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Perturbation treatment of electronically nonadiabatic collisions

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The electronically inelastic two-state problem is solved by using a double perturbation theory. The wave function is expressed as a set of coupled differential equations in a diabatic representation, and the elastic wave functions are removed from the exact wave functions to give a set of coupled differential equations for the coefficients of the elastic functions. These are then linearized about the crossing point in the potential-energy curves and solved as in the Landau–Zener approximation. The approximate, Landau–Zener coefficients are then removed from the exact coefficients to give a set of differential equations for the resulting second-level coefficients. Having removed most of the problem in these two steps, the resulting second-level equations can usually be solved accurately by an exponential perturbation theory. The theory is designed as a prototype for more complicated inelastic and spectroscopic problems for which a computer solution of the Schrödinger equation is impractical.

INTRODUCTION

One of the first scattering problems to be studied quantum mechanically was the electronically inelastic scattering of atoms and atomic ions. This usually, but not always, involved charge exchange. Of all the methods used, the Landau–Zener approximation has been by far the most popular.[1–5] By linearizing the problem around the point where two potential-energy curves cross, Landau and Zener were able to solve the Schrödinger equation using a semiclassical, time-dependent perturbation theory and get a simple answer for the probability for inelastic scattering. With modern computers, of course, the two-state problem can be solved without approximation in a matter of seconds. However, there is a large variety of more complicated problems which embody the Landau–Zener approximation as a component part. Many spectroscopic problems involve autoionization and predissociation. A molecule is excited to an electronic surface which then crosses one or more other surfaces in the electronic or vibrational continuum. The dynamics near this crossing region are closely related to the problem of electronically inelastic scattering. Many chemical reactions involve two or more potential-energy surfaces, and the treatment of these cases must involve nonadiabatic transitions. For example, the Preston–Tully trajectory surface hopping model[6] uses the Landau–Zener approximation to calculate the probability of jumping from one surface to another. Thus, the theory of nonadiabatic dynamics is still very active.[7,8]

We present here a perturbation treatment of the electronically inelastic problem which uses the Landau–Zener approximation as a zero-order, unperturbed solution. The goal is to incorporate this theory as part of one of the problems mentioned above. A forthcoming paper will use it as part of a semiclassical treatment of molecular charge exchange.[9] Here, the problem is complicated by the vast number of rotational and vibrational states of the two colliding molecules. The treatment given here is actually a double perturbation theory. The inelastic two-state problem is set up in a diabatic representation, and the radial wave functions for the elastic scattering are removed from the solutions to give a set of coupled differential equations for the coefficients of these elastic wave functions. These differential equations are linearized as in the Landau–Zener approximation and then solved in closed form to give an approximate Landau–Zener coefficient. Finally, the Landau–Zener coefficient is removed from the exact coefficient to give a set of differential equations for the resulting second-level coefficients. Having removed most of the interaction in these two steps we can then solve what is left by a simple perturbation approximation. The basic method for the multiple perturbation theory has been described in detail in Ref. 10 (referred to hereafter as I). The process is called the "onion method" because it resembles the peeling of an onion, layer by layer. The final scattering matrix also has an onion-like structure, with various layers coming from each of the zero-order solutions which have been removed from the problem.

BASIC THEORY

In the case of electronically inelastic scattering, as opposed to charge exchange, we set up the problem in a diabatic representation. There will then be two potential-energy curves which cross each other at some point R_0. The radial Schrödinger equation is given by

$$u_i^{(e)\prime\prime} + \left[k_i^2 - \frac{l_i(l_i+1)}{R^2}\right] u_i^{(e)} - \sum_j \langle i|U(R)|j\rangle u_j^{(e)}(R) = 0, \tag{1}$$

where l is the orbital angular momentum quantum number, $k_i^2 = 2\mu(E_{\rm tot} - E_i)/\hbar$, and $U(R) = 2\mu V(R)/\hbar$ is proportional to the potential V; i and j are 1 and 2 for the two states. The exact radial wave function is written as $u^{(e)}(R)$ to distinguish it from the approximate u's that will be used later. The theory generalizes in a rather obvious way to the case of more than two states.

In the case of charge exchange Stechel, Schmalz, and Light (SSL)[11] have argued that one must use a theory designed for reactive scattering because the quantum states of the products are different from those of the reactants, and therefore one cannot expand the wave function in a single basis set. They argue further that the common adiabatic theories[12] for charge exchange do not give the correct asympto-

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tic form for the wave function and are therefore incorrect. They formulated a theory for charge exchange based on a set of nonorthogonal, diabatic basis electronic basis functions centered on each of the colliding nuclei. The coupled equations are

$$\mathbf{S}\mathbf{u}^{(e)\prime\prime} + \left[\mathbf{k}^2\mathbf{S} - \frac{\mathbf{N}}{r^2} - \mathbf{U}(R)\right]\mathbf{u}^{(e)} = 0, \tag{2}$$

where $\mathbf{S}$ is the overlap integral for the nonorthogonal basis functions and $\mathbf{N}$ is the matrix corresponding to the orbital angular momentum operator. This reduces to $l(l+1)$ for the case of no electronic angular momentum. It is clear that left multiplication by $\mathbf{S}^{-1}$ will convert Eq. (2) into the same form as Eq. (1). Equation (2) omits two small terms in the SSL theory of the order of the electron mass to the nuclear mass, but these, again, do not change the overall form of the coupled equations. The general methods developed here can be used on either type of equation. We will refer to Eq. (1) with the understanding that, with the appropriate changes, the method can be used for the case of charge exchange as well.

If we have a set of N coupled second-order differential equations, we will have $2N$ constants of integration. These will then specify N well-behaved solutions which go to 0 as $R\rightarrow 0$ and N singular solutions. We represent each solution as a column vector. The N well-behaved solutions form an $N\times N$ matrix $\mathbf{u}_a^{(e)}$. Similarly, the N singular solutions can be grouped into an $N\times N$ matrix $\mathbf{u}_b^{(e)}$. We also define the $2N\times 2N$ matrix $\mathbf{u}^{(e)}$ as

$$\mathbf{u}^{(e)}(R) = \begin{pmatrix} \mathbf{u}_a^{(e)} & \mathbf{u}_b^{(e)} \\ \mathbf{u}_a^{(e)\prime} & \mathbf{u}_b^{(e)\prime} \end{pmatrix}, \tag{3}$$

where the prime indicates differentiation with respect to R. Equation (1) then becomes

$$\mathbf{u}^{(e)\prime} = \begin{pmatrix} 0 & 1 \\ \mathbf{P}+\mathbf{U} & 0 \end{pmatrix}\mathbf{u}^{(e)} = \mathbf{A}^{(e)}(R)\mathbf{u}^{(e)}(R), \tag{4}$$

where $\mathbf{P}$ is the diagonal matrix of $k_i^2 - l_i(l_i+1)/R^2$. If we neglect the off-diagonal elements of $U(R)$, then the coupled equations in Eq. (1) decouple completely, and those in Eq. (4) break up into 2×2 blocks. These can be solved easily, e.g., by the WKB approximation, and will define our zero-order elastic wave functions. As before there will be N well-behaved solutions $\mathbf{u}_a^{(0)}$ and N singular solutions $\mathbf{u}_b^{(0)}$. Both matrices are diagonal. They satisfy the differential equation

$$\mathbf{u}^{(0)\prime} = \begin{pmatrix} 0 & 1 \\ \mathbf{P}+\mathbf{U}_d & 0 \end{pmatrix}\mathbf{u}^{(0)} = \mathbf{A}^{(0)}(R)\mathbf{u}^{(0)}(R), \tag{5}$$

where $\mathbf{U}_d(R)$ consists of the diagonal elements of $\mathbf{U}(R)$. We now express $\mathbf{u}^{(e)}$ in terms of $\mathbf{u}^{(0)}$,

$$\mathbf{u}^{(e)}(R) = \mathbf{u}^{(0)}(R)\mathbf{X}^{(1)}(R) = \mathbf{u}^{(e)}\begin{pmatrix} \mathbf{X}_{aa}^{(1)} & \mathbf{X}_{ab}^{(1)} \\ \mathbf{X}_{ba}^{(1)} & \mathbf{X}_{bb}^{(1)} \end{pmatrix}. \tag{6}$$

The differential equation for $\mathbf{X}^{(1)}$ is

$$\mathbf{X}^{(1)\prime} = \mathbf{u}^{(0)-1}[\mathbf{A}^{(e)} - \mathbf{A}^{(0)}]\mathbf{u}^{(0)}\mathbf{X}^{(1)} = \mathbf{A}^{(1)}\mathbf{X}^{(1)}. \tag{7}$$

We can write $\mathbf{A}^{(1)}$ as a set of four $N\times N$ blocks as we did for $\mathbf{X}^{(1)}$ in Eq. (6). They are given in I by

$$A_{aaij}^{(1)} = \tfrac{1}{2}u_{bi}^{(0)}U_{ij}u_{aj}^{(0)}, \tag{8a}$$

$$A_{abij}^{(1)} = \tfrac{1}{2}u_{bi}^{(0)}U_{ij}u_{bj}^{(0)}, \tag{8b}$$

$$A_{baij}^{(1)} = -\tfrac{1}{2}u_{ai}^{(0)}U_{ij}u_{aj}^{(0)}, \tag{8c}$$

$$A_{bbij}^{(1)} = -\tfrac{1}{2}u_{ai}^{(0)}U_{ij}u_{bj}^{(0)}. \tag{8d}$$

At small R we must have $\mathbf{X}_{ba}^{(1)} = 0$ in order that $\mathbf{u}_a^{(e)}$ go to zero. Let $\mathbf{X}_{aa}^{(1)} = \mathbf{X}_0^{(1)}$ at some suitably small value of R. Then at large R, we have

$$\mathbf{X}_{aa}^{(1)} \sim [\mathbf{1} + \mathbf{E}^{(1)}]\mathbf{X}_0^{(1)}, \quad \mathbf{X}_{ba}^{(1)} \sim \mathbf{F}^{(1)}\mathbf{X}_0^{(1)}. \tag{9}$$

In the limit of a small perturbation both $\mathbf{E}^{(1)}$ and $\mathbf{F}^{(1)}$ are first order in the perturbation. There are no clear boundary conditions on $\mathbf{X}_{ab}^{(1)}$ and $\mathbf{X}_{bb}^{(1)}$ since they determine the singular solutions $\mathbf{u}_b^{(e)}$. The exact scattering matrix is given by

$$\mathbf{S}^{(e)} = \exp(i\boldsymbol{\eta}_0)\mathbf{S}^{(1)}\exp(i\boldsymbol{\eta}_0), \tag{10}$$

where $\boldsymbol{\eta}_0$ is the diagonal matrix of phase shifts obtained from the asymptotic behavior of $\mathbf{u}_a^{(0)}$. The modified S matrix $\mathbf{S}^{(1)}$ is

$$\mathbf{S}^{(1)} = [\mathbf{1} + \mathbf{E}^{(1)} + i\,\mathbf{F}^{(1)}][\mathbf{1} + \mathbf{E}^{(1)} - i\,\mathbf{F}^{(1)}]^{-1}. \tag{11}$$

The onion structure of the theory is already apparent from Eq. (10). The outside factors depend on the zero-order solutions while the inner part depends on the perturbation.

If the coupling between the electronic states is localized around the crossing point as is usually the case, then the elastic wave functions will give a reasonable description of the scattering except near the crossing point. This means that $\mathbf{X}^{(1)}$ is roughly constant except near R_0. By removing $\mathbf{u}^{(0)}$, we have taken care of the asymptotic behavior at small and large R. We have also removed the diagonal elements in the coupling matrix. The next stage is to use the Landau–Zener approximation to get an approximate form for $\mathbf{X}^{(1)}$, which we call $\mathbf{X}^{(L)}$. We can then remove $\mathbf{X}^{(L)}$ from the exact $\mathbf{X}^{(1)}$ in the same way we removed $\mathbf{u}^{(0)}$ from $\mathbf{u}^{(e)}$ to obtain a set of second-level coefficients $\mathbf{X}^{(2)}$. The process can be continued, but, at this stage, the coupling matrix $\mathbf{A}^{(2)}$ is usually small enough that a perturbation solution to the coupled equations is quite accurate.

THE LANDAU–ZENER APPROXIMATION

Having taken care of the parts of the wave function far from the crossing point, we can now simplify the potential near R_0. First, we assume that $\mathbf{u}^{(0)}$ is given by the asymptotic WKB approximation[13]

$$u_{ai}^{(0)} \approx (2/p_i)^{1/2}\sin[\xi_i + \pi/4], \tag{12a}$$

$$u_{bi}^{(0)} \approx (2/p_i)^{1/2}\cos[\xi_i + \pi/4], \tag{12b}$$

where p_i is proportional to the classical radial momentum

$$p_i^2 = k_i^2 - U_{ii}(R) - l_i(l_i+1)/R^2, \tag{13}$$

and the classical phase ξ_i is

$$\xi_i(R) = \int_{R_c}^{R} p_i(R)dR, \tag{14}$$

and R_c is the classical turning point where $p_i(R_c) = 0$. This assumption means that the approximation will not work unless R_0 is outside the classical turning points for both potential-energy curves. Next, we linearize the problem about R_0 so that

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$$\xi_1 - \xi_2 = \Delta\xi = \Delta\xi_0 + \tfrac{1}{2}(p_1' - p_2')(R - R_0)^2$$
$$= \Delta\xi_0 + \tfrac{1}{2}\Delta p' \Delta R^2. \quad (15)$$

We assume that $U_{12} = U_{21}$ and p are both constant. Then the coupling elements in Eq. (7) are given in the Landau–Zener approximation[3] by

$$A^{(L)}_{aa12} = -\frac{U_{12}}{2p}\sin(\Delta\xi), \quad A^{(L)}_{ab12} = \frac{U_{12}}{2p}\cos(\Delta\xi),$$
$$A^{(L)}_{ba12} = -\frac{U_{12}}{2p}\cos(\Delta\xi), \quad A^{(L)}_{bb12} = -\frac{U_{12}}{2p}\sin(\Delta\xi). \quad (16)$$

We have neglected the rapidly oscillating terms involving $\xi_1 + \xi_2$. Each solution of Eq. (7) will give a column of the 4×4 matrix $\mathbf{X}^{(L)}$. We can break the coupling matrix $\mathbf{A}^{(L)}$ into two 2×2 blocks with the transformation

$$\begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} -1 & i & -i & 1 \\ 1 & -i & -i & 1 \\ 1 & i & i & 1 \\ -1 & -i & i & 1 \end{pmatrix}\begin{pmatrix} X_{a1} \\ X_{a2} \\ X_{b1} \\ X_{b2} \end{pmatrix} = \mathbf{T}^{\dagger}\mathbf{X}^{(L)}. \quad (17)$$

Then

$$\mathbf{Y}' = \frac{\Delta U_{12}}{2p}\begin{pmatrix} 0 & -e^{-i\Delta\xi} & 0 & 0 \\ e^{i\Delta\xi} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{-i\Delta\xi} \\ 0 & 0 & -e^{i\Delta\xi} & 0 \end{pmatrix}\mathbf{Y}. \quad (18)$$

Note that the equations for Y_3 and Y_4 are completely decoupled from those of Y_1 and Y_2, and the equations for Y_3 and Y_4 can be obtained from those for Y_1 and Y_2 by substituting $U_{12} \rightarrow -U_{12}$. If we convert the dependent variable from R to t ($R = vt$) and change the phase of $\mathbf{Y}$, we get the coupled equations in time that are usually used in the Landau–Zener approximation.[3] However, the boundary conditions are different as is described below. By using a scattering formulation rather than a time-dependent one, we keep the proper phase and use the correct boundary conditions.

The coupled differential equations for $\mathbf{Y}$ in Eq. (18) are solved in the Appendix. The solutions are

$$Y_1 = A_1 f - A_2 g^*, \quad (19a)$$
$$Y_2 = A_1 g + A_2 f^*, \quad (19b)$$
$$Y_3 = A_3 f + A_4 g^*, \quad (19c)$$
$$Y_4 = -A_3 g + A_4 f^*, \quad (19d)$$

where $x = \frac{1}{2}\Delta p' \Delta R^2$ and the functions $f(x)$ and $g(x)$ are given by

$$f(x) = M(-i\beta, 1/2, -ix)$$
$$\sim [\cosh(\pi\beta)]^{1/2} e^{-\pi|\beta|/2}\exp(iz_1)$$
$$- i[\sinh|\pi\beta|]^{1/2} e^{-\pi|\beta|/2}$$
$$\times \exp(iz_2 - i\Delta\xi_0)\left(\frac{\beta}{x}\right)^{1/2} e^{-ix}, \quad (20a)$$

$$g(x) = \frac{U_{12}}{2p}\Delta R \exp(-i\Delta\xi_0) M(1/2 + i\beta, 3/2, ix)$$
$$\sim [\sinh|\pi\beta|]^{1/2} e^{-\pi|\beta|/2}\frac{\Delta R}{|\Delta R|}\exp(-iz_2)$$
$$- i\frac{\Delta R}{|\Delta R|}[\cosh(\pi\beta)]^{1/2} e^{-\pi|\beta|/2}$$
$$\times \exp(iz_1 + i\Delta\xi_0)\left(\frac{\beta}{x}\right)^{1/2} e^{ix}, \quad (20b)$$

where M is the confluent hypergeometric function,[14] $\beta = U_{12}^2/(8p^2\Delta p')$, and z_1 and z_2 are given by Eq. (A16). Figure 1 shows a plot of $f(x)$ and $g(x)$ and the asymptotic forms given in Eq. (20) for $\beta = 0.2$. The parameter β governs the strength of the coupling; $\beta = 0$ is the diabatic limit where there is no coupling between the diabatic curves. The limit $\beta = \infty$ is the adiabatic limit. In both limits the probability for inelastic scattering is zero. The maximum probability occurs at $\beta = (\ln 2)/4\pi = 0.0552$ (see below). Both functions show a rapid change in the range of $x = 0$–4 followed by a slowly oscillating change which persists indefinitely. Since $x = \Delta\xi - \Delta\xi_0$, this initial change is over within a few deBroglie wavelengths of the crossing point.

We can cast Eq. (19) in a convenient matrix form,

$$\mathbf{Y}(R) = \mathbf{G}(R)\mathbf{A}, \quad (21)$$

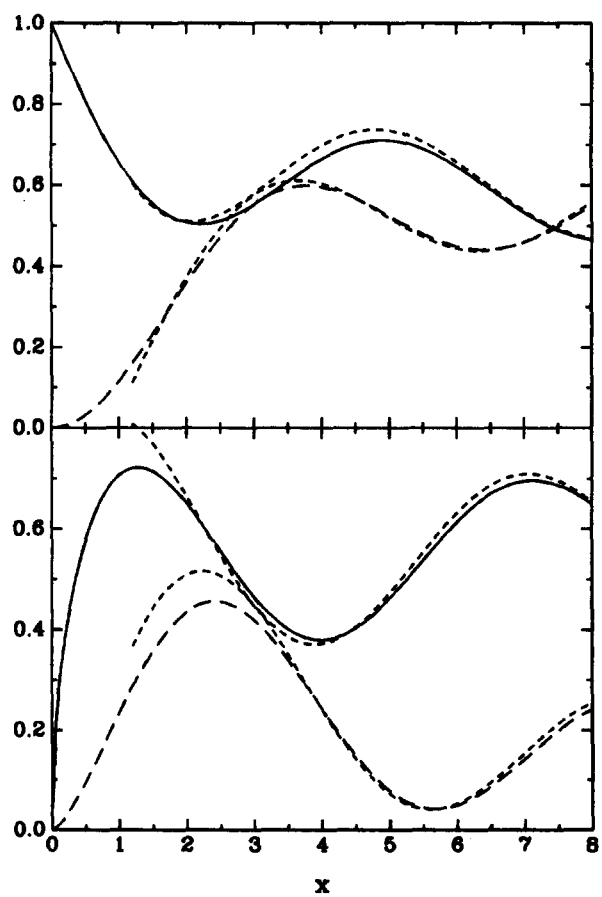

FIG. 1. The top panel shows the function $f(x)$ given in Eq. (20a) and the bottom panel the function $g(x)$ given in Eq. (20b) for $\beta = 0.2$. The solid lines give the real component while the long dashes give the imaginary component. The asymptotic values given by Eq. (30) are shown by short dashes.

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where

$$\mathbf{G}(R)=\begin{pmatrix} f & -g^* & 0 & 0 \\ g & f^* & 0 & 0 \\ 0 & 0 & f & g^* \\ 0 & 0 & -g & f^* \end{pmatrix}. \tag{22}$$

This formulation allows us to separate the wave functions from the boundary conditions in a convenient fashion. To obtain the scattering matrix we need to examine the behavior at large and small R. Unfortunately, a glance at Eq. (20) shows that f and g do not become constant for large ΔR but instead oscillate slowly. This comes from the assumption that $U_{12}(R)$ is constant. In the time-dependent form usually used in the Landau–Zener approximation we can choose A_1 and A_2 so that either Y_1 or Y_2 is zero at large negative ΔR.[3] In the scattering problem, however, we must have $X_{bi}^{(L)}=0$, and this requires that $Y_1=-Y_2$ at large negative ΔR. This cannot be done for all R. As a compromise, we evaluate the boundary conditions as some large but finite ΔR_1. We do not need rigorous boundary conditions on $\mathbf{X}^{(L)}$ because we can impose them on the final $\mathbf{X}^{(2)}$. Because $\mathbf{X}^{(L)}$ oscillates slowly at large ΔR, the coefficients $\mathbf{X}^{(2)}$ must also oscillate. Using only the first asymptotic term in Eq. (20) gives the asymptotic form

$$\mathbf{G}(\pm\Delta R_1)=\mathbf{G}_{\pm}=\begin{pmatrix} C & \mp S & 0 & 0 \\ \pm S^* & C^* & 0 & 0 \\ 0 & 0 & C & \pm S \\ 0 & 0 & \mp S^* & C^* \end{pmatrix}, \tag{23}$$

where the top signs refer to positive ΔR_1 and the bottom signs to negative ΔR_1:

$$C=[\cosh|\pi\beta|]^{1/2}e^{-\pi|\beta|/2}\exp[iz_1(\Delta R_1)], \tag{24a}$$

$$S=[\sinh|\pi\beta|]^{1/2}e^{-\pi|\beta|/2}\exp[iz_2(\Delta R_1)]. \tag{24b}$$

We note that the determinant of $\mathbf{G}_{\pm}$ is one and that $\mathbf{G}_{\pm}$ is unitary. The determinant of $\mathbf{G}$ is $D=[|f|^2+|g|^2]^2$. From Eq. (A10) we can see that $D'=0$ so that $\mathbf{G}$ is unitary at all R.

We have four constants of integration A_1–A_4 corresponding to four linearly independent solutions (the four columns) of $\mathbf{X}^{(L)}$. We can choose the A's in a number of ways, but the most convenient way is to set $\mathbf{X}^{(L)}(-\Delta R_1)=1$, the unit matrix. This automatically satisfies the boundary condition that $X_{ba}^{(L)}=0$ as is required to make the well-behaved solutions go to zero at small R. The first two columns of $\mathbf{X}^{(L)}$ then give the well-behaved solution and the last two the singular solution. The first column puts all the intensity into state 1 and the second into state 2:

$$\mathbf{X}^{(1)}(-\Delta R_1)=\mathbf{1}=\mathbf{T}\mathbf{Y}(-\Delta R_1)=\mathbf{T}\mathbf{G}_{-}\mathbf{A}, \tag{25}$$

where the adjoint of $\mathbf{T}$ is given by Eq. (17). Then $\mathbf{A}$ is given by

$$\mathbf{A}=\mathbf{G}_{-}^{\dagger}\mathbf{T}^{\dagger}, \tag{26}$$

$$\mathbf{X}^{(L)}=\mathbf{T}\mathbf{G}\mathbf{G}_{-}^{\dagger}\mathbf{T}^{\dagger}, \tag{27}$$

$$\mathbf{X}^{(L)}(+\Delta R_1)=\mathbf{T}\mathbf{G}_{+}\mathbf{G}_{-}^{\dagger}\mathbf{T}^{\dagger}. \tag{28}$$

Then $\mathbf{X}^{(L)}(\Delta R_1)$ can be obtained by straightforward if messy algebra to give

$$\mathbf{X}^{(L)}(\Delta R_1)=\begin{pmatrix} e^{-2\pi|\beta|} & B\sin(z_1+z_2) & 0 & B\cos(z_1+z_2) \\ -B\sin(z_1+z_2) & e^{-2\pi|\beta|} & B\cos(z_1+z_2) & 0 \\ 0 & -B\cos(z_1+z_2) & e^{-2\pi|\beta|} & B\sin(z_1+z_2) \\ -B\cos(z_1+z_2) & 0 & -B\sin(z_1+z_2) & e^{-2\pi|\beta|} \end{pmatrix}, \tag{29}$$

where

$$B=[1-e^{-4\pi|\beta|}]^{1/2}. \tag{30}$$

THE SECOND PERTURBATION

We can now remove the Landau–Zener solutions from $\mathbf{X}^{(1)}$ to get a double perturbation theory:

$$\mathbf{X}^{(1)}=\mathbf{X}^{(L)}\mathbf{X}^{(2)}. \tag{31}$$

Then

$$\mathbf{X}^{(2)\prime}=\mathbf{X}^{(L)-1}[\mathbf{A}^{(1)}-\mathbf{A}^{(L)}]\mathbf{X}^{(L)} \tag{32}$$

$$=\mathbf{T}\mathbf{G}_{-}\mathbf{G}^{\dagger}\mathbf{T}^{\dagger}[\mathbf{A}^{(1)}-\mathbf{A}^{(L)}]\mathbf{T}\mathbf{G}\mathbf{G}_{-}\mathbf{T}^{\dagger}, \tag{33}$$

where Eq. (27) has been used to obtain $\mathbf{X}^{(L)}$ and its inverse. $\mathbf{A}^{(1)}$ is the exact coupling matrix, and $\mathbf{A}^{(L)}$ is the approximate, linearized form used to obtain the Landau–Zener approximation. If the equations are expressed in the transformed basis, the T's disappear. This may be the more convenient basis set for most cases. The boundary conditions are such that $\mathbf{X}_{ba}^{(2)}(-\Delta R_1)=0$ to make sure that $\mathbf{X}_{ba}^{(1)}(-\Delta R_1)=0$. We can also use $\mathbf{X}_{aa}^{(2)}=\mathbf{1}$. As discussed above, $\mathbf{X}^{(L)}$ is not properly behaved at small R. If U_{12} goes to zero away from the crossing point, then $\mathbf{X}^{(1)}$ will be constant, but, since $\mathbf{X}^{(L)}$ oscillates slowly, $\mathbf{X}^{(2)}$ must also oscillate. At large positive ΔR, we have, in analogy to Eq. (9),

$$\mathbf{X}_{aa}^{(2)}\sim[\mathbf{1}+\mathbf{E}^{(2)}],\quad \mathbf{X}_{ba}^{(2)}\sim\mathbf{F}^{(2)}. \tag{34}$$

We then have

$$[\mathbf{1}+\mathbf{E}^{(1)}]=\mathbf{X}_{aa}^{(L)}(\Delta R_1)[\mathbf{1}+\mathbf{E}^{(2)}]+\mathbf{X}_{ab}^{(L)}(\Delta R_1)\mathbf{F}^{(2)}, \tag{35a}$$

$$\mathbf{F}^{(1)}=\mathbf{X}_{ba}^{(L)}(\Delta R_1)[\mathbf{1}+\mathbf{E}^{(2)}]+\mathbf{X}_{bb}^{(L)}(\Delta R_1)\mathbf{F}^{(2)}. \tag{35b}$$

The four quadrants of $\mathbf{X}^{(L)}$ can be obtained from Eq. (29). Then

$$\mathbf{S}^{(1)}=\{[\mathbf{X}_{aa}^{(L)}+i\,\mathbf{X}_{ba}^{(L)}][\mathbf{1}+\mathbf{E}^{(2)}]+[\mathbf{X}_{ab}^{(L)}+i\,\mathbf{X}_{bb}^{(L)}]\mathbf{F}^{(2)}\}$$
$$\times\{[\mathbf{X}_{aa}^{(L)}-i\,\mathbf{X}_{ba}^{(L)}][\mathbf{1}+\mathbf{E}^{(2)}]+[\mathbf{X}_{ab}^{(L)}-i\,\mathbf{X}_{bb}^{(L)}]\mathbf{F}^{(2)}\}^{-1}. \tag{36}$$

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From Eq. (29) we see that

$$\mathbf{X}^{(L)}_{\pm} = \mathbf{X}^{(L)}_{aa} \pm i\,\mathbf{X}^{(L)}_{ba} = \pm i\,[\mathbf{X}^{(L)}_{ab} \pm i\,\mathbf{X}^{(L)}_{bb}]$$
$$= \begin{pmatrix} e^{-2\pi|\beta|} & \mp iB\exp(\pm iz_1 \pm iz_2) \\ \mp iB\exp(\mp iz_1 \mp iz_2) & e^{-2\pi|\beta|} \end{pmatrix}, \quad (37)$$

where B is given by Eq. (30). Then

$$\mathbf{S}^{(1)} = \mathbf{X}^{(L)}_{+}[\mathbf{1}+\mathbf{E}^{(2)} + i\,\mathbf{F}^{(2)}][\mathbf{1} + \mathbf{E}^{(2)} - i\,\mathbf{F}^{(2)}]^{-1}\mathbf{X}^{(L)-1}_{-} \quad (38)$$
$$= \mathbf{X}^{(L)}_{+}\mathbf{S}^{(2)}\tilde{\mathbf{X}}^{(L)}_{+}, \quad (39)$$

where $\tilde{\mathbf{X}}^{(L)}_{+}$ is the transpose of $\mathbf{X}^{(L)}_{+}$. We note that $\mathbf{X}^{(L)}_{\pm}$ is unitary so that the full S matrix is unitary.

A special case of Eq. (39) is the Landau–Zener approximation itself. It is obtained, of course, by setting $\mathbf{A}^{(1)} = \mathbf{A}^{(L)}$ so that $\mathbf{X}^{(2)} = \mathbf{1} = \mathbf{S}^{(2)}$. Then

$$S^{(1)} = \begin{pmatrix} e^{-4\pi|\beta|} - B^2\exp(2iz_1 + 2iz_2) & -2iB\,e^{-2\pi|\beta|}\cos(z_1+z_2) \\ -2iB\,e^{-2\pi|\beta|}\cos(z_1+z_2) & e^{-4\pi|\beta|} - B^2\exp(-2iz_1 - 2iz_2) \end{pmatrix}. \quad (40)$$

The probability for curve crossing is

$$P_{12} = P_{21} = 4\,e^{-4\pi|\beta|}[1 - e^{-4\pi|\beta|}]\cos^2(z_1+z_2). \quad (41)$$

To make the connection with the usual Landau–Zener formula we note that: $R = vt$, $p = \mu v/\hbar$, $\Delta p' = -(2p)^{-1}\partial(U_{11} - U_{22})/\partial R = -(\hbar v^2)^{-1}\partial\Delta V/\partial t$. Using Eq. (A3) for β gives

$$|\beta| = \frac{\Delta V_{12}^2}{2\hbar|\partial\Delta V/\partial t|} = \gamma/2\pi, \quad (42)$$

where γ is the usual Landau–Zener coupling parameter.[3] The probability obtained from the usual time-dependent formulation is[3]

$$P_{LZ} = 2\,e^{-2\gamma}[1 - e^{-2\gamma}] = 2\,e^{-4\pi|\beta|}[1 - e^{-4\pi|\beta|}]. \quad (43)$$

Equations (41) and (43) differ by a factor of $2\cos^2(z_1+z_2)$. This is not surprising since the time-dependent formulation neglects the interference between the incoming and outgoing branches of the trajectory. The $\cos^2$ factor will average out to give 1/2, and the two agree on the average as is true of many classical–semiclassical comparisons.

We can cast Eq. (39) into the form of a phase shift. Because $\mathbf{X}^{(L)}_{+}$ is unitary, we can set $\mathbf{X}^{(L)}_{+} = \exp[i\boldsymbol{\Delta\eta}^{(L)}]$, where $\boldsymbol{\Delta\eta}^{(L)}$ is a Hermitian matrix; $\boldsymbol{\Delta\eta}^{(L)}$ can be found by diagonalizing $\mathbf{X}^{(L)}_{+}$. The eigenvalues $\mathbf{X}^{(L)}_{+}$ are easily found to be $e^{-2\pi|\beta|} \pm iB$. The eigenvalues of $\boldsymbol{\Delta\eta}^{(L)}$ are then given by $\pm\arctan[B/e^{-2\pi|\beta|}] = \pm\arcsin B$. We can then transform back to the original representation to get

$$\boldsymbol{\Delta\eta}^{(L)} = \begin{pmatrix} 0 & -\arcsin B\exp(iz_1 + iz_2) \\ -\arcsin B\exp(-iz_1 - iz_2) & 0 \end{pmatrix}. \quad (44)$$

We can express $S^{(2)}$ in terms of a phase-shift matrix to get

$$\mathbf{S}^{(e)} = \exp[i\boldsymbol{\eta}^{(0)}]\exp[i\boldsymbol{\Delta\eta}^{(L)}]\exp[2i\boldsymbol{\Delta\eta}^{(2)}]$$
$$\times\exp[i\tilde{\boldsymbol{\Delta}}\tilde{\boldsymbol{\eta}}^{(L)}]\exp[i\boldsymbol{\eta}^{(0)}]. \quad (45)$$

We can solve Eq. (33) by using an exponential perturbation theory to get $\boldsymbol{\Delta\eta}^{(2)}$. This gives[10]

$$\boldsymbol{\Delta\eta}^{(2)} = \mathbf{F}^{(2)} = \int_{-\Delta R_i}^{\Delta R_i}\mathbf{A}^{(2)}(R)\,dR. \quad (46)$$

The use of an exponential perturbation theory preserves the unitarity of the S matrix. It has also been found in the case of rotationally and vibrationally inelastic scattering that the quadratic and higher-order terms in the expansion of the exponential approximate the terms in a higher-order perturbation theory so that the exponential perturbation theory is very much more accurate than a straight first-order perturbation theory such as the distorted-wave approximation.[15]

DISCUSSION

We have used a double perturbation theory to simplify the problem of two-state electronically inelastic scattering. First, we remove the elastic scattering from the exact wave functions and then the Landau–Zener approximation. What is left is usually small and can be solved by using an exponential perturbation theory. As explained in the Introduction, this is a prototype problem, and we are really interested in many other, more complicated problems of which this is a component part. If we have many curve crossings which are not too close together, we can make a composite, multistate $\mathbf{X}^{(L)}$ by using the Landau–Zener approximation for each crossing separately. If the Landau–Zener wave functions nearly reach their asymptotic forms between the crossings, this method should be accurate. In the case of photodissociation, we can use the same basic theory. However, we need to change the boundary conditions. We are currently developing a semiclassical treatment of molecular charge exchange.[9] Here the electronic curve crossing is complicated by the huge number of vibrational and rotational states which must be considered along with the electronic states. Clearly, a numerical solution of the exact coupled equations is out of the question. The perturbation theory for the electronic part fits in nicely with the very similar treatment of the rotation and vibration.

APPENDIX: SOLUTION OF THE LANDAU–ZENER EQUATIONS

The solution of the coupled differential equations for $\mathbf{Y}$ is cumbersome but straightforward. If we change the dependent variable to $x = \frac{1}{2}\Delta p'\Delta R^2$. Then

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$$\begin{pmatrix} Y_1' \\ Y_2' \end{pmatrix} = \frac{U_{12}}{2p(2\Delta p' x)^{1/2}} \begin{pmatrix} 0 & -\exp[-i\Delta\xi_0 - ix] \\ \exp[i\Delta\xi_0 + ix] & 0 \end{pmatrix} \begin{pmatrix} Y_1 \\ Y_2 \end{pmatrix}. \tag{A1}$$

By differentiating Eq. (A1) and substituting we get

$$Y_1'' + (1/2x + i)Y_1' + (\beta/x)Y_1 = 0, \tag{A2}$$

where

$$\beta = U_{12}^2/[8p^2\Delta p']. \tag{A3}$$

In a similar fashion,

$$Y_2'' + (1/2x - i)Y_2' + (\beta/x)Y_2 = 0. \tag{A4}$$

The substitution $y = -ix$ converts Eq. (A2) into Kummer's differential equation, the solutions of which are the confluent hypergeometric functions[14]

$$Y_1 = A_1 M(-i\beta, 1/2, -ix) + B_1 \Delta R M(1/2 - i\beta, 3/2, -ix). \tag{A5}$$

Similarly, if we let $y = ix$, then

$$Y_2 = A_2 M(i\beta, 1/2, ix) + B_2 \Delta R M(1/2 + i\beta, 3/2, ix). \tag{A6}$$

In the present case the confluent hypergeometric functions are equivalent to the parabolic cylinder (Weber) functions usually used in the Landau–Zener theory.[3] They can be evaluated as a rapidly converging power series.[14] The extra differentiations in deriving Eqs. (A2) and (A4) have introduced two new constants of integration. By substituting Eqs. (A5) and (A6) into the original coupled equations (18) we see that

$$B_1 = -\frac{U_{12}}{2p}\exp(-i\Delta\xi_0)A_2, \tag{A7}$$

$$B_2 = \frac{U_{12}}{2p}\exp(i\Delta\xi_0)A_1. \tag{A8}$$

We define the two functions

$$f(x) = M(-i\beta, 1/2, -ix), \tag{A9a}$$

$$g(x) = \frac{U_{12}}{2p}\Delta R \exp(i\Delta\xi_0) M(1/2 + i\beta, 3/2, ix). \tag{A9b}$$

When ΔR is expressed in terms of x, $g(x)$ is seen to be proportional to $\pm(\beta x)^{1/2}$. From Eq. (18) we see that

$$\frac{df}{dR} = -\frac{\Delta U_{12}}{2p} e^{-i\Delta\xi} g, \tag{A10a}$$

$$\frac{dg}{dR} = \frac{\Delta U_{12}}{2p} e^{i\Delta\xi} f. \tag{A10b}$$

Then we have

$$Y_1 = A_1 f - A_2 g^*, \tag{A11a}$$

$$Y_2 = A_1 g + A_2 f^*, \tag{A11b}$$

$$Y_3 = A_3 f + A_4 g^*, \tag{A11c}$$

$$Y_4 = -A_3 g + A_4 f^*. \tag{A11d}$$

The solutions for Y_3 and Y_4 are obtained by replacing U_{12} by $-U_{12}$, A_1 by A_3, and A_2 by A_4.

For large $\pm\Delta R = (R - R_0)$ we have[14]

$$M(a,b,z) = \frac{\Gamma(b)e^{\pm i\pi a} z^{-a}}{\Gamma(b-a)} + \frac{\Gamma(b)e^z z^{a-b}}{\Gamma(a)}, \tag{A12}$$

where the top sign is used if $-\pi/2 < \arg z < 3\pi/2$, and the lower sign if $-3\pi/2 < \arg z \leqslant -\pi/2$. We must take account of the possibility that $\Delta p'$ can be positive which means that both β and x are positive, or all three can be negative. The case where $\Delta p' \approx 0$ corresponds to the case where the two potential-energy curves are nearly parallel, and here the Landau–Zener approximation breaks down. Also U_{12} can be both positive or negative. Since a is complex, we must evaluate the gamma function of a complex argument. For $b = \frac{1}{2}$, this is[16]

$$\Gamma(1/2 \pm i\beta) = \left[\frac{\pi}{\cosh(\pi\beta)}\right]^{1/2} \exp(\pm i\theta_1). \tag{A13}$$

The argument of the gamma function θ_1 can be evaluated by using a rapidly converging series.[16] Similarly,

$$\Gamma(1 \pm i\beta) = \left[\frac{\pi\beta}{\sinh(\pi\beta)}\right]^{1/2} \exp(\pm i\theta_2). \tag{A14}$$

Putting the pieces together gives

$$f \sim [\cosh(\pi\beta)]^{1/2} e^{-\pi|\beta|/2} \exp(iz_1) - i[\sinh|\pi\beta|]^{1/2} e^{-\pi|\beta|/2} \times \exp(-iz_2 - i\Delta\xi_0)\left(\frac{\beta}{x}\right)^{1/2} e^{-ix}, \tag{A15a}$$

$$g \sim [\sinh|\pi\beta|]^{1/2} e^{-\pi|\beta|/2} \frac{\Delta R}{|\Delta R|} \exp(-iz_2) - i\frac{\Delta R}{|\Delta R|}[\cosh(\pi\beta)]^{1/2} e^{-\pi|\beta|/2} \times \exp(iz_1 + i\Delta\xi_0)\left(\frac{\beta}{x}\right)^{1/2} e^{ix}, \tag{A15b}$$

where

$$z_1 = \beta \ln|x| - \theta_1 \tag{A16a}$$

$$z_2 = \beta \ln|x| - \theta_2 - \Delta\xi_0 - n_1\pi/4 + n_2\pi, \tag{A16b}$$

and where $n_1 = 1$ for $\beta > 0$ ($\Delta p' > 0$), and $n_1 = -1$ for $\beta < 0$; $n_2 = 0$ for $\Delta U_{12} \geqslant 0$, and $n_2 = 1$ for $\Delta U_{12} < 0$. These asymptotic forms are shown in Fig. 1.

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