RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 49, NUMBER 4 APRIL 1994

Nonadiabatic transitions and gauge structure

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(Received 18 January 1994)

We examine the role of fictitious gauge structure in nonadiabatic transitions for transport in open paths. Local features of the gauge potential modify the nature of the intersection of the adiabatic energy surfaces and thereby affect crucially the Landau-Zener formula for a single-passage transition rate.

PACS number(s): 03.65.Bz, 32.80.Bx

The discovery of quantum adiabatic phase accompanying transport along closed paths has already had a great impact on various fields of physics and chemistry. This global phase, originally discussed in connection with the intersection of molecular energy surfaces, is attributed to connections in the Hilbert bundle, i.e., to a fictitious gauge potential [1].

A generalization of the influence of the quantum adiabatic phase to the nonadiabatic transitions is nontrivial, because we capture the local (rather than global) structure of the novel gauge potential via the transition rate. While several studies are concerned with this theme, most of the efforts have concerned finding corrections to the global geometric phase factor for closed or near-closed paths [2].

Nonadiabatic transitions, however, occur widely for both open and closed paths and they provide a key to understanding a variety of state-changing phenomena; e.g., two-level dynamics in the presence of magnetic and/or electric fields, atomic and molecular collisions, Zener tunneling, etc. [3,4]. This kind of transition is induced at the avoided crossings of the potential surfaces.

In this Rapid Communication, we consider nonadiabatic transitions between a pair of states as a mechanism for nonadiabatic transport along open paths. In particular, we consider the influence of the fictitious gauge potential on the transition rate. Although we use, as a prototype, the dynamics of a single spin in the presence of a time-dependent magnetic field, the analysis presented is applicable to other systems; e.g., two-level systems subjected to time-dependent laser fields.

In the magnetic field $\mathbf{B}(t) = (B_x(t), B_y(t), B_\parallel(t))$, the spin dynamics is described by the Schrödinger equation, $i\hbar d\Psi/dt = H(\mathbf{B}(t))\Psi$, with

$$H(\mathbf{B}(t)) = \tfrac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{B}(t) = \frac{1}{2}\begin{pmatrix} B_\parallel(t) & B_x(t) - iB_y(t) \\ B_x(t) + iB_y(t) & -B_\parallel(t) \end{pmatrix}, \quad (1)$$

where the negative of the Bohr magneton μ_B has been suppressed for simplicity. With the choice $B_\parallel = vt$, $B_x = \Gamma$, and $B_y = 0$, we obtain the Landau-Zemer (or curve-crossing) model. In our study, both B_x and B_y are assumed nonvanishing and time dependent: $\mathbf{B}(t)$ executes a winding (besides a translational) motion. We shall evaluate the transition amplitude from one adiabatic state at $t = -\infty$ to another at $t = +\infty$.

First we briefly summarize the existing formulas [5,6] for the transition rate in the presence of winding motion. Choosing the adiabatic basis $\alpha(t)$ and $\beta(t)$, $\Psi(t)$ is written as $\Psi(t) = C_1(t)\alpha(t) + C_2(t)\beta(t)$ and the Schrödinger equation reduces to

$$\begin{aligned} i\hbar\dot{C}_1 &= [E_1(t) - A_1(t)]C_1 - i\hbar\langle\Psi_1|\dot{\Psi}_2\rangle C_2, \\ i\hbar\dot{C}_2 &= [E_2(t) - A_2(t)]C_2 - i\hbar\langle\Psi_2|\dot{\Psi}_1\rangle C_1, \end{aligned} \quad (2)$$

with

$$A_i = i\hbar\langle\Psi_i|\dot{\Psi}_i\rangle \quad (i = 1, 2), \quad (3)$$

where overdots denote time derivative, the $\{E_i\}$ are the eigenvalues of H in (1) at particular times (adiabatic energies), and the $\{A_i\}$ are (mutually different) fictitious gauge potentials [1]. In our notation $i = 1$ and 2 are associated with the lower- and higher-energy states, respectively. This gauge structure leads to a novel geometric phase for adiabatic transport along closed paths. As for nonadiabatic transport, use of the path-integral method and the stationary phase approximation leads to the following for the transition rate for a single passage of the avoided crossing: $p = \exp(-2\delta)$ with [5,6]

$$\delta = \frac{1}{\hbar}\mathrm{Im}\int_0^{t_c} dt[\Delta E(t) - \Delta A(t)], \quad (4)$$

where $\Delta E = E_2 - E_1$, $\Delta A = A_2 - A_1$, and t_c is the complex crossing point at which ΔE vanishes. According to the rigorous treatment given below, however, the gauge potentials enter into the phase integral in a much more intricate way and (4) is valid only in a very special limit.

We now examine the quantum dynamics for the Hamiltonian (1) using a diabatic (time-independent) basis. Transforming to polar coordinates defined by $B_x(t) - iB_y(t) = B_\perp(t)\exp[-i\Phi(t)]$ and introducing the unitary transformation

$$U(t) = \begin{pmatrix} e^{-i\Phi/2} & 0 \\ 0 & e^{i\Phi/2} \end{pmatrix},$$

we introduce a new wave function $\tilde{\Psi}$ defined by $\Psi = U\tilde{\Psi}$. Then $\tilde{\Psi}$ satisfies

$$i\hbar d\tilde{\Psi}/dt = \tilde{H}(t)\tilde{\Psi} = \frac{1}{2}\begin{pmatrix} B_{\parallel} - \hbar\dot{\Phi} & B_{\perp} \\ B_{\perp} & -(B_{\parallel} - \hbar\dot{\Phi}) \end{pmatrix}\tilde{\Psi}. \tag{5}$$

The transformed Hamiltonian $\tilde{H}$ given by (5) is now analytic throughout some strip of the complex-time plane centered on the real axis, and it satisfies $|\tilde{H}_{12}|/|\tilde{H}_{22} - \tilde{H}_{11}| \to 0$ for $|t| \to \infty$ (i.e., absence of mixing between diabatic states). In this situation we can apply the phase-integral method by Stückelberg [7], then obtaining for the full transition rate

$$P = 4p(1-p)\sin^2(\cdots)$$

with the single-passage rate $p = \exp(-2\delta)$. [In this Rapid Communication we are not interested in the phase-interference factor, $\sin^2(\cdots)$, proper to the passage of successive avoided crossings.] δ is now given by

$$\delta = \frac{1}{\hbar}\mathrm{Im}\int_0^{\hat{t}_c} dt[\Delta\hat{E}(t)] \tag{6}$$

with

$$\Delta\hat{E} = \sqrt{\{(B_{\parallel} - \hbar\dot{\Phi})^2 + B_{\perp}^2\}} = \sqrt{(B_{\parallel}^2 + B_{\perp}^2 - 2\hbar\dot{\Phi}B_{\parallel} + \hbar^2\dot{\Phi}^2)} \tag{7}$$

the difference between adiabatic energies of $\tilde{H}$ in (5). Note that $\hat{t}_c$ is the complex crossing point $[\Delta\hat{E}(\hat{t}_c) = 0]$ nearest the real axis. Equations (6) and (7) are exact. In the near-adiabatic region of the winding Landau-Zener model, $B_{\perp}(=\Gamma)$ is constant and predominant, whereas $\dot{\Phi}$ and $B_{\parallel}$ are slow and small variables in the transition region near the avoided crossing. In this extreme case, (7) is expanded in one of the slowest variables as

$$\Delta\hat{E} \sim \begin{cases} \sqrt{B_{\perp}^2 + B_{\parallel}^2} - \hbar\dot{\Phi}B_{\parallel}/\sqrt{B_{\parallel}^2 + B_{\perp}^2} + O(\hbar^2\dot{\Phi}^2) & \text{for } \hbar\dot{\Phi} \ll B_{\parallel}, \quad (8a) \\ \sqrt{B_{\perp}^2 + \hbar^2\dot{\Phi}^2} + O(B_{\parallel}) & \text{for } \hbar\dot{\Phi} \gg B_{\parallel}, \quad (8b) \end{cases}$$

followed by the corresponding expansion of $\hat{t}_c$ in (6).

While the results in (6)–(8) are derived using the diabatic basis, we now rewrite them in terms of the adiabatic basis: Definition (3) yields $\Delta A = A_2 - A_1 = \hbar\dot{\Phi}B_{\parallel}/\Delta E$ and $\sum A = A_2 + A_1 = \hbar\dot{\Phi}$ with $\Delta E = (B_{\perp}^2 + B_{\parallel}^2)^{1/2}$. Using these expressions in (7), we have

$$\Delta\hat{E} = \left\{\left[\Delta E^2 - 2\Delta A\Delta E + \left(\sum A\right)^2\right]\right\}^{1/2}. \tag{9}$$

With the same replacement in (8), the asymptotic behavior is given by

$$\Delta\hat{E} \approx \begin{cases} \Delta E - \Delta A & \text{for } \hbar\dot{\Phi} \ll B_{\parallel}, \quad (10a) \\ \left[B_{\perp}^2 + (\sum A)^2\right]^{1/2} & \text{for } \hbar\dot{\Phi} \gg B_{\parallel}, \quad (10b) \end{cases}$$

with $\hat{t}_c$ approximated by the values at which ΔE and $[B_{\perp}^2 + (\sum A)^2]^{1/2}$ vanish in (10a) and (10b), respectively. Therefore (4) is justified in the special limit when the winding motion is much slower than the translational motion. In the opposite limit the sum of gauge potentials is needed and, in the general case, we should use (9).

We shall now apply the results in (6), (9), and (10) to a winding Landau-Zener (curve crossing) model where $B_{\parallel} = vt$, $B_x = \Gamma\cos\Phi$, and $B_y = \Gamma\sin\Phi$ with $\Phi = wt^n/n$ $(n = 1, 2, \ldots)$. For simplicity, v, Γ, and w are assumed to be positive.

Below we shall use $\Delta E = [\Gamma^2 + (vt)^2]^{1/2}$, irrespective of the value of n.

Case of n=1. In this case, the Galilean transformation $(t \to t' = t - \hbar w/v)$ smears out the phase factor, so that there is no gauge structure and the ordinary Landau-Zener transition rate $p_{LZ} = \exp[-\pi\Gamma^2/(2\hbar v)]$ is applicable.

Case of n=2. Using in (10) $\Delta A = \hbar v w t^2/\Delta E$ and $\sum A = \hbar w t$, we have from (6)

$$\delta = \begin{cases} [\pi\Gamma^2/(4\hbar v)](1 + \hbar w/v) & \text{for } \hbar w \ll v, \quad (11a) \\ \pi\Gamma^2/(4\hbar^2 w) & \text{for } \hbar w \gg v. \quad (11b) \end{cases}$$

With the same expression for gauge potentials in (9), (6) with $\hat{t}_c = i\Gamma/|v - \hbar w|$ yields $\delta = \pi\Gamma^2/(4\hbar|v - \hbar w|)$, which recovers the two limits in (11). While Berry carefully analyzed the $n = 2$ case [6], he was mainly concerned

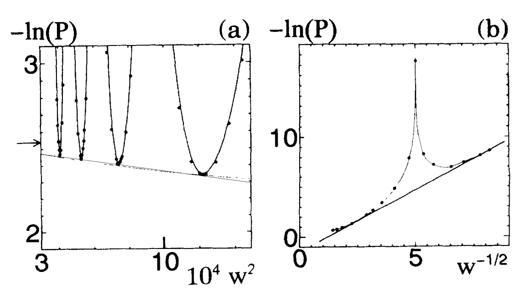

FIG. 1. Full transition rate P for the winding Landau-Zener model with $\hbar = 1$ and $\Gamma = 1$. Filled circles denote values obtained by numerical iteration of (1): (a) $4\hbar w\Gamma \ll v^2$ with $v = 0.4$; (b) $4\hbar w\Gamma \gg v^2$ with $v = 0$. Envelope lines in (a) and (b) represent $-\ln P = -2\ln 2 - \ln p$ with p in (12a) and (12b), respectively. Arrow in (a) corresponds to the limit $p = p_{LZ}$.

with (10a) and (11a), showing neither (9) nor (10b).

Case of n=3. In this case, $\Delta A = \hbar w v t^3/\Delta E$ and $\sum A = \hbar w t^2$. The formula in (4) or (10a) here yields no correction to the Landau-Zener result, since the integration of ΔA does not have any imaginary component. On the other hand, from (10b) we have $\delta = 0.61[\Gamma^3/(\hbar^3 w)]^{1/2}$. In terms of a scaled time τ, the most general result available from (9) is

$$\delta(\varepsilon) = [\Gamma^3/(\hbar^3 w)]^{1/2}\mathrm{Im}\int_0^{\tau_c}[(\tau^2-\varepsilon)^2+1]^{1/2}d\tau,$$

with $\varepsilon = v^2/(4\Gamma\hbar w)$ and $\tau_c = (\varepsilon + i)^{1/2}$. Noting the asymptotic expansions $\delta(\varepsilon)/[\Gamma^3/(\hbar^3 w)]^{1/2} \sim (\pi/8\varepsilon^{1/2})[1 - 3/(32\varepsilon^2) + 565/(2^{14}\varepsilon^4) + \cdots]$ for $\varepsilon \gg 1$ and $\sim 0.61 - 0.42\varepsilon$ for $\varepsilon \ll 1$, we have

$$p = \begin{cases} p_{\mathrm{LZ}}\exp\left([3\pi\hbar w^2\Gamma^4/(4v^5)]\{1-(565/1536)(4\hbar w\Gamma/v^2)^2+\cdots\}\right) & \text{for } 4\hbar w\Gamma \ll v^2, \quad (12a)\\ \exp\left(-2[\Gamma^3/(\hbar^3 w)]^{1/2}\{0.61-0.42v^2/(4\hbar w\Gamma)+\cdots\}\right) & \text{for } 4\hbar w\Gamma \gg v^2. \quad (12b)\end{cases}$$

The asymptotic behaviors in (12) are in excellent agreement with an envelope of the full transition rate $P(\cong 4p)$ in Fig. 1 obtained by our numerical iteration of the time-dependent Schrödinger equation (1) for $n = 3$. [Spiking oscillations in P are attributed to the multiplicative phase-interference factor in the equation above Eq. (6).] We here assert that (i) even when the winding motion is slower than the translational motion, the existing formula (4) fails in providing a leading-order correction to p_{LZ}; (ii) in the opposite case, the formula in (10b), consisting only of a sum of gauge potentials, can give accurate leading-order values for the transition rate; and (iii) in general, (9) indicates that the transition rate depends on the difference and sum of a pair of gauge potentials in intricate ways, according to the adiabaticity ratio of the winding and translational motions.

The present formula in (9) and (10), with a slight modification, can also be used in other winding models in the near-adiabatic region. Consider, for instance, a winding Demkov (exponential) model [8] with $B_{\parallel} = \Gamma$, $B_{\perp} = \gamma\cos\kappa\exp(-vt)$, and $\Phi(t) = [\gamma/(\hbar v)]\sin\kappa\exp(-vt)$ in the case $\hbar v \ll \Gamma$. Interchanging $B_{\parallel}$ and $B_{\perp}$, the formulas from (8) through (10) still hold; this interchange comes from the predominance of $B_{\parallel}$ in this model. Noting the gauge potentials $\Delta A = -\Gamma\gamma\sin\kappa\exp(-vt)/\Delta E$ and $\sum A = -\gamma\sin\kappa\exp(-vt)$ with $\Delta E = [\Gamma^2 + \gamma^2\cos^2\kappa\exp(-2vt)]^{1/2}$, we have from (10) and (9)

$$p/p_{\mathrm{Demk}} = \begin{cases}\exp[-\pi\Gamma\kappa/(\hbar v)] & \text{for } \kappa \ll \pi/2, \quad (13a)\\ \exp[-\pi\Gamma/(\hbar v)] & \text{for } \kappa \approx \pi/2 \quad (13b)\end{cases}$$

and

$$p/p_{\mathrm{Demk}} = \exp[-\pi\Gamma\sin\kappa/(\hbar v)], \quad (14)$$

respectively [9], where $p_{\mathrm{Demk}} = \exp[-\pi\Gamma/(\hbar v)]$. The winding Demkov model, after a unitary transformation (5), turns out the exactly solvable Nikitin model, whose known solution [8] justifies (13) and (14) in the near-adiabatic region.

In conclusion, when the applied magnetic and/or electric fields show time dependence in both the amplitude and the polarization vector, the local aspect of the gauge potentials greatly affects the intersection of adiabatic energy surfaces. The formula for the nonadiabatic transition rate includes a pair of gauge potentials in intricate ways, depending on the ratio of the adiabaticities of the winding and translational motions of applied fields.

We are grateful to M. V. Berry, P. Gaspard, and H. Nakamura for valuable discussions in the early stages of the present work.

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