Rabi Oscillation between States of a Coupled Harmonic Oscillator

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Rabi oscillation between bound states of a single potential is well known. However the corresponding formula between the states of two different potentials has not been obtained yet. In this work, we derive Rabi formula between the states of a coupled harmonic oscillator which may be used as a simple model for the electron transfer. The expression is similar to typical Rabi formula for a single potential. This result may be used to describe transitions between coupled diabatic potential curves.

Key Words : Rabi oscillation, Diabatic potentials, Harmonic oscillator

Introduction

An electron transfer between two sites involves transitions which require two different potential energies. A pair of adiabatic Born-Oppenheimer potential surfaces are often introduced and the transition probabilities from the lower surface to the upper surface are calculated. Altenatively coupled diabatic potential surfaces can be used and the electron transfer probabilities are calculated by time-dependent methods.[1] Typical time-dependent methods include various exact propagation schemes, the time-dependent self-consistent field approximation (TDSCF), and the locally propagating gaussian (LPG) approximation.[2-4] Since the transition dipole moment is usually assumed constant and is treated by the constant coupling of the two diabatic potentials. Rabi oscillation between states of coupled potentials may also be used to determine the transition probabilities between two sites.

In this work, two coupled one-dimensional harmonic oscillators are introduced as a simple model and the Rabi oscillations are determined between two states of the coupled oscillators.

Derivation of Rabi Formula

The model Hamiltonian for the two site electron transfer is chosen as[3]

$$\boldsymbol{H} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\frac{p^2}{2m} + \begin{pmatrix} k_1 & 0 \\ 0 & k_2 \end{pmatrix}\frac{x^2}{2} + \begin{pmatrix} \varepsilon_1 & \Gamma \\ \Gamma & \varepsilon_2 \end{pmatrix} + \begin{pmatrix} \Delta & 0 \\ 0 & -\Delta \end{pmatrix}x \tag{1}$$

where two shifted harmonic oscillator potentials are coupled by a constant Γ and they are given as

$$V_1(x) = \frac{k}{2}\left(x + \frac{\Delta}{k}\right)^2 + \varepsilon_1 - \frac{\Delta^2}{2k};$$
$$V_2(x) = \frac{k}{2}\left(x - \frac{\Delta}{k}\right)^2 + \varepsilon_2 - \frac{\Delta^2}{2k} \tag{2}$$

where the force constants of two oscillators are set to be equal for simplicity. Writing the Hamiltonian as a sum of site Hamiltonians

$$\boldsymbol{H} = \boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{\Gamma} \tag{3}$$

where the coupling between sites is $\boldsymbol{\Gamma} = \Gamma\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$. If we expand the wavefunction of $\boldsymbol{H}$ in terms of site wavefunctions as

$$\Psi(x,t) = c_1(t)\Psi_1(x,t) + c_2(t)\Psi_2(x,t), \tag{4}$$

and set up the Schrödinger equation (with $\hbar = 1$) as

$$(\boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{\Gamma})(c_1\Psi_1 + c_2\Psi_2) = i\frac{\partial}{\partial t}(c_1\Psi_1 + c_2\Psi_2) \tag{5}$$

where $\Psi_i(x,t) = e^{-iE_{\upsilon_i}t}\psi_{\upsilon_i}(x)$ $(i = 1, 2)$ and E_{υ_i} and $\psi_{\upsilon_i}(x)$ are υ_i-th eigenvalue and eigenfunction of the ith oscillator, we have

$$c_2e^{-iE_{\upsilon_2}t}\boldsymbol{H}_1\psi_{\upsilon_2} + c_1e^{-iE_{\upsilon_1}t}\boldsymbol{\Gamma}\psi_{\upsilon_1} + c_1e^{-iE_{\upsilon_1}t}\boldsymbol{H}_2\psi_{\upsilon_1} + c_2e^{-iE_{\upsilon_2}t}\boldsymbol{\Gamma}\psi_{\upsilon_2} = i\left(\dot{c}_1e^{-iE_{\upsilon_1}t}\psi_{\upsilon_1} + \dot{c}_2e^{-iE_{\upsilon_2}t}\psi_{\upsilon_2}\right). \tag{6}$$

where $\dot{c}_1 = \frac{\partial c_1}{\partial t}$, etc. Multiplying ψ_{υ_i} with Eq. (6) and integrating it with respect to x, we will have following equations.

$$c_2e^{-iE_{\upsilon_2}t}\boldsymbol{H}_{22}^{(1)} + c_1e^{-iE_{\upsilon_1}t}\Gamma S_{21} + c_1e^{-iE_{\upsilon_1}t}E_{\upsilon_2}S_{12} = i(\dot{c}_1e^{-iE_{\upsilon_1}t}S_{21} + \dot{c}_2e^{-iE_{\upsilon_2}t}) \tag{7a}$$

$$c_2e^{-iE_{\upsilon_2}t}E_{\upsilon_1}S_{21} + c_1e^{-iE_{\upsilon_1}t}H_{11}^{(2)} + c_2e^{-iE_{\upsilon_2}t}\Gamma S_{12} = i(\dot{c}_1e^{-iE_{\upsilon_1}t} + \dot{c}_2e^{-iE_{\upsilon_2}t}S_{12}) \tag{7b}$$

where $H_{ii}^{(k)} = \int \psi_{\upsilon_i}H_k\psi_{\upsilon_i}dx$ $(k = 1, 2)$ and $S_{ij} = \int \phi_{\upsilon_i}\phi_{\upsilon_j}dx$ and $\Gamma_{ii} = 0$ is assumed. Solving Eqs. (7a) and (7b), we would have

$$\begin{pmatrix}\dot{c}_1\\ \dot{c}_2\end{pmatrix} = \frac{i}{1-S_{21}S_{12}}\begin{pmatrix} S_{12}^2(E_{\upsilon_2}+\Gamma)-H_{11}^{(2)} & e^{-i\omega_{21}t}S_{21}(H_{22}^{(1)}-E_{\upsilon_1}-\Gamma) \\ e^{i\omega_{21}t}S_{12}(H_{11}^{(2)}-E_{\upsilon_2}-\Gamma) & S_{21}^2(E_{\upsilon_1}+\Gamma)-H_{22}^{(1)}\end{pmatrix}\begin{pmatrix}c_1\\ c_2\end{pmatrix} \quad (8)$$

where $\omega_{21} = E_{\upsilon_2} - E_{\upsilon_1}$. Overlap matrix between the states of two shifted oscillators is not symmetric so that $S_{ij} \neq S_{ji}$ and explicit expressions for $H_{ij}^{(k)}$ and S_{ij} will be given later. The second-order differential equations for $c_1(t)$ and $c_2(t)$ are obtained as follows

$$\ddot{c}_1 - (F\mathrm{tr}U - i\omega_{21})\dot{c}_1 + F(F\det U - i\omega_{21}U_{11})c_1 = 0 \quad (9a)$$

$$\ddot{c}_2 - (F\mathrm{tr}U + i\omega_{21})\dot{c}_2 + F(F\det U + i\omega_{21}U_{22})c_2 = 0 \quad (9b)$$

where $F = \dfrac{i}{1-S_{21}S_{12}}$ and the elements of U are given as

$$U_{11} = S_{12}^2(E_{\upsilon_2}+\Gamma) - H_{11}^{(2)},$$

$$U_{12} = e^{-i\omega_{21}t}S_{21}(H_{22}^{(1)} - E_{\upsilon_1} - \Gamma)$$

$$U_{21} = e^{i\omega_{21}t}S_{12}(H_{11}^{(2)} - E_{\upsilon_2} - \Gamma),$$

$$U_{22} = S_{21}^2(E_{\upsilon_1}+\Gamma) - H_{22}^{(1)} \quad (10)$$

If we put $e^{\lambda t}$ in Eq. (9a) for $c_1(t)$, we have a following equation for λ

$$\lambda^2 - (F\mathrm{tr}U - i\omega_{21})\lambda + F(F\cdot\det U - i\omega_{21}U_{11}) = 0. \quad (11)$$

Roots of Eq. (11) are obtained as

$$\lambda_\pm = \frac{1}{2}\{(F\mathrm{tr}U - i\omega_{21}) \pm\sqrt{(F\mathrm{tr}U - i\omega_{21})^2 - 4F(F\cdot\det U - i\omega_{21}U_{11})}\} \quad (12)$$

For $c_2(t)$, we obtain following roots from Eq. (9b) if we assume $c_2(t) \sim e^{\mu t}$

$$\mu_\pm = \frac{1}{2}\{(F\mathrm{tr}U + i\omega_{21}) \pm\sqrt{(F\mathrm{tr}U + i\omega_{21})^2 - 4F(F\cdot\det U + i\omega_{21}U_{22})}\} \quad (13)$$

Then $c_1(t)$ and $c_2(t)$ will be given as follows

$$c_1(t) = \mathrm{A}e^{\lambda_+ t} + \mathrm{B}e^{\lambda_- t} \quad (14a)$$

$$c_2(t) = \mathrm{C}e^{\mu_+ t} + \mathrm{D}e^{\mu_- t} \quad (14b)$$

where A, B, C, and D are determined from initial conditions. We now evaluate $H_{ij}^{(k)}$ and S_{ij} so that $c_1(t)$ and $c_2(t)$ are explicitly calculated. They are given as

$$H_{11}^{(2)} = \left(\upsilon_1 + \frac{1}{2}\right)\hbar\omega + \frac{3\Delta^2}{2k} + \varepsilon_2 \quad (15a)$$

$$H_{22}^{(1)} = \left(\upsilon_2 + \frac{1}{2}\right)\hbar\omega + \frac{3\Delta^2}{2k} + \varepsilon_1 \quad (15b)$$

and[5]

$$S_{ij} = \sqrt{\pi}\alpha N_{\upsilon_i}N_{\upsilon_j}e^{-\beta^2} \sum_{l=0}^{\min(\upsilon_i,\upsilon_j)} \frac{(-1)^{\upsilon_j - l}(2\beta)^{\upsilon_i - \upsilon_j - 2l}\upsilon_i!\,\upsilon_j!}{2^l l!(\upsilon_i - l)!(\upsilon_j - l)!} \quad (16)$$

where $\alpha = (mk)^{-\frac{1}{4}}$, $\beta = \dfrac{\Delta}{\alpha k}$, and $N_{\upsilon_i} = \left(\dfrac{\alpha}{2^{\upsilon_i}\upsilon_i!\sqrt{\pi}}\right)^{\frac{1}{2}}$. We note that $S_{ji} = (-1)^{\upsilon_j - \upsilon_i}S_{ij}$. When the minima of the two oscillators are same so that $H_{11}^{(2)} = E_{\upsilon_1} + \dfrac{2\Delta^2}{k}$, $H_{22}^{(1)} = E_{\upsilon_2} + \dfrac{2\Delta^2}{k}$, we obtain $\lambda_\pm$ from Eqs. (12), (15a), and (15b) as follows

$$\lambda_\pm = -i\left[(E_{\upsilon_2}+\Gamma) + \frac{1}{1-S_{12}^2}\left\{\left(\frac{2\Delta^2}{k} - \Gamma\right) \mp\sqrt{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2}\right\}\right] \quad (17)$$

and $\mu_\pm$ given as

$$\mu_\pm = \lambda_\pm + i\omega_{21} \quad (18)$$

In order to specify $c_1(t)$ and $c_2(t)$ completely, we assume that the electron is entirely at site 1 when $t = 0$. From $c_1(0) = A + B = 1$ and $c_2(0) = C + D = 0$, we would have

$$\mathrm{A} = \frac{\omega_{21} + \sqrt{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2}}{2\sqrt{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2}} \quad (19a)$$

$$\mathrm{B} = -\frac{\omega_{21} - \sqrt{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2}}{2\sqrt{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2}} \quad (19b)$$

The probability $P_1(t)$ between υ_1-th state of oscillator 1 and υ_2-th state of oscillator 2 is then

$$P_1(t) = |c_1(t)|^2 = \cos^2\left\{\frac{1}{1-S_{12}^2}\sqrt{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2}\right\}t + \frac{\omega_{21}^2\sin^2\left\{\frac{1}{1-S_{12}^2}\sqrt{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2}\right\}t}{(1-S_{12}^2)\omega_{21}^2 + S_{12}^2\left(\frac{2\Delta^2}{k} - \Gamma\right)^2} \quad (20)$$

which shows typical Rabi formula and dependence of the Rabi frequency on the overlap between the states of coupled oscillators.

Conclusion

We derive Rabi formula between the states of a coupled harmonic oscillator which could be used as a simple model for transitions between coupled bound diabatic potential curves of constant transition dipole moment. The expression is similar to the standard Rabi formula for a single potential except the dependence of the Rabi frequency on the overlap of states of coupled potentials.

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