CONCERNING THE PROBABILITIES OF NONADIABATIC TRANSITIONS NEAR THE TURNING POINTS

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A generalization of the formula of Landau for the probabilities w of nonadiabatic transitions in a system of two atoms is obtained for the case where the energy of the system in the initial state, E, can be close to total value of the potential energy U_0 at the point where the terms of the initial and final states intersect, and the interaction energy V between the terms is sufficiently large.

As is well known, the probability of nonadiabatic transition in a system of two particles which interact in a centrally-symmetrical manner is given, in the case when the terms of the initial and final states $(U_1 \text{ and } U_2)$ intersect (Fig. 1) and the matrix element of the nonadiabatic interaction V is sufficiently large, by the Landau formula^[1]:

$$w = 2e^{-\kappa_0}, \ \kappa_0 = 2\pi V^2 / \hbar v \Delta F, \tag{1}$$

where v is the velocity at the point of term crossing r_0 , $\Delta F = F_1 - F_2$, and $F_{1,2} = dU_{1,2}/dr$ for $r = r_0$. However, this formula cannot be used if the turning points r_1 and r_2 are sufficiently close to r_0 , for in this case the velocity of the particles cannot be regarded as constant in the vicinity of r_0 , as is assumed in the derivation of (1). A similar situation is possible, for example, upon collision of two atoms with kinetic energy E, slightly exceeding U_0 , and also in the case of predissociation from a state corresponding to a vibrational level close to U_0 .

In the present paper we present a derivation of a formula for w, valid for any distance between the turning points $r_{1,2}$ and r_0 , that is, for any energy excess $\epsilon = E - U_0$. This derivation is based on replacing in the first approximation the crossing terms $U_{1,2}$ by "regular" noncrossing terms,





constructed with allowance for the interactions that cause the transitions (see [2], page 356).

Namely, let the wave equation of the system of two atoms be

$$-\frac{\hbar^2}{2m}\,\Delta_{\mathbf{r}} + H + \hat{V}\Big)\,\Psi = E\Psi,\tag{2}$$

where $\Delta_{\mathbf{r}}$ — operator of relative motion of the two atoms, \mathbf{r} — distance between them, \mathbf{H} — Hamiltonian of electron motion in the system of the two atoms, in which the interaction that leads to the nonadiabatic transition has not been turned on, \mathbf{E} — kinetic energy of relative motion of the atoms, and m — their reduced mass. Let, further, $\varphi_{1,2}$ be orthonormal electron functions corresponding to the crossing terms $U_{1,2}$, that is, $\mathbf{H}\varphi_{1,2} = U_{1,2}(\mathbf{r})$ $\varphi_{1,2}$. We introduce along with $\varphi_{1,2}$ wave functions $\Phi_{1,2}$ satisfying the equation $(\mathbf{H} + \hat{\mathbf{V}}) \Phi_{1,2} = W_{1,2}(\mathbf{r})$ $\Phi_{1,2}$, the eigenvalues of which $W_{1,2}(\mathbf{r})$ represent regular non-crossing terms $W_1(\mathbf{r})$ and $W_2(\mathbf{r})$. The approximate construction (see ^[2], page 305) leads, as is well known, to the following formulas:

$$W_{1,2} = \frac{1}{2} (\tilde{U}_1 + \tilde{U}_2) \pm \left\{ \frac{1}{4} (\tilde{U}_1 - \tilde{U}_2)^2 + |V_{12}|^2 \right\}^{1/2}, \quad (3)$$

where $\widetilde{U}_i = U_i + V_{ii}$, $V_{ik} = \int \varphi_i^* \widehat{V} \varphi_k d\xi$, i, k = 1, 2; ξ — aggregate of electron coordinates,

$$\Phi_{1} = -\phi_{1} \cos g(r) + \phi_{2} \sin g(r),$$

$$\Phi_{2} = \phi_{1} \sin g(r) + \phi_{2} \cos g(r), \quad \text{tg } g = 2V_{12}/(\tilde{U}_{1} - \tilde{U}_{2}).$$
(4)*

We write the complete wave function Ψ in the form $\Psi = F_1(\mathbf{r})\Phi_1 + F_2(\mathbf{r})\Phi_2$, and assume that all the interactions are centrally symmetrical, that is, the functions $F_{1,2}$ of the relative motion of the atoms can be expanded in spherical functions

^{*}tg = tan.

$$F_{1,2} = \frac{1}{r} \sum f_{1,2}^{(l)} (r) P_l (\cos \theta).$$

Then for each pair of radial functions $F_{1,2}^{(l)}$ we obtain a system of equations ^[3] (the prime denotes differentiation with respect to r):

$$\begin{aligned} f_1^{"} &+ 2mh^{-2} \left(E - W_1 \right) f_1 = 2g'f_2' + g''f_2, \\ f_2^{"} &+ 2mh^{-2} \left(E - W_2 \right) f_2 = -2g'f_1' - g''f_1 \end{aligned} \tag{5}$$

(here $W_{1,2}$ includes the centrifugal energy $h^2 l^2/2mr^2$). The final-state wave function satisfies the additional condition

$$f_{2}^{(l)}_{r \to \infty} = \eta_l e^{ik_2 r} / k_2, \qquad k_2 = \sqrt{2m (E - W_2(\infty))} / h.$$

The quantity $w_l = |\eta_l|^2$ is the probability of nonadiabatic transition. If we assume that it is small, then the right half in the first equation of (5) can be set equal to zero and then we write, after elementary transformation, the following expression for w (^[3], page 386)

$$w = \left| \frac{\pi}{2} \int_{0}^{\infty} \sqrt{\alpha^{2} + \psi^{2}} \widetilde{f}_{1} \widetilde{f}_{2} \operatorname{arc} \operatorname{tg} \frac{\alpha}{\psi} dr \right|^{2}, \qquad (6)^{*}$$

where

$$\psi = m \; ({\widetilde U}_1 - \; {\widetilde U}_2)/h^2, \;\;\; {lpha}^2 = \; 2m \; | \; V_{12} \; |^2/h^2$$

and $\widetilde{f}_{1,2}$ — solution of the equation

$$\widetilde{f}_{1,2}'' + \widetilde{k}_{1,2}^2(r) \ \widetilde{f}_{1,2} = 0, \qquad \widetilde{k}_{1,2}^2 = 2m (E - W_{1,2}(r))/\hbar^2,$$

which are normalized to a δ function in $k_{1,2}$ and for which the following quasiclassical approximation is valid:

$$\widetilde{f}_{1,2} = \sqrt{\frac{2}{\pi}} \, \widetilde{k}_{1,2}^{-1/2} \cos \Big(\int_{r_{1,2}}^{r} \widetilde{k}_{1,2} \, dr - \frac{\pi}{4} \Big) \,. \tag{7}$$

The integral in (6) can be calculated by the stationary-phase method, for which it is necessary to employ analytic continuations of (7) in those parts of the plane of complex variable r, where there are located the points of the stationary phase $r_{\rm C}$, defined by the relations $\tilde{k}_1 = \tilde{k}_2$, that is, $\psi^2(r_{\rm C}) + \alpha^2(r_{\rm C}) = 0$. In other words, we must assume

$$\widetilde{f}_{1,2} = C_{1,2} \widetilde{k}_{1,2}^{-1/2} \exp\left(\pm i \int_{r_{1,2}}^{r} \widetilde{k}_{1,2} dr\right),$$

where $C_{1,2}$ are numerical coefficients which take into account the Stokes phenomenon.

On the basis of the general method ([2], page 212) we have

$$w = Ce^{-\varkappa}, \qquad \varkappa = 2 \operatorname{Im} \left(\int_{r_1}^{r_c} (\widetilde{k}_1 dr - \int_{r_2}^{r_c} \widetilde{k}_2 dr) \right).$$
 (8)

*arctg = tan.1

The coefficient C, as shown by the investigation (see the appendix) turns out to be a numerical constant which does not depend on the dimensional parameters and consequently is equal to 2, since (8) goes over into (1) at large energy excess ϵ [see formula (13)].

It must be noted that the use of the WBK approximation (7) for the wave functions $f_{1,2}$ in calculating the transition probability calls for some justification, since the approximation (7) does not hold in the vicinity of the turning points $r_{1,2}$. This justification, from which follow some limitations on the region of applicability of the main formula (8), consists in the following.

The condition for the validity of the analytic continuation of the function (7)

$$\widetilde{f}_{1,2} = C_{1,2}\widetilde{k}_{1,2}^{-1/2} \exp\left(-\int_{r_{1,2}}^{r} k_{1,2} dr\right)$$

in the upper half-plane of the complex variable r coincides with the ordinary quasiclassical condition

$$mh \frac{dW_{1,2}}{dr} / (2m (E - W_{1,2}))^{3/2} \bigg| \ll 1.$$

We use here and throughout a linear approximation for the terms $U_{1,2}$ in the vicinity of the point r_0 where the terms cross: $U_{1,2} = U_0 + F_{1,2}x$, $x = r - r_0$, that is,

$$2m (E - W_{1,2}) = 2m \left[\varepsilon + Fx \pm \sqrt{V^2 + \frac{1}{4} (x \Delta F)^2} \right],$$

$$V^2 = |V_{1,2} (r_0)|^2, \quad F = -\frac{1}{2} (F_1 + F_2), \quad \varepsilon = E - U_0.$$

Inasmuch as the principal role in the calculation of the integral in (6) is assumed by the region of values of r close to r_c , the condition for the applicability of the linear approximation

$$d^2 U_{1,2}/dr^2 \mid_{r_{\bullet}} x^2 \ll dU_{1,2}/dr \mid_{r_{\bullet}} x$$

can be written in the form of the inequality

$$|r_{c} - r_{0}| = \frac{2V}{\Delta F} \ll \left(\frac{d \ln F_{1,2}}{dr}\right)^{-1} \Big|_{r=r_{0}}, \text{ i.e. } V \ll r_{0} \Delta F,$$

which, roughly speaking, reduces to the usually satisfied requirement that the splitting of the terms V be small compared with the quantity $U_0F^{-1}\Delta F$.

On the other hand, using the linear approximation $U_{1,2} = U_0 + F_{1,2}x$ we can write the quasiclassical condition, under the most unfavorable case $\epsilon \rightarrow 0$ with $r \sim r_c$, in the form

$$\left| mh \frac{dW_{1,2}}{dr} \right| (2m (E - W_{1,2}))^{3/2} \right| \sim \frac{hF}{V \sqrt{2mV}} \ll 1.$$

This inequality, which is satisfied in many cases (for example, $V\sqrt{2mV/hF} \sim 10$ for the transition

Li + H \rightarrow Li⁺ + H⁻ which is considered at the end of this article), signifies in fact that the probability w is exponentially small [see formula (11)]. We emphasize that in the other limiting case $hF/V\sqrt{2mV} \gg 1$, that is, for sufficiently small term splittings V, the transition probability near the turning points is given by a known formula ([2], page 360, problem 3), according to whichw ~ $(V\sqrt{2mV}/h\Delta F)^{4/3}$, that is, is not exponentially small. For $hF/V\sqrt{2mV} \gg 1$, the method which we employ to calculate the integral (6), and which leads to formula (8), is obviously not applicable and we must express the functions $f_{1,2}$ in this case in terms of Airy functions (see [2], page 360). Thus, depending on the value of the parameter $hF/V\sqrt{2mV}$, the probabilities of the transitions near the turning points are given either by the formula on page 360 of ^[2] when $hf/V\sqrt{2mV} \gg 1$, or by our formula (8). In the intermediate case $hF/V\sqrt{2mV} \sim 1$, it is apparently necessary to solve the system (5) rigorously in order to obtain w.

Let us investigate the exponent κ , which determines (8), using the linear approximation $U_{1,2} = U_0 + F_{1,2}x$, $x = r - r_0$. Then κ is written in the form

$$\kappa = \frac{2 \sqrt{2m}}{h} \operatorname{Im} \left(\int_{0}^{x_{0} i} \left[\varepsilon + Fx + \sqrt{V^{2} + \frac{1}{4} (x \Delta F)^{2}} \right]^{1/2} - \int_{x_{1}}^{x_{0}} \left[\varepsilon + Fx - \sqrt{V^{2} + \frac{1}{4} (x \Delta F)^{2}} \right]^{1/2} dx \right), x_{1} \neq r_{1} - r_{0};$$
(9)
$$V^{2} = |V_{12} (r_{0})|^{2}, \qquad F = -\frac{1}{2} (F_{1} + F_{2}),$$

$$x_{0} = \frac{2V}{\Delta F}.$$
(10)

Introducing the dimensionless parameters $\nu = V/\epsilon$ and $a = 2F/\Delta F$, we represent κ in the form

$$\varkappa = 4 \frac{\sqrt{2mV}}{h} \frac{V}{\Delta F} \chi (\nu, a),$$

$$\chi (\nu, a) = \nu^{-1/2} \operatorname{Im} \left(\int_{0}^{t} [1 + \nu a\xi + \sqrt{\xi^{2} + 1}]^{1/2} d\xi - \int_{\xi_{1}}^{\xi} [1 + \nu a\xi - \sqrt{\xi^{2} + 1}]^{1/2} d\xi \right).$$
(11)

We make a change of variable $\xi = i \sin t$, such that*

$$a\xi \pm \sqrt{\xi^2 + 1} = A \sin(t \pm \delta), t \pm \delta = \tau;$$

$$A = iv \sqrt{a^2 - 1}, \quad \delta = -i \operatorname{Arth} \frac{1}{a} \quad \text{for } a > 1,$$

$$A = v \sqrt{1 - a^2},$$

$$\delta = \frac{\pi}{2} + i \operatorname{Arch} \frac{1}{\sqrt{1 - a^2}} \quad \text{for } a < 1.$$

*Arth = tanh⁻¹, Arch = cosh⁻¹

We can then express the function $\chi(\nu, a)$ in terms of hypergeometric functions, which also reduce to elliptic intergrals with real moduli and limits. The results of such a reduction, and consequently the behavior of the function χ , turns out to be essentially different in two regions of variation of the parameters ν and a, defined by the inequalities $a \leq 1$.

1) Region $a \ge 1$:

$$\chi = v^{1/2} f(\lambda), \qquad \lambda = v \sqrt{a^2 - 1},$$

$$f(\lambda) = \frac{2}{\lambda} \operatorname{Im} \int_{0}^{\pi/2} (1 + i\lambda \sin \tau)^{1/2} \sin \tau \, d\tau$$

$$= 4k^2 \frac{(1 + \lambda^2)^{3/4}}{\lambda^2} \int_{0}^{\pi/2} \sin^2 \varphi \sqrt{1 - k^2 \sin^2 \varphi} \, d\varphi$$

$$= \pi \lambda^{-2} \left(1 + \lambda^2\right)^{3/4} k^2 F\left(\frac{3}{2}, -\frac{1}{2}, 2, k^2\right),$$

$$k^2 = \frac{1}{2} \left(1 - 1/\sqrt{\lambda^2 + 1}\right), \qquad (12)$$

 $F(\alpha, \beta, \gamma; k^2)$ — hypergeometric function.

The expansion of $f(\lambda)$ in powers of λ takes, in accordance with (12), the form

$$f(\lambda) = \frac{\pi}{4} \sum_{n=0}^{\infty} (-1)^n \frac{(4n-1)!!}{2^{4n}(n+1)!} \lambda^{2n}$$
$$= \frac{\pi}{4} \left(1 - \frac{3}{2^5} \lambda^2 + \frac{35}{2^{10}} \lambda^4 - \dots \right).$$
(13)

From (12) and (13) follows the interesting conclusion that $f(\lambda) \equiv \pi/4$ when a = 1 and $\lambda = 0$, that is, in this case (a = 1, $\nu \leq 1$) the Landau formula (1) is rigorously correct.

The function $f(\lambda)$ can be represented also in the form of an expansion in powers of the parameter $\rho = 1/\sqrt{1 + \lambda^2}$ or $1/\lambda$

$$f(\lambda) = \frac{\pi}{2} \frac{\rho^{1/2}}{1+\rho} \sum_{n=0}^{\infty} (-1)^n \frac{d^n F(^{3}/_{2}, -\frac{1}/_{2}, 2, x)}{dx^n} \bigg|_{x=^{1}/_{2}} \left(\frac{\rho}{2}\right)^n$$

= $\lambda^{-1/2} \left(1.23 - 0.88 \frac{1}{\lambda} + \dots\right).$ (14)
2) Region $a \le 1$:¹⁾

$$\chi (v, a) = v^{1/2} f(\lambda), \qquad \lambda = v \sqrt{1 - a^2};$$

 $f(\lambda) = \frac{1}{\lambda} \int_{-\pi/2}^{\pi/2} (1 + \lambda \sin \tau)^{1/2} \sin \tau d\tau$
 $= 2 \frac{\sqrt{1 + \lambda}}{\lambda} \int_{0}^{\pi/2} (1 - 2 \sin^2 \varphi) \sqrt{1 - k^2 \sin^2 \varphi} d\varphi$

¹⁾The condition $a \leq 1$ corresponds to Fig. 1, that is, in this case w has the meaning of a probability of predissociation from the state characterized by the term W_2 . Therefore in formula (15) the only physically meaningful quantities are $\epsilon \geq V$, i.e., $\nu \leq 1$, i.e., $\lambda \leq 1$.

$$= \pi \frac{\sqrt{1+\lambda}}{\lambda} \left[F\left(\frac{1}{2}, -\frac{1}{2}, 1; k^2\right) - F\left(\frac{3}{2}, -\frac{1}{2}, 2; k^2\right) \right], \quad k^2 = \frac{2\lambda}{1+\lambda}.$$
 (15)

The expansion of (15) in powers of λ is of the form

$$f(\lambda) = \frac{\pi}{4} \sum_{n=0}^{\infty} \frac{(4n-1)!!}{2^{4n}(n+1)!} \lambda^{2n}.$$
 (16)

It is of interest in principle to investigate the behavior of κ as a $\rightarrow \infty$, since the condition a = $2F/\Delta F \gg 1$ signifies that the forces acting on the particles which move over different terms are approximately the same, that is, in this case it becomes possible to introduce the concept of the particle trajectory and to use nonstationary perturbation theory for the calculation of w^[3].

Let us see first how we can simplify our formulas (12) and (17), which correspond to a > 1as $a \rightarrow \infty$. According to (12), in the case $a \gg 1$ we can replace the parameter $\lambda = \nu (a - 1)^{1/2}$ by the parameter $\lambda = \nu a$, and $(a^2 - 1)^{1/2}$ can be replaced by a.

We compare these formulas with the results of the nonstationary perturbation theory, which can be obtained by expanding the roots in (11) in powers of $\nu\sqrt{\xi^2 + 1}/(1 + a\nu\xi)$. We have²⁾

$$\chi = v^{1/2} f(\lambda), \qquad f(\lambda) = \operatorname{Im} \int_{0}^{1} \frac{\sqrt{\xi^{2} + 1}}{\sqrt{1 + \lambda\xi}} d\xi, \qquad \lambda = av.$$
 (17)

The function $f(\lambda)$ in (17) can be readily reduced to an expression which coincides exactly with (12), in which we must put $\lambda = a$.

We thus arrive at the following deduction: the probability of the transition, determined by introducing a classical trajectory in accordance with (17), coincides with the exact quantum mechanical probability, determined from (12), if we assume for the average force which sets the classical theory not $F = (F_1 + F_2)/2$, but $F = \sqrt{F_1F_2}$ (the replacement of $(F_1 + F_2)/2$ by $\sqrt{F_1F_2}$ in (17) is equivalent to replacing a by $(a^2 - 1)^{1/2}$, which indeed yields the exact formula (12)).

In conclusion we note that the energy dependence of $\kappa = \kappa(\epsilon)$, given by (12) and differing essentially from that given by the Landau formula (1), can be quite pronounced, for example, for the process Li + H \rightarrow H⁻¹ + Li⁺ (the transition X' Σ^+ \rightarrow A' Σ^+), for in this case V is quite large, V ~ 1 eV (see the term scheme of the LiH system in ^[5]). I am grateful to A. S. Kompaneets and M. Ya. Ovchinnikova for a discussion of this work and

for many useful indications.

APPENDIX³⁾

The integral contained in (6) can be represented in the form

$$J = 2C_1 C_2 \int_{-\infty}^{\infty} \widetilde{k}_1^{-1/2} \widetilde{k}_2^{-1/2} \sqrt{\alpha^2 + \psi^2} e^{S(r)} \operatorname{arc} \operatorname{tg} \frac{\alpha}{\psi} dr,$$

$$S(r) = i \left(\int_{r_1}^r \widetilde{k}_1 dr - \int_{r_2}^r \widetilde{k}_2 dr \right).$$
(A.1)

In the plane of complex r, the situation is that shown in Fig. 2.

Here r_c —point of the stationary phase, determined by the equation $\psi^2 + \alpha^2 = 0$. The lines l_1, l_2 , and l_3 are the level lines Re S(r) = Re S(r_c). In the shaded region between the abscissa axis and the lines l_1 and l_3 , we have Re S(r) < 0. On the lines l'_1 and l'_2 , which are the lines of steepest descent, we have

Re
$$S_0(r) < 0$$
, $S_0 = i \int_{r_c}^r (\tilde{k}_1 - \tilde{k}_2) dr$.

We replace J by an integral along a contour consisting of the lines l_1 and l_2 . We can do this by virtue of the regularity of the integrand of (A.1) in the shaded region. The main contribution is made to J by the vicinity of the point r_c where the contour of integration can be deformed along the steepest descent lines l'_1 and l'_2 . We denote this part of the contour in the vicinity of r_c by C. Then (A.1) can be rewritten in the form

$$J = iC_{1}C_{2}e^{S_{0}(r_{c})^{*}}p\int_{C} \exp\left(\frac{2}{3}ipz^{3/2}\right)\sqrt{z} \ln z \, dz,$$

$$z = r - r_{c}, \quad \psi(r) - i\alpha(r) = \psi'(r_{c}) z,$$

$$p = [i\alpha(r_{c})\psi'(r_{c})/\phi(r_{c})]^{1/2},$$

$$\phi(r_{c}) = h^{-1}\sqrt{m(\widetilde{U}_{1} + \widetilde{U}_{2})}|_{r=r_{c}}.$$
 (A.2)

Since $ipz^{3/2} < 0$ on l'_1 and l'_2 , and since the angle between these lines is $4\pi/3$, we obtain, putting ${}^{2}/_{3}ipz^{3/2} = -\tau$ and recognizing that the angle $4\pi/3$ rotates in this case through 2π ,

$$J = -\frac{1}{3} C_1 C_2 e^{S_0(r_c)} \int_{C'} e^{-\tau} \ln \tau \, d\tau, \qquad (A.3)$$

²⁾It must be noted that the expansion of $f(\lambda)$ in powers of $\lambda = a\nu$, obtained by Nikitin^[4] on the basis of (17) (formula (10) in^[4]) differs from our expansion (13). According to a private communication from Nikitin, this discrepancy is a consequence of a computational error on his part.

 $^{^{3)}} This investigation was made by M. I. Fedoryuk, to whom I am deeply grateful for his help.$



FIG. 2

where the integral is taken along the contour C', that is, on both edges of the cut (formed by the positive part of the real axis) of length ϵ (Fig. 2). It is equal to

$$\int_{0}^{\varepsilon} e^{-\tau} \ln \tau \, d\tau - \int_{0}^{\varepsilon} e^{-\tau} \left(\ln \tau + 2\pi i \right) d\tau = -2\pi i.$$

We ultimately get

$$J = \frac{2\pi i}{3} C_1 C_2 \exp i \left(\int_{r_1}^{r_c} \widetilde{k}_1 dr - \int_{r_2}^{r_c} \widetilde{k}_2 dr \right), \quad (A.4)$$

That is, as already indicated, the factor preceding the exponent in J does not depend on the dimensional constants.

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