Damping of states in the problem of intersecting terms

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The effect of damping of states on the transition between quasi-intersecting terms is investigated by solving the Schrödinger equation in the energy representation with a Landau-Zener model Hamiltonian. It is shown that the damping of the states can lead to a substantial change of the time dependence of the reaction amplitudes, in comparison with the case when the damping can be neglected, and also to a change of the effective region of the term interaction. However, the damping of the states does not influence (if the trivial $e^{-2\Gamma t}$ dependence is neglected) the probability of remaining in the initial state and the probability of going over to another state within a time longer than the effective transition time.

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1. INTRODUCTION

The problem of transition between electron terms that have a quasi-intersection point was first considered in the classical papers of Landau[1] and Zener.[2] Various aspects of this problem were subsequently investigated by many workers. A list of papers is contained, e.g., in the review of Nikitin and Ovchinnikova.[3] In all these studies, however, they neglected the influence of the terms on the probability of a transition between them.

The damping of states following a double intersection of the terms was first taken into account, apparently, by Kishinevskiĭ and Parilis,[4] who calculated the probability of the Auger ionization in the collision of a multiply charged ion and a neutral atom. It was assumed in that paper that the damping of the states does not influence the transition probability at the "point" of quasi-intersection of the term. On the other hand, the decrease of the populations of the states during the time t_{12} between two successive quasi-intersections of terms was taken into account via trivial factors of the type $\exp(-2\Gamma t_{12})$. This approach is justified if the characteristic time of the transition between terms is much shorter than the lifetime of the damped state. In the opposite case it is necessary, in general, to take into account the damping of the states in the process of the transition from term to term.

The theory of inelastic transitions in a two-level system, when only one term is assumed to be stationary, was considered by Kogan, Lisitza, and Selidovkin,[5] In particular, by starting from the formalism of a multiplicative integral, they obtained in that paper a general formula (6.12) for the probability of remaining on an undamped term. This formula, as shown by them, leads to a reasonable result if, neglecting the damping, the amplitude of the probability of a transition to another state is equal to zero during the entire time of the process. It appears that the validity of their formula (6.12) is restricted to the class of problems considered in[5] as an example. An attempt to apply this formula to the Landau-Zener problem leads, in our opinion, to an incorrect result: the probability of remaining on an undamped term as the latter crosses an arbitrarily weak damped term remains equal to zero.

The influence of the finite level lifetime on the probability of nonradiative transitions in the presence of quasi-intersection of terms is the subject of a paper by Karas', Moiseev, and Novikov[6]. In that paper, by a method analogous to that used by Stückelberg[7], it is shown that a finite lifetime of the levels can lead to an appreciable change of the probability of a transition between doubly-intersecting terms in comparison with the usual Landau-Zener expression.[1,2] In particular, according to the results of[6], the transition probability can become equal to zero at a certain critical damping parameter. There is, however, an essential (in our opinion) remark concerning the probabilities calculated by them with the aid of wave functions in the WKB approximation. Formulas (6) used in[6], as noted by Stückelberg[7] (p. 400), are valid for real values of the parameters τ, β, and γ. When damping is taken into account, these quantities[1)] as defined in[6] are generally speaking complex. As a result, the general expression (6) obtained by them for the transition probability is incorrect. In particular, it does not describe the change of the populations of the states during the time t_{12} between the points of the quasi-intersection considered by Kinshinevskiĭ and Parilis,[4] although this effect becomes appreciable even in the first approximation in Γ.

This raises the question of correct allowance for the influence of the damping of states in the problem of transitions between terms having a quasi-intersection point. As will be shown below, in this approach the Schrödinger equation in the energy representation with a Landau-Zener model Hamiltonian is solved exactly even when account is taken of the damping of both terms. In addition, this method makes it possible to trace the time variation of the reaction amplitudes, and to determine by the same token the effective region of the term interaction near the quasi-intersection point.

2. FORMULATION OF PROBLEM AND FORMAL SOLUTION

We consider the problem of a transition between electronic terms having a quasi-intersection point. The system of differential equations for the probability amplitudes $c_1(t)$ and $c_2(t)$ of finding an electron respectively in states $|1\rangle$ or $|2\rangle$ corresponding to these terms at the instant of time t, with allowance for the possible damping of the state, is written in the form (cf. formula (4) of Zener's paper[2])

$$
\begin{aligned}
i\dot{c}_1 &= -(\tfrac{1}{2}\Delta Fvt + i\Gamma_1)c_1 + V_{12}c_2,\\
i\dot{c}_2 &= (\tfrac{1}{2}\Delta Fvt - i\Gamma_2)c_2 + V_{21}c_1.
\end{aligned}
\tag{1}
$$

Here F_1 and F_2 are the forces on the corresponding terms; $\Delta F = F_2 - F_1$; $V_{12} = V_{21}^*$ is the matrix element of the Hamiltonian of the interaction leading to the considered transitions; Γ_1 and Γ_2 are the damping constants of states $|1\rangle$ and $|2\rangle$ (in particular, radiative damping); v is the velocity of the relative motion of the colliding atomic particles. The foregoing quantities are assumed, with sufficient accuracy, equal to their values at the term quasi-intersection point $t = 0$. We note, however, that introduction of the damping of the states calls for an additional investigation of such a possibility in comparison with the Landau-Zener problem, when the damping of the states is neglected (see below).

Taking into account the equalities

$$\frac{dD_p(z)}{dz} = pD_{p-1}(z) - \frac{z}{2}D_p(z) = \frac{z}{2}D_p(z) - D_{p+1}(z),$$

where $D_p(z)$ is a parabolic-cylinder function with index p, we can easily verify by direct substitution that the general solution of the system (1) can be represented in the form

$$c_1(t) = \exp\left\{-\frac{\Gamma_1+\Gamma_2}{2}t\right\}\sqrt{-p}[A_1D_{p-1}(z) - A_2D_{p-1}(-z)],$$
$$c_2(t) = \exp\left\{-\frac{\Gamma_1+\Gamma_2}{2}t\right\}[A_1D_p(z) + A_2D_p(-z)], \quad (2)$$
$$p = -iV^2/\Delta Fv, \quad z = (i\Delta Fv)^{1/2}(t - i\Delta\Gamma/\Delta Fv),$$
$$\Delta\Gamma = \Gamma_2 - \Gamma_1, \quad V^2 \equiv V_{12}V_{21}.$$

To determine the integration constants A_1 and A_2 we use the initial conditions, which we choose in the form

$$\lim|c_1(t_0)| = 1, \quad \lim|c_2(t_0)| = 0 \text{ for } t_0 \to -\infty. \quad (3)$$

Using the solution (2), we can show that when the time origin t_0 is chosen to satisfy the condition

$$|t_0| \gg t_{eff},$$
$$t_{eff} = \max\left[\frac{V}{|\Delta Fv|}, \frac{1}{(|\Delta Fv|)^{1/2}}, \frac{|\Delta\Gamma|}{|\Delta Fv|}(1+|p|)\right], \quad (4)$$

the constants A_1 and A_2 depend on t_0 only via a trivial factor of the form $\exp(\Gamma_1 T_0)$:

$$A_1 = |p|^{1/2}\frac{|\Gamma(-p)|}{(2\pi)^{1/2}}\exp(-3i\pi p/4 + \Gamma_1 t_0),$$
$$A_2 = |p|^{1/2}\frac{|\Gamma(-p)|}{(2\pi)^{1/2}}\exp(i\pi p/4 + \Gamma_1 t_0), \quad (5)$$

where $\Gamma(z)$ is the Gamma function of z. This factor is the only consequence of the damping of the initial state $|1\rangle$ from the instant of its "preparation" to the instant $t = 0$ of quasi-intersection of the terms (see (11) and the text that follows).

The quantity t_{eff} in (4) can be interpreted as the effective time of transition of the electron between the considered states. Indeed, as follows from the solution (7) given above, amplitudes $c_1(t)$ and $c_2(t)$ are substantially altered by the interaction V mainly in the vicinity of the quasi-intersection point $|t| \le t_{eff}$. According to (4), allowance for the damping of the states at sufficiently large $|\Delta\Gamma|$ can lead to an appreciable increase of the effective term-interaction time in comparison with t_{eff} in the case when $|\Delta\Gamma|$ can be neglected. On the other hand, as already noted above, for the employed model to be equivalent to the real problem it is necessary that t_{eff} be sufficiently small, in order to be able to confine oneself to the first nonvanishing terms of the expansion of the parameters of the problem in a series in the vicinity of the quasi-intersection point. Thus, the employed approach is limited by the condition

$$\left|\frac{dV}{dt}\right|_{t=0} t_{eff} \ll V, \quad (6)$$

if, as usual (see, e.g.,[8]) the parameter that varies most rapidly with time is an off-diagonal matrix element of the interaction Hamiltonian V. If the damping of the states can be neglected, condition (6) coincides with the well known criterion[9] for the validity of the Landau-Zener model.

Substituting the obtained constants A_1 and A_2 in the general solution (2) and using also the recurrence relation

$$D_p(z) = e^{-i\pi p}D_p(-z) + \frac{(2\pi)^{1/2}}{\Gamma(-p)}e^{-i\pi(p+1)/2}D_{-p-1}(iz),$$

we obtain a solution of the system (1) for the probability amplitudes; this solution satisfies the chosen initial condition (3) and is given by

$$c_1(t) = \exp\left(-\frac{\Gamma_1+\Gamma_2}{2}t + \Gamma_1 t_0 - \frac{\pi V^2}{4|\Delta Fv|}\right)D_{-p}[i(i\Delta Fv)^{1/2}(t - i\Delta\Gamma/\Delta Fv)],$$
$$c_2(t) = \frac{Vi^{1/2}}{(|\Delta Fv|)^{1/2}}\exp\left(-\frac{\Gamma_1+\Gamma_2}{2}t + \Gamma_1 t_0 - \frac{\pi V^2}{4|\Delta Fv|}\right) \quad (7)$$
$$\times D_{-p-1}[i(i\Delta Fv)^{1/2}(t - i\Delta\Gamma/\Delta Fv)].$$

Expressions (7) enable us to calculate the probabilities of processes occurring in the case of quasi-intersection of terms, with allowance for their damping.

3. SOME PARTICULAR CASES

We now obtain the probability $w_1(t)$ that the electron will remain in state $|1\rangle$, and the probability $w_2(t)$ of going over to the state $|2\rangle$ at an arbitrary instant of time $t > 0$, in some limiting cases.

In the particular case when the damping constants are equal, $\Gamma_1 = \Gamma_2 = \Gamma$, we obtain in accord with (7) the following expressions for the probabilities:

$$w_1(t) = \exp[-2\Gamma(t-t_0)]\exp\left(-\frac{\pi V^2}{2|\Delta Fv|}\right)|D_{-p}(i(i\Delta Fv)^{1/2}t)|^2,$$
$$w_2(t) = \exp[-2\Gamma(t-t_0)]\frac{V^2}{|\Delta Fv|}\exp\left(-\frac{\pi V^2}{2|\Delta Fv|}\right) \cdot \quad (8)$$
$$\times|D_{-p-1}(i(i\Delta Fv)^{1/2}t)|^2.$$

It is seen from these expressions that $w_1(t)$ and $w_2(t)$ are equal to the corresponding probabilities calculated without allowance for the damping of the states, multiplied by the probabilities of remaining in these states in purely radiative transitions (the factor $\exp[-2\Gamma(t - t_0)]$).

Another limiting case, when the probabilities $w_1(t)$ and $w_2(t)$ of the considered processes have a relatively simple form, corresponds to large absolute values of the arguments of the D-functions in (7):

$$|z|^2 = |\Delta F|vt^2 + \frac{|\Delta\Gamma|^2}{|\Delta F|v} \gg \max(1+|p|). \quad (9)$$

In this case it is possible to use the asymptotic representations of the D-functions. In particular under condition (9) and if[2)] $t > 0$, the following expressions hold for the probabilities $w_1(t)$ and $w_2(t)$:

$$w_1(t) = \exp[-2\Gamma_1(t-t_0)]\exp\left[-\frac{2V^2}{|\Delta Fv|}\left(\frac{\pi}{2} + \operatorname{arctg}\frac{|\Delta Fv|t}{|\Delta\Gamma|}\right)\right], \quad (10)$$
$$w_2(t) = \exp[-2\Gamma_2 t + 2\Gamma_1 t_0]\left[1 - \exp\left(-\frac{2\pi V^2}{|\Delta Fv|}\right)\right]$$
$$\times\exp\left[-\frac{2V^2}{|\Delta Fv|}\left(\frac{\pi}{2} - \operatorname{arctg}\frac{|\Delta Fv|t}{|\Delta\Gamma|}\right)\right].$$

At a relatively small difference between the damping constants

$$|\Delta\Gamma| \lessdot (|\Delta Fv|)^{1/2}(1+|p|)^{1/2}$$

the inequality (9) is satisfied at values of the time

$$t \gg |\Delta F v|^{-1/2}(1+|p|)^{1/2}.$$

In this case the arctangent in the exponents of (10) can be approximated by $\pi/2$. Then the time dependence in the expressions for the probabilities $w_1(t)$ and $w_2(t)$ remains only in the form of the trivial exponential factors

$$\begin{aligned} w_1(t) &= \exp[-2\Gamma_1(t-t_0)]\exp[-2\pi V^2/|\Delta F v|], \\ w_2(t) &= \exp[-2\Gamma_2 t+2\Gamma_1 t_0][1-\exp(-2\pi V^2/|\Delta F v|)]. \end{aligned} \tag{11}$$

The factor $\exp(2\Gamma_1 t_0)$ is connected with the decay of the initial state by the instant $t = 0$ of the quasi-intersection of the terms, while the factors $\exp(-2\Gamma_1 t)$ and $\exp(-2\Gamma_2 t)$ are connected with the decays of the corresponding states after the instant of the quasi-intersection of the terms.

However, if the values of $|\Delta\Gamma|$ are large enough,

$$|\Delta\Gamma| \gg (|\Delta F v|)^{1/2}(1+|p|)^{1/2},$$

then the inequality (9) is satisfied at all times t. The probabilities $w_1(t)$ and $w_2(t)$ then depend on the ratio $|\Delta F v| t/|\Delta\Gamma|$ (see (10)). If this ratio is large, i.e., $t \gg |\Delta\Gamma|/|\Delta F v|$, then we can use for the functions $w_1(t)$ and $w_2(t)$ the simpler expressions (11). In comparison with the previously considered case, however, that of relatively small $|\Delta\Gamma|$, the asymptotic values of the probabilities (11) are reached much later, and this, as already noted, corresponds to a relative increase of the effective interaction time (see (4)).

The probability $W_2(t)$ of a transition by the instant of time t to the state $|2\rangle$, and the probability $W_1(t)$ of remaining in the state $|1\rangle$ as a result of passing twice through the intersection point can be easily obtained if the effective transition time t_{eff} is small in comparison with the interval between the instant $t = 0$ of term quasi-intersection and the instant $t_{12} > 0$ ($t_{\text{eff}} \ll t_{12}$):

$$\begin{aligned} W_1(t) &= \exp[-2\Gamma_1(t-t_0)][e^{-2\delta}+(1-e^{-\delta})^2\exp\{-2(\Gamma_2-\Gamma_1)t_{12}\}], \\ W_2(t) &= \exp[2\Gamma_1 t_0-2\Gamma_2 t]e^{-\delta}(1-e^{-\delta})[1+\exp\{-2(\Gamma_2-\Gamma_1)t_{12}\}], \\ & t-t_{12} \gg t_{eff}, \quad \delta = 2\pi V^2/|\Delta F v|. \end{aligned} \tag{12}$$

At $\Gamma_1 = \Gamma_2 = 0$ formulas (12) go over into the known formulas of Landau[1] and Zener.[2] If we neglect the damping of the state $|1\rangle$, we obtain a result that agrees with the hypothesis of Kishinevskiĭ and Parilis.[4]

4. CONCLUSION

Thus, the damping of the states has no influence (apart from a trivial dependence of the type $e^{-2\Gamma t}$, due to the decays of the terms) on the probability of remaining in the initial state or on the probability of going over to another state after a time t longer than the effective term interaction time. At times shorter than the effective transition time, the damping of the states leads to a more complicated time dependence of the probabilities than the exponential dependence (see (7)). Then both the dimensions of this region and the character of the time behavior of the probabilities depend essentially on the difference $|\Delta\Gamma|$ between the damping constants.

It follows from the presented results that with increasing $|\Delta\Gamma|$ the effective term interaction times increases, and this can make the Landau-Zener model unsuitable for the description of transitions with large damping-constant differences $|\Delta\Gamma|$. It is necessary in this case to use a more realistic Hamiltonian (see, e.g., the papers of Demkov[10] and Nikitin[11]). We note, however, that in the case of sufficiently strong damping $|\Delta\Gamma| \gtrsim \Delta\Gamma_{cr}$ ($\Delta\Gamma_{cr} = |\Delta F|^2 v^2 t_{12}/V^2$) the transitions cannot be regarded at all as pointlike. For example, at $|\Delta F| \approx 10^8$ eV/cm, $v \approx 10^6$ cm/sec, $t_{12} = 10^{-14}$ sec, and $V \approx 1$ eV, values typical of collisions in the presence of a term quasi-intersection point,[12] the critical values is $\Delta\Gamma_{cr} \approx 10^{14}$ sec^{-1}.

Let us consider in conclusion certain concrete physical processes in which it may be necessary to take into account the damping of the quasi-intersecting terms. It is known that the charge exchange of an ion with a neutral atom, which is the reaction of interest, e.g., in connection with attempts to produce laser sources for the far ultraviolet and x-ray regions of the spectrum, is usually considered in the Landau-Zener approximation.[8] For ions with charge $z \sim 10$, however, the radiative-damping constant of the term with which charge exchange is possible has the value $\Gamma \sim 10^{12}$ sec^{-1}. Therefore, as follows from the results of Sec. 3, at relative velocities $v \lesssim 10^5$ cm/sec of the atom and ion the effective charge-exchange time exceeds the corresponding value calculated in accord with the Landau-Zener theory, and also exceeds the decay time of the excited state produced as a result of the charge exchange. This effect can influence the line width of the spontaneous emission accompanying the charge exchange.

On the other hand, when a multiply-charged ion comes close to a neutral atom, decay of the quasi-molecule via the Auger effect is possible.[4] This Auger-ionization process, which results in production of an electron and two ions in the final state, is essential in the study of ionization phenomena accompanied by hard x-ray emission in gases. The damping constant due to the Auger transitions can reach values $\Gamma \sim 10^{14} - 10^{15}$ sec^{-1}.[14] The Auger-electron spectrum, which yields important information on the ionization mechanism, depends here essentially on the term damping even at relative velocities $v \lesssim 10^7$ cm/sec of the ion and atom, and at velocities $v \lesssim 10^6$ cm/sec allowance for the damping makes the Landau-Zener model unsuitable, since the assumption that the interaction is pointlike no longer holds.

Allowance for the damping of the states may be essential for a plasma, where the finite lifetime is due to collisions. In addition, the problem considered has a bearing on a large number of effects of disintegration of metastable states located near other states, damped, in the presence of an external field.[5]

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1)In the absence of damping, the quantities τ, β, and γ have the meaning of phase factors.

2)The time region $t<0$ corresponds to points of the complex z plane on the other side of the Stokes line, where another asymptotic representation of the D-functions must be used.

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