



Effect of curve crossing induced dissociation on absorption and resonance Raman spectra: An analytically solvable model



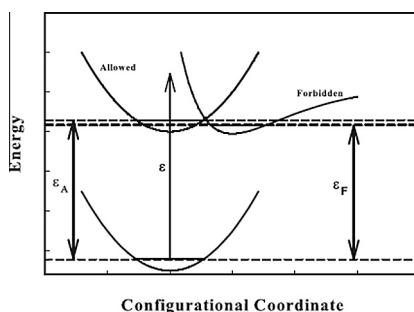
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HIGHLIGHTS

- Model consisting of harmonic oscillator and Morse potential is solved.
- Dirac Delta function and Greens function is used.
- Absorption spectra and resonance Raman excitation profile is studied.

GRAPHICAL ABSTRACT



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ABSTRACT

An analytically solvable model for the crossing of a harmonic and a Morse potential coupled by Dirac Delta function has been proposed. Further we explore the electronic absorption spectra and resonance Raman excitation profile using this model and found that curve crossing had significant effect on the resonance Raman excitation profile.

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1. Introduction

In various atomic and molecular processes we have different type of transitions which occur between two atomic/molecular states and it is worthwhile to say that potential energy curve crossing plays a key role in such kind of transitions. Nonadiabatic transitions (transitions between two adiabatic states or diabatic states) generally occur between bound states [1]. Nonadiabatic transitions also play a very important role in change of state/phase [2–6] in different kind of dynamic processes occurring in the field of

biology, chemistry and physics. Similarly, various spectroscopic, collisions processes and different kind of reactions are governed by nonadiabatic transitions at crossing or avoided crossing of the potential energy surfaces [7]. Radiationless transitions in condense matter physics, fluorescence quenching, self-trapping of excitons, laser assisted collisions reactions are some of the other examples [8,9] where nonadiabatic transitions due to curve crossing or avoided crossing play an important role. Other important fields of study related to nonadiabatic transitions include the Zener transitions in flux driven metallic rings [10], superconducting Josephson junctions [11], nuclear collisions and reactions in nuclear physics [12], electron proton transfer processes in biological molecules [13]. Such kind of transitions also play a very

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important role in neutrino conversion in the sun and provide an evidence for its existence in the mutability of the universe [14]. It has been also commented by Shaik [15] that curve crossing/avoided crossing could be interpreted as a general mechanism of rearrangement of electrons by molecules leading to the formation and breaking of bonds. Nonadiabatic transitions have been also studied as a mechanism of dissociation of molecules on metal surfaces as reported by Kosloff [16] in his studies. The first report on such kind of transitions came into existence into 1932, when the pioneering works were published by Landau [17], Zener [18] and Stueckelberg [19] and by Rosen and Zener [20]. Since 1932, there are numerous research papers have been published in this area using analytical as well as computational approach [21–33]. In our earlier publications we have reported analytical solution in those cases where two or more arbitrary potentials are coupled by Dirac Delta interactions [34,37,35,38,36,39]. Recently we have extended our research to deal with the cases where two potentials are coupled by any arbitrary interaction [40]. One of the great advantage of Dirac Delta coupling model is that we can find exact analytical solution using this model.

2. Mathematical model

We consider the crossing of two diabatic curves (a harmonic potential and a Morse potential in the present case) and the coupling between them is assumed to be a Dirac Delta function which is responsible for transitions between these two considered diabatic curves. Nonadiabatic transition due to curve crossing would occur in the neighborhood of the crossing point or in other words is given by

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

In the above equation x is the nuclear coordinate and x_c is considered as crossing point. $V_1(x)$ and $V_2(x)$ are the diabatic potentials (and $V(x_c)$ represent the coupling between them. In real systems the transitions between the two diabatic potentials occurs at the crossing point. This can be attributed to the fact that necessary energy transfer between the electronic and nuclear degrees of freedom is minimum at this point, hence it is worthful to analyze a coupling which is localized near the crossing point rather than using a model where coupling is constant or same elsewhere. Thus we put (see Appendix A for more details on diabatic coupling, where we do a calculation on real system like Lithium chloride i.e. (Eq. (2), Fig. 4))

$$V(x) = k_0 \delta(x - x_c), \quad (2)$$

here k_0 is a constant. This model has the advantage that it can be analytically solved.

3. Exact analytical approach

In this section we derive exact analytical expressions for wave function and Green's function which are needed to study the effect of curve crossing on electronic absorption and resonance Raman excitation profile. We write the probability amplitude for the two included states as

$$\Phi(x, t) = \begin{pmatrix} \phi_1(x, t) \\ \phi_2(x, t) \end{pmatrix}, \quad (3)$$

where $\phi_1(x, t)$ and $\phi_2(x, t)$ are the probability amplitude for the two states. $\Phi(x, t)$ obey the time dependent Schrodinger equation. In the subsequent calculations as well as the present one (we take $\hbar = 1$)

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

H is given by

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

where $H_i(x)$ is

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

the half Fourier transform $\bar{\Phi}(\omega)$ of $\Phi(t)$ is defined by

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

writing the half Fourier transform of Eq. (4) gave us

$$\bar{\Phi}(\omega) = iG(\omega)\Phi(0), \quad (8)$$

where $G(\omega)$ is defined by

$$(\omega - H)G(\omega) = I. \quad (9)$$

In the position representation, the above equation may be written as

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

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 applying the partitioning technique 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 potential $V(x)$. Our equation is further simplified if V is a delta function located at the crossing point

$$G_{11}(x, x_0; \omega) = G_1^0(x, x_0; \omega) + \frac{K_0^2 G_1^0(x, x_c; \omega) G_2^0(x_c, x_c; \omega) G_1^0(x_c, x_0; \omega)}{1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)}, \quad (14)$$

where

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

The above value of Green's function 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. In a similar fashion one can get

$$G_{12}(x, x_0; \omega) = \frac{K_0 G_1^0(x, x_c; \omega) G_2^0(x_c, x_0; \omega)}{1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)}. \quad (16)$$

The expressions for $G_{22}(x, x_0; \omega)$ and $G_{21}(x, x_0; \omega)$ can be further derived by using a similar approach as shown in the last section. We can calculate $\bar{\Phi}(\omega)$ explicitly by using these expressions for the Green's function in Eq. (8).

The expressions that we have obtained for $\bar{\Phi}(\omega)$ 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 Morse oscillator is one of them [41].

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