METHODOLOGICAL NOTES

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The Majorana formula and the Landau – Zener – Stückelberg treatment of the avoided crossing problem

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Abstract. **The Majorana formula for the probability of spin-flipping in a time-dependent magnetic field which almost vanishes at a certain moment is discussed in connection with the celebrated work by Landau, Zener, and Stückelberg for nonadiabatic dynamics in the avoided crossing situation.**

In 1932, E Majorana published a paper on the dynamics of an arbitrary quantum angular momentum in a time-dependent magnetic field [1]. The paper consists essentially of two parts: the first dealing with the reduction of the general problem to that for the spin 1/2, and the second describing the dynamics of a two-state system in a time-dependent potential. The first part of the paper, the results of which were rederived later [2, 3] and attracted much attention, has been widely commented on (see, e.g., Ref. [4]) and cited in textbooks on quantum mechanics [5]. The second part is not mentioned often, and one of its results, the fate of the spin 1/2 in a magnetic field with one component changing sign linearly with time, has been virtually neglected. However, the analytical solution of the latter problem has much in common with the results of other well-known papers of 1932 dealing with nonadiabatic transitions in atomic collisions for the so-called avoided crossing situation [6 – 9]. The purpose of the present note is to place Majorana's work in the context of other works [6 – 9] which are of paramount importance in the theory of low-energy atomic and molecular collisions. We also take this opportunity to indicate differences in treating the avoided crossing problem by Landau [6, 7], Zener [8], and Stückelberg [9], the differences which, we believe, are not reflected properly in the existing literature on this subject.

The problem of nonadiabatic dynamics for a two-state one-dimensional system in atomic collisions was treated in Refs [6 – 9] under two assumptions. The first concerns the form of the energy matrix in the avoided crossing region, and the second the kinetic energy of the nuclei in this region.

The potential energy 2×2 matrix V (the matrix of the electronic Hamiltonian) in a region of nonadiabatic coupling was taken in the form that contains a single coordinate (interatomic distance) R

$$\mathbf{V}(R) = \begin{pmatrix} E_c - F_2(R - R_c) & a \\ a & E_c - F_1(R - R_c) \end{pmatrix}, \qquad (1)$$

where E_c, R_c, F_1, F_2, and a are free R-independent parameters. The matrix V completely defines the two-state problem in adiabatic approximation, since the eigenvalues of this matrix are identified with the adiabatic potential curves in the avoided crossing region. Note that the form of this matrix is consistent with the pattern of narrow avoided crossing, since away from R_c the spacing between eigenvalues can be made much larger than the minimum spacing at $R = R_c$, which is $2a$.

To go beyond adiabatic approximation, one has to consider the motion of nuclei with a finite, nonzero, velocity. The assumption about collision velocity, adopted in papers [6 – 9], was formulated as the condition that the local kinetic energy of the nuclei at the center of the avoided crossing region, at $R = R_c$, is substantially higher than the adiabatic splitting $2a$:

$$\frac{\mu v_c^2}{2} \gg 2a\,. \qquad (2)$$

Here, μ is the reduced mass of two nuclei, and v_c is the velocity of the relative motion at $R = R_c$. Note that condition (2) means that the avoided crossing region is not located too close to the turning points at which the kinetic energy vanishes. The quantities entering into the interaction matrix in Eqn (1) can be combined with the velocity entering into the inequality in Eqn (2) to form a dimensionless ratio

$$\zeta = \frac{2\pi a^2}{\hbar\,|F_1 - F_2|\,v_c}\,, \qquad (3)$$

which has the sense of the Massey parameter in the avoided crossing region.

L Landau in his first paper [6] calculated the transition probability in the near-sudden limit (NS, under condition $\zeta \ll 1$) using the first-order perturbation approach on an adiabatic basis within the WKB (Wentzel – Kramers – Brillouin) approximation. The transition probability for a double passage of the coupling region takes the form

$$\mathsf{P}_{\mathrm{WKB}}^{\mathrm{L,NS}} = 4\zeta \sin^2(\Phi^{\mathrm{L}})\,, \qquad (4)$$

where Φ^{L} is a certain phase accumulated by the system during its motion from the avoided crossing region to the turning points and back. The inequality (2) translates into the condition $\Phi^{\mathrm{L}} \gg 1$. Once $\mathsf{P}_{\mathrm{WKB}}^{\mathrm{L,NS}}$ is averaged over rapid

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oscillations, it yields the phase-averaged probability $\bar{\mathsf{P}}^{\mathrm{L,NS}}_{\mathrm{WKB}} = 2\zeta$.

In his second paper [7], Landau calculated the transition probability in the near-adiabatic limit (NA, under condition $\zeta \gg 1$) using the perturbation approach on an adiabatic basis and introducing the analytical continuation of adiabatic PES into the complex region of internuclear separations R. The expression for the single-passage transition probability reads

$$P^{\mathrm{L,NA}}_{\mathrm{JWKB}} = C\exp(-\zeta)\,, \tag{5}$$

where the prefactor C is, according to Landau, presumably of the order of unity.

Zener [8] considered a single passage for the time-dependent Hamiltonian

$$\hat{H}(t) = \hat{V}[R(t)]\,,$$

putting

$$R - R_c = v_c t$$

into Eqn (1). He set up two time-dependent coupled equations, which describe the nonadiabatic quantum dynamics of electrons in the avoided crossing region for a uniform classical motion of the nuclei (the so-called semi-classical approximation, SC). Two first-order coupled equations were transformed into one second-order equation, and the latter was solved in terms of parabolic cylinder functions. Using the known asymptotics of these functions (from the 'bible' on transcendental functions [10]), Zener found the accurate transition probability

$$P^{\mathrm{Z}}_{\mathrm{SC}} = \exp(-\zeta)\,. \tag{6}$$

If one ignores Zener's comment [8] that the exponent in formula (6) differs from that in the Landau formula (5) (communicated to him by Rosenkewitsch) by a factor of 2π, one finds that the factor C in Eqn (5) should be unity and that the exponential form of the transition probability in formula (5) is valid for any values of ζ, and not just for $\zeta \gg 1$. Actually, the Zener comment was due to a misunderstanding since Landau used the character h to represent $\hbar$.

Had one gone further and expressed a general phase-averaged double-passage transition probability $\bar{\mathsf{P}}$ through the single-passage transition probability P as

$$\bar{\mathsf{P}} = 2P(1-P)\,, \tag{7}$$

one would have found that the Zener result also reproduces the phase-averaged double-passage Landau formula which follows from Eqn (4). Therefore, it is customary to call the expression for the single-passage transition probability

$$P^{\mathrm{LZ}} = \exp(-\zeta) \tag{8}$$

the Landau – Zener formula.

Stückelberg [9] considered two coupled coordinate-dependent second-order wave equations with the Hamiltonian

$$\hat{H}(R) = \hat{T}(R) + U(R)\,,$$

where $\hat{T}(R)$ is the operator of the kinetic energy of the nuclei, and $\hat{U}(R)$ is an arbitrary matrix potential that is approximated by $\mathbf{V}(R)$ within the avoided crossing region. In using the WKB approximation, he encountered the problem of the analytical continuation of the WKB solution across the so-called Stokes lines. A rather complicated procedure in solving this problem led to the following expression for double-passage transition probability $\mathsf{P}^{\mathrm{St}}_{\mathrm{WKB}}$ in the JWKB approximation:

$$\mathsf{P}^{\mathrm{St}}_{\mathrm{WKB}} = 4\exp(-\zeta)\big[1-\exp(-\zeta)\big]\,\sin^2(\Phi^{\mathrm{St}})\,. \tag{9}$$

Here, Φ^{St} is what is now known as the Stückelberg phase depending on adiabatic potentials in the region between the avoided crossing point and turning points. Stückelberg cited the Landau work [5] and noted that the results in Ref. [5] are only correct for $\zeta \ll 1$ and that Φ^{St} coincides with Φ^{L} in this limit. When formula (9) is averaged over the phase (or over the Stückelberg oscillations) and is then compared to expression (7), one recovers the single-passage Stückelberg transition probability

$$P^{\mathrm{St}} = \exp(-\zeta)\,. \tag{10}$$

We see that the WKB approximation for the transition probability derived by Stückelberg coincides with the accurate semiclassical transition probability found by Zener. This is expected under the condition formulated in Eqn (2).

In a quite different context, a problem similar to the narrow avoided crossing was considered by E Majorana who discussed the dynamic behavior of the spin 1/2 in a time-dependent magnetic field that almost vanishes at a certain moment [1]. The Hamiltonian describing the evolution of the spin in such a situation was taken in the form

$$\hat{H}(t) = \gamma\dot{B}_z t\hat{s}_z + \gamma B_x\hat{s}_x\,, \tag{11}$$

where γ is the gyromagnetic ratio, and $\dot{B}_z$, B_x are time-independent parameters. The time-dependent probability amplitudes of two spin functions were represented as contour integrals taken over the auxiliary variable. In particular, the time-dependent survival amplitude f expressed as a function of the dimensionless time $\tau \propto t$ assumes the form

$$f(\tau) = \frac{\sqrt{k}\exp(-k\pi/8)}{2(1+\mathrm{i})\sqrt{\pi}}\int_L s^{k/4\mathrm{i}-1}\exp\left(\frac{s^2}{8\mathrm{i}}+s\tau\right)\mathrm{d}s\,, \tag{12}$$

where $k = \gamma B_x^2/(\hbar\dot{B}_z)$, L is a properly chosen integration contour, and f is normalized in such a way as to give $|f(\tau)|^2_{\tau\to-\infty} = 1$. Then, the asymptotic survival probability is just $|f(\tau)|^2_{\tau\to\infty}$, and the nonadiabatic transition probability (i.e., the probability of spin-flipping with respect to the asymptotic direction of the magnetic field) becomes $P^{\mathrm{M}} = 1 - |f(\tau)|^2_{\tau\to\infty}$. The explicit expression for P^{M} reads

$$P^{\mathrm{M}} = \exp\left(-\frac{\pi\gamma B_x^2}{\hbar\dot{B}_z}\right). \tag{13}$$

Now, the Hamiltonian in Eqn (11) is similar to that considered by Zener. With proper identifications of the parameters $\gamma B_x = a$ and $\gamma\dot{B}_z = |F_1 - F_2|v_{\mathrm{c}}$, the exponent in formula (13) can be expressed through $P^{\mathrm{M}} = \exp(-\zeta)$, which is the same as P^{LZ} and P^{St}. Two comments will be appropriate in connection with expressions (12) and (13). First, a close inspection of the Majorana integral reveals that it is related to the integral representation of the parabolic cylinder functions; this establishes the connection with the Zener treatment of the problem. Second, formula (12) was derived in Ref. [1] without any reference to the properties of higher transcendental functions; this makes the Majorana treatment of the problem quite appropriate for incorporation into advanced textbooks on quantum mechanics as an exercise problem. Up to now, the standard reference for the accurate nonadiabatic transition probability in the narrow avoided crossing case is the Zener paper, which lacks the conciseness and simplicity normally needed for a textbook. Since $P^{\mathrm{LZ}} = P^{\mathrm{St}} = P^{\mathrm{M}}$, it would be appropriate to call the single-passage transition probability the Landau – Zener – Stückelberg – Majorana formula:

$$P^{\mathrm{LZStM}} = \exp\left(-\frac{2\pi a^2}{\hbar\,|F_1 - F_2|\,v_{\mathrm{c}}}\right). \tag{14}$$

Unfortunately, the Majorana name is never mentioned in connection with the formula (14) though his elegant approach nicely complements the artistic derivation by Landau, straightforward solution by Zener, and sophisticated treatment by Stückelberg. One may say that five papers of 1932 laid the foundation of different methods in the theory of nonadiabatic transitions: expressing the solution as an integral representation, using the analytical continuation of classical dynamical quantities into a complex plane, resorting to well-documented higher transcendental functions, and understanding the role of the Stokes phenomenon in quasiclassical analysis of coupled wave equations. References for the appropriate papers can be found in the review [11] and the collection of papers [12].

We hope that this note will partly rectify historical neglect of the Majorana contribution [1] to the theory of nonadiabatic transitions, which, regrettably, is not properly acknowledged in current reference lists, including those [11, 13] by one of the authors of this paper. Also, our note can be regarded as a small addition to the impressive description of the Majorana contribution to theoretical physics, as presented by Amaldi [14].

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