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Comment

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Comment on “The Landau–Zener Formula”

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The Landau–Zener formula was derived in 1932 and since then has remained an important tool in molecular dynamics and spectroscopy. In 2005, C. Witting proposed a simple derivation of the formula;[1] it looks very useful and probably will be widely used.

In this Comment, a new derivation of the Landau–Zener formula is proposed. Several shortcomings of Witting's derivation are overcome; now it is really “a single line” derivation.

Let there be two nonperturbed diabatic states, labeled 1 and 2, and the energy difference between them is

$$E_{12}(t) \equiv E_1(t) - E_2(t) = \hbar\alpha t = v(F_1 - F_2)t \tag{1}$$

where v is velocity, t is time, and $F_1 \equiv \mathrm{d}U_1/\mathrm{d}r$ and $F_2 \equiv \mathrm{d}U_2/\mathrm{d}r$ are the slopes of the potential energy curves. We search for the perturbed wave function in the form $A(t)\Psi_1(r, t) + B(t)\Psi_2(r, t)$, where $\Psi_1(r, t)$ and $\Psi_2(r, t)$ are eigenfunctions of the nonperturbed Hamiltonian. The perturbation is given by time-independent off-diagonal matrix elements H_{12} and $|H_{12}| \equiv \hbar\omega_{12}$.

Putting the wave function into the time-dependent Schrödinger equation yields the second-order differential equation

$$\ddot{B}(t) + i\alpha t\dot{B}(t) + \omega_{12}^2 B(t) = 0 \tag{2}$$

where B is a complex function and all other parameters are real. We assume that $|B(-\infty)| = 1$ and the aim is to find $|B(+\infty)| \equiv B_f$. Note that at large t the first term is negligible in comparison with the other two and the solution of eq 2 is $B(t \to \pm\infty) = B(\pm\infty)(\pm t)^{i(\omega_{12}^2/\alpha)}$. From this asymptotic behavior, one obtains

$$(\ddot{B}/B)_{t\to\pm\infty} = -(\omega_{12}^2 + i\alpha)\omega_{12}^2/(\alpha t)^2 \tag{3}$$

From this equation, we shall use only one consequence: $(\ddot{B}/B)_{t\to\pm\infty}$ varies as t^{-2}.

After dividing eq 2 by tB and integrating over t, one obtains

$$\ln B_f = \int_{-\infty}^{\infty} \frac{\dot{B}\,\mathrm{d}t}{B} = -\frac{1}{i\alpha}\int_{-\infty}^{\infty}\left[\frac{\omega_{12}^2 + \ddot{B}/B}{t}\right]\mathrm{d}t \equiv -\frac{I_x}{i\alpha} \tag{4}$$

Here the integral at the right side is denoted as I_x.

From this point, we follow our own logic, which is different from that of Wittig. We will evaluate I_x by expressing it as a part of the contour integral along the contour that goes along the real axis from $t = -T$ to $t = +T$ and then along a semicircle centered at 0 from $t = +T$ to $t = -T$, where $T \to \infty$. From eq 2, it follows that the expression in square brackets has no pole at $t = 0$. Thus, the I_x integral may be calculated from the relation $I_x + I_C = 0$, where I_C is the contour integral that goes along an infinitely large semicircle centered at 0 and placed either in upper or lower parts of the complex plane. The I_C integral may be obtained from the integral of eq 4 by replacing real t by complex variable $z = |z|e^{i\phi}$

$$\begin{aligned} I_C &\equiv \oint\left[\frac{\omega_{12}^2 + \ddot{B}(z)/B(z)}{z}\right]\mathrm{d}z \\ &= i\int_0^{\pm\pi}(\omega_{12}^2 + \ddot{B}/B)_{|z|\to\infty}\,\mathrm{d}\phi \\ &= \pm i\pi\omega_{12}^2 \end{aligned} \tag{5}$$

where the upper and the lower signs correspond to semicircles in the upper and lower part of the complex plane, respectively. According to eq 3, $(\ddot{B}/B)_{|z|\to\infty} \sim z^{-2}$; hence, this term vanishes. Substituting the result from eq 5 in eq 4 gives

$$B_f = \exp(\pm\pi\omega_{12}^2/\alpha) \tag{6}$$

Since B is a wave function coefficient, it should be $|B| \leq 1$; this condition makes one of the signs impossible. Finally, using definitions from eq 1, we obtain the Landau–Zener formula for the probability of nonadiabatic transition P_{LZ}:

$$P_{LZ} = |B_f|^2 = \mathrm{e}^{-2\pi\omega_{12}^2/|\alpha|} = \mathrm{e}^{-2\pi\hbar^2\omega_{12}^2/v|F_1 - F_2|}$$

Surely, the introduction of the time of flight through the interaction region $\tau_d \equiv \omega_{12}/\alpha$ in this expression is very useful for a qualitative understanding of the nature of nonadiabatic transitions. In summary, all present simplifications of the Wittig's approach are based on two notes: the expression in square brackets in eq 4 has no pole at $t = 0$, and the condition $|B| \leq 1$ helps to choose the correct solution in eq 6.

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Notes

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