INFLUENCE OF PSEUDO-INTERSECTING TERMS ON ADIABATIC TRANSITIONS IN INELASTIC ATOMIC COLLISIONS

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We evaluate the probability for an adiabatic transition between two terms in the case when one of them has a "break" caused by the pseudo-intersection with a third term. We show that for small velocities when the "break" is important, it is necessary to take transitions in the vicinity of the "break" into account.

It is well known that inelastic transitions between non-intersecting terms have an adiabatic character and that at low velocities the probability for a transition is exponentially small. In the case of two terms transitions are then "realized" in complex points where the terms "intersect."[1]

The situation may change appreciably if one of the terms has for one reason or another a "singularity." In that case it is necessary to take into account the influence of these regions on the transition probability. This, if we consider the generally speaking non-physical case of a system with two terms when one of them has a break (approximated by a hyperbola) we can easily show using perturbation theory that in the region of the break the transition probability is $P \sim v^3$ for low velocities v of the colliding particles.

One of the reasons for the occurrence of a singularity of the "break" type is the pseudo-intersection of a term with a third term which does not intersect with the first one (Figs. 1 and 2). Such a situation is very often encountered in the spectra of colliding atoms.

In the following we evaluate the probability for the transition between levels E_3 and E_1 under the assumption that the transitions are caused in the main region of the "break" ΔR of the levels.

1. In Fig. 1 we have depicted three levels, two of which (E_3 and E_2) have a pseudo-intersection point while E_1 is in the region ΔR at a distance ω_0 where $\omega_0 \gg \Delta$ (Δ is the separation of the levels E_3 and E_2 in that region). E_3^0, E_2^0, and E_1^0 are the zeroth approximation levels corresponding to the case where there is no interaction between the terms (Fig. 2). The levels E_3 and E_2 have no intersection whatever with E_1.

The system of equations for the transition amplitude in the time-dependent theory have the form

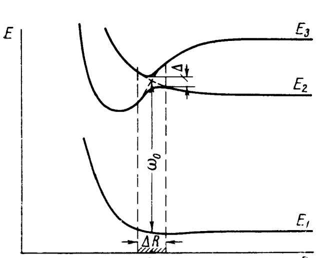

FIG. 1.

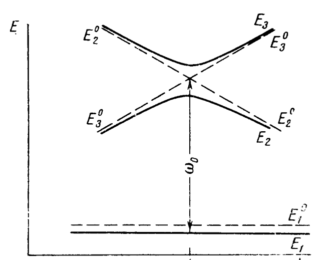

FIG. 2.

$$\dot{C}_m(t) = -\sum_{m\neq n} C_n(t) d_{mn} \exp\Big(i\int^t \omega_{mn}\,dt\Big). \tag{1}$$

Here $m, n = 1, 2, 3$; $\omega_{mn} = E_m - E_n$; $d_{mn} = \int\psi_m\dot{\psi}_n dr$; E_n and ψ_n are the eigenvalues and eigenfunctions when the interaction is taken into account, and depend on t as a parameter. The set of three equations (1) can not be solved in general form but the way the problem is stated enables us to apply perturbation theory. Indeed, since the coupling is large between the levels E_3 and E_2 and small between E_2 and E_1 (E_2 and E_1), we can put $C_1 = 0$ or 1 (depending on the initial conditions) and in first approximation find C_2 and C_3 by solving a set of two equations; after that we find C_1 in the next approximation, using the values of C_2 and C_3 found in the first approximation.

2. To evaluate the matrix elements d_{12} and d_{13} we expand ψ_n in terms of the eigenfunctions ψ_n^0 of the unperturbed problem corresponding to the intersecting terms:

$$\psi_n = \sum_{m=1}^{3} b_m\psi_m^0,$$

and, as usual, we find the expansion coefficients b_m from the set of equations for the stationary problem

$$\begin{aligned}(E_1^0 + V_{11} - E)b_1 + V_{12}b_2 + V_{13}b_3 &= 0,\\ (E_2^0 + V_{22} - E)b_2 + V_{21}b_1 + V_{23}b_3 &= 0,\\ (E_3^0 + V_{33} - E)b_3 + V_{31}b_1 + V_{32}b_2 &= 0\end{aligned} \tag{2}$$

together with the normalization condition $|C_1|^2 + |C_2|^2 + |C_3|^2 = 1$. The set (2) can be solved approximately by bearing in mind that in the regions close to the roots E_n of the secular equation, the difference $E_1^0 - E_n \approx \Delta_{1n} \gg V_{1n}$ (V_{32}), where $n = 2, 3$, and $\Delta_{1n} = E_1^0 - E_n^0$. The terms E_n and the coefficients b_n have, up to terms of first order in V_{mn}/Δ_{1n} with $n = 2, 3$, the following form:

1. The root $E = E_1^0$:

$$b_1^{(1)} = 1;\quad b_2^{(1)} = \frac{V_{12}}{\Delta_{21}};\quad b_3^{(1)} = -\frac{V_{13}}{\Delta_{31}}. \tag{3}$$

2. The root $E_2 = -\tfrac{1}{2}(E_2^0 + E_3^0 - \sqrt{\Delta_{32}^2 + 4V_{32}^2})$:

$$b_1^{(2)} = \frac{1}{\sqrt{2}\Delta_{21}}[-V_{12}(1+k)^{1/2} + V_{13}(1-k)^{1/2}]; \tag{4}$$

$$b_2^{(2)} = -\frac{1}{\sqrt{2}}(1+k)^{1/2},\quad b_3^{(2)} = \frac{1}{\sqrt{2}}(1-k)^{1/2}.$$

3. The root $E_3 = -\tfrac{1}{2}(E_2^0 + E_3^0 + \sqrt{\Delta_{32}^2 + 4V_{32}^2})$:

$$b_1^{(3)} = \frac{1}{\sqrt{2}\Delta_{31}}[V_{12}(1-k)^{1/2} + V_{13}(1+k)^{1/2}]; \tag{5}$$

$$b_2^{(3)} = \frac{1}{\sqrt{2}}(1-k)^{1/2};\ b_3^{(3)} = \frac{1}{\sqrt{2}}(1+k)^{1/2},$$

where

$$k = \Delta_{32}/\sqrt{\Delta_{32}^2 + 4V_{32}^2}. \tag{6}$$

Using the values from (3) to (6) the matrix elements become

$$d_{12} = -\frac{1}{\sqrt{2}}\frac{V_{12}}{\Delta_{21}}\frac{\dot{k}}{(1-k)^{1/2}},$$

$$d_{13} = -\frac{1}{\sqrt{2}}\frac{V_{12}}{\Delta_{31}}\frac{\dot{k}}{(1+k)^{1/2}}.$$

Here, and everywhere, we have taken into account only) terms in first order of $V_{mn}/\Delta_{n1}(n = 2, 3)$.

3. In the following we consider the particular case of the term behavior when the angles of inclination of E_2^0 and E_3^0 with respect to E_1^0 are the same in absolute magnitude (see Fig. 2); it is not difficult, as far as principle is concerned, to generalize this to arbitrary angles. Then

$$\omega_{12} = {}^1/_2\sqrt{\Delta_{32}^2 + 4V_{32}^2} - \omega_0, \tag{9}$$

$$\omega_{13} = -{}^1/_2\sqrt{\Delta_{32}^2 + 4V_{32}^2} - \omega_0, \tag{10}$$

where $\Delta_{32} = \alpha(t - t_0)$, V_{mn} = const, and t_0 is the point where the terms E_2^0 and E_3^0 intersect.

We look for the transition probability in the case when the system of colliding particles is initially in the upper level E_3:

$$C_1(-\infty) = 0,\quad C_2(-\infty) = 0,\quad |C_3(-\infty)| = 1. \tag{11}$$

The solutions of C_2 and C_3 are known in the first approximation of our problem. This are the Landau-Zener solutions of the problem in the adiabatic case.[2] Using the notation of[2], we write them as follows:

$$C_2 = \frac{i}{2}\left\{(A+iB)\left(\frac{\tau-i}{\tau+i}\right)^{1/4} - (A-iB)\left(\frac{\tau+i}{\tau-i}\right)^{1/4}\right\}$$

$$\times \exp\left(-\frac{i\mu}{2}\int^{\tau}\sqrt{1+x^2}\,dx\right), \tag{12}$$

$$C_3 = \frac{1}{2}\left\{(A+iB)\left(\frac{\tau-i}{\tau+i}\right)^{1/4} + (A-iB)\left(\frac{\tau+i}{\tau-i}\right)^{1/4}\right\}\exp\left(\frac{i\mu}{2}\int^{\tau}\sqrt{1+x^2}\,dx\right),$$

where

$$A = e^{-\pi\mu/16}D_{-i\mu/4}(\sqrt{\mu}e^{-3i\pi/4}\tau),$$

$$B = {}^1/_2\sqrt{\mu}e^{-\pi\mu/16}D_{-i\mu/4-1}(\sqrt{\mu}e^{-3i\pi/4}\tau). \tag{13}$$

Here $D_n(z)$ is a parabolic cylinder function and

$$\mu = 4V_{32}^2/\alpha,\quad \tau = \alpha(t-t_0)/2V_{32}. \tag{14}$$

Before finding the solution for C_1 we make some remarks. It is clear that the use of the linear terms E_2^0 and E_3^0 in the problem involves their asymptotic intersection with E_1^0. Since, however, this does not enter into the problem as stated, we restrict the region of the asymptotic behavior by the condition ${}^1/_2\alpha(t - t_0) \ll \omega_0$ which is natural as ω_0 is large and much larger than V_{32}. We do therefore not take into account singular points of the kind $\Delta_{21} = \Delta_{31} = 0$. It is also clear that if we expect that the region of the "break" will affect the level E_1, the solution for C_1 must have singularities in the same points of the complex plane as the solutions for C_2 and C_3, i.e., $\tau = \pm i$.

We now write down the value of the amplitude C_1 in terms of the variable τ, using (7), (8), and (12):

$$C_1 = G\int_{-\infty}\frac{MA+NB}{(1+\tau^2)^{3/2}}\exp\left(-i\omega_0\frac{\mu}{2V_{32}}\tau\right)d\tau, \tag{15}$$

where

$$G = V_{12}/2\sqrt{2}\omega_0,$$

$$M = i(\sqrt{1+\tau^2} - \tau)^{1/2}[(\tau-i)^{1/2} - (\tau+i)^{1/2}] + (\sqrt{1+\tau^2}+\tau)^{1/2}[(\tau-i)^{1/2} + (\tau+i)^{1/2}],$$

$$N = i(\sqrt{1+\tau^2}+\tau)^{1/2}[(\tau-i)^{1/2} - (\tau+i)^{1/2}] - (\sqrt{1+\tau^2}-\tau)^{1/2}[(\tau-i)^{1/2} + (\tau+i)^{1/2}]. \tag{16}$$

The integral in (15) can be obtained by shifting the integration path into the lower half-plane going round the cut which goes from the point $\tau = -i$ to $-i\infty$. The integrand can be expanded in a power series in the vicinity of $\tau = -i$ and we take into account the first term in the expansion. As a result the probability for the transition from the level E_3 to the level E_1 is of the form

$$P_{31} = \frac{\pi\mu V_{12}^2}{\omega_0 V_{32}}\exp\left\{-\frac{\pi\mu}{8} - \frac{\omega_0\mu}{V_{32}}\right\}\Big|D_{-i\mu/4}(\sqrt{\mu}\,e^{3i\pi/4}) + \frac{i\sqrt{\mu}}{2}D_{-i\mu/4-1}(\sqrt{\mu}e^{3i\pi/4})\Big|^2. \tag{17}$$

Using the asymptotic value of the D-function and using the fact that $\omega_0 \gg V_{32}$ we get for large μ

$$P_{31} = 8\pi\frac{V_{12}^2V_{32}}{v\omega_0(F_3-F_2)}\exp\left\{\frac{-4\omega_0V_{32}}{v(F_3-F_2)}\right\}(1-\cos\theta), \tag{18}$$

where v is the radial velocity in the region ΔR and F_3 and F_2 are forces (slopes of the terms E_3^0 and E_2^0). The phase

$$\theta = \frac{\mu}{2} - \frac{\mu}{4}\ln\mu + \frac{3}{4}\pi + 0{,}27 + \arg\Gamma\left(\frac{i\mu}{4}\right)$$

appears due to the interference of the solutions for C_2 and C_3 and although for low velocities of the colliding particles the oscillations are appreciable, cases are possible where the averaging over the velocities does not lead to the vanishing of the oscillating term. It is therefore retained in Eq. (18).

Unfortunately, it is not possible to compare directly the transition probability obtained here with the one from the paper by Dykhne[1] since to do that it is necessary to consider an actual case; however, because of its character the exponent in Eq. (18) can give a very insignificant contribution in contrast to the corresponding formula in[1]. At the same time we must note that the factor of the exponent in (18) may be small. We note also that in the case when $E_3(E_2)$ and E_1 are terms of different symmetry, transitions will be induced by a rotation of the internuclear axis. In that case, apparently, which is of most interest, the nature of the matrix elements $V_{12}(V_{13})$ and V_{32} will be different. While $V_{32} = \Delta/2$ = const, V_{12} = const·v. In that case it follows from (18) that

$$P_1 \sim (\Delta v/a\omega_0^2)\,e^{-a\Delta/v}$$

(here a are the dimensions of the system, Δ the separation of the terms E_3 and E_2) while in the purely adiabatic case $P_2 \sim e^{-a\omega_0/v}$. Bearing in mind that $\omega_0 \gg \Delta$ we must expect for small $v = v'$ that $P_1(v') > P_2(v')$. When the velocity increases, beginning with a well-defined value $v = v''$, $P_1(v'') \leq P_2(v'')$. This is connected with the fact that when the velocity increases $E_3 \to E_3^0 (E_2 \to E_2^0)$, the terms will intersect almost exactly, the "break" vanishes, and the transition probability will be determined by the quantity P_2. Thus, Eq. (18) is applicable in the velocity range

$$v_{qu} < v \lesssim \frac{a(\Delta - \omega_0)}{\ln (v\Delta / a\omega_0^2)},$$

where v_{qu} is the velocity at which the classical approach to the solution is inapplicable.

In conclusion we give the formula for the transition probability for the case when the slopes of all terms are arbitrary:

$$P_{31} = 8\pi \frac{V_{12}^2 V_{32}^2}{v(F_3 - F_2)\omega_0^2} \left[\frac{(2F_1 - F_2 - F_3)^2}{(F_3 - F_2)^2} + \frac{\omega_0^2}{V_{32}^2} \right]^{1/2} \times \exp\left\{ -\frac{4\omega_0 V_{32}}{v(F_3 - F_2)} \right\} (1 - \cos\theta). \tag{19}$$

We must note that when evaluating P_{31} the principle of detailed balancing was not taken into account.

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[1] A. M. Dykhne, Zh. Eksp. Teor. Fiz. 41, 1324 (1961) [Sov. Phys.-JETP 14, 941 (1962)].

[2] A. M. Dykhne and A. V. Chaplik, Zh. Eksp. Teor. Fiz. 43, 889 (1962) [Sov. Phys.-JETP 16, 631 (1963)].

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