereby the one-dimensional problem is rather exceptional in nonadiabatic dynamics. Recall that the velocity-dependent terms arise from the outer product of the relevant vectors as the Lorentz force does. (Incidentally, another Lorentz-like force has been identified in classical dynamics in a curved space representing molecular internal shape space that is extracted from the total Euclidean space by removing the translational and rotational isotropic dimensionalities.[63])

Obviously, $\ddot{\mathscr{R}}^k_{IJ}$ constitutes a Hermitian matrix

$$\ddot{\mathscr{R}}^k = \begin{pmatrix} \ddot{R}^k_{11} & \ddot{R}^k_{12} & \cdots \\ \ddot{R}^k_{21} & \ddots & \\ \vdots & & \end{pmatrix} \tag{44}$$

because

$$\ddot{\mathscr{R}}^k_{IJ} = (\ddot{\mathscr{R}}^k_{JI})^* \tag{45}$$

In this representation, where $\mathbf{R}$ is assumed to remain in the real-valued space in contrast to Miller−George theory,[34] a complex valued force $\ddot{\mathscr{R}}^k_{IJ}$ arises for the electronic state to shift from the Jth state to the Ith one. Therefore these off-diagonal complex forces manifest quantum dynamics of mixing the electronic states in a way that does not have a classical counterpart. Therefore one should remove the off-diagonal elements to retain the view of classical path.

B. Force Diagonalization. This matrix, which we call the force matrix, can be diagonalized so that its diagonal elements represent the real-valued eigenforces,

$$\mathbf{U}^k(\mathbf{R})\ddot{\mathscr{R}}^k\mathbf{U}^k(\mathbf{R})^{-1} = \begin{pmatrix} F^k_1 & 0 & \cdots \\ 0 & F^k_2 & \\ \vdots & & \ddots \end{pmatrix} \tag{46}$$

with the associated electronic basis-set transformation

$$\mathbf{U}^k(\mathbf{R})\begin{pmatrix} \Phi_1(\mathbf{r};\mathbf{R}) \\ \Phi_2(\mathbf{r};\mathbf{R}) \\ \vdots \end{pmatrix} = \begin{pmatrix} \lambda^k_1(\mathbf{r};\mathbf{R}) \\ \lambda^k_2(\mathbf{r};\mathbf{R}) \\ \vdots \end{pmatrix} \tag{47}$$

The original force matrix elements in eq 41 could be represented in either the adiabatic representation or other unitary transformed variants, but the diagonalization of eq 47 uniquely fixes the representation.

Note that the above diagonalization can be done in each direction k, and it is obvious that the unitary matrix $\mathbf{U}^k(\mathbf{R})$ should depend on k. Furthermore, it is "path-dependent," that is, it depends on the velocity of trajectories through the presence of $\dot{R}_l$ in eq 41. Therefore, there should not exist in principle a matrix that diagonalizes the force matrix in any direction simultaneously and at any velocity. However, because we are moving along a classical path, which is essentially a one-dimensional object in N-dimensional configuration space, it suffices to choose the direction of a trajectory as the direction of the diagonalization.[64] This may not be a simple procedure though (see below).

On the basis of this idea, we can construct a diabatic representation for the potential energy curves along a non-Born−Oppenheimer path, which are connected asymptotically to the ordinary adiabatic potential energy surfaces. First we recall that the force matrix $\ddot{\mathscr{R}}^k$ is diagonal from the outset if the off-diagonal matrix elements are all vanishing, that is

$$H^{\rm el}_{IJ}(\mathbf{R}) = 0 \qquad X^k_{IJ}(\mathbf{R}) = 0 \tag{48}$$

and therefore trajectories run on one of the adiabatic potential energy surfaces in those areas. Suppose that a classical trajectory, having started on an adiabatic potential surface, enters a crossing region, where the off-diagonal elements are not small. As the couplings become significant, we diagonalize $\ddot{\mathscr{R}}^k_{IJ}$ in the direction of trajectory, which is denoted as $\ddot{\mathscr{R}}^{\rm tr}_{IJ}$. This procedure may require an iterative process, because the direction of a trajectory $\dot{\mathbf{R}}(t + \Delta t)$ deviates slightly from $\dot{\mathbf{R}}(t)$, and the direction of $\dot{\mathbf{R}}(t{+}\Delta t)$, where Δt is a time step for integration of the classical equations of motion, is not known beforehand. We thus find the direction along which the path proceeds.

It is interesting to recall that the geometrical dependence of the nonadiabatic coupling terms ($H^{\rm el}_{IJ}(\mathbf{R})$ and/or $X^k_{IJ}(\mathbf{R})$) is vital for determining the nonadiabatic transitions. If they are very small in the direction of a path, no significant transition among the potential energy surfaces is expected along this path. This fact is widely recognized already and actually taken into account in various approximations to nonadiabatic transition in multidimensional systems. Consider, for instance, a trajectory hopping at a crossing seam. A usual practice is that the multidimensional nonadiabatic transition is reduced to a one-dimensional problem along this classical path, and the coupling element is taken to be proportional to the inner product between the directions of the trajectory and the crossing seam. In the present approach, too, such a geometrical dependence should be appropriately taken into account.

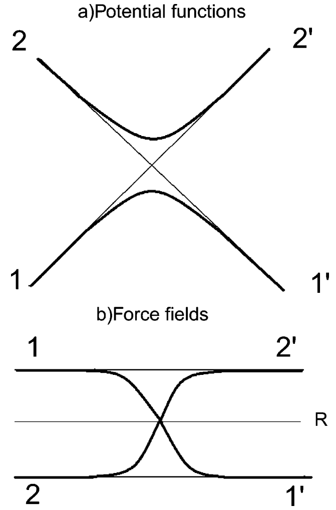

Figure 1. (a) Schematic view of potential curves in adiabatic (thick curves) and a typical diabatic (thin straight lines) representations. (b) Corresponding force fields. The adiabtic potential curves avoid crossing, but the forces in the diabatic representation do cross. (The diabatic representation adopted in this figure does not necessarily represent the force-diagonalizing states.)

C. Natural Diabatic Representation along the Force-Diagonalizing Paths. The force-diagonalizing paths thus formulated should be propagated simultaneously with the electronic wavepacket dynamics of eq 40, because they have been born from the same Hamiltonian, eq 19. However, to highlight a property of this non-Born−Oppenheimer path, we here track the geometrical property of these paths, disregarding the electron dynamics of eq 40 in the meantime.

Because the matrix $\dot{\mathscr{R}}^{\mathrm{tr}}$ is Hermitian, the resultant eigenvalues should repel each other as in energy-level repulsion, and therefore it is expected that the eigenforces do not cross each other unless an accidental degeneracy occurs. Let us take an example from a one-dimensional two-level problem (see Figure 1). Suppose we adopt the adiabatic representation, where the simple force matrix is

$$\ddot{\mathscr{R}}^{k}_{IJ} = -[X^{k}_{IJ}(\mathbf{R})\, H^{\mathrm{el}}_{J}(\mathbf{R}) - H^{\mathrm{el}}_{I}(\mathbf{R})\, X^{k}_{IJ}(\mathbf{R}) + (\partial_k H^{\mathrm{el}}_{I}(\mathbf{R}))\delta_{IJ}] \tag{49}$$

Thus, the off-diagonal terms $-X^{k}_{IJ}(\mathbf{R})\, H^{\mathrm{el}}_{J}(\mathbf{R}) + H^{\mathrm{el}}_{I}(\mathbf{R})\, X^{k}_{IJ}(\mathbf{R})$ bring about a repulsion between the Born−Oppenheimer forces $-\partial_k H^{\mathrm{el}}_{1}(\mathbf{R})$ and $-\partial_k H^{\mathrm{el}}_{2}(\mathbf{R})$. Thus the eigenforces should avoid crossing. On the other hand, the Born−Oppenheimer forces $-\partial_k H^{\mathrm{el}}_{1}(\mathbf{R})$ and $-\partial_k H^{\mathrm{el}}_{2}(\mathbf{R})$ should cross to avoid the crossing of the potential energy curves in the adiabatic representation (see Figure 1). Thus, the paths guided smoothly by the diagonalized forces should give rise to a natural diabatic representation. This avoided-crossing feature in the eigenforces is retained even if the velocity dependent terms (the last terms in eq 41) are taken into account in a multidimensional system. (Note that the ordering of the eigenvalues of the force matrix has nothing to do with the ordering of the adiabatic potential energy surfaces.)

V. Entanglement between Electron Wavepackets and the Force-Diagonalizing Paths in Mixed Quantum-Classical Representation

There can be many ways to evolve in time the electronic wavepacket dynamics of eq 40 along the force-diagonalizing paths of eq 46, which should be integrated simultaneously. Here we consider a rather straightforward method, in which we repeat a combination of the short-time (theoretically infinitesimally short-time) evolution of the paths and the electron wavepackets many times for a finite time elapse as in the Trotter product formula.[65] This is essentially a rigorous way to integrate the electron−nuclei dynamics and is not necessarily practical in actual applications. We need to devise a reasonable approximation, which will be studied in our future publications.[66]

We here explore the characteristics of the above solutions, which give a view of how "classical" nuclear dynamics can be involved in the quantum entanglement. This is a nontrivial extension of the semiclassical Ehrenfest theory and the on-the-fly molecular dynamics methods, because a total wavefunction starting from the following form

$$\Psi(\mathbf{r},\mathbf{R}(0),t) = \Phi(\mathbf{r},0;\mathbf{R}(0))\, \delta(\mathbf{R}-\mathbf{R}(0)) \tag{50}$$

in these methods remains in the product form as

$$\Psi(\mathbf{r},\mathbf{R}(t),t) = \Phi(\mathbf{r},t;\mathbf{R}(t))\, \delta(\mathbf{R}-\mathbf{R}(t)) \tag{51}$$

with the electron wavepacket being represented as in eq 14. The discussion made here is mainly devoted to conceptual and theoretical aspects, rather than numerical issues. We note again that the numerical realization of the following scheme is not easy.

A. Scheme of Computation. We outline the procedure in a recursive manner.

Step 1. Suppose, we have an arbitrary electronic wavepacket at a position ($\mathbf{R}(t)$, $\dot{\mathbf{R}}(t)$) in nuclear phase space such that

$$\Phi(\mathbf{r},t;\mathbf{R}(t)) = \sum_I C_I(t)\, \Phi_I(\mathbf{r};\mathbf{R})|_{\mathbf{R}=\mathbf{R}(t)} \tag{52}$$

which we would like to propagate to $t + \Delta t$.

Step 2. At this nuclear position, we first solve the electronic Schrödinger equation, eq 39 or 40 (or approximately eq 28), which should give

$$\Phi(\mathbf{r},t+\Delta t;\mathbf{R}(t)) = \sum_I C_I(t+\Delta t)\, \Phi_I(\mathbf{r};\mathbf{R}) \tag{53}$$

Step 3. Diagonalize the force matrix in the direction of the trajectory, obtaining the eigenfunctions $\lambda^{\mathrm{tr}}_{K}(\mathbf{r};\mathbf{R})$ for the corresponding eigenforces $F^{\mathrm{tr}}_{K}(K=1,2,...)$.

Step 4. Expand $\Phi(\mathbf{r},t+\Delta t;\mathbf{R}(t))$ in $\lambda^{\mathrm{tr}}_{K}(\mathbf{r};\mathbf{R}(t))$

$$\Phi(\mathbf{r},t+\Delta t;\mathbf{R}(t)) = \sum_K D_K(t+\Delta t)\, \lambda^{\mathrm{tr}}_{K}(\mathbf{r};\mathbf{R}(t)) \tag{54}$$

with $D_K(t+\Delta t)$ being the coefficients.

Step 5. The individual pieces of this electronic wavefunction $D_K(t+\Delta t)\ \lambda^{\mathrm{tr}}_{K}(\mathbf{r};\mathbf{R}(t))$ should be pushed to their neighboring positions by the individual eigenforces

$$\mathbf{R}_K(t+\Delta t) = \mathbf{R}(t) + \Delta\mathbf{R}_K \tag{55}$$

where $\Delta\mathbf{R}_K$ is to be obtained by solving Newton's equation

$$\ddot{\mathbf{R}}(t) = F^{\mathrm{tr}}_{K} \tag{56}$$

for a small time-interval Δt. The differences in $\Delta\mathbf{R}_K$ among $K = 1, 2, ...$ after a very short time propagation must be small, but they should become significant after some finite time.

Step 6. We thus have a time-propagation

$$\Phi(\mathbf{r},t;\mathbf{R}(t)) \rightarrow \sum_K D_K(t+\Delta t,\mathbf{R}_K(t+\Delta t))\, \lambda_K^{\mathrm{tr}}(\mathbf{r};\mathbf{R}_K(t+\Delta t)) \tag{57}$$

To recall that the coefficients D_K depend not only on time but on the path position, we explicitly write it as $D_K(t+\Delta t,\mathbf{R}_K(t+\Delta t))$.

Step 7. Go back to step 1 by identifying $D_K(t+\Delta t,\mathbf{R}_K(t+\Delta t))$ $\lambda_K^{\mathrm{tr}}(\mathbf{r};\mathbf{R}_K(t+\Delta t))$ as $\Phi(\mathbf{r},t;\mathbf{R}(t))$ of eq 52. $\lambda_K^{\mathrm{tr}}(\mathbf{r};\mathbf{R}_K(t+\Delta t))$ can be expanded in terms of the basis functions $\{\Phi_I(\mathbf{r};\mathbf{R}_K(t+\Delta t))\}$.

B. Final Wavefunctions. In the above procedure, the short-time electronic propagation and the transport of the electronic wavepackets along the nuclear coordinates are performed alternately. It is quite natural that the eigenforces ($F_K^{\mathrm{tr}}(\mathbf{R})$) of the force matrix are responsible for carrying their corresponding eigenfunctions ($\lambda_K^{\mathrm{tr}}(\mathbf{R})$) in step 6, because the eigenforces can shift the nuclear positions without mixing among $\{\lambda_K^{\mathrm{tr}}(\mathbf{R})|, K = 1, 2, ...\}$.

A wavepacket initially prepared at a point $\mathbf{R}(t)$ in step 1 is to be propagated to points $\{\mathbf{R}_K(t+\Delta t), K = 1, 2, ...\}$. These points are in turn followed individually to $\{\mathbf{R}_K(t+2\Delta t), K = 1, 2, ...\}$, which carry the dynamics to the next time steps. Therefore we should be careful about the precise histories of the paths. For instance, the position $\mathbf{R}_M(t+2\Delta t)$ of a path $\mathbf{R}(t) \rightarrow \mathbf{R}_K(t+\Delta t) \rightarrow \mathbf{R}_M(t+2\Delta t)$ is generally different of $\mathbf{R}_M(t+2\Delta t)$ of $\mathbf{R}(t) \rightarrow \mathbf{R}_L(t+\Delta t) \rightarrow \mathbf{R}_M(t+2\Delta t)$ and must be distinguished from each other. To make this difference explicit, we should denote these points as $\mathbf{R}_{KM}(t+2\Delta t)$ and $\mathbf{R}_{LM}(t+2\Delta t)$, respectively. The present situation reminds us of the Feynman path integration. Thus, the electronic wavefunctions carried over a finite time is now written as

$$\Phi(\mathbf{r},t;\mathbf{R}(t)) \rightarrow \sum_K \sum_{His}^{K} \lambda_K^{\mathrm{tr}}(\mathbf{r};\mathbf{R}_{His,K}(t+n\Delta t))\, D_{His,K}(t+n\Delta t,\mathbf{R}_{His,K}(t+n\Delta t)) \tag{58}$$

where $\sum_{His}^{K}$ implies the summation over the possible histories of paths before they came to the Kth electronic state at time $t + n\Delta t$.

In this way, path positions undergo a cascade-like branching. Even though these points are determined in a completely deterministic manner as shown above, it may seem to be a stochastic process, if one tracks the position of a single path like $\mathbf{R}(t) \rightarrow \mathbf{R}_K(t+\Delta t) \rightarrow \mathbf{R}_M(t+2\Delta t)$. This seemingly stochastic behavior is one of the interesting manifestations of quantum fluctuation on a classical system directly coupled with a quantum system. This aspect is discussed elsewhere in a greater detail.

After the nonadiabatic interaction is switched off after passing the avoided crossing region ($n \rightarrow \infty$), the individual eigenfunctions $\lambda_K(\mathbf{r};\mathbf{R})$ become identical with one of the electronic wavefunctions in the adiabatic representation. Hence, even if we start from the product form of the total wavefunction as in eq 50, the wavefunction should end up with the form

$$\sum_K \sum_{His}^{K} \Phi_K^{\mathrm{ad}}(\mathbf{r};\mathbf{R}_{His,K}(t+n\Delta t))\, D_{His,K}(t+n\Delta t,\mathbf{R}_{His,K}(t+n\Delta t)) \tag{59}$$

Thus, the electronic wavefunction is distributed over the different adiabatic states, and moreover, on each adiabatic potential surface, e.g., the Kth one, it has a spatial distribution over the nuclear coordinates. Therefore, the accumulated coefficients $D_{His,K}(t+n\Delta t,\mathbf{R}_{His,K}(t+n\Delta t))$ may be regarded as a nuclear wavepacket spreading over the $\mathbf{R}$ coordinates, which is in a marked contrast to eq 51. In this way we have recovered the entangled form of nuclear and electronic motions as in eq 3 within quantum-classical mixed representation.

C. Nonadiabatic Transition Probability. After accumulating all these pieces of information, we finally obtain the nonadiabatic transition probability. Nevertheless, partial information about the transition amplitude will be provided by tracking each path, because the coefficient $D_K(t)$ is always associated with the path. Although the method described here is almost exact in the limit of $\Delta t \rightarrow 0$, more feasible (approximate) methods must be devised. This aspect will be discussed in our future papers.

VI. Concluding Remarks

We have studied two aspects of nonadiabatic transition from the view point of electronic wavepacket dynamics. In the first half of this paper, we have presented the total Hamiltonian for the coupled dynamics of electrons and nuclei in a molecule, in which the Hilbert and configuration spaces are adopted to represent the state of electrons and nuclei, respectively. With this quantum-classical mixed representation, we have established the theoretical foundation of the semiclassical Ehrenfest theory. In this conjunction, we have noted that the electronic Hamiltonian in the electronic Schrödinger equation should be corrected so as to include an additional term arising from a non-adiabatic coupling.

In the second half, a mixed quantum-classical study has been applied to resolve the difficulty inherent to the so-called semiclassical Ehrenfest theory, that is, after passing the avoided crossing region, a classical trajectory is forced to run on an averaged potential energy surface and thereby the Born−Oppenheimer view breaks down. Instead of wavepacket averaging of $\dot{\mathscr{R}}$, we propose diagonalizing the matrix representation of to determine the force acting on the nuclear coordinates $\mathbf{R}$, which gives rise to a natural extension of classical mechanics.

A non-Born−Oppenheimer path thus determined chooses one of the possible adiabatic potential energy surfaces as its destination after passing through an avoided crossing region. The final adiabatic potential surface chosen by such a path may sensitively depend on the initial condition of the path. A slight difference in the initial conditions (position and associated momentum), even starting on a same potential surface, can result in a large difference in the final potential surface arrived at. Nevertheless, the dynamics is entirely deterministic. Thus, this dynamics would reveal a new aspect of chaos. Note that such chaos can take place only in quantum mechanics, or in semiclassical dynamics of nonadiabatic transition and associated quantum entanglement.[67,68]

We thus have seen that the non-Born−Oppenheimer trajectory can be made compatible with the ordinary classical path that runs on a single adiabatic potential surface. We note that those "classical trajectories" may be utilized in any semiclassical theory[65,69−75] or Feynman path integrations to quantize the nuclear motions.

This paper has been the first report of the series of our studies on nonadiabatic electronic wavepacket dynamics and has covered only the theoretical and conceptual aspects. The present theory has already been extended so as to treat the dynamics of molecules in an intense laser field (classical electromagnetic vector field).[66] For practical applications, we have already implemented all the necessary matrix elements based upon ab initio quantum chemistry in our working program. Along with this theoretical extension, numerical studies based on appropriate approximations to the Trotter-like formula considered in section V will be reported in our future publications.[66]

Acknowledgment. I thank Dr. T. Yonehara for his valuable discussions. This work has been supported in part by the Grant-in-Aid for Basic Science and the 21st Century COE Program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

(1) McCullough, E. A.; Wyatt, R. E., Jr. *J. Chem. Phys.* **1969**, *51*, 1253.

(2) McCullough, E. A.; Wyatt, R. E., Jr. *J. Chem. Phys.* **1969**, *55*, 3578.

(3) For an update see: Wyatt, R. E.; Babyuk, D. *Phys. Rev. E* **2006**, *73*, 046701. See also the publication list of R. Wyatt in this volume.

(4) Gruebele, M.; Zewail, A. *J. Chem. Phys.* **1993**, *98*, 883.

(5) Zewail, A. H. *J. Phys. Chem. A* **2000**, *104*, 5660.

(6) Dantus, M.; Zewail, A. *Chem. Rev.* **2004**, *104*, 1717.

(7) Arasaki, Y.; Takatsuka, K.; Wang, K.; McKoy, V. *Chem. Phys. Lett.* **1999**, *302*, 363; *J. Chem. Phys.* **2000**, *112*, 8871.

(8) Arasaki, Y.; Takatsuka, K.; Wang, K.; McKoy, V. *Phys. Rev. Lett.* **2003**, *90*, 248303; *J. Chem. Phys.* **2003**, *119*, 7913.

(9) Arasaki, Y.; Yamazaki, K.; Varella, M.; Takatsuka, K. *Chem. Phys* **2005**, *311*, 255.

(10) Varella, M. T. N.; Arasaki, Y.; Ushiyama, H.; Takatsuka, K.; Wang, K.; McKoy, V. *J. Chem. Phys.* **2007**, *126*, 054303.

(11) Arasaki, Y.; Takatsuka, K. *Chem. Phys.* To be published.

(12) Hentschel, M.; Kienberger, R.; Spielmann, C.; Reider, G. A.; Milosevi, N.; Brabec, T.; Corkum, C.; Heinzmann, U.; Drescher, M.; Krausz, F. *Nature* **2001**, *414*, 509.

(13) Niikura, H.; Légaré, F.; Hasban, R.; Bandrauk, A. D.; Ivanov, M. Y.; Villeneuve, D. M.; Corkum, P. B. *Nature* **2002**, *417*, 917.

(14) Baltuška, A.; Udem, Th.; Uiberacker, M.; Hentschel, M.; Goulielmakis, E.; Gohle, Chapter; Holzwarth, R.; Yakovlev, V. S.; Scrinzi, A.; Hänsch, A.; Krausz, F. *Nature* **2003**, *421*, 611.

(15) Nabekawa, Y.; Shimizu, T.; Okino, T.; Furusawa, K.; Hasegawa, K.; Yamanouchi, K.; Midorikawa, K. *Phys. Rev. Lett.* **2006**, *96*, 083901.

(16) Amano, M.; Takatsuka, K. *J. Chem. Phys.* **2005**, *122*, 084113.

(17) Ushiyama, H.; Takatsuka, K. *Angew. Chem. Intl. Ed.* **2007**, *46*, 587.

(18) Yagi, N.; Takatsuka, K. *J. Chem. Phys.* **2005**, *123*, 224103.

(19) Yamanouchi, K. *Science* **2002**, *295*, 1659.

(20) Levine, I. N. *Quantum Chemistry*; Prentice Hall:Englewood Cliffs, NJ, 2000.

(21) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; John-Wiley: New York, 2000.

(22) Takahashi, S.; Takatsuka, K. *J. Chem. Phys.* **2006**, *124*, 144101.

(23) Bittner, E. R.; Rossky, P. J. *J. Chem. Phys.* **1995**, *103*, 8130; *J. Chem. Phys.* **1997**, *107*, 8611.

(24) Wong, K. F.; Rossky, P. *J. Chem. Phys.* **2002**, *116*, 8418; **2002**, *116*, 8429.

(25) Hack, M. D.; Truhlar, D. G. *J. Chem. Phys.* **2001**, *114*, 9305.

(26) Jasper, A. W.; Hack, M. D.; Chakraborty, A.; Truhlar, D. G.; Piecuch, P. *J. Chem. Phys.* **2001**, *115*, 7945.

(27) Zhu, C.; Jasper, A. W.; Truhlar, D. G. *J. Chem. Phys.* **2004**, *120*, 5543.

(28) Zhu, C.; S. Nangia; Jasper, A. W.; Truhlar, D. G. *J. Chem. Phys.* **2004**, *121*, 7658.

(29) Child, M. S. *Molecular Collision Theory*; Academic Press: New York, 1974. *Semiclassical Mechanics with Molecular Approximations*; Clarendon Press: Oxford, U.K., 1991.

(30) Nakamura, H. *Nonadiabatic Transition*; World Scientific: Singapore, 2002.

(31) Jasper, A. W.; Kendrick, B. K.; Mead, C. A.; Truhlar, D. G. *Modern Trends in Chemical Reaction Dynamics*; Yang, X., Liu K., Eds.; World Scientific: Singapore, 2004; p 329.

(32) Baer, M. *Beyond Born-Oppenheimer*; Wiley: Hoboken, NJ, 2006.

(33) Pechukas, P. *Phys. Rev.* **1969**, *181*, 174.

(34) Miller, W. H.; George, T. F. *J. Chem. Phys.* **1972**, *56*, 5637.

(35) Tully, J. C.; Preston, R. K. *J. Chem. Phys.* **1971**, *55*, 562.

(36) Bjere, A.; Nikitin, E. E. *Chem. Phys. Lett.* **1967**, *1*, 179.

(37) Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061.

(38) Jasper, A. W.; Stechmann, S. N.; Truhlar, D. G. *J. Chem. Phys.* **2002**, *115*, 5424.

(39) Nangia, S.; Jasper, A. W.; Miller, T. F., III; Truhlar, D. G. *J. Chem. Phys.* **2002**, *120*, 3586. One can see an extensive list of publications in the trajectory surface-hopping method.

(40) Doltsinis, N. L.; Marx, D. *Phys. Rev. Lett.* **2002**, *16*, 166402.

(41) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*, *Non-relativistic Theory*; Addison-Wesley: New York, 1965.

(42) Zhu, C.; Nakamura, H.; Re, N.; Aquilanti, V. *J. Chem. Phys.* **1992**, *97*, 1892.

(43) Zhu, C.; Nakamura, H. *J. Chem. Phys.* **1992**, *97*, 8497.

(44) Blais, N.; Truhlar, D. G. *J. Chem. Phys.* **1983**, *79*, 1334.

(45) Delos, J. B. *Rev. Mod. Phys.* **1981**, *53*, 287.

(46) Meyer, H.-D.; Miller, W. H. *J. Chem. Phys.* **1979**, *70*, 3214.

(47) Meyer, H.-D.; Miller, W. H. *J. Chem. Phys.* **1980**, *72*, 2272.

(48) Kim, S. Y.; Hammes-Schiffer, S. *J. Chem. Phys.* **2003**, *119*, 4389 and references cited therein.

(49) Terashima, T.; Shiga, M.; Okazaki, S. *J. Chem. Phys.* **2001**, *114*, 5663.

(50) Sergi, A.; Kapral, R. *J. Chem. Phys.* **2003**, *119*, 12776.

(51) Hanna, G.; Kapral, R. *J. Chem. Phys.* **2005**, *122*, 244505.

(52) Yamashita, T.; Takatsuka, K. *J. Chem. Phys.* **2007**, *126*, 074304.

(53) Takatsuka, K., *J. Chem. Phys.* **2006**, *124*, 064111.

(54) $|\Phi_I(\mathbf{R})\rangle$ is a state vector for an electronic state at a nuclear position $\mathbf{R}$ and should not be confused with an electronic wavefunction having the electronic coordinates $\mathbf{r}$ as independent variables. More explicitly, $\Phi_I(\mathbf{r};\mathbf{R}) = \langle \mathbf{r}|\Phi_I(\mathbf{R}(t))\rangle$ and $\Phi(\mathbf{r},t;\mathbf{R}(t)) = \sum C_I(t)\langle \mathbf{r}|\Phi_I(\mathbf{R}(t))\rangle|_{\mathbf{R}=\mathbf{R}(t)}$ in eq 15.

(55) It would be instructive to compare our Hamiltonian with the one employed in the classic work of Meyer and Miller,[46] that is, $H = {}^1/_2\sum_k P_k{}^2 + \sum_{I,J}|\Phi_I(\mathbf{R})\rangle H^{\mathrm{el}}_{IJ}(\mathbf{R})\langle\Phi_J(\mathbf{R})|$.

(56) Schatz, G. C.; Ratner, M. A. *Quantum Mechanics in Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1993.

(57) It should be noted that these canonical equations of motion do not always give consistent results depending on the electronic wavefunctions we adopt. This is due to the replacement of $\hat{P}_k$ with P_k; the mixed treatment of quantum and classical quantities.

(58) The terms $\partial_k X^l_{IJ}(\mathbf{R})$ have already appeared in the equations of nuclear motion in Appendix B of ref 46.

(59) Tully, J. C. In *Dynamics of Molecular Collisions*; Miller, W. H., Ed.; Plenum: New York, 1976.

(60) Schiff, L. I. *Quantum Mechanics*; McGraw-Hill: New York, 1968.

(61) Dirac, P. A. M. *Proc. Cambridge Philos. Soc.* **1930**, *26*, 376.

(62) Frenkel, J. *Wave Mechanics*; Clarendon Press: Oxford, U.K., 1934.

(63) Teramoto, H.; Takatsuka, K. *J. Chem. Phys.* **2005**, *122*, 074101.

(64) The idea to make a diabatic representation along a path is not new. For instance, Granucci et al. proposed the matrix $\sum_k \dot{R}^k(t)X^k_{IJ}$ in eq 28 to be diagonalize only along a path in the surface hopping method, which they termed a locally diabatic representation. See: Granucci, G.; Persico, M.; Toniolo, A. *J. Chem. Phys.* **2001**, *114*, 10608.

(65) Schulman, L. S. *Techniques and Applications of Path Integration*; Wiley: New York, 1981.

(66) Yonehara, T.; Takatsuka, K. To be published.

(67) Fujisaki, H.; Takatsuka, K. *Phys. Rev. E* **2001**, *63*, 066221.

(68) Higuchi, H.; Takatsuka, K. *Phys. Rev. E* **2002**, *66*, 035203(R).

(69) Miller, W. H. *Adv. Chem. Phys.* **1974**, *25*, 69.

(70) Berry, M. V.; Mount, K. E. *Rep. Prog. Phys.* **1972**, *35*, 315.

(71) Miller, W. H. *Adv. Chem. Phys.* **1975**, *30*, 77.

(72) Gaspard, P.; Alonso, D.; Burghardt, I. *Adv. Chem. Phys.* **1995**, *90*, 105.

(73) Brack, M.; Bhaduri, R. K. *Semiclassical Physics*; Addison-Wesley: Reading, MA, 1997.

(74) Takatsuka, K.; Inoue, A. *Phys. Rev. Lett.* **1997**, *78*, 1404. Inoue-Ushiyama, A.; Takatsuka, K. *Phys. Rev. A* **1999**, *59*, 3256; **1999**, 60, 112.

(75) Takatsuka, K. *Phys. Rev. E* **2001**, *64*, 016224. Hotta, K.; Takatsuka, K. *J. Phys. A* **2003**, *36*, 4785. Teramoto, H.; Takatsuka, K. *J. Chem. Phys.* **2006**, *125*, 194301. Takatsuka, K.; Takahashi, S.; Yang Wei, K; Yamashita, T. *J. Chem. Phys.*, **2007**, *126*, 021104.