

# Curve Crossing Problems: Analytically solvable model

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We propose an exactly solvable model for the two state curve crossing problems. Our model assumes the coupling to be a delta function. It is used to calculate the effect of curve crossing on electronic absorption spectrum and resonance Raman excitation profile.

## INTRODUCTION

Nonadiabatic transition due to potential curve (or surface) crossing is one of the most important mechanisms to effectively induce electronic transitions in collisions [1]. This is a very interdisciplinary concept and appears in various fields of physics and chemistry, even in biology [2]. The most typical examples are, of course, a variety of atomic and molecular processes such as atomic and molecular collisions, chemical reactions and molecular spectroscopic processes. Attempts have been made to classify organic reactions by curve crossing diagrams [3]. Other examples are nuclear collisions and reactions in nuclear physics [4, 5], dynamic processes on solid surfaces, energy relaxation and phase transitions in condensed phase physics [6, 7], and electron and proton transfer processes in biology [8, 9]. Two state curve crossing can be classified into the following two cases according to the crossing scheme: (1) Landau-Zener (L.Z) case, in which the two diabatic potential curves have the same signs for the slopes and (2) non-adiabatic tunnelling (N.T) case, in which the diabatic curves have the opposite sign for slopes. There is also a non-crossing non-adiabatic transition called the Rosen-Zener-Demkov type [1, 2], in which two adiabatic potentials are in near resonance at large  $R$ . The theory of non-adiabatic transitions dates back to 1932, when the pioneering works for curve-crossing and non-crossing were published by Landau [10], Zener [11] and Stueckelberg [12] and by Rosen and Zener [13] respectively. Since then numerous papers by many authors have been devoted to these subjects, especially to curve crossing problems. Two categories might be classified for finding an exact analytical solution of the curve crossing problem. The first is that an exact analytical solution can be obtained for the whole region of the variable (say  $x$  here, see in the next section). For example, Osherov and Voronin solved the case where two diabatic potentials are constant with exponential coupling [14]. C. Zhu solved the case where two diabatic potentials are exponential with exponential coupling [15]. The second is that an exact analytical solution is not possible for the whole region of the variable, but is possible for the asymptotic region. Then, physical quantities such as eigenvalues, scattering matrices can still be solved in an exact analytical form, providing that the connection problem of the asymptotic solution is known. The Stokes phenomenon

[16] of asymptotic solution of the ordinary differential equation provides a powerful tool to deal with these kinds of problems [17, 18, 19]. Generalizing the real variable to the complex variable and tracing the asymptotic solution around the complex plane, the connection matrix which connects the asymptotic solution in the complex plane can be expressed in terms of Stokes constants. Recent work by Zhu and Nakamura [19] found an exact analytical solution of the Stokes constants for the second-order ordinary differential equation with the coefficient function as the fourth-order polynomial. In this way, exact analytical solutions of scattering matrices were obtained for the two state linear curve crossing problem with constant coupling [20].

## THE MODEL

We consider two diabatic curves, crossing each other. There is a coupling between the two curves, which causes transitions from one curve to another. This transition would occur in the vicinity of the crossing point. In particular, it will occur in a narrow range of  $x$ , given by

$$|V_1(x) - V_2(x)| \simeq |V(x_c)|. \quad (1)$$

where  $x$  denotes the nuclear coordinate and  $x_c$  is the crossing point.  $V_1$  and  $V_2$  are the diabatic curves and  $V$  represent the coupling between them. Therefore it is interesting to analyze a model, where coupling is localized in space near  $x_c$ . Thus we put

$$V(x) = K_0 \delta(x - x_c), \quad (2)$$

here  $K_0$  is a constant. This model has the advantage that it can be exactly solved (delta function sink model for electronic relaxation in solution is known in literature [21]). One can roughly estimate the value of  $K_0$  as follows. If the two curves are approximated as linear near the vicinity of crossing, then the energy separation between the two is  $\approx \left[ \frac{\partial}{\partial x}(V_1 - V_2) \right]_{x_c} (x - x_c)$ . This will be of the order of  $\Delta V(x_c)$ , if  $(x - x_c)$  takes the value  $\simeq \frac{\Delta V(x_c)}{\left( \frac{\partial}{\partial x}(V_1 - V_2) \right)_{x_c}}$ . So it is reasonable to put

$$K_0 = \left| \frac{2V(x_c)}{\left( \frac{\partial}{\partial x}(V_1 - V_2) \right)_{x_c}} \right| \times V(x_c).$$

## EXACT ANALYTICAL SOLUTION

We start with a particle moving on any of the two diabatic curves. The problem is to calculate the probability that the particle will still be on any one of the diabatic curves after a time  $t$ . We write the probability amplitude as

$$\Psi(x, t) = \begin{pmatrix} \psi_1(x, t) \\ \psi_2(x, t) \end{pmatrix}, \quad (3)$$

where  $\psi_1(x, t)$  and  $\psi_2(x, t)$  are the probability amplitude for the two states.  $\Psi(x, t)$  obey the time dependent Schrödinger equation (we take  $\hbar = 1$  here and in subsequent calculations)

$$i \frac{\partial \Psi(x, t)}{\partial t} = H \Psi(x, t). \quad (4)$$

$H$  is defined by

$$H = \begin{pmatrix} H_1(x) & V(x) \\ V(x) & H_2(x) \end{pmatrix}, \quad (5)$$

where  $H_i(x)$  is

$$H_i(x) = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} + V_i(x). \quad (6)$$

We find it convenient to define the half Fourier Transform  $\bar{\Psi}(\omega)$  of  $\Psi(t)$  by

$$\bar{\Psi}(\omega) = \int_0^\infty \Psi(t) e^{i\omega t} dt. \quad (7)$$

Half Fourier transformation of Eq. (4) leads to

$$\begin{pmatrix} \bar{\psi}_1(\omega) \\ \bar{\psi}_2(\omega) \end{pmatrix} = i \begin{pmatrix} \omega - H_1 & V \\ V & \omega - H_2 \end{pmatrix}^{-1} \begin{pmatrix} \psi_1(0) \\ \psi_2(0) \end{pmatrix}. \quad (8)$$

$$(\omega - H_1 - K_0^2 G_2^0(x_c, x_c; \omega) S)^{-1} = (\omega - H_1)^{-1} + (\omega - H_1)^{-1} K_0^2 G_2^0(x_c, x_c; \omega) S [\omega - H_1 - K_0^2 G_2^0(x_c, x_c; \omega) S]^{-1}. \quad (16)$$

Inserting the resolution of identity  $I = \int_{-\infty}^\infty dy |y\rangle \langle y|$  in the second term of the above equation, we arrive at

$$G_{11}(x, x_0; \omega) = G_1^0(x, x_0; \omega) + K_0^2 G_1^0(x, x_c; \omega) \quad (17)$$

$$\times G_2^0(x_c, x_c; \omega) G_{11}(x_c, x_0; \omega). \quad (18)$$

Putting  $x = x_c$  in Eq. (17) and solving for  $G_{11}(x_c, x_0; \omega)$

This may be written as

$$\bar{\Psi}(\omega) = i G(\omega) \Psi(0). \quad (9)$$

$G(\omega)$  is defined by  $(\omega - H) G(\omega) = I$ . In the position representation, the above equation may be written as

$$\bar{\Psi}(x, \omega) = i \int_{-\infty}^\infty G(x, x_0; \omega) \bar{\Psi}(x_0, \omega) dx_0, \quad (10)$$

where  $G(x, x_0; \omega)$  is

$$G(x, x_0; \omega) = \langle x | (\omega - H)^{-1} | x_0 \rangle. \quad (11)$$

Writing

$$G(x, x_0; \omega) = \begin{pmatrix} G_{11}(x, x_0; \omega) & G_{12}(x, x_0; \omega) \\ G_{21}(x, x_0; \omega) & G_{22}(x, x_0; \omega) \end{pmatrix} \quad (12)$$

and using the partitioning technique [22] we can write

$$G_{11}(x, x_0; \omega) = \langle x | [\omega - H_1 - V(\omega - H_2)^{-1} V]^{-1} | x_0 \rangle. \quad (13)$$

The above equation is true for any general  $V$ . This expression simplify considerably if  $V$  is a delta function located at  $x_c$ . In that case  $V$  may be written as  $V = K_0 S = K_0 |x_c\rangle \langle x_c|$ . Then

$$G_{11}(x, x_0; \omega) = \langle x | [\omega - H_1 - K_0^2 G_2^0(x_c, x_c; \omega) S]^{-1} | x_0 \rangle, \quad (14)$$

where

$$G_2^0(x, x_0; \omega) = \langle x | (\omega - H_2)^{-1} | x_0 \rangle, \quad (15)$$

and corresponds to propagation of the particle starting at  $x_0$  on the second diabatic curve, in the absence of coupling to the first diabatic curve. Now we use the operator identity

gives

$$G_{11}(x_c, x_0; \omega) = G_1^0(x_c, x_0; \omega) \quad (19)$$

$$\times [1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)]^{-1}. \quad (20)$$

This when substituted back into Eq. (17) gives

$$G_{11}(x, x_0; \omega) = G_1^0(x, x_0; \omega) + \frac{K_0^2 G_1^0(x, x_c; \omega) G_2^0(x_c, x_c; \omega) G_1^0(x_c, x_0; \omega)}{1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)}. \quad (21)$$

Using the same procedure one can get

$$G_{12}(x, x_0; \omega) = \frac{K_0 G_1^0(x, x_c; \omega) G_2^0(x_c, x_0; \omega)}{1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)}. \quad (22)$$

Similarly one can derive expressions for  $G_{22}(x, x_0; \omega)$  and  $G_{21}(x, x_0; \omega)$ . Using these expressions for the Green's function in Eq. (9) we can calculate  $\overline{\Psi}(\omega)$  explicitly.

The expressions that we have obtained for  $\overline{\Psi}(\omega)$  are quite general and are valid for any  $V_1(x)$  and  $V_2(x)$ . However, their utility is limited by the fact that one must know  $G_1^0(x, x_0; \omega)$  and  $G_2^0(x, x_0; \omega)$ . It is possible to find  $G_i^0(x, x_0; \omega)$  only in a few limited cases and the harmonic oscillator is one of them.

### ELECTRONIC ABSORPTION SPECTRA AND RESONANCE RAMAN EXCITATION PROFILE

In this section we apply the method to the problem involving harmonic potentials. We consider a system of three potential energy curves, ground electronic state and two 'crossing' excited electronic states (electronic transition to one of them is assumed to be dipole forbidden and while it is allowed to the other) [23, 24]. We calculate the effect of 'crossing' on electronic absorption spectra and on resonance Raman excitation profile. The propa-

gating wave functions on the excited state potential energy curves are given by solution of the time dependent Schrödinger equation

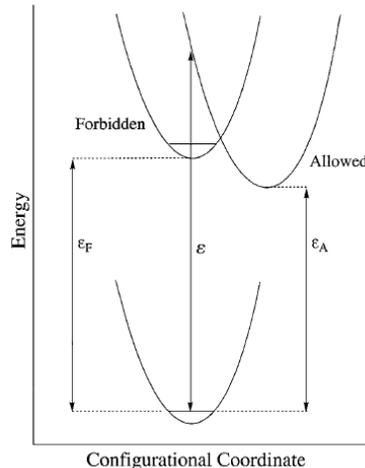


FIG. 1: Schematic diabatic potential energy curves that illustrate the model. The forbidden state is labeled F; the allowed state is labeled A.

$$i \frac{\partial}{\partial t} \begin{pmatrix} \psi_1^{vib}(x, t) \\ \psi_2^{vib}(x, t) \end{pmatrix} = \begin{pmatrix} H_{vib,e1}(x) & V_{12}(x) \\ V_{21}(x) & H_{vib,e2}(x) \end{pmatrix} \begin{pmatrix} \psi_1^{vib}(x, t) \\ \psi_2^{vib}(x, t) \end{pmatrix}. \quad (23)$$

In the above equation  $H_{vib,e1}(x)$  and  $H_{vib,e2}(x)$  describes the vibrational motion of the system in the first electronic excited state (allowed) and second electronic excited state (forbidden) respectively

$$H_{vib,e1}(x) = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega_A^2 (x - a)^2 \quad (24)$$

and

$$H_{vib,e2}(x) = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega_F^2 (x - b)^2. \quad (25)$$

In the above  $m$  is the oscillator's mass,  $\omega_A$  and  $\omega_F$  are the vibrational frequencies on the allowed and forbidden states and  $x$  is the vibrational coordinate. Shifts of the vibrational coordinate minimum upon excitation are given

by  $a$  and  $b$ , and  $V_{12}$  ( $V_{21}$ ) represent coupling between the two harmonic potentials which is taken to be

$$V_{21}(x) = V_{12}(x) = K_0 \delta(x - x_c), \quad (26)$$

where  $K_0$  represent the strength of the coupling. The intensity of electronic absorption spectra is given by [24, 25]

$$I_A(\omega) \propto \text{Re} \left[ \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx_0 \Psi_i^{vib*}(x) iG(x, x_0; \omega + i\Gamma) \Psi_i^{vib}(x_0) \right], \quad (27)$$

where

$$G(x, x_0; \omega + i\Gamma) = \langle x | [(\omega_0/2 + \omega - \omega_{eg}) + i\Gamma - H_{vib,e}]^{-1} | x_0 \rangle. \quad (28)$$

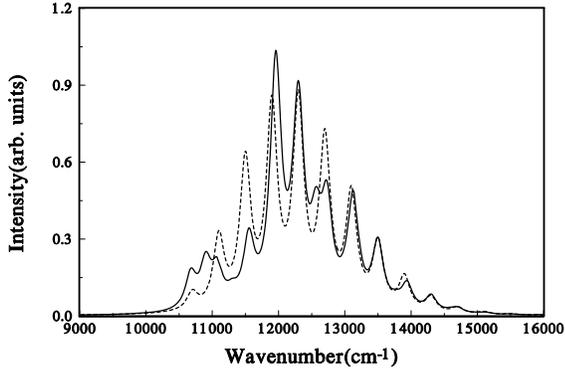


FIG. 2: Calculated electronic absorption spectra with coupling (solid line) and without coupling (dashed line). Here the values for the simulations are  $\omega_0 = \omega_A = \omega_F = 400 \text{ cm}^{-1}$ ,  $\Gamma = 100 \text{ cm}^{-1}$ ,  $\varepsilon_A = 10700 \text{ cm}^{-1}$ ,  $\varepsilon_F = 11000 \text{ cm}^{-1}$ ,  $K_0 = 5.9643 \times 10^{-15} \text{ erg}\cdot\text{\AA}$ , and  $x_c = 0.0895 \text{ \AA}$ .

and

$$H_{vib,e} = \begin{pmatrix} H_{vib,e1}(x) & K_0|x_c\rangle\langle x_c| \\ K_0|x_c\rangle\langle x_c| & H_{vib,e2}(x) \end{pmatrix} \quad (29)$$

Here,  $\Gamma$  is a phenomenological damping constant which account for the life time effects.  $\Psi_i^{vib}(x, 0)$  is given by

$$\Psi_i^{vib}(x, 0) = \begin{pmatrix} \chi_i(x) \\ 0 \end{pmatrix}, \quad (30)$$

where  $\chi_i(x)$  is the ground vibrational state of the ground electronic state,  $\omega_0$  is the vibrational frequency on the ground electronic state,  $\varepsilon_A$  is the energy difference between the excited (allowed) and ground electronic state, and for the forbidden electronic state it's value is  $\varepsilon_F$ . Similarly resonance Raman scattering intensity can be expressed in terms of Green's function and is given by [24, 25].

$$I_R(\omega) \propto \left| \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx_0 \Psi_f^{vib*}(x, 0) iG(x, x_0; \omega + i\Gamma) \Psi_i^{vib}(x_0, 0) \right|^2. \quad (31)$$

In the above  $\Psi_f^{vib}(x, 0)$  is given by

$$\Psi_f^{vib}(x, 0) = \begin{pmatrix} \chi_f(x) \\ 0 \end{pmatrix}, \quad (32)$$

where  $\chi_f(x)$  is the final vibrational state of the ground electronic state. As  $G_i^0(x, x_0; \omega)$  for the harmonic potential is known [26], we can calculate  $G(x, x_0; \omega)$ . We use Eq. (31) to calculate the effect of curve crossing on resonance Raman excitation profile.

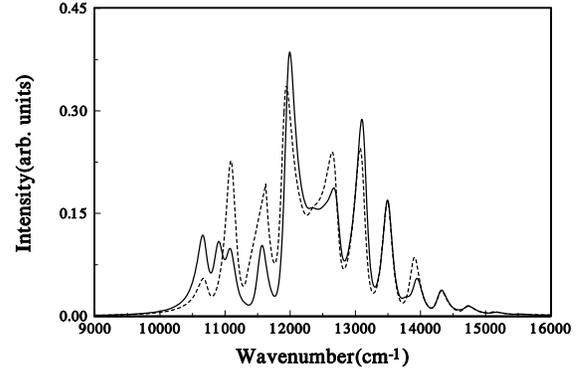


FIG. 3: Calculated resonance Raman excitation profile for excitation from the ground vibrational state to the first excited vibrational state, with coupling (solid line) and without coupling (dashed line). Here the values for the simulations are  $\omega_0 = \omega_A = \omega_F = 400 \text{ cm}^{-1}$ ,  $\Gamma = 100 \text{ cm}^{-1}$ ,  $\varepsilon_A = 10700 \text{ cm}^{-1}$ ,  $\varepsilon_F = 11000 \text{ cm}^{-1}$ ,  $K_0 = 5.9643 \times 10^{-15} \text{ erg}\cdot\text{\AA}$ , and  $x_c = 0.0895 \text{ \AA}$ .

## Results using the model

In the following we give results for the effect of curve crossing on electronic absorption spectrum and resonance Raman excitation profile in the case where one dipole allowed electronic state crosses with a dipole forbidden electronic state as in Fig. 1. As in [24], the ground state curve is taken to be a harmonic potential energy curve with its minimum at zero. The curve is constructed to be representative of the potential energy along a metal-ligand stretching coordinate. We take the mass as  $35.4 \text{ amu}$  and the vibrational wavenumber as  $400 \text{ cm}^{-1}$  [24] for the ground state. The first diabatic excited state potential energy curve is displaced by  $0.197 \text{ \AA}$  and is taken to have a vibrational wavenumber of  $400 \text{ cm}^{-1}$ . Transition to this state is allowed. The minimum of the potential energy curve is taken to be above  $10700 \text{ cm}^{-1}$  of that of the ground state curve. The second diabatic excited state potential energy curve is taken to be an un-displaced excited state. On that potential energy curve, the vibration is taken to have same wavenumber of  $400 \text{ cm}^{-1}$ . Its minimum is  $11000 \text{ cm}^{-1}$  above that of the ground state curve. Transition to this state is assumed to be dipole forbidden. The two diabatic curves cross at an energy of  $11673.6 \text{ cm}^{-1}$  with  $x_c = 0.0895 \text{ \AA}$ . Value of  $K_0$  we use in our calculation is  $K_0 = 5.9643 \times 10^{-15} \text{ erg}\cdot\text{\AA}$ . The lifetime of both the excited states are taken to be  $100 \text{ cm}^{-1}$ . The calculated electronic absorption spectra is shown in Fig. 2. The profile shown by the dashed line is in the absence of any coupling to the second potential energy curve. The full

line has the effect of coupling in it. The calculated resonance Raman excitation profile is shown in Fig. 3. The profile shown by the full line is calculated for the coupled potential energy curves. The profile shown by the dashed line is calculated for the uncoupled potential energy curves. It is seen that curve crossing effect can alter the absorption and Raman excitation profile significantly. However it is the Raman excitation profile that is more effected. Even though our calculations are for a simple model (which has the convenience that everything can be found analytically), similar conclusions are valid for more complicated couplings [24].

## CONCLUSIONS

We have proposed a simple model for the two state curve crossing problem which can be analytically solved. Our solution is quite general and is valid for any potentials for which Green's functions for the motion in the absence of coupling is known. The model is used to calculate the effect of curve crossing on electronic absorption spectrum and on resonance Raman excitation profile. We find that Raman excitation profile is affected much more by the crossing, than the electronic absorption spectrum.

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