Geometrical quantization of nonadiabatic systems

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We present a geometrical quantization condition, i.e., quantum–classical correspondence, for steady states of nonadiabatic systems consisting of fast and slow degrees of freedom (DOFs) by extending Gutzwiller’s trace formula using an approach based on the nonadiabatic path integral. Quantum-classical correspondence indicates that a set of primitive hopping periodic orbits of the slow DOF that are invariant under time evolution in phase space should be quantized. We apply the geometrical quantization to a simple nonadiabatic model that accurately reproduces the exact quantum energy levels.

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Nonadiabatic transitions are universal quantum phenomena of coupled systems with fast and slow degrees of freedom (DOFs), e.g., electrons and nuclei\textsuperscript{1,2}, and have been studied since the formulation of quantum mechanics. These transitions arise in surface scattering\textsuperscript{3}, vision\textsuperscript{4}, molecular dynamics control\textsuperscript{5}, quantum computing\textsuperscript{6}, and organic solar cell\textsuperscript{7,8} contexts. Transition probabilities in one-dimensional systems can be described by the Landau–Zener\textsuperscript{9,10} and St"{u}ckelberg\textsuperscript{11} formulae or the more sophisticated and applicable Zhu–Nakamura formula\textsuperscript{12–15}. A number of theoretical frameworks\textsuperscript{16–27} and numerical codes\textsuperscript{28–30} for investigating the nonadiabatic dynamics in realistic and atomistic models have also been presented.

However, the quantization mechanism, i.e., the quantum–classical correspondence, in nonadiabatic systems has not yet been fully revealed. Revealing classical counterparts of nonadiabatic transitions will promote further understanding of quantum mechanics because quantum mechanics should be constructed on the correspondence principle. To this end, there have been some semiclassical studies such as that of Miller and coworkers\textsuperscript{31,32}, who re-quantized a classical electron analog model obtained through Ehrenfest treatments, and that of Stock and Thoss\textsuperscript{33}, who re-quantized a classical analog of a continuous fast quantum DOF that is mapped from a discrete fast quantum DOF, but in both these studies, the analogical fast and slow DOFs were quantized on an equal footing. Although the nonadiabatic transitions were well reproduced semiclassically, there was no clear classical counterpart of the nonadiabatic transition between adiabatic surfaces because classical mechanics on and transitions between adiabatic surfaces were not used explicitly.

In this Letter, we propose a new semiclassical formulation to describe the quantization mechanism of nonadiabatic systems. In contrast to previous studies, we focus explicitly on the quantization of the nonadiabatic dynamics of the slow DOF evolving on an adiabatic surface and hopping between adiabatic surfaces. Namely, a classical counterpart holding the physical concept of a transition between adiabatic surfaces is revealed, which can be addressed by recent progresses of the path integral for nonadiabatic phenomena\textsuperscript{34,35}.

In geometrical quantization, the quantization is performed using geometrical quantities such as periodic orbits and tori that are invariant under time evolution in phase space. Geometrical quantities are basic concepts in obtaining the quantum steady states of the old quantum theory, i.e., the Bohr\textsuperscript{36}, Bohr–Sommerfeld\textsuperscript{37}, and Einstein–Brillouin–Keller\textsuperscript{38} quantum conditions, and are considered to be classical counterparts to quantum steady states.
We begin by considering a one-dimensional adiabatic system for which Gutzwiller’s trace formula\textsuperscript{39}, based on the path integral representation of the density of states (DOS) $\Omega(E)$, also offers a geometrical quantization condition:

$$\Omega(E) \propto \sum_{\lambda \in \text{PPOs}} \sum_{k=0}^{\infty} G^k, \quad (1)$$

$$G_\lambda = \exp \left[ \frac{i}{\hbar} \left( S_{\lambda}^{cl} - \frac{\hbar \pi}{2} \nu_\lambda \right) \right], \quad (2)$$

Here, only the part that causes divergence of the DOS at the quantum energy levels is shown. Each primitive periodic orbit (PPO) that is not a repeated cycle of another periodic orbit (PO) is indexed by $\lambda$, and $S^{cl}$ is a classical action integral written as

$$S^{cl} = \int dt P \frac{dR}{dt} - H(P, R) + E = \int dRP, \quad (3)$$

where $R$, $P$, and $H(P, R)$ are the coordinates, momenta, and Hamiltonian of the system under consideration. Thus, $S^{cl}$ is the phase space surrounded by each PPO. The Maslov index $\nu$ denotes the number of times the momentum is 0 during one cycle, i.e., the number of times the PPO intersects the $R$-axis in phase space. Therefore, $G$ is the geometrical quantity of each PPO. The summation over $k$ takes into account $k$ cycles of each PPO. Considering that only one PPO exists at each energy in a one-dimensional adiabatic system, we can rewrite the DOS as $\Omega(E) = (1 - G)^{-1}$, and the quantization condition of an adiabatic system is thus $G = 1$. For the example of a quantum harmonic oscillator, i.e., $H(p, q) = p^2/2m + m\omega^2q^2/2$, a phase space area of $2\pi E/\omega$, and $\nu = 2$, the quantization condition is $G = \exp \left[ \frac{i}{\hbar} \left( \frac{2\pi E}{\omega} - \hbar \pi \right) \right] = 1$; that is, we recover the well-known $E_n = \hbar \omega \left( n + \frac{1}{2} \right)$ energy levels.

For nonadiabatic systems, we present the geometrical quantization condition in a similar manner. In this case, a nonadiabatic path integral\textsuperscript{34,35} is needed to formulate the nonadiabatic trace formula (semiclassical treatments are described in\textsuperscript{35}). In this nonadiabatic path integral, overlap integrals of the fast DOF between different slow coordinates, $\langle n'; R'|n; R \rangle$, are a key factor for the nonadiabatic transitions. Here, $\langle n; R \rangle$ is the $n$-th eigenstate of the fast DOF, and these eigenstates are adiabatic states that depend parametrically on the coordinates of the slow DOF $R$. The time evolution of the fast DOF is exactly adiabatic if the overlap integrals of the same eigenstate are equal to 1 when the slow DOF changes from $R$ to $R'$. In contrast to adiabatic systems, the quantum population probability is transferred nonadiabatically to different eigenstates if the overlap integrals of different eigenstates
are not zero. These non-zero values of overlap integrals cause breakdown of the quantum adiabatic theorem.

The nonadiabatic kernel can then be written with the overlap integrals and trajectories that experience hopping between adiabatic surfaces:

\[
K(R_f, n_f, t_f; R_i, n_i, t_i)
\equiv \langle n_f; R_f | \langle R_f | \exp \left[ \frac{i}{\hbar} \hat{H} (t_f - t_i) \right] | R_i \rangle | n_i, R_i \rangle
\]

\[
= \int \mathcal{D} [\mathcal{R}(\tau), n(\tau)] \xi \exp \left[ \frac{i}{\hbar} S \right],
\]

where \( \mathcal{D} \) denotes the path integral of all paths that start from \( R_i \) on the \( n_i \)-th adiabatic surface at time \( t_i \), hop between adiabatic surfaces, and end at \( R_f \) on the \( n_f \)-th adiabatic surface at \( t_f \). The Hamiltonian \( \hat{H} \) is that of the total system consisting of fast and slow DOFs, and \( \xi \) is an infinite product of the overlap integrals along each path:

\[
\xi \equiv \lim_{J \to \infty} \prod_{j=0}^{J-1} \langle n(t_{j+1}); R(t_{j+1}) | n(t_j); R(t_j) \rangle,
\]

where \( t_j \equiv (t_f - t_i)/J + t_i, t_i = t_0, \) and \( t_f = t_J \). Applying the stationary phase approximation to Eq. (4) leads to the nonadiabatic semiclassical kernel:

\[
K_{sc} = (2\pi i\hbar)^{-1/2} \sum_{\lambda} \xi_{\lambda} \left| \frac{\partial R_f}{\partial P_i} \right|_{R_i}^{-1/2} \exp \left[ \frac{i}{\hbar} S_{cl}^{\lambda} - i\frac{\pi}{2} \nu_{\lambda} \right].
\]

There are two differences between this nonadiabatic semiclassical kernel and the usual adiabatic semiclassical kernel. The first is that all the variables in Eq. (6) are calculated along a trajectory that experiences momentum-conserving hopping between adiabatic surfaces. After such a hop and before the next hop, the trajectory evolves on the adiabatic surface according to the first derivative of the adiabatic surface. The second difference is that \( \xi \) is a prefactor of the exponential term. In addition, it should be noted that there are multiple hopping trajectories that have identical starting (and/or ending) phase space points (thus necessitating the sum over \( \lambda \)).

By using the nonadiabatic path integral, the extension of Gutzwiller’s trace formula to nonadiabatic systems is fairly straightforward:

\[
\Omega(E) \propto \sum_{\lambda \in \text{PHPOs}} \sum_{k=0}^{\infty} \mathcal{G}_{\lambda}^{k}
\]

\[
\mathcal{G}_{\lambda} = \xi_{\lambda} \exp \left[ \frac{i}{\hbar} \left( S_{\lambda}^{cl} - \frac{\hbar \pi}{2} \nu_{\lambda} \right) \right].
\]
Note that here the primitive hopping periodic orbit (PHPO) is not a repeated cycle of another hopping periodic orbit (HPO) and that $\xi$ is along each PHPO. Because $\xi$ is in general less than 1, the quantization cannot be performed with a single PHPO, unlike the adiabatic case in which a single PPO was sufficient.

Owing to an infinite number of possible hopping trajectories, there are a countably infinite number of PHPOs, and as a result, care must be taken in performing the summation over $\lambda$ in Eq. (7). To enable the summation, we introduce $S$ for each adiabatic surface. This $S$ defines a set of PHPOs that (i) pass through the same phase space point and (ii) cannot be factorized as a combination of other PHPOs in $S$; that is, any pair of PHPOs in $S$ is coprime: $\{\forall \Gamma, \forall \Gamma' \in S | \Gamma' \not\subset \Gamma \vee \Gamma \setminus \Gamma' \notin S\}$. Rewriting Eq. (7) in terms of $S$ leads to

$$\Omega(E) \propto \sum_{\mathcal{S}_i \in \{\mathcal{S}\}} \Omega_{\mathcal{S}_i}(E), \quad (9)$$

$$\Omega_{\mathcal{S}_i}(E) \equiv \sum_{k=0}^{\infty} \left\{ \sum_{\lambda \in \mathcal{S}_i} \mathcal{G}_\lambda \right\}^k = \frac{1}{1 - \left\{ \sum_{\lambda \in \mathcal{S}_i} \mathcal{G}_\lambda \right\}}, \quad (10)$$

where $\{\mathcal{S}\}$ is a set of sets. The number of elements of $\{\mathcal{S}\}$ equals the number of adiabatic surfaces considered. In Eq. (10), any PHPO can be included as a combination of elements of the set $\mathcal{S}_i$; the number of elements in each $\mathcal{S}_i$ is finite for one-dimensional systems, and so the summation over $\lambda$ can be performed concretely. We therefore conclude from Eq. (10) that a geometrical quantization condition for one-dimensional nonadiabatic systems is

$$\sum_{\lambda \in \mathcal{S}} \mathcal{G}_\lambda = 1. \quad (11)$$

We apply this geometrical quantization to a simple nonadiabatic model consisting of two adiabatic quantum harmonic oscillators, $V_I(R)$ and $V_{II}(R)$, as shown in Fig. 1(a). The eigenstates corresponding to these two adiabatic surfaces are represented as $|I; R\rangle$ and $|II; R\rangle$, respectively, and to induce nonadiabatic transitions, these adiabatic eigenstates are defined by a set of diabatic states $|\Psi_\lambda\rangle$ and $|\Psi_B\rangle$:

$$\begin{pmatrix}
|I; R\rangle \\
|II; R\rangle
\end{pmatrix} = (1 - \theta(R)) \begin{pmatrix}
|\Psi_A\rangle \\
|\Psi_B\rangle
\end{pmatrix} + \theta(R) \begin{pmatrix}
\cos \phi & -\sin \phi \\
\sin \phi & \cos \phi
\end{pmatrix} \begin{pmatrix}
|\Psi_A\rangle \\
|\Psi_B\rangle
\end{pmatrix}, \quad (12)$$
FIG. 1. (a) Two adiabatic harmonic surfaces: $V_I(R) = m\omega_I R^2/2$ and $V_{II}(R) = m\omega_{II} R^2/2$ where $\omega_I = 27.6 \text{ [kcal}^{1/2}\text{mol}^{-1/2}\text{Å}^{-1}\text{amu}^{-1/2}\text{], } \omega_{II} = 82.8 \text{ [kcal}^{1/2}\text{mol}^{-1/2}\text{Å}^{-1}\text{amu}^{-1/2}\text{], and } m \text{ is 1 [amu].}$

(b) Phase space area surrounded by classical trajectories on $V_I$ and $V_{II}$ are represented by the light and dark gray ellipses, respectively. The area of former and latter are referred as $S_I^{cl}$ and $S_{II}^{cl}$ in the text, respectively.
where \( \theta(R) \) is the Heaviside step function. The overlap integrals of the adiabatic eigenstates can thus be expressed as

\[
\begin{pmatrix}
\langle I; R' | I; R \rangle \\
\langle II; R' | I; R \rangle
\end{pmatrix}
\begin{pmatrix}
\langle I; R' | II; R \rangle \\
\langle II; R' | II; R \rangle
\end{pmatrix}
\begin{cases}
\begin{pmatrix}
\cos \phi & -\sin \phi \\
\sin \phi & \cos \phi
\end{pmatrix} & \text{for } R' < 0 \land 0 \leq R, \\
\begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix} & \text{otherwise}
\end{cases}
\]

The first-order derivative couplings (e.g., \( \langle I; R | \frac{\partial}{\partial R} | II; R \rangle \)) calculated using Eq. (12) diverge at the origin of the \( R \)-axis only. Therefore, wavepackets can nonadiabatically transfer to another adiabatic surface only when the wavepackets pass through the origin of the \( R \)-axis.

In semiclassical treatments, trajectories can hop to another adiabatic surface only when the trajectories pass through the origin.

Let us consider a set \( \mathcal{S}_I \) of PHPOs that start from the phase space point “p” in Fig. 1(b):

\[
p \rightarrow q \rightarrow p,
p \rightarrow s \rightarrow p,
p \rightarrow q \rightarrow p \rightarrow s \rightarrow p,
p \rightarrow q \rightarrow r \rightarrow s \rightarrow p,
\]

To simplify the representation, we assign a bit sequence to each PHPO such that “0” (“1”) indicates that a PHPO has passed through “p” or “q” (“r” or “s”). The PHPOs in Eq. (14) are then denoted by

\[
\dot{0}, \dot{1}, \dot{00} \dot{1}, \dot{001} \dot{1}, \ldots,
\]

where the dots indicate the start and end points of one cycle. If these cyclic bit sequences are considered as fractional parts of real numbers, then all the cyclic bits correspond to a subset of rational numbers between 0 and 1/2. To ensure that any pair of PHPOs in \( \mathcal{S}_I \) is coprime, we need to exclude abundant PHPOs. For example, \( \dot{00} \dot{1} \) is not coprime with \( \dot{0} \dot{0} \) and \( \dot{0} \dot{1} \) because \( \dot{00} \dot{1} \) is a combination of 00 and 01. We can thus exclude abundant PHPOs by retaining only PHPOs in which odd-numbered bits, except for the first bit, are 1.
denote bit sequences in which all odd-numbered bits are 1 (e.g., 1, 101, 111, 10101, \cdots, 1011101\cdots1, etc.) as $1$, and so all the elements in $\mathcal{S}_I$ can be listed as
\[ \mathcal{S}_I = \{\ddot{0}\ddot{0}, \ddot{0}\ddot{1}, \ddot{0}\dot{0}1\ddot{0}, \ddot{0}\dot{1}1\ddot{0}, \dot{0}\ddot{1}\ddot{0}, \dot{0}\ddot{1}\dot{1}\ddot{1}\}. \] (16)

Each PHPO in $\mathcal{S}_I$ is shown graphically in Fig. 2.

To calculate $G$ [Eq. (8)], we note from Fig. 2 that the geometries of $\ddot{0}\ddot{0}1\dot{1}$ and $\ddot{0}\dot{1}1\ddot{0}$ are identical, and so
\[ S_{\ddot{0}\ddot{0}1\dot{1}}^{cl} = S_{\ddot{0}\dot{1}1\ddot{0}}^{cl}, \quad \xi_{\ddot{0}\ddot{0}1\dot{1}} = \xi_{\ddot{0}\dot{1}1\ddot{0}}, \quad \nu_{\ddot{0}\ddot{0}1\dot{1}} = \nu_{\ddot{0}\dot{1}1\ddot{0}}. \] From Fig. 1(b) in which the areas of the light and dark gray ellipses are $S_{I}^{cl}$ and $S_{II}^{cl}$, respectively, we find that
\[ S_{\ddot{0}\ddot{0}}^{cl} = S_{I}^{cl}, \] (17)
\[ S_{\ddot{0}\ddot{1}}^{cl} = \frac{1}{2} S_{I}^{cl} + \frac{1}{2} S_{II}^{cl}, \] (18)
\[ S_{\ddot{0}\dot{0}1\ddot{0}}^{cl} = \frac{3}{2} S_{I}^{cl} + \frac{1}{2} S_{II}^{cl}, \] (19)
\[ S_{\ddot{0}\dot{0}1\ddot{1}}^{cl} = S_{I}^{cl} + S_{II}^{cl}, \] (20)
\[ S_{\ddot{0}\ddot{1}\dot{1}}^{cl} = \frac{1}{2} S_{I}^{cl} + \frac{3}{2} S_{II}^{cl}, \] (21)
where $S_{I}^{cl} = 2\pi E/\omega_I$ and $S_{II}^{cl} = 2\pi E/\omega_{II}$. In calculating $\xi$, we use the overlap integrals defined in Eq. (13) when the PHPO passes through the origin of the $R$-axis, and therefore,
\[ \xi_{\ddot{0}\ddot{0}} = \cos^2 \phi, \] (22)
\[ \xi_{\ddot{0}\ddot{1}} = \sin^2 \phi, \] (23)
\[ \xi_{\ddot{0}\dot{0}1\ddot{0}} = \cos^2 \phi \sin^2 \phi, \] (24)
\[ \xi_{\ddot{0}\dot{0}1\dot{1}} = -\cos^2 \phi \sin^2 \phi, \] (25)
\[ \xi_{\ddot{0}\ddot{1}\dot{1}} = \cos^2 \phi \sin^2 \phi. \] (26)

The Maslov indexes for these cycles are $\nu_{\ddot{0}\ddot{0}} = \nu_{\ddot{0}\ddot{1}} = 2$ and $\nu_{\ddot{0}\dot{0}1\ddot{0}} = \nu_{\ddot{0}\dot{0}1\dot{1}} = \nu_{\ddot{0}\ddot{1}\ddot{0}} = \nu_{\ddot{0}\ddot{1}\dot{1}} = 4$. We are now able to calculate $G_{\ddot{0}\ddot{0}}$, $G_{\ddot{0}\ddot{1}}$, $G_{\ddot{0}\dot{0}1\ddot{0}}$, $G_{\ddot{0}\dot{0}1\dot{1}}$, $G_{\ddot{0}\ddot{1}\ddot{0}}$, and $G_{\ddot{0}\ddot{1}\dot{1}}$, but we have not yet considered
the sequences represented by 1. As these sequences include all combinations of 10 and 11, the contribution to the DOS can be summarized as

\[
\Omega_1 \equiv \sum_{k=0}^{\infty} (g_{\hat{I}0} + g_{\hat{I}1})^k = \frac{1}{1 - (g_{\hat{I}0} + g_{\hat{I}1})},
\]

where \(g_{\hat{I}0}\) and \(g_{\hat{I}1}\) can be calculated in a similar manner to \(g_{\hat{0}1}\) and \(g_{\hat{0}0}\), respectively, by exchanging \(\omega_I\) and \(\omega_{II}\). We then find that

\[
\begin{align*}
g_{0010} &= g_{0010} \Omega_1, \quad g_{0011} = g_{0011} \Omega_1, \\
g_{0110} &= g_{0110} \Omega_1, \quad g_{0111} = g_{0111} \Omega_1.
\end{align*}
\]

We can now perform an analytical calculation of the DOS, Eq. (10), and the geometrical quantization condition, Eq. (11), for the set \(\mathcal{S}_I\).

To calculate the total DOS, Eq. (9), a set \(\mathcal{S}_{II}\) and the corresponding geometrical quantities for each element are also required. All the PHPOs in \(\mathcal{S}_{II}\) start from “r”, and using the same arguments, this set is given by

\[
\mathcal{S}_{II} = \{\hat{1}\hat{1}, \hat{1}\hat{0}, \hat{1}\hat{0}\hat{1}, \hat{1}\hat{0}\hat{0}, \hat{1}\hat{0}\hat{1}, \hat{1}\hat{0}\hat{0}\},
\]

where \(0\) represents bit sequences in which all odd-numbered bits are 0. The geometrical quantities for \(\mathcal{S}_{II}\) can then calculated in the same way as those for \(\mathcal{S}_I\). These two sets and the corresponding geometrical quantities thus enable an analytical calculation of the total DOS in Eq. (9).

Figure 3 compares three DOSs in the case of \(\phi = \pi/3\). The first DOS (solid blue line) is calculated using the present geometrical quantization for nonadiabatic systems, Eq. (27), and second (dashed red line) with the numerically exact method for nonadiabatic systems, while the third (dotted black line) is an adiabatic DOS calculated analytically on each adiabatic harmonic surface (and therefore does not contain any nonadiabatic effects). Because the energy levels of the quantum steady states are indicated by the divergence of the DOS, we see that the energy levels determined by the present geometrical quantization agree with the numerically exact nonadiabatic energy levels rather than the adiabatic energy levels. We also note that in the nondegenerate case at the origin, the first integral in Eq. (3) should be used to calculate the classical action integrals because the energies of the PHPOs are not conserved quantities.
FIG. 3. (color online). Absolute value of DOSs. Blue solid, red broken, and black dot lines represent DOSs calculated by Geometrical nonadiabatic, numerically exact nonadiabatic, and numerically exact adiabatic quantizations, respectively.

In summary, we have presented the trace formula and geometrical quantization condition for one-dimensional nonadiabatic systems. The present approach shows that the quantization mechanism is based on a set of PHPOs $\mathcal{S}$. Namely, $\mathcal{S}$, which is invariant under time evolution in phase space, corresponds to quantum eigenstates in the classical limit. Further investigations of remaining problems, e.g. multidimensional problems such as conical intersections\textsuperscript{40}, quantitative analyses of violation of the quantum adiabatic theorem\textsuperscript{41–44}, and relation to the Riemann Hypothesis through zeta-functions should be addressed in future work to gain further insight into nonadiabatic transitions.

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