Control of Time-Dependent Nonadiabatic Processes by an External Field

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(Received 4 May 1998)

A new idea of controlling nonadiabatic transitions by an external field is proposed. The basic principle is to periodically sweep an external field at each level crossing to make the overall transition probability from an initial state to any desirable final state equal to unity. The recently completed semiclassical theory of nonadiabatic transition enables us to analytically deal with this problem. The present idea may be applicable to various physical and chemical problems, whenever level crossings are created by an external field. [S0031-9007(98)07054-9]

PACS numbers: 32.80.Bx, 33.80.Be, 34.50.Rk, 75.40.Gb

Recently, there has been a growing interest, both experimentally and theoretically, in controlling atomic and molecular processes by external fields. Control of reactions by using either laser coherence (coherence control) or laser pulse (pulse shape driven control) is one typical example [1–4]. Control of dynamic processes can also be realized to some extent by creating so-called dressed states in a laser field [2,5,6]. Time-dependent electric and/or magnetic fields are also used to control various transitions; examples are the current driven tunnel junction and field driven Zener tunneling [7–11]. In many of the processes mentioned above, nonadiabatic transitions at level or potential curve crossings play crucial roles, since they are effective to enhance transitions. Recently, a complete set of practically useful analytical solutions have been derived for the Landau-Zener-Stueckelberg–type curve crossing problems in both time-independent [12–16] and time-dependent [16] cases.

In this Letter, based on this achievement, we propose a new idea to control nonadiabatic processes so that an overall transition probability to any specified state in a multichannel curve crossing system becomes unity. This can be realized by periodically sweeping the external field in time at the crossing point. By periodically changing the field, we can use not only the nonadiabatic transition probability for one passage of crossing point but also the phases and the number of periods as control parameters. Taking a simple two-state curve crossing as a function of time (see Fig. 1), we explain and formulate our basic idea. It should be emphasized that the theory proposed here can be applied to general multichannel problems, since the basic theory of Zhu and Nakamura works nicely for them [17].

The transition matrix I which describes the transition from F_a to F_b (see Fig. 1) is given by

$$I = \begin{bmatrix} \sqrt{1-p}\, e^{i(\phi+\sigma_1+\sigma_2)} & -\sqrt{p}\, e^{i(\sigma_0-\sigma_2+\sigma_1)} \\ \sqrt{p}\, e^{-i(\sigma_0-\sigma_2+\sigma_1)} & \sqrt{1-p}\, e^{-i(\phi+\sigma_1+\sigma_2)} \end{bmatrix}, \quad (1)$$

while the transpose of this matrix, I^t, describes the backward transition from F_b to F_a. Here p represents the nonadiabatic transition probability by one passage of the crossing point F_x, ϕ is the Stokes phase, and σ_0, σ_1, and σ_2 are the phase factors which are defined, respectively, by

$$\sigma_0 = \mathrm{Re}\left(\int_{F_x}^{F_*} \Delta E(F)\,\frac{dt}{dF}\,dF\right) = \mathrm{Re}\left(\int_{t_x}^{t_*} \Delta E(t)dt\right), \quad (2)$$

$$\sigma_1 = \frac{1}{2}\int_{F_a}^{F_x} \Delta E(F)\,\frac{dt}{dF}\,dF = \frac{1}{2}\int_{t_a}^{t_x} \Delta E(t)dt\,, \quad (3)$$

and

$$\sigma_2 = \frac{1}{2}\int_{F_x}^{F_b} \Delta E(F)\,\frac{dt}{dF}\,dF = \frac{1}{2}\int_{t_x}^{t_b} \Delta E(t)dt\,, \quad (4)$$

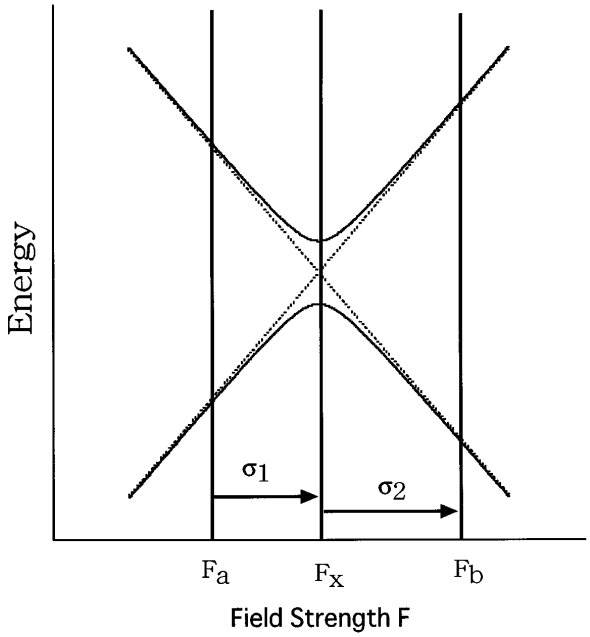

FIG. 1. Schematic two diabatic (dotted lines) and two adiabatic (solid lines) potentials. External field oscillates between F_a and F_b, striding the avoided crossing point F_x. The phase σ_1 (σ_2) can be controlled by changing F_a (F_b).

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where $\Delta E(F)$ is the adiabatic energy difference at the field strength F, F_* is the solution of $\Delta E(F_*) = 0$, and F_x is the field strength corresponding to the crossing point. The time t_α for $\alpha = a, b, x$, and $*$ is the time at which $F(t_\alpha) = F_\alpha$ is satisfied. Since $\Delta E \neq 0$ on the real axis, F_* and t_* are complex numbers. Explicit compact expressions of p and ϕ can be found in Refs. [12–16]. It should be noted that compact analytical expressions of these quantities are available even for the cases that the two diabatic potentials tangentially touch each other ($F_b = F_x$) or avoid crossing ($F_b < F_x$).

The final overall transition matrix T_n after n periods of oscillation between F_a and F_b is expressed as

$$T_n = T^n, \tag{5}$$

where T is the transition matrix for one period which is given by

$$T \equiv I^t I = \begin{bmatrix} \{p + (1-p)e^{2i\psi}\}e^{-i\sigma} & -2i\sqrt{p(1-p)}\sin\psi \\ -2i\sqrt{p(1-p)}\sin\psi & \{p + (1-p)e^{-2i\psi}\}e^{i\sigma} \end{bmatrix} \tag{6}$$

with $\psi \equiv \phi + \sigma_0 + \sigma_1$ and $\sigma \equiv 2\sigma_0 + \sigma_1 - \sigma_2$.

In the case of n and half periods of traversing the crossing point, the overall transition matrix is given by

$$T_{n+1/2} = I(I^t I)^n = IT^n. \tag{7}$$

It should be noted that the adiabatic potentials and thus the parameters p, ψ, and σ_i ($i = 0$–2) are dependent on the external field. Roughly speaking, the nonadiabatic transition probability p, the Stokes phase ϕ, and the phase σ_0 are dependent on the local functionality of the adiabatic potentials around the crossing point, namely, the sweep velocity (dF/dt) of the external field at the crossing point, while the phase factors σ_1 and σ_2 are dependent on the global functionality of the adiabatic potentials in the range (F_a, F_b) of the field. We try to find conditions for the parameters $[n, p, \psi, \sigma_i\ (i = \sim 1$–$2)]$ to satisfy

$$P_{12}^{(n)} \equiv |(T_n)_{12}|^2 = 0 \quad \text{or} \quad 1 \tag{8}$$

or

$$P_{12}^{(n+1/2)} \equiv |(T_{n+1/2})_{12}|^2 = 0 \quad \text{or} \quad 1\,. \tag{9}$$

Using the Lagrange-Sylvester formula, we obtain

$$T_n = T^n = \frac{\lambda_+\lambda_-(\lambda_-^{n-1} - \lambda_+^{n-1})}{\lambda_+ - \lambda_-} E + \frac{\lambda_+^n - \lambda_-^n}{\lambda_+ - \lambda_-} T\,, \tag{10}$$

where E is the unit matrix and $\lambda_\pm$ are the eigenvalues of T, which are given by

$$\lambda_\pm = e^{\pm i\xi}, \tag{11}$$

where

$$\cos\xi = (1-p)\cos(2\psi - \sigma) + p\cos(\sigma)\,. \tag{12}$$

The unitarity of the matrix T requires ξ to be real. Equation (12) implies that the nonadiabatic transition probability p should satisfy

$$\frac{1 - |\cos\xi|}{2} \leq p \leq \frac{1 + |\cos\xi|}{2}\,. \tag{13}$$

Then the requirements of Eq. (8) lead, respectively, to

$$P_{12}^{(n)} = \left| \frac{\lambda_+^n - \lambda_-^n}{\lambda_+ - \lambda_-} T_{12} \right|^2 = 4\frac{\sin^2(n\xi)}{\sin^2\xi} p(1-p)\sin^2\psi = 0 \tag{14}$$

or

$$P_{12}^{(n)} = 4\frac{\sin^2(n\xi)}{\sin^2\xi} p(1-p)\sin^2\psi = 1\,. \tag{15}$$

In the case of Eq. (14) we simply have the condition $\sin(n\xi) = 0$ or $\sin\psi = 0$. It is more interesting and worthwhile to consider Eq. (15). If $P_{12}^{(n)} = 1$ holds for n periods, then $P_{12}^{(2n)} = 0$ must be satisfied for $2n$ periods; thus Eq. (15) for n may be divided into the following two conditions:

$$\sin(2n\xi) = 0 \tag{16}$$

and

$$4p(1-p)\sin^2\psi = \sin^2\xi\,. \tag{17}$$

Since $\sin(n\xi) \neq 0$ in general because of Eq. (15), Eq. (16) leads to

$$\sin^2(n\xi) = 1\,. \tag{18}$$

This equation determines ξ for a given n, and Eq. (17) gives a condition for p and ψ for a given ξ. The phase σ may be determined form Eq. (12). Equation (17) implies that p must satisfy the following condition:

$$p(1-p) \geq \tfrac{1}{4}\sin^2\xi\,, \tag{19}$$

which is the same as Eq. (13).

The above analysis can be summarized as follows: (i) For a given system, the nonadiabatic transition probability p is estimated as a function of the external field. (ii) From Eq. (18), ξ is determined for an appropriately specified n. If p is not in the range of Eq. (13), the external field (mainly the sweep velocity) and/or n should be modified so that this condition is satisfied. (ii) The phase ψ is controlled by changing σ_1 to satisfy Eq. (17), while σ is controlled by changing σ_2 to satisfy Eq. (12). These can be realized by adjusting the oscillation period n and the range (F_a, F_b) of the field. When the above procedure is completed, then we can achieve $P_{12}^{(n)} = 1$. The

required range of p as a function of ξ given by Eq. (13) can easily be drawn and be used to search for appropriate conditions for the parameters.

Let us next consider n and half periods of oscillation of the external field [see Eq. (9)]. This case together with the n-period case discussed above is useful to treat general multilevel problems, since this enables us to follow any specified path from any initial state to any desirable final state. If either one of the conditions of Eq. (9) is satisfied for n and half periods, then $P_{12}^{(2n+1)} = 0$ must be satisfied for $2n + 1$ periods. Then from Eq. (14) we have

$$\sin^2[(2n + 1)\xi] = 0 . \tag{20}$$

Now, the condition $P_{12}^{(n+1/2)} = 0$ can be explicitly expressed as

$$4(1 - p)\sin^2(\psi - \sigma) = \frac{\sin^2\xi}{\sin^2(n\xi)} , \tag{21}$$

which tells

$$(1 - p) \geq \frac{\sin^2\xi}{4\sin^2(n\xi)} . \tag{22}$$

On the other hand, the condition $P_{12}^{(n+1/2)} = 1$ can be reduced to the following equation:

$$4p\sin^2(\psi - \sigma) = \frac{\sin^2\xi}{\sin^2(n\xi)} , \tag{23}$$

which implies

$$p \geq \frac{\sin^2\xi}{4\sin^2(n\xi)} . \tag{24}$$

From Eqs. (20), (22), and (24), we end up with the same condition for the range of p as Eq. (13).

A search for the best condition of the parameters can be done in the same way as in the n-period case. In the case of the requirement $P_{12}^{(n+1/2)} = 0$, Eq. (18) in the above step (ii) should be replaced by Eq. (20), and Eq. (17) has to be replaced by Eq. (21). In the case of $P_{12}^{(n+1/2)} = 1$, on the other hand, Eqs. (20) and (23) take the place of Eqs. (18) and (17) in the procedure.

An example of multilevel crossing is shown in Fig. 2, which is taken from the quantum tunneling of the magnetization of $Mn_{12}Ac$ in a time-dependent magnetic field [18–20]. Here, we consider the lowest three adiabatic states 1–3, and demonstrate control of the nonadiabatic processes by our idea presented above. The Hamiltonian is taken from Eq. (1) of Ref. [20]. In Fig. 2, the energy is scaled by the anisotropy energy D. Figure 3 shows the time evolution of the state probability from the point "a"

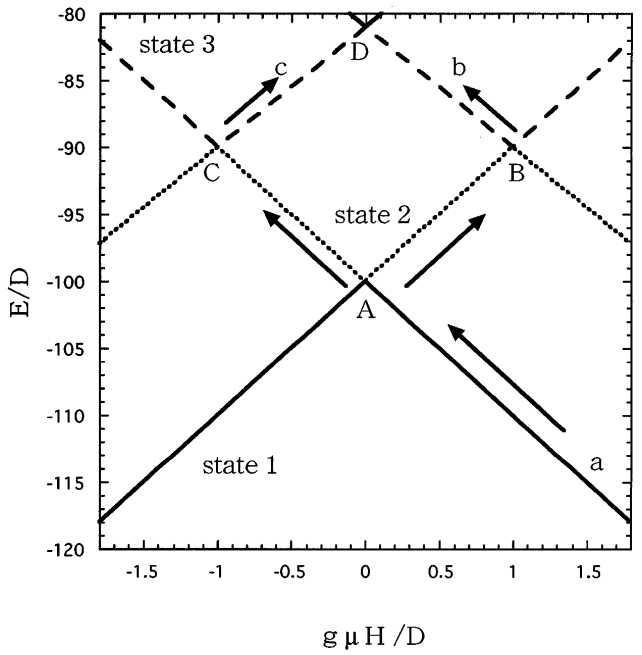

FIG. 2. Adiabatic spin states as a function of an external magnetic field, $g\mu_\beta H$: Three lowest levels (scaled by the anisotropy energy D) are shown, where g is the Landé g-factor, μ_B is the Bohr magneton, and H is the magnetic field. The nonadiabatic probabilities p at avoided crossings $A-C$ are 0.039, 0.977, and 0.977, respectively.

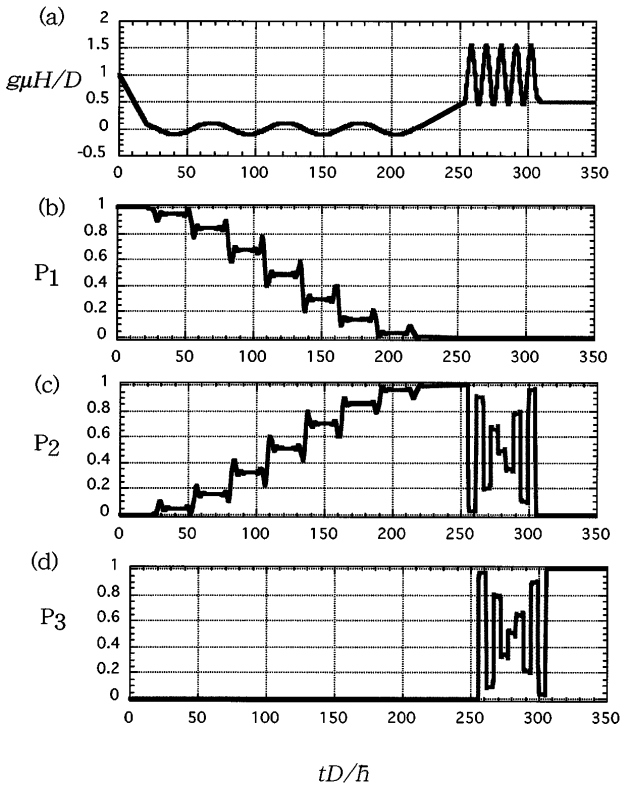

FIG. 3. Controlled nonadiabatic processes, starting from "a" on state 1 and ending at "b" on state 3 via avoided crossings A and B (see Fig. 2). (a) Variation of the external magnetic field as a function of time, $tD/\hbar$. The first four-period oscillation around $g\mu_\beta H/D = 0$ corresponds to the control at the avoided crossing A. The second five-period oscillation around $g\mu_\beta H/D = 1.0$ corresponds to the control at B. (b) Time evolution of the probability P_1 for the system to be staying on the state 1. (c) Time evolution of P_2. (d) Time evolution of P_3.

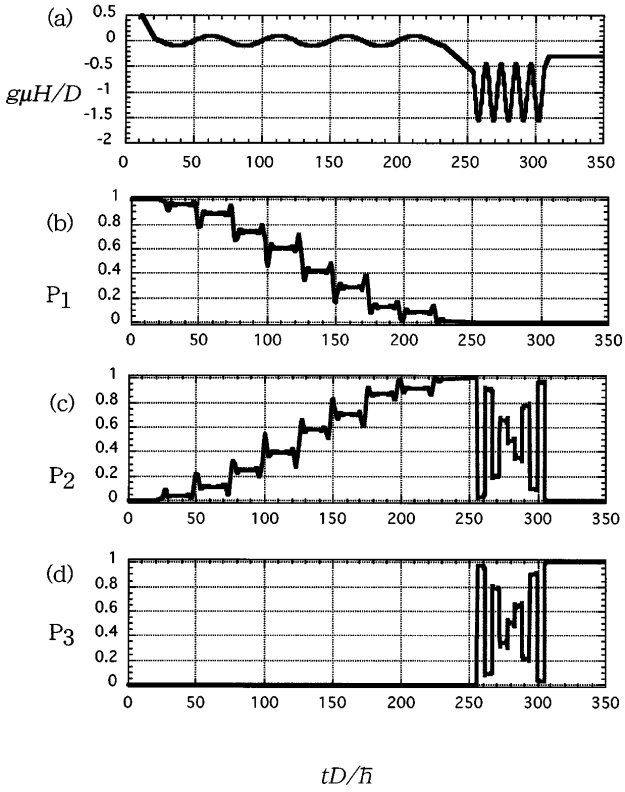

FIG. 4. The same as Fig. 3 but for a process from a to c.

on state 1 to "b" on state 3 via two avoided crossings A and B. At the avoided crossing $A(B)$ four-(five-) period oscillations of the field are applied. This is shown in Fig. 3a. The probability of the state $1(P_1)$ becomes zero after the four periods, as is seen in Fig. 3b. The probability P_2 reaches unity when P_1 becomes zero, and after five periods at B it becomes zero (Fig. 3c) at which time P_3 reaches unity (Fig. 3d). Figure 4 demonstrates another path from "a" on state 1 to "c" on state 3 via two avoided crossings A and C. In this case we have applied $4 + 1/2$ (five) periods of oscillation of the field at the avoided crossing $A(C)$. This example clearly demonstrates that we can choose any path to reach any specified final state with unity probability.

Figures 3 and 4 are the results of the numerical solution of the coupled Schrödinger equation, but we have confirmed that the semiclassical theory developed by the present authors [16] based on the Zhu-Nakamura theory for time-independent Landau-Zener–type nonadiabatic transition gives results almost indistinguishable from Figs. 3b–3d and 4b–4d except for the humps and dips which appear when the probability jumps abruptly. This guarantees that we do not have to solve multichannel coupled equations numerically, and that we can formulate all necessary conditions of control analytically.

The present idea of controlling nonadiabatic processes may be widely applied to various physical and chemical problems, whenever level crossings are induced by an external field. Examples are Rydberg atoms in an electric/magnetic field [21], current driven tunnel junction, field driven Zener tunneling [7–11], and isomerization of a molecule [22]. Collision as well as reaction processes which contain potential curve crossing may be controlled by the same idea. Even when the system does not contain any curve crossing, we can apply a static field to create crossing dressed states and control transition there by applying an oscillatory field.

This work was supported partially by the Grand-in-Aid for Scientific Research on Priority Area "Quantum Tunneling of Group of Atoms as Systems with Many Degrees of Freedom" from the Ministry of Education, Science, Sports, and Culture of Japan.

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