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Landau-Zener problem for energies close to potential crossing points

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We examine one overlooked in previous investigations aspect of well – known Landau – Zener (LZ) problem, namely, the behavior in the intermediate, i.e. close to a crossing point, energy region, when all four LZ states are coupled and should be taken into account. We calculate the 4×4 connection matrix in this intermediate energy region, possessing the same block structure as the known connection matrices for the tunneling and in the over-barrier regions of the energy, and continously matching those in the corresponding energy regions. Applications of the results may concern the various systems of physics, chemistry or biology, ranging from molecular magnets and glasses to Bose condensed atomic gases.

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Standard textbook Landau–Zener (LZ) theory [1] treats of two linear diabatic potentials $U^{\#} \pm FX$ crossing problem ($X = 0$ is the crossing point). However, in spite of more than half of century history, semiclassical solutions of this problem have been found only in the limits of small or large energies E (we will term these regions as tunneling or over-barrier, respectively), i.e. for

$$|U^{\#} - E| \gg U_{12}; \quad |U^{\#} - E| \ll U_{12}, \tag{1}$$

where U_{12} is inter level interaction which in LZ model does not depend on X. For the intermediate energy region

$$|U^{\#} - E| \leq U_{12}, \tag{2}$$

there known only interpolating relations between exponentially decaying solutions in the tunneling and oscillating solutions in the over-barrier energy regions (see e.g. [2, 3]). Analytical and numerical study of this region (2) is the objective of this paper.

Our approach is motivated by semiclassical instanton approximation [4 – 6]. The idea is to construct two linearly independent continuous (with continuous first derivatives) approximate solutions to the Schrödinger equation, which in the asymptotic region coincide with semiclassic solutions, and in the vicinity of the turning points – with the exact solutions of the so-called comparison equation (i.e. the exact solution of the Schrödinger equation for the chosen appropriately approximate near the turning points potentials). In what follows the Weber equation [7] will be used as the comparison equation, valid in the vicinity of the second order turning points for an anharmonic potential [3, 8, 9]. To justify this choice it is sufficient to note that anharmonic corrections remain semiclassically small (i.e., proportional to higher orders of $\hbar$ series) in the region where the solutions of the comparison equation have to be matched smoothly with the semiclassical solutions. Luckily the analogous approach is valid to treat two diabatic potential crossing point (LZ problem), and the comparison equations for this case are two coupled Weber equations with the indices and arguments determined by the solutions of algebraic characteristic equation.

LZ problem for crossing diabatic potentials is equivalent to the coupled Schrödinger equations which can be transformed by the substitution

$$\Psi = \exp(\kappa X)\Phi \tag{3}$$

into the 4-th order linear differential equation with independent of coordinates coefficients at the derivatives

$$D^4\Phi + 4\kappa D^3\Phi + (6\kappa^2 - 2\alpha\gamma^2)D^2\Phi + \\ + 4(\kappa^3 - \alpha\gamma^2\kappa - \tfrac{1}{2}\gamma^2 f)D\Phi + \\ [\kappa^4 - 2\alpha\gamma^2\kappa^2 - 2\gamma^2 f\kappa + \gamma^4(\alpha^2 - u_{12}^2 - f^2X^2)]\Phi = 0, \tag{4}$$

where $D^n \equiv d^n/dX^n$, and $\gamma \gg 1$ is the dimensionless semiclassical parameter which is determined by the ratio of the characteristic potential scale over the zero oscillation energy, and all other dimensionless appropriately rescaled variables are

$$\alpha = 2\frac{U^{\#} - E}{\gamma\hbar\Omega}, \quad f = \frac{2a_0 F}{\gamma\hbar\Omega}, \quad u_{12} = \frac{2U_{12}}{\gamma\hbar\Omega}, \tag{5}$$

where scale for the energy is given by $\Omega^2 = F^2/mU_{12}$ (m is a mass), and space scale is determined by the characteristic size a_0 of the potential in the vicinity of the crossing point.

The Eq. (4) admits semiclassical solutions by Fedoryuk method [10 – 12] since the coefficients at the n-th order derivatives proportional to γ^{-n}, and all the four asymptotic solutions read as

$$\Psi_j^{(sc)} = (u_{12}^2 + f^2X^2)^{-1/4} \exp\left(\int_0^X \lambda_j(x)dx\right), \quad j = (++, +-, -+, --), \tag{6}$$

where we designated

$$\lambda_j = \lambda_j^0 + u_j, \quad \lambda_j^0 = \pm\sqrt{\gamma(\alpha \pm \sqrt{u_{12}^2 + f^2X^2})},$$

$$\text{and } u_j = \gamma f((\lambda_j^0)^2 - \alpha\gamma)^{-1}.$$

The equation (4), up to anharmonic terms proportional to $X^2D\Phi$, $X^3\Phi$, $X^4\Phi$, can be formally derived by simple manipulations (two sequential differentiations and summations) from the following second order equation

$$D^2\Phi + (a_0 + a_1X + a_2X^2)\Phi = 0, \tag{7}$$

where the coefficients are

$$a_0 = \kappa^2 - \alpha\gamma^2 - \frac{\gamma^2 f}{2\kappa}(1+\delta); \quad a_1 = \gamma^2 f\delta; \quad a_2 = -\gamma^2 f\kappa\delta, \tag{8}$$

where the equation for κ referred in what follows by the characteristic equation is

$$\kappa^4 - \alpha\gamma^2\kappa^2 + \frac{1}{4}\gamma^4u_{12}^2 = -\kappa^4\delta^2(1+2\delta) + R(\kappa,\delta), \tag{9}$$

where

$$R(\kappa,\delta) = (2\kappa^6)^{-1}(1-3\delta)(1+\delta)^{-3}(1 - Q - \sqrt{1-2Q^2});$$

$$Q = 8\delta^2(1+\delta),$$

and

$$\delta = \frac{\gamma^2 f}{4\kappa^3}. \tag{10}$$

The fundamental solutions to (7) read as

$$D_p\left[\pm\left(\frac{\gamma^4 f^2}{\kappa^2}\right)^{1/4}\left(X - \frac{1}{2\kappa}\right)\right], \tag{11}$$

where

$$p = -\frac{1}{2} + \left(\frac{\gamma^4 f^2}{\kappa^2}\right)^{-1/2}\left(a_0 - \frac{a_1^2}{4a_2}\right). \tag{12}$$

In the tunneling and over-barrier regions of energies, where $\delta < 1/4$, these 4 solutions (2 solutions of (11) for two largest modulus roots of the characteristic Eq. (9)) can be separated into two independent pairs (orthogonality of the Weber functions with different indices). Thus one can say that the crossing point is equivalent to two second order turning points with different Stokes constants (see e.g., [13]).

In the tunneling region the two largest modulus roots of (9) are (two other roots are small and do not satisfy semiclassical approach)

$$\kappa = \pm\kappa_0\left(1 \pm \frac{\delta^2}{2}\frac{\kappa_0^2}{2\kappa_0^2 - \alpha\gamma^2}\right); \quad \kappa_0 = \frac{\gamma}{\sqrt{2}}\left(\alpha + \sqrt{\alpha^2 - u_{12}^2}\right)^{1/2}, \tag{13}$$

and the four linearly independent solutions (11) are matched to the semiclassical solutions (5) in the region $\alpha > f|X| > u_{12}$, where the exponent of the wave function can be expanded over small parameter δ

$$\Phi \propto \exp\left(\kappa X + \delta(\kappa X)^2 - \frac{2}{3}\delta^2(\kappa X)^3 + \ldots\right). \tag{14}$$

Since $\kappa|X| \le (4\delta)^{-1}$, the convergent with alternating signs expansion (13) determines the accuracy of the asymptotically smooth transformation. Putting altogether we end up at the conclusion that anharmonic corrections to the Weber functions (11) are small (by other words the parameter δ determines the accuracy of our approximation). The same kind of analysis can be performed in the over-barrier region, where one finds two imaginary largest modulus roots of the characteristic equation (see details in [9]).

More difficult task is to find solutions in the intermediate energy region, where two roots of the characteristic equation are real and two are imaginary ones having the same modulus, i.e. moving upon α variation along a circle with the radius $\gamma\sqrt{u_{12}/2}$. In this case the semiclassical solutions can be presented as certain linear combinations of the comparison equation solutions, and the roots are

$$\kappa_{1,2} \simeq \pm\gamma\sqrt{\frac{u_{12}}{2}}\exp(i\varphi);$$
$$\kappa_{3,4} \simeq \pm i\gamma\sqrt{\frac{u_{12}}{2}}\exp(-i\varphi), \qquad (15)$$

where

$$\tan\varphi = \sqrt{\frac{u_{12}-\alpha}{u_{12}+\alpha}}. \qquad (16)$$

Correspondingly to these roots (16) the arguments and the indices of the Weber functions (11), (12) read as

$$z_1 = z_2 =$$
$$2\kappa_{\rm int}\sqrt{\delta_{\rm int}}\exp(-i\varphi/2)(X-(2\kappa_{\rm int})^{-1}\exp(-i\varphi), \qquad (17)$$

$$z_3 = z_4 = 2\kappa_{\rm int}\sqrt{\delta_{\rm int}}\exp(i\varphi/2)(X-(2\kappa_{\rm int})^{-1}\exp(i\varphi),$$

and

$$p_1 = p_2 - 1 =$$
$$= -1 - \frac{1}{4\delta_{\rm int}}\exp(-i\varphi)(1+2\delta_{\rm int}^2\exp(-2i\varphi)), \qquad (18)$$

$$p_4 = p_3 - 1 = -1 - \frac{1}{4\delta_{\rm int}}\exp(i\varphi)(1+2\delta_{\rm int}^2\exp(2i\varphi)),$$

where

$$\kappa_{\rm int} = \gamma(u_{12}/2)^{1/2}; \quad \delta_{\rm int} = (\gamma^2 f)/(4\kappa_{\rm int}^3). \qquad (19)$$

The semiclassical solutions (6) are matched asymptotically smoothly to the linear combinations of the Weber functions in the region $u_{12} > f|X|$. Since from (17), (18) follow that at large $\delta_{\rm int}$ the indices of the Weber functions are also large, one can use known due to Olver [14, 15] asymptotics of the Weber functions with large arguments and indices

$$D_p(z) \propto \exp\left[-\frac{1}{2}\int\left(z^2 - 4\left(p+\frac{1}{2}\right)\right)^{1/2}dz\right]. \qquad (20)$$

At $z^2 \gg 4|p+(1/2)|$ (20) is reduced to the usual asymptotic expansion of the large argument Weber functions, and in the opposite limit (i.e. in the intermediate region) (20) corresponds to the expansion of the exponent over odd powers of z. We can also find asymptotics to the solutions of (7)

$$\Phi_0 \propto \exp\left(-i\int\sqrt{a_0 + a_1X + a_2X^2}dx\right) \qquad (21)$$

valid at arbitrary values of the parameters a_i ($a_2 = 0$ including).

The fundamental solutions to the comparison equation are the asymptotics for the wave functions in the form (3), namely,

$$\Psi_j^{\pm} = \exp(\kappa X)D_p(\pm z_j(X)), \qquad (22)$$

and

$$\Psi_1^+, \Psi_4^+ \propto \exp(F_1(X)),\ \Psi_2^-, \Psi_3^- \propto \exp(-F_1(X)),$$
$$\Psi_1^-, \Psi_3^- \propto \exp(iF_2(X)),\ \Psi_2^+, \Psi_4^- \propto \exp(-iF_2(X)), \qquad (23)$$

where

$$F_{1,2}(X) =$$
$$= \gamma\sqrt{u_{12}\pm\alpha}(1+\delta_{\rm int})X - \kappa_{\rm int}^2\delta_{\rm int}^2\exp(-2i\varphi)X^2 +$$
$$+\frac{\gamma f^2}{12u_{12}\sqrt{u_{12}\pm\alpha}}\left(1\pm\frac{\alpha}{u_{12}} - \delta_{\rm int}\right)X^3. \qquad (24)$$

The wave functions (23) asymptotically smoothly turn into the semiclassical functions (6). The accuracy of this matching is determined by the anharmonic corrections, i.e. by the parameter $\delta_{\rm int}$ (19), and the Olver asymptotic (20) works even on the boundary $z^2 \simeq 4|p+(1/2)|$. The parameter $\delta_{\rm int}$ is no more small one, when simultaneously

$$|\alpha| \le \left(\frac{f}{\gamma}\right)^{2/3} = \left(\frac{u_{12}}{2\gamma^2}\right)^{1/3}; \quad u_{12} \le \frac{2}{\gamma}. \qquad (25)$$

However the asymptotic matching of the solutions should be performed at small $|X| < \gamma^{-1}$, where the comparison equation (12), and, therefore, the characteristic Eq. (9) are valid, even though upon increasing $\delta_{\rm int}$ the potential becomes more and more anharmonic one. At $\alpha = 0$, and $u_{12} = 0$, the Eq. (9) (with the term $R(\kappa,\delta)$ taking into account) has the doubly degenerate root $\kappa = 0$, i.e. in terms of (12) $a_1 = \pm\gamma^2 f$, $a_2 = 0$. Thus in this limit (12) is equivalent to two decoupled Airy equations, corresponding to the diabatic potentials. These solutions turns smoothly into the semiclassical ones (6), and the anharmonic corrections in the matching region are small over the parameter $\gamma^{-1/2}$.

We conclude that in the both intermediate energy subregions: large κ (i.e.$\propto\gamma$), and small small κ (i.e.

$\propto \sqrt{\gamma}$) the comparison Eq. (12) is reduced to two decoupled equations, Weber or Airy ones, respectively. This simple observation enables us to construct the universal connection matrix for the both intermediate energy region by using Olver asymptotic expansion (21). The four roots (15) distributed over the circle with the radius $\gamma\sqrt{u_{12}/2}$ on the comples plane determine the following combinations of the comparison equation solutions matching the semiclassical solutions (6). Namely

$$\Psi_1^+ + \Psi_4^+ \to \Psi_{++}^{sc};\ \ \Psi_2^- + \Psi_3^- \to \Psi_{+-}^{sc};$$
$$\Psi_1^- + \Psi_3^+ \to \Psi_{-+}^{sc};\ \ \Psi_2^+ + \Psi_4^- \to \Psi_{--}^{sc}, \tag{26}$$

where the superscript sc points out the semiclassical solutions. Combining together the asymptotic expansions for these combinations, we find at the crossing point, the matrix $\hat{U}_c''$ is

$$\hat{U}_c'' = \begin{bmatrix} (\sqrt{2\pi}/\Gamma(q^*))\exp(-2\chi(q^*)) & 0 & 0 & -\exp(-2\pi q_2)\cos(\pi q_1) \\ 0 & (\Gamma(q)/\sqrt{2\pi})\exp(2\chi(q))(1-\exp(-2\pi q_2)\cos^2(\pi q_1)) & -\exp(-2\pi q_2)\cos(\pi q_1) & 0 \\ 0 & \exp(-2\pi q_2)\cos(\pi q_1) & (\sqrt{2\pi}/\Gamma(q))\exp(2\chi(q)) & 0 \\ \exp(-2\pi q_2)\cos(\pi q_1) & 0 & 0 & (\Gamma(q^*)/\sqrt{2\pi})\exp(2\chi(q^*))(1-\exp(-2\pi q_2)\cos^2(\pi q_1)) \end{bmatrix}, \tag{27}$$

where

$$q = q_1 + iq_2;\ q_{1,2} = \frac{\gamma u_{12}\sqrt{u_{12} \pm \alpha}}{4f};\ q^* = q_1 - iq_2, \tag{28}$$

and, besides, we introduce the following abridged notations

$$\chi = \chi_1 + i\chi_2;\ 2\chi_1 = q_1 - \left(q_1 - \frac{1}{2}\right)\ln|q| + \varphi q_2, \tag{29}$$

and analogously

$$2\chi_2 = q_2 - q_2\ln|q| - \varphi\left(q_1 - \frac{1}{2}\right), \tag{30}$$

where φ is defined by (16).

The connection matrix (27) in the intermediate energy region is our main result and the motivation of this publication. This matrix generalizes the results we presented in [3]. It is ready for further applications and to reap the fruits of the result we compute the LZ transition probability $|T|^2$ universally valid for the tunneling, over-barrier and intermediate energy regions (solid line in the Figure). It is instructive to compare our result with the perturbative Landau approach (see e.g. [1]) valid at small coupling constants. In the first order perturbation theory the transition amplitude $A_{LZ}^{(1)}$ reads

$$A_{LZ}^{(1)} = 2iu_{12}\sqrt{\frac{\pi}{\varepsilon}}\mathrm{Ai}(2^{2/3}\varepsilon), \tag{31}$$

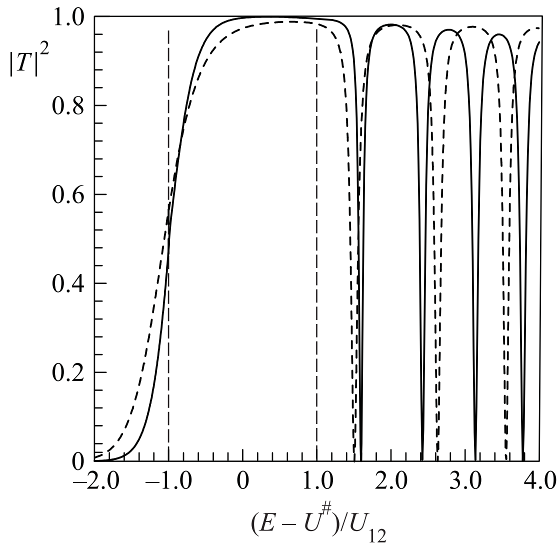
where we designated $\varepsilon = -\alpha f^{-2/3}$, and Ai is the first kind Airy function. All even higher order terms equal zero, and odd terms read as

$$A_{LZ}^{(2n+1)} = (A_{LZ}^{(1)})^{2n+1}. \tag{32}$$

Therefore the series can be easily sum up giving the generalized Landau formula

$$A_{LZ} = A_{LZ}^{(1)}\left[1 + (A_{LZ})^2\right]^{-1}. \tag{33}$$

We show this perturbative solution by the dashed line on the Figure. Note that although the Eq. (32) reproduces the oscillating energy dependence of the LZ transition amplitudes, the equation gives the period of the oscillations which are quite different from those we calculated by our 4×4 connection matrix (27). The difference occurs because the perturbation (say 2) method disregards the contributions from the increasing solutions to the Schrödinger equation, which are relevant in the intermediate energy region.



Energy dependent LZ transition probability: Solid line – the 4×4 connection matrix (27) calculations; Dashed line – the generalized perturbative Landau formula (33)

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1. L. D. Landau and E. M. Lifshits, *Quantum Mechanics (non-relativistic theory)*, Pergamon Press, New York, 1965.
2. C. Zhu, Y. Teranishi, and H. Nakamura, Adv. Chem. Phys. **117**, 127 (2001).
3. V. A. Benderskii, E. V. Vetoshkin, and E. I. Kats, JETP **97**, 232 (2003).
4. A. M. Polyakov, Nucl. Phys. **B129**, 429 (1977).
5. S. Coleman, *Aspects of Symmetry, Cambridge University Press*, Cambridge, 1985.
6. V. A. Benderskii, D. E. Makarov, and C. A. Wight, *Chemical Dynamics at Low Temperatures*, Willey-Interscience, New York, 1994.
7. A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions*, vol.**1** – vol.**3**, McGraw Hill, New York, 1953.
8. V. A. Benderskii, E. V. Vetoshkin, and E. I. Kats, JETP **95**, 645 (2002).
9. V. A. Benderskii, E. V. Vetoshkin, and E. I. Kats, Phys. Rev. **A69**, 062508 (2004).
10. M. V. Fedoryuk, Proc. Russian Acad. of Sci., **158**, 540 (1964).
11. M. V. Fedoryuk, Proc. Russian Acad. of Sci. **162**, 287 (1965).
12. M. V. Fedoryuk, Russian Math. Survey **21**, 1 (1966).
13. J. Heading, *An Introduction to Phase-Integral Methods*, Wiley – Interscience, London, 1962.
14. F. W. J. Olver, J. Res. Nat. Bur. Stand. **63B**, 131 (1959).
15. F. W. J. Olver, *Asymptotics and Special Functions*, Acad. Press., New York, 1974.