PROBABILITY OF A NON-ADIABATIC TRANSITION NEAR THE TURNING POINT

V. K. BYKHOVSKIĬ, E. E. NIKITIN, and M. Ya. OVCHINNIKOVA

Institute of Chemical Physics, Academy of Sciences, U.S.S.R.

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It is demonstrated that the quasi-classical and the quantum-mechanical treatment are completely equivalent for the case of two linear electron terms connected by a constant interaction matrix element. Formulae are obtained for the transition probability in various limiting cases. Their validity embraces the greater part of the range of the two characteristic parameters, ϵ and b. In the intermediate range of ϵ and b the system of coupled wave equations is integrated numerically.

THE evaluation of the probability of a non-adiabatic transition in the vicinity of quasi-crossing points of electronic terms is the fundamental problem in the calculation of the cross section of inelastic atomic collisions, of the rate of radiationless transitions in complicated molecules, etc. In the general case the problem reduces to the solution of a system of coupled second order wave equations for the wave function describing the nuclear motion. At the present time even for only two coupled levels a general solution has been obtained only for the case where the distance between the point of the term crossing and the turning point is sufficiently large.[1] This condition is frequently violated for slow atomic collisions. It is thus necessary to find the transition probability for the case where the turning point and the crossing point are close together.

The simplest way to perform such a calculation is in the classical approximation.[2] There the motion of the nuclei is treated classically by introducing a kind of mean trajectory whose parameters correspond to a certain average of the characteristics of the two considered electronic terms. In the following we shall consider a situation arising typically in slow atomic collisions, viz., the case of two linear terms which cross in zero-order approximation and whose interaction is given by a constant matrix element. The given one-dimensional treatment can immediately be generalized to the case of three-dimensional scattering in a central field.

1. CONNECTION BETWEEN THE CLASSICAL APPROXIMATION AND THE EXACT QUANTUM MECHANICAL SOLUTION FOR TWO STATES

The system of coupled wave equations has the form

$$\frac{\hbar^2}{2m}\frac{d^2u_1}{dx^2} + (E + F_1x)\,u_1 + au_2 = 0,$$
$$\frac{\hbar^2}{2m}\frac{d^2u_2}{dx^2} + (E + F_2x)\,u_2 + au_1 = 0. \qquad (1)$$

Here a is the interaction matrix element, F_1 and F_2 are the forces at the point x = 0 where the terms cross in zero order approximation, and $E \equiv mv^2/2$ is the energy measured from that point. For the following it is convenient to introduce the mean force

$$F \equiv (F_1F_2)^{1/2}, \qquad (2)$$

and also the quantities

$$E' \equiv 2mE/\hbar^2, \quad F_i' \equiv 2mF_i/\hbar^2, \quad a' \equiv 2ma/\hbar^2. \qquad (3)$$

We try to obtain a solution of (1) in terms of the following contour integral:

$$u_i(x) = \frac{1}{\sqrt{\pi}}\int_l \exp\left[ikx - i\frac{F_1' + F_2'}{2F_1'F_2'}\left(\frac{k^3}{3} - E'k\right)\right] \times \frac{1}{\sqrt{F_i'}}\varphi_i(k)\,dk, \qquad (4)$$

where l is a contour such that at its endpoints the integrand vanishes. The functions $\varphi_i(k)$ then have

to obey the equation

$$i\frac{d\varphi_1}{dk}=\frac{\Delta F'}{2F_1'F_2'}(k^2-E')\varphi_1-\frac{a'}{(F_1'F_2')^{1/2}}\varphi_2,$$

$$i\frac{d\varphi_2}{dk}=-\frac{\Delta F'}{2F_1'F_2'}(k^2-E')\varphi_2-\frac{a'}{(F_1'F_2')^{1/2}}\varphi_1,$$

$$\Delta F'\equiv F_2'-F_1'>0. \qquad (5)$$

The adiabatic approximation for the functions $\varphi_i(k)$ is obtained from this system after diagonalization of the right-hand side of (5). In that approximation no transitions occur between the terms. The nuclei then move on the deformed terms [in the variables z, ϵ and b the adiabatic splitting between the terms equals to the square root in the integrand of (13b)].

Introducing new functions and a new argument by

$$A_i\equiv\varphi_i\exp\left[\pm\frac{1}{2}i(F')^{-2}\Delta F'\left(\frac{k^3}{3}-E'k\right)\right],\quad t\equiv\frac{\hbar}{F}k, \qquad (6)$$

we obtain from (5) the following system of equations, which is identical with the equations of the classical approximation:[2]

$$i\dot{A}_1=-\frac{a}{\hbar}\exp\left[i\int\frac{\Delta Fx(t)}{\hbar}dt\right]A_2,\quad i\dot{A}_2$$

$$=-\frac{a}{\hbar}\exp\left[-i\int\frac{\Delta Fx(t)}{\hbar}dt\right]A_1;$$

$$x(t)=Ft^2/2m-mv^2/2F. \qquad (7)$$

The main terms of the asymptotic expansion of φ_i (or A_i) can be obtained by solving (5) with the assumption $\Delta F|x(t)|\gg a$; this yields

$$\varphi_{1,2}\sim C_{1,2}\exp\left[\mp\frac{1}{2}i(F')^{-2}\Delta F'\left(\frac{k^3}{3}-E'k\right)\right]. \qquad (8)$$

Here the constants C_1 and C_2 depend on the argument of k at which $|k|\to\infty$. Let C_1^+ and C_2^+ be the values of these constants for $k\to+\infty$ and C_1^- and C_2^- their values for $k\to-\infty$. Inserting (8) in (4) and investigating the asymptotic behavior of $u_i(x)$ as $|x|\to\infty$ one finds that the $u_i(x)$ are exponentially damped only if one takes for the contour l a straight line parallel to the real axis and shifted into the lower half-plane of k. Then for $x\to+\infty$ the asymptotic behavior of $u_i(x)$ is determined by the two saddle points $k_0=\pm(F_1'x+E')^{1/2}$ in (3). As $x\to+\infty$ we obtain $|k_0|\to\infty$; the use of the asymptotic solutions (8) instead of the exact functions $\varphi_i(k)$ is thus justified. Evaluation of (4) for $x\to+\infty$ yields

$$u_n(x)\sim iC_n^+(F_n'x)^{-1/4}\exp\left[\frac{2}{3}i(F_n')^{1/2}x^{3/2}+\frac{i\pi}{4}\right]$$

$$+iC_n^-(F_n'x)^{-1/4}\exp\left[-\frac{2}{3}i(F_n')^{1/2}x^{3/2}-\frac{i\pi}{4}\right],\ n=1,2. \qquad (9)$$

The boundary conditions for the non-adiabatic transitions are as follows: unit incoming flux in state 1 and no incoming flux in level 2, i.e., $C_2^-=0$ and $|C_1^-|=1$. One sees from the asymptotic expression (8) that $|C_i^{\mp}|=|\varphi_i(\mp\infty)|$, i.e., $|C_i^{\mp}|^2=|A_i(\mp\infty)|^2$. Thus the system of wave equations (1) together with the indicated boundary conditions is fully equivalent to the system (5) with initial conditions $A_2(-\infty)=0$ and $|A_1(-\infty)|=1$. At the same time the system (5) together with these initial conditions corresponds exactly to the problem of non-adiabatic transitions formulated in the classical approximation.[2] The probability of non-adiabatic transitions is given in any calculation (classical or quantum-mechanical) by $P_{12}=|A_2(+\infty)|^2$.

The validity of the previously used classical approximation[2] was shown only for small values of $\Delta F/F$. It follows from the above discussion that this approximation is valid in fact for arbitrary values of $\Delta F/F$ if one takes the value[1] $(F_1F_2)^{1/2}=F$ for the force which determines the classical trajectory. The only limitation is the requirement that F be real; for $F_1F_2<0$ the system (5) is non-Hermitian. This is not surprising since in this case the non-adiabatic transition corresponds to a transition across a repulsive barrier (or a tunnelling through it), where the analogy with a classical motion is completely lost; the current conservation equation then acquires an entirely different form.

2. FORMULAE FOR THE TRANSITION PROBABILITY IN DIFFERENT LIMITING CASES

The system of equations for the wave functions describing the nuclear motion contains three dimensionless parameters which can be constructed from the four quantities E, F_1, F_2, and a. Nevertheless the transition probability depends only on two dimensionless parameters. It is convenient to choose for these the quantities $\epsilon\equiv E\Delta F/2aF$ and $b\equiv 4a\hbar^{-1}(ma/F\Delta F)^{1/2}$ (these definitions coincide with those of [2]). If we introduce the dimensionless quantity $\tau\equiv 2at/\hbar$, the system (5) takes the form

$$idA_{1,2}/d\tau=\tfrac{1}{2}\exp[\pm i(\tau^3/3b^2-\epsilon\tau)]A_{2,1}. \qquad (10)$$

Let us trace through the way in which we can obtain from (10) the well-known Landau-Zener equation.[4] For that it is necessary that the sta-

[1] This fact was noted by Sayasov[3] for the case of an exponentially small transition probability. However, it must be noted that the expression given in that paper for the pre-exponential factor is valid only for the condition $\delta\gg 1$.

tionary phase points $\tau = \pm b\epsilon^{1/2}$ in the exponent of (10) be sufficiently far apart so that the function $f(\tau) \equiv \tau^2/3b^2 - \epsilon\tau$ can be represented at both places by $\epsilon^{1/2}b^{-1}(\tau \pm b\epsilon^{1/2})$ + const. Then the system (10) is equivalent to a twice repeated transit through the nonadiabaticity region with linear crossing zero-order terms. After averaging over the phase difference $f(b\epsilon^{1/2}) - f(-b\epsilon^{1/2})$ between the two transition points we then obtain

$$P_{12} = 2e^{-2\pi\delta}(1 - e^{-2\pi\delta}), \qquad (11)$$

where $\delta \equiv b/8\epsilon^{1/2}$.

The conditions requiring a large phase difference and a small non-adiabatic region compared with the distance between the points of stationary phase have the form

$$S \equiv b\varepsilon^{2/3} \gg 1, \qquad \varepsilon \gg 1. \qquad (12)$$

These conditions, which determine the region of validity of the Landau-Zener formula, are considerably broader than the conditions contained in the literature.[3] The earlier derivations of the Landau-Zener formula[4,5] assume that the turning points at both levels are far removed from the crossing points. In fact, the formula is valid also in those cases where the conditions for a quasiclassical motion can be violated. In particular, Eq. (11) is valid at all energies ϵ in the case where two zero-order linear terms cross and one of the terms has zero slope.[6]

By solving the system (10) we find for the probability P_{12} at small and large values of the parameter b the expressions[2]

$$P_{12} = \pi b^{4/3}\Phi^2(-\varepsilon b^{2/3}), \quad b \ll 1, \qquad (13a)$$

$$P_{12} = B\exp\left\{2\,\mathrm{Re}\, ib\int_0^{\xi_0}[1 + (z^2 - \varepsilon)^2]^{1/2}dz\right\}, \quad b \gg 1, \qquad (13b)$$

where Φ is the Airy function. In Eq. (13b) the parameter ξ_0 denotes that root of the integrand closest to the real axis. The relation (13a) follows from usual perturbation theory for the expansion in terms of the small parameter b; the expression (13b) is obtained from the adiabatic perturbation theory. The pre-exponential factor B in (13b) should be obtained by solving the system (10) in the vicinity of the zero of the integrand in (13b). In the considered case there are four such points. They are symmetrical about both the real and the imaginary axis of z. The condition $b \gg 1$ indicates in all cases except for $\epsilon \ll 1$ that the phase differences between these points is sufficiently large so that one may neglect interference between the probability amplitudes. Then one does not have to solve the corresponding equations, since an analogous situation obtains in the well known Landau-Zener case, where B = 2.

The computation of B for the cases $b \gg 1$ and $\epsilon \ll -1$ requires special discussion. Physically, it is clear that for large negative ϵ (where the nonadiabatic transition occurs by tunnelling from below the crossing point) both approximation methods (the adiabatic perturbation theory and the perturbation theory for small b) must lead to the same result. For this to be true one has to choose for the coefficient B the value $\pi b/4\epsilon^{1/2}$.[2] This differs from the above value 2 for the following reasons. For $\epsilon \ll -1$ two branch points of the integrand of (13b) approach each other so that it is not possible to neglect the interference between the probability amplitudes. As $\epsilon \to -\infty$ these points move in the z-plane along the imaginary axis; their arguments being then equal to $\pi/2 \pm \arg(i + \epsilon)^{1/2}$.

In order to account fully for the interference one has to solve the system (5) in the vicinity of the indicated zeros.[7] Then the system (5) leads to the second-order equation for the parabolic cylinder functions. Omitting the intermediate steps we give directly the final expression for B, which is valid for $\epsilon \ll -1$ and $|\epsilon|^{1/2}b^{1/3} \gg 1$ (i.e., the conditions where one can limit oneself to the contributions from only one pair of the branch points):

$$B = 2\pi\delta[\Gamma(1 - \delta)]^{-2}\delta^{-2\delta}e^{2\delta}, \quad \delta \equiv b/8|\varepsilon|^{1/2}. \qquad (14)$$

One can neglect the interference if it is permissible to average B over a small energy interval $\Delta\epsilon$ by replacing rapidly oscillating factors by their average values. Transforming the Γ function in (14) by means of the formula $\Gamma(x)\Gamma(1-x) = \pi/\sin\pi x$ we find

$$B = 2\pi^{-1}\delta\sin^2\pi\delta\Gamma^2(\delta)e^{2\delta}\delta^{-2\delta}. \qquad (15)$$

The averaging over the oscillations can be performed if $\delta \gg 1$. When approximating $\Gamma(\delta)$ by its asymptotic expression we find upon averaging that B = 2. In the opposite case, for $\delta \ll 1$, it follows from (14) that $B = 2\pi\delta$. This way we finally obtain these expressions for B:

$$B = 2 \quad \text{for} \quad \varepsilon > 0, \quad b \gg 1 \quad \text{and} \quad \varepsilon \ll -1, \quad b \gg 8|\varepsilon|^{1/2}, \qquad (16a)$$

$$B = \pi b/4|\varepsilon|^{1/2} \quad \text{for} \quad \varepsilon \ll -1, \quad b \ll 8|\varepsilon|^{1/2}. \qquad (16b)$$

It is of interest to point out that the parameter δ coincides with Massey's parameter ξ, which for the present problem is $\xi = 2a\Delta l/\hbar v$, where v is the velocity of the transition through the region of non-adiabaticity, 2a is the minimum in the split-

ting of the terms, and Δl is a characteristic dimension of the region. For linear zero-order terms the terms actually differ considerably from the linear terms over the interval $\Delta l \sim 2a/\Delta F$. From this follows that $\xi \sim a^2/\Delta F\hbar v \equiv \delta$. This way we see that the usual perturbation theory is applicable for the computation of the transition probability at large velocities v independently of whether the transition occurs above the barrier ($a^2/\Delta F\hbar v \ll 1$) or by tunnelling ($a^2/\Delta F\hbar|iv| \ll 1$). We further note that the parameter $S \equiv \epsilon b^{2/3}$ has the meaning of a dimensionless distance (in units of $\hbar$) between the crossing point and the turning point on the average trajectory [in the sense of (2)].

3. THE GENERAL DEPENDENCE OF THE TRANSITION PROBABILITY ON THE ENERGY AND ON THE FORM OF THE ADIABATIC TERMS

The approximate expressions for the transition probability given above allow the evaluation of P_{12} in a very wide region of the variables ϵ and b. In Fig. 1 we have shown the region in the (ϵ, b) plane where the different expressions for P_{12} are applicable:

1. In the region I, for $b \ll 1$, formula (13a) holds (the figure shows the region $b < 1/3$).

2. In the region II, for $S \gg 1$ and $\epsilon \gg 1$, the Landau-Zener formula is applicable. However, it should be kept in mind that for $S \gg 1$ and $\epsilon \sim 1$ the transition probability is exponentially small and can be computed from (13b) with B = 2. Therefore, one can use in the whole region II the Landau-Zener formula with an exponent given by (13b). In the figure this region corresponds to the part in the (ϵ, b) plane where $\epsilon b^{2/3} > 3$. In addition, the

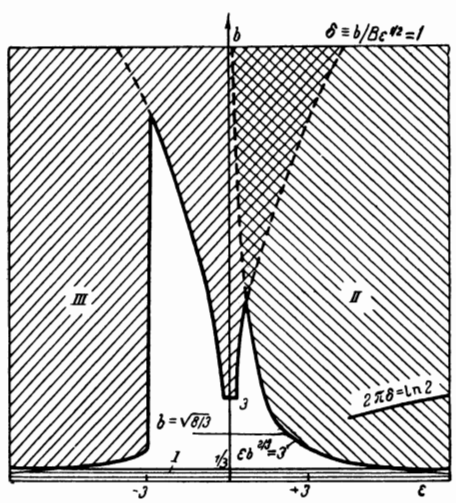

FIG. 1. Regions of applicability of the diverse limiting formulae for the probability of a non-adiabatic transition.

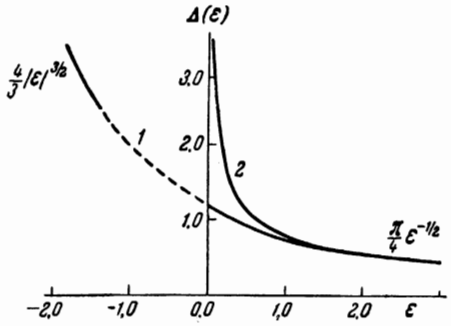

FIG. 2. Influence of the turning point on the probability of a non-adiabatic transition, P_{12}. Curve 1: the function $\Delta(\epsilon)$, which determines the transition probability for the case of exponentially small P_{12} [see Eq. (18)]; Curve 2: result of the Landau-Zener approximation (the turning point is not taken into account).

curve $2\pi\delta = \ln 2$ is also shown; this is the locus for the maximum of P_{12} which then has the value $1/2$.

3. In the region III with $\epsilon \ll 1$, $|S| \gg 1$ the transition probability is exponentially small. It can be computed from (13b) with a pre-exponential factor B [see Eq. (15)], i.e.,

$$P_{12} = B(\varepsilon)\exp(-b\Delta(\varepsilon)), \tag{17}$$

$$\Delta(\varepsilon) \equiv \mathrm{Re}\, 2i\int_0^{\xi_0} [1+(z^2-\varepsilon)^2]^{1/2}dz. \tag{18}$$

The function $\Delta(\epsilon)$ was computed numerically in the region $\epsilon > 0$ in steps of 0.01. It is shown in Fig. 2.

All these regions overlap pairwise: regions I and II overlap for $b \ll 1$ and $\epsilon b^{2/3} \gg 1$, regions II and III for $\epsilon b^{2/3} \gg 1$ and $(b/8\epsilon^{1/2}) \gg 1$, and regions III and I for $\epsilon b^{2/3} \ll -1$ and $b \ll 1$.

In connection with the above discussion it is of interest to report that Dykhne and Chaplik[8] have pointed out that the Landau-Zener formula is correct within the framework of time-dependent perturbation theory for all values of the splitting since for an exponentially small probability this formula coincides with the general expression for the transition probability in the adiabatic approximation.[8] From the above discussions one sees that this result turns out to be valid in the larger region of applicability of the Landau-Zener relation, where account is taken of the influence of the turning points and the motion of the nuclei above the barrier is described quantum-mechanically. For tunnelling non-adiabatic transitions ($\epsilon < 0$) at sufficiently low energy the interference of the probability amplitudes from two zeros of the function $\Delta(\epsilon)$ is always important. Then the pre-exponential factor is smaller than 2 and the generalized

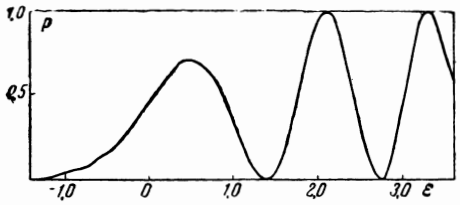

FIG. 3. Transition probability P obtained from numerical integration of the system (5).

Landau-Zener formula (Eq. (15) of [2]) is not applicable.

In the intermediate region ($|\epsilon| \sim 1$, $b \sim 1$) the system (10) was integrated numerically by the Runge-Kutta method. The parameter $b = (8/3)^{1/2}$ was chosen such that for $|\epsilon| \gg 1$ the solution lies in the region of maximum probability, as computed by the Landau-Zener formula (this probability is maximal on the parabola $2\pi\delta = \ln 2$ and has the value $1/2$ after averaging over the oscillations). The graph of $P_{12}(\epsilon)$, Fig. 3, shows that P_{12} approaches the asymptotic value quite fast.

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