The Landau−Zener Formula†

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Received: September 24, 2004; In Final Form: March 4, 2005

The Landau−Zener formula for the probability that a nonadiabatic transition has taken place is derived without solving directly the usual second-order differential equation. This is achieved in just a few steps by using contour integration.

Introduction

In 1932, Clarence Zener published the exact solution to a one-dimensional semi-classsical model for nonadiabatic transitions.[1] In the model, nuclear motion is treated classically, in which case, it enters the electronic transition problem as an externally controlled parameter. As Landau had formulated and solved the same model independently (albeit in the perturbative limit and with an error of a factor of 2π),[2] it came to be known as the Landau−Zener model. Despite its limitations, it remains an important example of a nonadiabatic transition. Even in systems for which accurate calculations are possible, application of the Landau−Zener model can provide useful "first estimates" of nonadiabatic transition probabilities. Alternatively, for complex systems, it may offer the only feasible way to obtain transition probabilities.

Figure 1 depicts the model's salient features. It is assumed that nuclear motion is classical, the slopes F_1 and F_2 of the intersecting diabatic potential curves are each constant, and H_{12}, the coupling matrix element in the diabatic basis, is constant. The assumption that F_1, F_2, and H_{12} are each constant takes into account the fact that, for a diabatic basis, these parameters change over distances (say $\sim a_0$) that are large compared to the interaction region near the crossing point, i.e., the region where nearly all of the transitions take place. In the model, interaction ceases far from the crossing point because the energy difference between the diabats exceeds greatly the magnitude of the coupling matrix element.

In the model, the nuclear dynamics are assumed to be 100% classical. There is no quantum mechanics whatsoever insofar as the nuclear degree of freedom is concerned. Nuclear motion enters parametrically. In polyatomic molecules, this results in geometric phase and associated phenomena. Here, it means that electron dynamics result from the perturbation brought about by the imposed nuclear motion.

In the diabatic $\phi_{1,2}$ basis, the wave function is given by

$$\psi = A\,\phi_1 \exp\{-i\int^t E_1\, \mathrm{d}_t\} + B\,\phi_2 \exp\{-i\int^t E_2\, \mathrm{d}t\} \qquad (1)$$

where the convention $\hbar = 1$ has been used and A and B are expansion coefficients. Putting ψ into the time-dependent Schrödinger equation yields the coupled equations

$$\dot{A} = -iH_{12}B \exp\{i\int^t E_{12}\, \mathrm{d}_t\} \qquad (2)$$

$$\dot{B} = -iH_{21}A \exp\{-i\int^t E_{12}\, \mathrm{d}_t\} \qquad (3)$$

where $E_{12} = E_1 - E_2$. Further differentiation of, and substitutions between, eqs 2 and 3 yields the second-order differential equations

$$\ddot{A} - iE_{12}\dot{A} + |H_{12}|^2 A = 0 \qquad (4)$$

$$\ddot{B} + iE_{12}\dot{B} + |H_{12}|^2 B = 0 \qquad (5)$$

Zener introduced the assumption $E_{12} = \alpha t$, where α is a constant. Referring to Figure 1, when the slopes F_1 and F_2 are each constant, the parameter α is equal to $v\,F_{12}$, where v is the magnitude of the relative velocity, which is assumed to remain constant throughout, and $F_{12} = F_1 - F_2$. Note that F_1, F_2, and F_{12} are all negative for the case shown in Figure 1; consequently, $\alpha = -\,v\,|F_{12}|$. It is difficult to visualize the behavior of $\dot{A}$ and $\dot{B}$ by a cursory inspection of eqs 2 and 3. For example, the fact that $\dot{B} \to 0$ as $t \to \infty$ is obvious on physical grounds, because interaction ceases at $t = \infty$, and B cannot sustain a phase oscillation in this limit (i.e., of the form $\exp(i\Omega t)$, lest it becomes a quasi-classical wave function. Thus, any phase oscillation that B might have must become immaterial at sufficiently long times. Equation 3, however, is less transparent on this point, as it contains an increasingly rapid phase oscillation due to the $E_{12} = \alpha t$ variation.

With $E_{12} = \alpha t$, eq 5 becomes

$$\ddot{B} + i\alpha\, t\dot{B} + |H_{12}|^2 B = 0 \qquad (6)$$

which is the equation to be solved. The desired quantity is the value of B after all interaction has ceased, i.e., $B_f \equiv B(t = \infty)$. An important point is that it is not necessary to find $B(t)$ unless this is needed to obtain B_f. Indeed, we shall obtain B_f directly. The derivation is concise and does not require sophisticated mathematics. It is aimed at a broad range of scientists (mainly experimentalists) who use the Landau−Zener model in their research.

Perturbative Limit

First, let us review the perturbative limit, which the exact solution must satisfy as a limiting case. We shall enlist this limiting case later on. The $t \to \infty$ solution of eq 2 is readily obtained for $B \cong 1$. Using $B = 1$ and replacing the integral

† Part of the special issue "George W. Flynn Festschrift".

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10.1021/jp040627u CCC: $30.25
Published on Web 03/24/2005

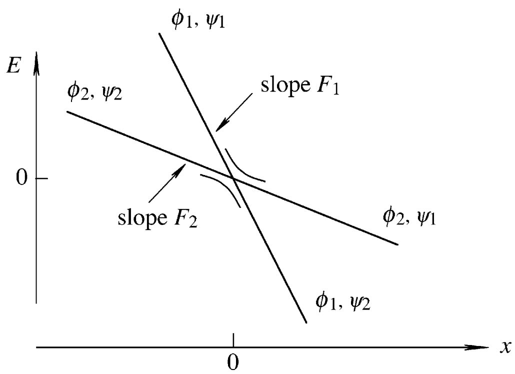

Figure 1. Diabats $\phi_{1,2}$ are coupled by H_{12}. Where interaction is negligible, adiabats $\psi_{1,2}$ are identified with the $\phi_{1,2}$, namely, for $x \ll 0$, $\psi_1 = \phi_1$ and $\psi_2 = \phi_2$, while for $x \gg 0$, $\psi_1 = \phi_2$ and $\psi_2 = \phi_1$.

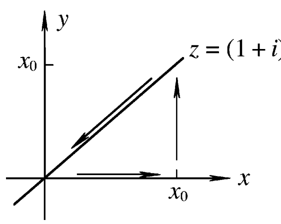

Figure 2. Contour in the complex plane used to integrate $\exp(ix^2)$.

with $\alpha\, t^2/2$ gives $\dot{A} = -i\, H_{12} \exp\{i\alpha\, t^2/2\}$, and with $x = (\alpha/2)^{1/2}\, t$, this yields

$$A_f = -iH_{12}\,[2/\alpha]^{1/2} \int_{-\infty}^{+\infty} \mathrm{d}x \exp(ix^2) \qquad (7)$$

The integral is evaluated by following the contour shown in Figure 2. From $x = 0$ to x_0 on the x-axis, we have $\mathrm{d}z = \mathrm{d}x$ and $\exp\{iz^2\} = \exp\{ix^2\}$. For the vertical path starting at $x = x_0$ and $y = 0$ and ending at $x = x_0$ and $y = x_0$, we have $\mathrm{d}z = i\,\mathrm{d}y$ and $\exp\{iz^2\} = \exp\{i(x_0 + iy)^2\} = \exp\{i(x_0{}^2 - y^2) - 2\,x_0 y\}$. Finally, returning to the origin along the straight line $z = (1 + i)\,x$, we have $\mathrm{d}z = (1 + i\,)\,\mathrm{d}x$ and $\exp\{iz^2\} = \exp\{-2x^2\}$. As no pole is enclosed by the path shown in Figure 2, the above contributions yield

$$\int_0^{x_0} \mathrm{d}x \exp\{ix^2\} = -\int_0^{x_0} i\,\mathrm{d}y \exp\{i(x_0{}^2 - y^2) - 2x_0 y\} - (1 + i\,)\int_{x_0}^{0} \mathrm{d}x \exp\{-2x^2\} \quad (8)$$

In the limit $x_0 \rightarrow \infty$, the integration over y vanishes and the right-hand side of eq 8 becomes $\pi^{1/2}\, e^{i\pi/4}/2$. Using this with eq 7 yields $A_f = H_{12}\,[2\pi/\alpha]^{1/2}\, e^{-i\pi/4}$. This result can also be obtained by substituting $x = x'\sqrt{i}$, with the Gaussian integral giving $\sqrt{\pi}$. Thus, the probability that a nonadiabatic transition has taken place, $P_{na} = 1 - |A_f|^2$, is given by

$$P_{na} = 1 - 2\pi\, \omega_{12}\, \tau_d \qquad (9)$$

where (with $\hbar$ explicit) $\omega_{12} \equiv |H_{12}|/\hbar$ and $\tau_d \equiv |H_{12}|/v|F_{12}|$. The parameter ω_{12} is a characteristic frequency. For example, at $x = 0$ (see Figure 1), it is the Rabi frequency with which the system oscillates between diabats. The parameter τ_d represents the duration of the interaction, which we take to be l/v, where l is an "interaction length" given by $|H_{12}|/|F_{12}|$.

This result is valid for the limit in which the system evolves mainly on a single diabat. In this case, the probability that a nonadiabatic transition has taken place is slightly less than unity. The exact solution of eq 6, when taken to this limit, must yield eq 9, which will be used shortly.

In examining eq 6, we see that, as t approaches infinity, $t\dot{B}$ remains proportional to B, as the second and third terms must cancel one another. In this regime, $\dot{B}$ varies as t^{-1}, and eq 6 can be approximated by the neglect of $\ddot{B}$ (i.e., note that $\ddot{B}$ varies as t^{-2} when $\dot{B}$ varies as t^{-1}). The resulting equation, which is valid as $t \rightarrow \infty$, is

$$i\alpha\, t\dot{B} + |H_{12}|^2 B = 0 \qquad (10)$$

Equation 10 indicates that, at long times, the time dependence of B is due to its phase variation, because $\dot{B}$ is proportional to i. Straightforward integration of eq 10 yields

$$B(t) = B_0 \exp\{-i\, \omega_{12}\, \tau_d \ln(t/t_0)\} \qquad (11)$$

where B_0 and t_0 are arbitrary beginning values of B and t, albeit restricted to the large-t regime. This shows the anticipated phase variation. The large-t advancement of the phase becomes insignificant because of the logarithmic behavior. Differentiation of eq 11 shows that $\ddot{B}/B$ approaches zero as t^{-2}, in accord with our neglect of $\ddot{B}$ in obtaining a solution of eq 6 valid for $t \rightarrow \infty$. The t^{-2} variation of $\ddot{B}/B$ at large t is used later to show that an integral vanishes. Alternatively, in the limit $t \rightarrow 0$, eq 6 indicates that $\ddot{B}(0)/B(0)$ is equal to $-|H_{12}|^2$. This appears later as an integration residue.

Derivation of the $t \rightarrow \infty$ Solution

Zener manipulated eq 6 into the form of the Weber equation, whose asymptotic ($t \rightarrow \infty$) solution yields B_f for an initial condition $B = 1$. Despite the fact that this derivation is tedious and contains a number of steps that are less than transparent, it remains the standard method of solution.[3−6] In this article, it is shown that eq 6 yields B_f in just a few steps that involve contour integrations, obviating the need to solve the second-order differential equation directly.

Dividing eq 6 by B yields an equation that is well behaved with respect to B. In general, B is complex, and its magnitude does not go to zero as a function of t in the complex t-plane. It only approaches zero as the result of one (or more) of the parameters of the model being assigned an extreme value that is unrealistic within the context of the model, e.g., $|H_{12}| \rightarrow \infty$. Multiplying eq 6 by $\mathrm{d}t/t$ and integrating from $-\infty$ to $+\infty$ yields

$$i\alpha \int_1^{B_f} \frac{\mathrm{d}B}{B} = -\,|H_{12}|^2 \int_{-\infty}^{+\infty} \frac{\mathrm{d}t}{t} - \int_{-\infty}^{+\infty} \frac{\mathrm{d}t}{t}\, \ddot{B}(t)/B(t) \quad (12)$$

The second term in eq 6 has become the logarithmic integration of B, i.e., the term on the left-hand side of eq 12. The fact that B_f appears as an integration limit enables it to be obtained without first determining $B(t)$ and then finding the $t \rightarrow \infty$ asymptotic value. Integration of the expression on the left-hand side of eq 12 yields $i\alpha \ln B_f$. The integral in the first term on the right-hand side of eq 12 gives $\pm\, i\pi$, where a semicircular path of infinitesimal radius ϵ passes either counterclockwise or clockwise around $t = 0$, yielding $+\, i\pi$ or $-\, i\pi$, respectively. The choice of sign will be discussed below. Thus, eq 12 becomes

$$\ln B_f = \pm\pi\omega_{12}\tau_d - i\,\frac{\tau_d}{|H_{12}|} \int_{-\infty}^{+\infty} \frac{\mathrm{d}t}{t}\, \ddot{B}(t)/B(t) \qquad (13)$$

where $\alpha = -v|F_{12}|$ has been used, with $\omega_{12} = |H_{12}|$ and $\tau_d = |H_{12}|/v|F_{12}|$.

By closing a contour in the complex t-plane, the integral in eq 13 can be expressed in terms of the $t = 0$ residue and a large$-R$ semicircle in the limit $R \to \infty$, where $R = |t|$. It is assumed that $\ddot{B}(t)/B(t)$, which is well-behaved on the real axis, is analytic in the complex plane, enabling the residue theorem to be applied.[7] On the real axis, $\ddot{B}(t)/B(t)$ varies as t^{-2} as $t \to \infty$, and its higher order time variation can be obtained by iteration, with the result that $\ddot{B}(t)/B(t)$ is expressed as a series of t^{-n} terms, with $n = 2, 4, 6$, etc. Though the phase of $B(t)$ evolves throughout the interaction, neither $\dot{B}(t)/B(t)$ nor $\ddot{B}(t)/B(t)$ has phase variation (i.e., of the form $\exp(i\Omega t)$, ensuring convergence. Namely, any exponential dependence that $B(t)$ might have is absent in the ratios $\dot{B}(t)/B(t)$ and $\ddot{B}(t)/B(t)$. To see this, note that if $B(t) = g(t)\ e^{f(t)}$, then $\dot{B}(t)/B(t) = \dot{g}(t)/g(t) + \dot{f}(t)$. Thus, unless $f(t)$ itself has exponential dependence, which is not the case, $\dot{B}(t)/B(t)$ has no exponential dependence. Extension to $\ddot{B}(t)/B(t)$ is trivial.

The fact that $\ddot{B}(t)/B(t)$ has no exponential dependence enables us to analytically continue this function into the complex plane without dealing with exponential growth when t becomes complex and $|t| \to \infty$. Thus, contours are chosen that follow: (*i*) the real axis from $-R$ to $-\epsilon$; (*ii*) a semicircle of infinitesimal radius ϵ either above or below the real axis; (*iii*) the real axis from $+\epsilon$ to $+R$; and (*iv*) a semicircle of radius R in either the upper or lower half plane, the choice being dictated by the physical situation, as discussed below. The limit as $R \to \infty$ is then taken, and the integral in the second term on the right-hand side of eq 13 is given by

$$\int_{-\infty}^{+\infty} \frac{\mathrm{d}t}{t} \ddot{B}(t)/B(t) = -i|H_{12}|^2 (\pm 2\pi\delta) - \lim_{R\to\infty} \int_R i\ \mathrm{d}\theta\ \ddot{B}(t)/B(t) \quad (14)$$

where the $t = 0$ residue, $\ddot{B}(0)/B(0)$, is equal to $-|H_{12}|^2$, and the fact that $t = R\ e^{i\theta}$ on the R semicircle is used to write $\mathrm{d}t/t = i\ \mathrm{d}\theta$. When the closed contour contains $t = 0$, δ is equal to 1, and when $t = 0$ lies outside the closed contour, no pole is enclosed and $\delta = 0$. Because $\ddot{B}(t)/B(t)$ varies as t^{-2} as $t \to \infty$, the integration over θ vanishes and eq 13 becomes

$$B_f = \exp\{\omega_{12}\ \tau_d\ (\pm\pi \mp 2\pi\delta)\} \quad (15)$$

The signs depend on whether the ϵ semicircle is taken in the counterclockwise (upper sign) or clockwise (lower sign) direction, as discussed below.

Note that complex time is treated consistently in the integrals on the right-hand side of eq 12, as the ϵ semicircles are taken in the same direction in each integral. It is significant that powers of $|H_{12}|$ higher than two are absent in eq 15, as this facilitates a comparison with the perturbative limit. It remains to choose the ϵ and R semicircles, which must be done through consideration of the physical situation.

In the limit $|H_{12}| \to 0$, eq 15 must yield the expression for $|B_f|^2$ given by eq 9, which was derived for this perturbative limit. For example, referring to eq 15, a clockwise ϵ semicircle can be used with a counterclockwise R semicircle, in which case, $\delta = 0$, as indicated in Figure 3. Alternatively, a counterclockwise ϵ semicircle can be used with a counterclockwise R semicircle.

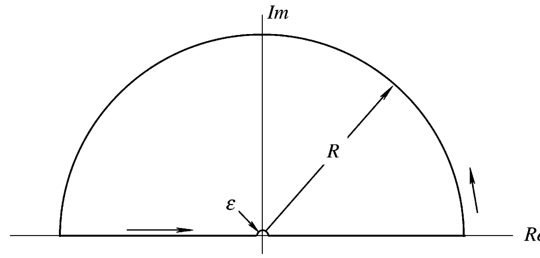

Figure 3. The large and small semicircles are denoted R and ϵ, respectively. Referring to eq 15, $\delta = 0$ because the pole at the origin is not enclosed, and the lower signs are taken because the ϵ semicircle around the origin is clockwise.

Here, $t = 0$ is enclosed, and the $\mp 2\pi\ \delta$ term in eq 15 becomes -2π. In both cases, the expression for B_f given by eq 15, when taken to the perturbative limit $|H_{12}| \to 0$, is in accord with eq 9. Thus, either choice is acceptable, while other contours are incompatible with the perturbative limit, giving incorrect exponential arguments in eq 15.

With the contour chosen to be in accord with the perturbative limit, P_{na} is given by

$$P_{na} = \exp\{-2\pi\ \omega_{12}\ \tau_d\} \quad (16)$$

where $\omega_{12} \equiv |H_{12}|/\hbar$ and $\tau_d \equiv |H_{12}|/v|F_{12}|$. As mentioned earlier, the parameter ω_{12} is the Rabi frequency at the crossing point, and the parameter τ_d is a measure of the duration of the interaction. Equation 16 is the Landau$-$Zener formula for the probability that a nonadiabatic transition has taken place following traversal through the interaction region.

In closing, it is pointed out that this approach can be extended to the more general case of nonconstant slopes F_1 and F_2 and velocity v. Namely, eq 12 is written

$$B_f = \exp\left\{|H_{12}|^2 \int_{-\infty}^{+\infty} \frac{i\ \mathrm{d}t}{\alpha t} + \int_{-\infty}^{+\infty} \frac{i\ \mathrm{d}t}{\alpha t} \frac{\ddot{B}(t)}{B(t)}\right\} \quad (17)$$

where α is no longer constant. For example, if $\alpha^{-1} = \alpha_0^{-1} + f(t)$, where α_0 is constant and $f(t)$ is small, the effect of nonconstant α is obtained in terms of residues of $f(t)$ and $f(t)\ddot{B}(t)/B(t)$.

Acknowledgment. This work was supported by the U.S. Department of Energy, Division of Basic Energy Sciences (DE FG03 85ER13363).

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