DEPENDENCE OF THE INELASTIC COLLISION CROSS SECTIONS OF ATOMS AND IONS ON VELOCITY IN THE CASE OF PSEUDO-INTERSECTION OF THE LEVELS

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The velocity dependence of the inelastic collision cross sections for atoms and ions is examined in the case of pseudo-intersection of the levels of the system of colliding particles. The time dependence of the electron wave functions is taken into account in terms of the radius vectors of the nuclei. The perturbation matrix element in the Landau-Zener formula includes the usual stationary separation of the levels and also a term that takes into account the indicated dependence of the electron wave functions on the time. Under certain conditions the cross section vs. velocity curves may have two peaks.

We assume that the nuclei of the colliding atoms move in a straight line and uniformly in the sense of classical mechanics. Then the probability of excitation of the atoms is determined by the impact parameter of the collision, p, and by the velocity of the relative motion of the nuclei, $\mathbf{R} = \mathbf{v}$.

If $v \ll e^2/\hbar$, it is natural to represent the wave function Ψ of the atomic electrons in the form of an expansion in the molecular wave functions χ_n with the nuclei stationary. The coordinates of the nuclei, $\mathbf{R}_a$ and $\mathbf{R}_b$, are contained as parameters in the Hamiltonian and in χ_n. If $R = |\mathbf{R}_a - \mathbf{R}_b| \to \infty$, the functions χ_n are transformed into products of the atomic wave functions corresponding to the given atomic state with index n (the products differ in the transposition of the electrons between the atoms). The eigenvalues E_n of the electron energy are also functions of R. The curves $E_n(R)$ and $E_{n'}(R)$ can, in principle, intersect. Most frequently, however, we seemingly encounter an intersection of these curves at the point $R = R_0$ where $E_n - E_{n'}$ so to speak vanishes and reverses sign on going through $R = R_0$. In fact, the curves $E_n(R)$ and $E_{n'}(R)$ pass very close to each other and then diverge again in such a way that $E_n - E_{n'}$ does not reverse its sign as R goes through R_0. Such a behavior of $E_n(R)$ is called a pseudo-intersection of the levels.

If there is no intersection or pseudo-intersection of $E_n(R)$ and $E_{n'}(R)$, then the probability of the (n, n') transition is exponentially small at small v. It is proportional to $\exp(-v_0/v)$; the greater $|E_n - E_{n'}|$, the greater v_0. Therefore, in the case of slow collisions, the (n, n') transitions are of practical importance only near the intersection or pseudo-intersection points of the levels E_n and $E_{n'}$. The theory of such transitions, given in the papers of Landau[1] and Zener,[2] seems to us insufficiently complete.* We shall show that the intersection of such transitions, expressed as a function of the velocity v, has in general two maxima.

In the case of slow inelastic collisions of atoms or ions, we can consider in the pseudo-intersection of the levels only the transition between the two terms near the "intersection" point ($R = R_0$).

The complete function of the system, $\Psi(R_a, R_b, \ldots r_i \ldots)$, satisfies the equation

$$i\hbar\partial\Psi/\partial t = H\Psi. \tag{1}$$

Let us expand this function in a series

$$\Psi = C_1\chi_1^0 + C_2\chi_2^0 + \sum_{n=3}^{\infty} C_n\chi_n, \tag{2}$$

where χ_1^0 and χ_2^0 are orthonormal to each other and to functions χ_n when $n \geq 3$. They are expressed linearly (see below) in terms of χ_1 and χ_2, which satisfy, for fixed nuclear coordinates $\mathbf{R}_a$ and $\mathbf{R}_b$ (n = 1, 2 . . .), the following equation:

$$H(\mathbf{R}_a, \mathbf{R}_b, \ldots, \mathbf{r}_i \ldots)\chi_n(\mathbf{R}_a, \mathbf{R}_b, \ldots, \mathbf{r}_i \ldots) = E_n(R)\chi_n(\mathbf{R}_a, \mathbf{R}_b, \ldots \mathbf{r}_i \ldots), \tag{3}$$

where $R = |\mathbf{R}_a - \mathbf{R}_b|$ and $\mathbf{r}_i$ are the radius vectors of the electrons.

For the coefficients C_m we obtain

$$i\hbar\dot{C}_m = E_m^0 C_m + \sum_{n+m}\left[H_{mn} - i\hbar\left(\frac{\partial}{\partial t}\right)_{mn}^0\right]C_n, \tag{4}$$

where $(\partial/\partial t)^0_{mn} = (\partial/\partial t)_{mn}$, $E^0_m = E_m$, and $H_{mn} = 0$ if $m > n$ and $n > 2$. If $m \leq 2$ and

*This theory is briefly developed in the book by Landau and Lifshitz.[3]

$n \leq 2$, then $H_{11} = E_1^0$, $H_{22} = E_2^0$, and $H_{12} = H_{21} = V$. Integration is carried out in the matrix elements only over the electron coordinates.

If we put

$$\chi_1^0 = q\chi_1 - \sqrt{1-q^2}\chi_2, \qquad \chi_2^0 = \sqrt{1-q^2}\,\chi_1 + q\chi_2 \quad (5)$$

and introduce a monotonic function $q(R)$ such that $q^2(R_0) = 1/2$, $q^2 \to 1$ when $R \gg R_0$ and $q^2 \to 0$ when $R \ll R_0$, then this function will satisfy the relations

$$q\sqrt{1-q^2} = V/(E_1 - E_2), \quad (6)$$

$$E_{12}^0 = (E_1 + E_2)/2 \pm (2q^2 - 1)(E_1 - E_2)/2. \quad (7)$$

If q tends to unity or to zero, then E_{12}^0 tends to E_{12} or to E_{21}, while χ_{12}^0 tends to χ_{12} or χ_{21}.

In the case of a pseudo-intersection of levels, the difference $E_1 - E_2$ ($E_1 > E_2$) reaches a minimum at a certain distance $R = R_0$ between the nuclei of the colliding particles. Then, putting $2V = (E_1 - E_2)_{min} \approx$ const, we obtain the intersection of the levels E_1^0 and E_2^0. It is obvious that if $(E_1 - E_2)_{min}$ is small, the perturbation of V will also be small.

Furthermore, neglecting in (4) the transitions of the system to the states with $n > 2$, we arrive at a system of equations

$$i\hbar\dot{C}_1 = E_1^0\dot{C}_1 + (V + K_{12}^0)C_2,$$

$$i\hbar\dot{C}_2 = (V + K_{12}^0)^*C_1 + E_2^0C_2. \quad (8)$$

This system differs from the analogous Zener equations[2] in the presence of the quantity K_{12}^0. This term has the form

$$K_{12}^0 = -i\hbar\int \chi_1^0\frac{\partial\chi_1}{\partial t}d\tau = -i\hbar\int\chi_1^0(\dot{\mathbf{R}}\nabla_a + \dot{\mathbf{R}}_b\nabla_b)\chi_2^0 d\tau$$
$$= -i\hbar(\dot{\mathbf{R}}_a\nabla_a + \dot{\mathbf{R}}_b\nabla_b)_{12}^0. \quad (9)$$

It takes into account the dependence of the electron wave functions χ^0 on the time through the radius vectors of the nuclei, which act as parameters.

The process is thus adiabatic and the matrix element K_{12}^0 can be considered constant in the vicinity of the point of "intersection." Actually,

$$K_{12} - K_{12}^0 = \frac{-i\hbar\dot{R}}{\sqrt{1-q^2}}\frac{dq}{dR} = -\frac{i\hbar V F_{12}^0\dot{R}}{(E_1 - E_2)^2}, \quad (9a)$$

Since

$$\left(\frac{\partial}{\partial R}\right)_{12} - \left(\frac{\partial}{\partial R}\right)_{12}^0 = \frac{1}{\sqrt{1-q^2}}\frac{dq}{dR} = \frac{VF_{12}^0}{(E_1 - E_2)^2},$$

$$F_{12}^0 = \frac{d}{dR}(E_1^0 - E_2^0).$$

The difference $K_{12} - K_{12}^0$ is a function that assumes a large value at the point of pseudo-intersection and diminishes rapidly with increasing

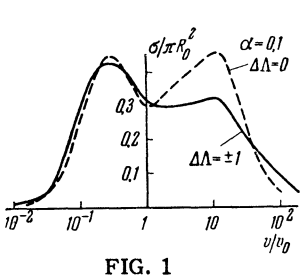

FIG. 1

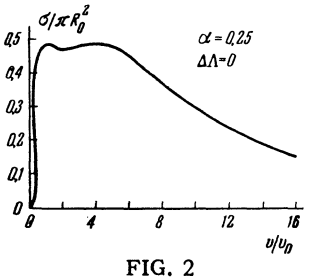

FIG. 2

distance from this point. The difference $E_1 - E_2$ changes rapidly near $R = R_0$. This is due to the singularity of the quantities χ_1 and χ_2, since the Hamiltonian H itself does not have any singularity as a function of R. It is therefore natural to assume that $(\partial/\partial R)_{12}^0$ is a smooth function, since E_1^0 and E_2^0 are smooth functions, whereas $(\partial/\partial R)_{12}$ includes a rapidly varying term $VF_{12}^0/(E_1 - E_2)^2$ [if we neglect $(\partial/\partial R)_{12}$, then in general there will be no such transitions].

We put

$$V' = V + K_{12}^0. \quad (10)$$

The solution of the system (8) can be found in the papers by Landau and Zener.[1,2] For the probability of transition of the system from state 2 into state 1 we obtain the Landau-Zener formula

$$w = 2e^{-S}(1 - e^{-S}), \quad (11)$$

$$S = 2\pi|V'|^2/\hbar v_R|F_{12}^0|. \quad (12)$$

Here $v_R = \dot{R}$ is the radial component of the relative velocity of the particle, while $F_{12}^0 = d(E_1^0 - E_2^0)/dR$. Formula (11) was derived under more general assumptions, with allowance for the dependence of the electron wave functions χ_n^0 on the time through the parameters $\mathbf{R}_a$ and $\mathbf{R}_b$.

We note that the matrix element K_{12} has, generally speaking, Galilean invariance. Actually,

$$\mathbf{R}_a\nabla_a + \dot{\mathbf{R}}_b\nabla_b = \tfrac{1}{2}(\dot{\mathbf{R}}_a - \dot{\mathbf{R}}_b)(\nabla_a - \nabla_b)$$
$$+ \tfrac{1}{2}(\dot{\mathbf{R}}_a + \dot{\mathbf{R}}_b)(\nabla_a + \nabla_b),$$

$$\dot{\mathbf{R}}_a - \dot{\mathbf{R}}_b = \dot{\mathbf{R}}, \quad \nabla_a - \nabla_b = \nabla_R.$$

The first term of the expression in the right half has Galilean invariance, while the second does not. It is easy to show that

$$(\nabla_a + \nabla_b)_{12}^0 = (\nabla_a + \nabla_b)_{12} = \hbar^{-2}m\mathbf{D}_{12}(E_1 - E_2), \quad (13)$$

where m is the electron mass and D is the dipole moment of the electrons. Therefore, in the case when $E_1 - E_2 \approx 0$, the matrix element K_{12} is approximately Galilean-invariant.

It is seen from (10) that the matrix element V' consists of a real and imaginary part. With allow-

ance for (9) and for the fact that $V = \frac{1}{2}(E_1 - E_2)_{min} = \Delta E/2$, the square of the modulus of this matrix element is

$$|V'|^2 = [(\Delta E)^2/4 + (\hbar(\dot{\mathbf{R}}\nabla_R)^0_{12})^2]_{R=R_0} = (\Delta E)^2/4 + \hbar^2 v_k^2 k^2,$$

$$\mathbf{k} = (\nabla_R)^0_{12}, \qquad (14)$$

where R is the radius vector joining the nuclei and v_k is the component of the velocity v in the direction of the vector k.

We thus obtain for S instead of (12) the expression

$$S = a/v_R + bv_k^2/v_R, \qquad v_k \sim v_R \sim v = |\dot{\mathbf{R}}|, \qquad (15)$$

$$a = \pi(\Delta E)^2/2\hbar|F^0_{12}|, \qquad b = 2\pi\hbar k^2/|F^0_{12}|. \qquad (16)$$

From an analysis of the dependence of the probability of transition w on the velocity v we see that the curve of this dependence has two maxima at values $v_k\sqrt{ab}/v_R = \alpha v_k/v_R < \frac{1}{2}\ln 2$; at values $\alpha v_k/v_R \geq \frac{1}{2}\ln 2$, both maxima merge into one.

The total effective cross section of the process is

$$\sigma = 2\pi\int_0^{R_0} wp\,dp, \qquad (17)$$

where p is the collision parameter.

We note that there are two possible types of transitions (Λ is the projection of the orbital momentum of the electrons on the axis joining the nuclei): 1) $\Delta\Lambda = 0$ (then $v_k = v_R$); 2) $\Delta\Lambda = \pm 1$ (then $v_k = v_\varphi$). For both cases we obtain one expression for the effective cross section σ:

$$\sigma = 2\pi R_0^2\int_0^1 2e^{-A/\eta - B\eta}(1 - e^{-A/\eta - B\eta})\,\eta\,d\eta, \qquad (18)$$

and if $\Delta\Lambda = 0$, then

$$A = \alpha v_0/v, \qquad B = \alpha v/v_0; \qquad (16a)$$

while if $\Delta\Lambda = \pm 1$, then

$$A = \alpha(v_0/v + v/v_0), \qquad B = -\alpha v/v_0. \qquad (16b)$$

Here

$$v_0 = \sqrt{a/b} = \Delta E/2\hbar k, \qquad \alpha = \pi\Delta E k/|F^0_{12}|.$$

The parameters A and B, generally speaking, vary within the limits $0 \leq A \leq +\infty$ and $-\infty < B < +\infty$. In addition, $A + B > 0$ when $\Delta\Lambda = \pm 1$.

We have calculated the cross section of the process by means of formula (18) for those values of the parameter α, at which the curves $w = w(v)$ have two maxima, i.e., $\alpha < \frac{1}{2}\ln 2$. In these cases the cross section $\sigma(v)$ also has two maxima with respect to the velocities; the two maxima are equal when $\Delta\Lambda = 0$ while the second maximum (at the higher velocity) is smaller than the first when $\Delta\Lambda = \pm 1$. The smaller α, the more separated are these maxima. It is obvious that when $\alpha \ll 0.3$ the first maximum in (15) is due to the first term at low velocities. This first term, as we have seen, is due to the minimal stationary splitting of the levels (spin-orbit and polarization effects). The second maximum is due to the second term in the expression for V' at high velocities. This term takes into account the dependence of the wave functions of the electrons on the time through the parameters (radius-vectors of the nuclei) i.e., it includes the interaction between the orbit and the motion of the nuclei.

When $\alpha \ll 0.01$ the two maxima are so separated, that in calculating the cross sections with these values of α, it is possible to consider in practice, for each of the maxima, either the first or the second terms in the expression (14) respectively.

References 4 — 6 consider several charge-exchange processes. In calculating the cross sections of these inelastic processes as functions of the velocity, these references took into account this dependence only in the first term of (14). Consequently the curves given there have only one maximum.

However, if α reaches a value 0.1, $\sigma(v)$ varies significantly even in the region of the first maximum. In half of the cases calculated by Bates, Moiseiwitsh, and Boyd,[4] α is found to be of order 0.1. For illustration, we give the plots of $\sigma(v)$ for $\alpha = 0.1$ and $\Delta\Lambda = \pm 1$ and 0 (Fig. 1) and for $\alpha = 0.25$ and $\Delta\Lambda = 0$ (Fig. 2). In the last case we see that $\sigma(v)$ is approximately constant in the interval $0.6\,v_0 < v < 6\,v_0$.

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