Quantum Dynamical Tunneling Suppression by a Laser Field

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Suppression of quantum dynamical tunneling is predicted to occur when a laser field drives a transition in an isolated, single molecule embedded in a host medium. [S0031-9007(96)00075-0]

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Quantum dynamical tunneling is one of the important processes occurring in different physical, chemical, and biological systems. It can be observed in systems whose potential energy V has at least two minima, with the form of the potential being locally symmetric. For the one-dimensional case, such a potential is a symmetric double well $V(x) = V(-x)$. At zero temperature, if the system is initially located in one of the wells of the potential, it will undergo quantum dynamical tunneling having period $T = 2\pi/\delta$, where $\hbar\delta$ is the small energy difference between the antisymmetric and symmetric states [1]. The dynamical tunneling occurs owing to the fact that initial localization in one of the wells implies a superposition of eigenstates having different energies. Physically, quantum dynamical tunneling describes the internal rotation in molecules [2], or the rotation of a single molecule in a crystalline or amorphous environment [3]. It also describes the more complex conformational changes in glasses [4], biological systems [5], etc. In this Letter we show how this quantum evolution, at first sight uncontrolled, can be suppressed dynamically by applying a coherent electromagnetic field.

To demonstrate this effect we assume that the symmetric double-well potential $V_g(x)$ (Fig. 1) corresponds to the electronically unexcited ground state. In addition, there is an electronically excited state. In the adiabatic approximation, the slow movement along the generalized coordinate x [6] in the excited state is defined by the excited-state potential $V_e(x)$, which we also take to be a double-well potential, but without symmetry about the point $x = 0$ (Fig. 1). The ground and excited states can interact through a coherent electromagnetic field having frequency ω_0. In the absence of the external radiation field, the lowest energy eigenstates of the ground electronic state are symmetric and antisymmetric states, denoted by $|1\rangle$ and $|2\rangle$, respectively. The corresponding normalized, approximate wave functions $\phi_{1,2}$ may be written in the form [1]

$$\phi_1(x) = [\phi(-x) + \phi(x)]/\sqrt{2}, \tag{1a}$$

$$\phi_2(x) = [\phi(-x) - \phi(x)]/\sqrt{2}, \tag{1b}$$

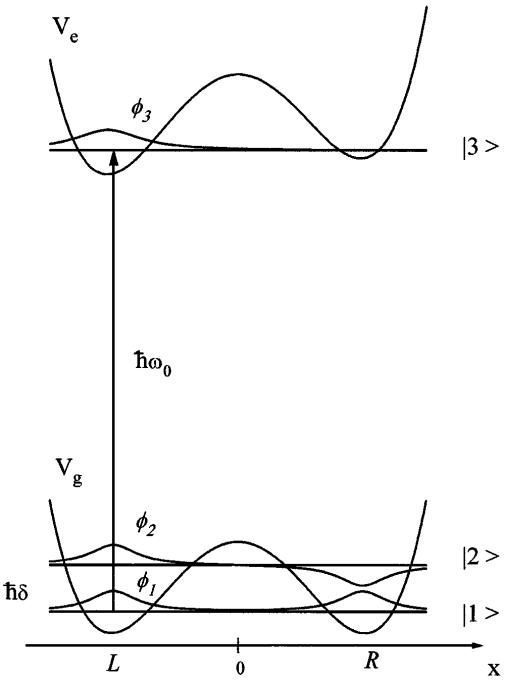

FIG. 1. Schematic representation of the quantum system under consideration. The system is characterized by two electronic states with double-well potentials for the ground $[V_g(x)]$ and excited $[V_e(x)]$ states. The ground state potential $V_g(x)$ is symmetric about the point $x = 0$, but the excited-state potential $V_e(x)$ does not possess this symmetry. The two lowest eigenstates $|1\rangle$ and $|2\rangle$ of the ground state potential have symmetric $[\phi_1(x)]$ and antisymmetric $[\phi_2(x)]$ wave functions, while the excited-state wave function $\phi_3(x)$ is localized in the left well of the excited-state potential. A coherent field having frequency ω_0 drives transitions between the ground and excited states.

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where $\phi(x)$ is a wave function localized in the right well. The energy of the antisymmetric state $|2\rangle$ is larger than that of the symmetric state $|1\rangle$ by the small difference [4]

$$\hbar\delta = E_2 - E_1 = \hbar\omega e^{-\lambda}, \tag{2}$$

where $\hbar\omega$ is an energy of order of the zero-point energy, and the factor $e^{-\lambda}$ represents the overlap between the wave functions for the two potential wells, $\lambda \simeq \Delta x(2mV)^{1/2}/\hbar$, with Δx being the distance between potential well minima, m the appropriate tunneling mass, and V the height of the barrier between the wells.

We suppose that initially (at $t = 0$) the system is localized in the left well,

$$|\psi(t = 0)\rangle = (|1\rangle + |2\rangle)/\sqrt{2}. \tag{3}$$

The spatial wave function for this state is $\phi(-x)$. For $t > 0$, this state evolves as

$$|\psi(t)\rangle = \left[\exp\left(-i\,\frac{E_1}{\hbar}\,t\right)|1\rangle + \exp\left(-i\,\frac{E_2}{\hbar}\,t\right)|2\rangle\right]\Big/\sqrt{2}, \tag{4}$$

which oscillates between states $|1\rangle$ and $|2\rangle$. The spatial wave function

$$\langle x\,|\,\psi(t)\rangle = \exp\left(-i\,\frac{E_2 + E_1}{2\hbar}\,t\right) \times \left[\phi(-x)\cos\frac{\delta t}{2} + i\phi(x)\,sin\,\frac{\delta t}{2}\right] \tag{5}$$

oscillates between the two wells, a process corresponding to dynamical quantum tunneling.

Now suppose that at time $t = 0$ a coherent electromagnetic field

$$E(t) = E\exp(-i\omega_0 t) + \text{c.c.}, \tag{6}$$

having frequency ω_0 quasiresonant with the transitions $|1\rangle \rightarrow |3\rangle$ and $|2\rangle \rightarrow |3\rangle$ (Fig. 1), is applied. State $|3\rangle$ is the lowest energy state for the electronically excited state described by the potential $V_e(x)$. As we have supposed that this potential is not symmetric about the point $x = 0$, its spatial wave function $\phi_3(x)$ is localized primarily in one of the wells (to be specific, it will be the left well). The interaction in this three-level Λ system can be described, in the rotating-wave approximation, by the semiclassical, interaction-picutre Hamiltonian:

$$\hat{H} = \hbar(\upsilon_{13}e^{i\delta_1 t}\hat{b}_{13} + \upsilon_{31}e^{-i\delta_1 t}\hat{b}_{31}) + \hbar(\upsilon_{23}e^{i(\delta_1+\delta)t}\hat{b}_{23} + \upsilon_{32}e^{-i(\delta_1+\delta)t}\hat{b}_{32}), \tag{7}$$

where $\delta_1 = \omega_0 - \omega_{31}$ and $\delta_1 + \delta = \omega_0 - \omega_{32}$ are the field-molecule detunings, ω_{31} and ω_{32} are the molecular transitions frequencies, $b_{ij} = |i\rangle\langle j|$ are the molecular raising and lowering operators, and

$$\upsilon_{ij} = -\frac{pE}{\hbar}\int dx\,\phi_i^*(x)\phi_j(x) \tag{8}$$

are the Rabi frequencies for the allowed transitions calculated in the adiabatic approximation. The solution of the Schrödinger equation with the interaction Hamiltonian (7) can be written as

$$|\psi(t)\rangle = \begin{pmatrix} e^{-i(\frac{E_1}{\hbar}-\delta_1)t} & 0 & 0 \\ 0 & e^{-i(\frac{E_1}{\hbar}-\delta_1)t} & 0 \\ 0 & 0 & e^{-iE_3 t} \end{pmatrix} \times e^{-i\hat{V}t}|\psi(t = 0)\rangle, \tag{9}$$

where the matrix $\hat{V}$ is given by

$$\hat{V} = \begin{pmatrix} \delta_1 & 0 & \upsilon_{13} \\ 0 & \delta_1 + \delta & \upsilon_{23} \\ \upsilon_{31} & \upsilon_{32} & 0 \end{pmatrix}. \tag{10}$$

The eigenvalues and eigenstates of the matrix V give the quasienergies and dressed states in the dressed picture representation [7]. In the case considered with the assumption that $|\delta| \ll |\upsilon_{31}|, |\upsilon_{32}|$ the dressed states are

$$|\psi_{+L}\rangle = \sin\theta(e^{i\varphi_1}\sin\eta|1\rangle + e^{i\varphi_2}\cos\eta|2\rangle) + \cos\theta|3\rangle, \tag{11a}$$

$$|\psi_{-L}\rangle = \cos\theta(e^{i\varphi_1}\sin\eta|1\rangle + e^{i\varphi_2}\cos\eta|2\rangle) - \sin\theta|3\rangle, \tag{11b}$$

$$|\psi_R\rangle = e^{i\varphi_1}\cos\theta|1\rangle - e^{i\varphi_2}\sin\theta|2\rangle, \tag{11c}$$

where $\sin\theta = \Omega/\sqrt{\Omega^2 + \mu^2}$, $\Omega = \sqrt{|\upsilon_{31}|^2 + |\upsilon_{32}|^2}$, $e^{i\varphi_1}\sin\eta = \upsilon_{13}/\Omega$, $e^{i\varphi_2}\cos\eta = \upsilon_{23}/\Omega$, $\mu = -\delta_1/2 + \Omega_1$, $\Omega_1 = \sqrt{\Omega^2 + \delta_1^2/4}$. The eigenvalues corresponding to the dressed states (11) are equal to

$$\lambda_{L\pm} = \delta_1/2 \pm \Omega_1, \qquad \lambda_R = \delta_1. \tag{12}$$

Because of the configuration chosen for the potentials, the Rabi frequencies for the transitions $|1\rangle \rightarrow |3\rangle$ and $|2\rangle \rightarrow |3\rangle$ practically coincide:

$$\upsilon_{13} = \upsilon + \Delta\upsilon, \qquad \upsilon_{23} = \upsilon - \Delta\upsilon, \tag{13}$$

where

$$\upsilon = -pE/\hbar\sqrt{2}\int \phi(-x)\phi_3(x)\,dx, \qquad \Delta\upsilon = -pE/\hbar\sqrt{2}\int \phi(x)\phi_3(x)\,dx. \tag{14}$$

For the present consideration, we neglect the term $\Delta\upsilon$ which is small (compared with υ) owing to the small penetration of the wave function $\phi_3(x)$ into the right well (see Fig. 1). As a result the dressed-state eigenfunctions (10) are simplified:

$$|\psi_{+L}\rangle = \sin\theta|\psi_L\rangle + \cos\theta|3\rangle, \qquad |\psi_{-L}\rangle = \cos\theta|\psi_L\rangle - \sin\theta|3\rangle, \qquad |\psi_R\rangle = (|1\rangle - |2\rangle)/\sqrt{2}, \tag{15}$$

where $|\psi_L\rangle \equiv (|1\rangle + |2\rangle)/\sqrt{2}$ is the state vector corresponding to localization in the left well. Therefore, in

accordance with Eq. (9), if the molecule starts in the initial state (3), it evolves as a two-state system [7] driven coherently between states $|\psi_L\rangle$ and $|3\rangle$:

$$|\psi(t)\rangle = e^{-i(E_3/\hbar+\delta_1/2)t}[(\cos\Omega_1 t + i\sin\Omega_1 t\cos 2\theta) \times e^{i\omega_0 t}|\psi_L\rangle - i\sin\Omega_1 t\sin 2\theta|3\rangle]. \quad (16)$$

Owing to the assumption that the upper-state wave function $\phi_3(x)$ is located mainly in the left well, tunneling from the left well to the right has been suppressed. The same effect occurs for initial localization in the right well of the ground-state potential when $|\psi(t=0)\rangle = |\psi_R\rangle$. In this case, the system remains in the right hand well; even though the external field does not produce any transitions to the excited state, it still suppresses the tunneling. For an arbitrary superposition of the left and right localized states $|\psi_L\rangle$ and $|\psi_R\rangle$, the presence of the coherent driving field isolates the right and left state wave functions; the probability for finding the molecule in the right well is constant in time. In effect, the external driving field suppresses the tunneling by lifting the degeneracy of the ground state, provided that the Rabi frequency υ is greater than the energy level separation δ.

In conclusion, we have shown that the property of quantum dynamical tunneling can be suppressed by means of coherent electromagnetic excitation. In the present discussion, we analyzed the simplest form of ground state potential exhibiting quantum dynamical tunneling—the symmetric, double-well potential [8]. A possible candidate for the observation of suppression of quantum dynamical tunneling is a quantum system (molecule, impurity center) embedded in a host environment that leads to a symmetric double-well potential for the ground electronic state and an asymmetric one for the excited electronic state of this quantum system. If the quantum system is initially localized in one of the wells, an external coherent field can be used to suppress the quantum mechanical tunneling and keep the quantum system in the same spatially localized position.

Two main conditions must be satisfied for experimental observation of the proposed suppression: (i) the ground and excited-state potentials must exhibit different symmetries (symmetric double-well potential for the ground state and asymmetric double-well potential for the excited state) and (ii) the Rabi frequency associated with the coherent driving field υ should be larger than the ground state double-well potential splitting δ. The first condition can be fulfilled, for example, for a molecule that is characterized by an internal, locally symmetric potential in the absence of interactions with its environment [9]. By placing this molecule in an appropriate host medium it may be possible to break the local symmetry associated with the excited-state potential. The second condition can be achieved easily for very low intensities of the coherent field. In connection with this fact, it should be noted that the suppression could be produced, in principle, by a cavity field in which there is, on average, less than one photon in the cavity.

Using the above-mentioned conditions we are able to choose a number of molecules, candidates, for an experimental verification of the predicted effect. Besides propionyl fluoride molecules [9] having two equivalent *gauche* conformations, other chromophores with substituted methyl groups [10] can be tested for this purpose. A possible candidate having an asymmetric ground state potential, but nearly degenerate ground state levels [8] is the 2-vinylantracene molecule which has different stable conformations for the excited (*s-cis* form) and ground (*s-trans* form) states [11]. The detailed considerations of the proposed systems will be done elsewhere.

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