

Non-Adiabatic Crossing of Energy Levels.

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1. Introduction.

The crossing of energy levels has been a matter of considerable discussion.* The essential features may be illustrated in the crossing of a polar and homopolar state of a molecule.

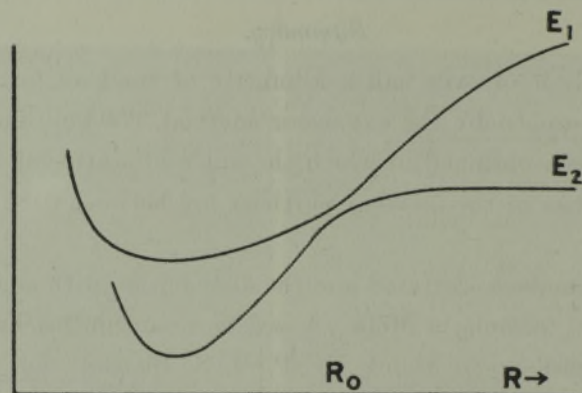


FIG. 1.—Crossing of polar and homopolar states.

Let $\psi_1(x/R)$, $\psi_2(x/R)$ be two electronic eigenfunctions of a molecule with stationary nuclei. Let these eigenfunctions have the property that for $R \gg R_0$, ψ_1 has polar characteristics, ψ_2 homopolar; while at $R \ll R_0$, ψ_2 has polar characteristics, ψ_1 homopolar. In the region $R = R_0$ these two eigenfunctions may be said to exchange their characteristics.

The adiabatic theorem tells us that if the molecule is initially in state ψ_2 , and R changes infinitely slowly from $R \gg R_0$ to $R \ll R_0$, then the molecule will remain in state ψ_2 . However, if R changes with a finite velocity, the final state $\psi(x/R)$ will be a linear combination

$$\psi(x/R) = A_1(R) \psi_1(x/R) + A_2(R) \psi_2(x/R). \quad (1)$$

Neumann and Wigner (*loc. cit.*) have found the conditions for which

$$A_1 \sim 0, \quad |A_2| \sim 1$$

and

$$|A_1| \sim 1, \quad A_2 \sim 0,$$

* Hund, 'Z. Physik,' vol. 40, p. 742 (1927); Neumann and Wigner, 'Phys. Z.,' vol. 30, p. 467 (1929); Kemble and Zener, 'Phys. Rev.,' vol. 33, p. 536 (1929).

respectively, without however obtaining the explicit dependence of the A 's upon the parameters of the system.

In order that the problem of obtaining this explicit dependence may be reduced to a precise soluble mathematical problem, it is desirable to specify the conditions of the transition as simply as possible, at the same time retaining the essential features.

Let ϕ_1, ϕ_2 be such linear combinations of ψ_1, ψ_2 , that for all values of R , ϕ_1 has the characteristics which ψ_1 has at $R \gg R_0$, while ϕ_2 has the characteristics which ψ_2 has at $R \gg R_0$. In our molecular example, ϕ_1 will be a pure polar state, ϕ_2 a pure homopolar state for all internuclear distances. While ϕ_1, ϕ_2 can be made orthogonal, they will not satisfy the wave equation for fixed nuclei, rather

$$\left. \begin{aligned} H\phi_1 &= \varepsilon_1 \phi_1 + \varepsilon_{12} \phi_2 \\ H\phi_2 &= \varepsilon_{12} \phi_1 + \varepsilon_2 \phi_2 \end{aligned} \right\} \quad (2)$$

The simplifications which will be made in order to obtain the explicit functions A_1, A_2 , are the following:—

- (a) $\varepsilon_{12}(R_0) \ll$ the relative kinetic energy of the two systems. Under this condition the motion of the centres of gravity of the two atoms, or in general of the two systems, may be treated as external parameters. That is, the variable R becomes a known function of time.
- (b) The transition region is so small that in it we may regard $\varepsilon_1 - \varepsilon_2$ as a linear function of time, and $\varepsilon_{12}(R)$, $\phi_1(x/R)$, $\phi_2(x/R)$ as independent of time. This condition is satisfied provided $\varepsilon_{12}(R_0)$ is sufficiently small. Since only the characteristics in the transition region are of importance, this condition enables us to replace the physical problem by an ideal problem in which

$$\left. \begin{aligned} \frac{2\pi}{h}(\varepsilon_1 - \varepsilon_2) &= \alpha t \\ \dot{\varepsilon}_{12} = \dot{\phi}_1 = \dot{\phi}_2 &= 0 \end{aligned} \right\} \quad (3)$$

for all time.

If the relative velocity of the atoms is constant, assumption (b) leads to the relationship shown in fig. 2 between $\varepsilon_1(R)$, $\varepsilon_2(R)$ and the eigenwerte of ψ_1, ψ_2 , namely $E_1(R)$, $E_2(R)$.

$E_1(R)$, $E_2(R)$ are hyperbolæ having $\varepsilon_1(R)$, $\varepsilon_2(R)$ as asymptotes. The closest distance between E_1 and E_2 , i.e., $E_1(R_0) - E_2(R_0)$, is given by $2\varepsilon_{12}(R_0)$.

2. Analysis.

In the analysis it has been found more convenient to use the linear combinations ϕ_1 , ϕ_2 of the exact adiabatic solutions ψ_1 , ψ_2 rather than these

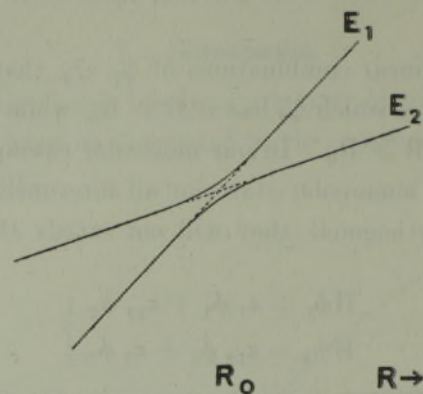


FIG. 2.—Crossing of energy levels in idealised problem. Full lines are adiabatic eigenwerte.

solutions themselves. Further, it has been found advantageous to start from the wave equation in the form

$$\left(H - \frac{\hbar}{2\pi i} \frac{\delta}{\delta t} \right) \left\{ C_1(t) e^{\frac{2\pi i}{\hbar} \int \epsilon_1 dt} \phi_1(x) + C_2(t) e^{\frac{2\pi i}{\hbar} \int \epsilon_2 dt} \phi_2(x) \right\} = 0.$$

The relations (2) reduce this wave equation to two simultaneous first order differential equations in the C 's.

$$\left. \begin{aligned} \frac{\hbar}{2\pi i} \frac{\delta C_1}{\delta t} &= \epsilon_{12} e^{-\frac{2\pi i}{\hbar} \int (\epsilon_1 - \epsilon_2) dt} C_2, \\ \frac{\hbar}{2\pi i} \frac{\delta C_2}{\delta t} &= \epsilon_{21} e^{\frac{2\pi i}{\hbar} \int (\epsilon_1 - \epsilon_2) dt} C_1. \end{aligned} \right\}. \quad (4)$$

The boundary conditions under which these equations are to be solved must correspond to our knowledge that initially the system is in state ψ_2 or ϕ_2 , which are equivalent when $R \gg R_0$. These conditions are thus

$$C_1(-\infty) = 0. \quad (5A)$$

$$|C_2(-\infty)| = 1. \quad (5B)$$

If we call $|A_1(R \ll R_0)|^2$ of (1) the probability P of a non-adiabatic transition, then

$$P = |C_2(\infty)|^2 = 1 - |C_1(\infty)|^2.$$

We thus need know only the asymptotic values of the solutions of (4).

Elimination of C_2 from (4) leads to the single equation

$$\frac{d^2 C_1}{dt^2} + \left\{ \frac{2\pi i}{h} (\varepsilon_1 - \varepsilon_2) - \frac{\dot{\varepsilon}_{12}}{\varepsilon_{12}} \right\} \frac{dC_1}{dt} + \left(\frac{2\pi \varepsilon_{12}}{h} \right)^2 C_1 = 0. \quad (6)$$

Substitution of the assumption (3), together with the definition

$$f = \frac{2\pi \varepsilon_{12}}{h}$$

and the substitution

$$C_1 = e^{-\frac{\pi i}{h} \int (\varepsilon_1 - \varepsilon_2) dt} U_1$$

reduces (6) to the Weber* equation

$$\frac{d^2 U_1}{dt^2} + \left(f^2 - \frac{i\alpha}{2} + \frac{\alpha^2}{4} t^2 \right) U_1 = 0.$$

This is thrown into the standard form

$$\frac{d^2 U_1}{dz^2} + \left(n + \frac{1}{2} - \frac{1}{4} z^2 \right) U_1 = 0,$$

by the substitutions

$$z = \alpha^{\frac{1}{2}} e^{-i\pi/4} t$$

$$n = if^2/\alpha.$$

The Weber function $D_{-n-1}(iz)$ is a particular solution of this equation which vanishes for infinite z along the directions $\propto \exp(-\frac{3}{4}\pi i)$ and $\propto \exp(-\frac{1}{4}\pi i)$. Hence the solution

$$U_1(z) = A_{\pm} D_{-n-1}(\mp iz), \quad \alpha \geq 0,$$

satisfies the first boundary condition (5A).

The constants A_{\pm} are determined from the asymptotic values

$$D_{-n-1}(iR e^{-\frac{1}{2}\pi i}) \xrightarrow{R \rightarrow \infty} e^{\frac{\pi}{4}(n+1)i} e^{iR^2/4} R^{-n-1},$$

$$D_{-n-1}(iR e^{-\frac{3}{4}\pi i}) \xrightarrow{R \rightarrow \infty} e^{-\frac{\pi}{4}(n+1)i} e^{-iR^2/4} R^{-n-1},$$

by means of the second boundary condition (5B). We find

$$|A_+| = |A_-| = \gamma^{\frac{1}{2}} e^{-\pi\gamma/4},$$

where

$$\gamma = f^2/|\alpha|.$$

* Those properties of this equation, and of its solutions, which are used in this analysis are fully discussed in Whitaker and Watson's "Modern Analysis," pp. 347-349, 4th ed.

Summarising,

$$e^{i\frac{\pi\alpha t}{h}} \underset{t \rightarrow \infty}{L} C_1(t) = \underset{z \rightarrow \alpha^{1/2} \infty \exp(-i\frac{1}{2}\pi)}{L} U_1(z) = \begin{cases} \gamma^{\frac{1}{2}} e^{-\pi\gamma/4} \underset{R \rightarrow \infty}{L} D_{-n-1}(iRe^{i\pi/4}), & \alpha > 0. \\ \gamma^{\frac{1}{2}} e^{-\pi\gamma/4} \underset{R \rightarrow \infty}{L} D_{-n-1}(iRe^{i\pi/4}), & \alpha < 0. \end{cases}$$

By use of the asymptotic values

$$\underset{R \rightarrow \infty}{L} D_{-n-1}(iRe^{i\pi/4}) = e^{i\pi(n+1)/4} e^{-iR^{3/4}/4} R^{-n-1} + \frac{\sqrt{2\pi}}{\Gamma(n+1)} e^{i\pi n/4} e^{iR^{3/4}/4} R^n,$$

$$\underset{R \rightarrow \infty}{L} D_{-n-1}(iRe^{i\pi/4}) = e^{-i\pi(n+1)/4} e^{iR^{3/4}/4} R^{-n-1} + \frac{\sqrt{2\pi}}{\Gamma(n+1)} e^{i\pi n/4} e^{-iR^{3/4}/4} R^n$$

we obtain

$$\begin{aligned} |C_1(\infty)|^2 &= \frac{2\pi\gamma e^{-\pi\gamma}}{\Gamma(i\gamma+1)\Gamma(-i\gamma+1)} = 2e^{-\pi\gamma} \sinh \pi\gamma \\ &= 1 - e^{-2\pi\gamma}. \end{aligned}$$

Therefore

$$P = e^{-2\pi\gamma}, \quad \gamma = \frac{2\pi}{h} \varepsilon_{12}^2 \left/ \left| \frac{d}{dt} (\varepsilon_1 - \varepsilon_2) \right| \right|.$$

Rosenkewitsch* states that Landau has obtained the formula

$$P \sim e^{-\frac{\pi}{2hv} \frac{\Delta^2}{F_1 - F_2}}$$

where $\Delta = 2\varepsilon_{12}$, v is the relative velocity, and F_1, F_2 are the "forces" acting upon the two states. If the identification $\frac{d}{dt} (\varepsilon_1 - \varepsilon_2) = v(F_1 - F_2)$ can be made, the exponent of Landau's formula is too small by a factor of 2π .

3. Discussion.

Equation (6), with $\varepsilon_1, \varepsilon_2, \varepsilon_{12}$, as arbitrary functions of time, is the general equation for a transition probability between two electronic states, provided (a) all other states may be neglected; (b) the motion of the atoms may be taken as external parameters; (c) changes in the "unperturbed" wave functions ϕ_1, ϕ_2 may be neglected. Two cases are of particular interest. In one $\varepsilon_1 - \varepsilon_2 = \Delta E$, a constant, and ε_{12} is a function having the general form of curve *a*, fig. 3. In the other $\varepsilon_1 - \varepsilon_2$ is a linear function, and ε_{12} is a constant.

* 'Phys. Z. U.S.S.R.', vol. 1, p. 426 (1932).

An investigation* of the first case has revealed that the transition probability P satisfies the inequality

$$P \leq \left| \frac{\int_{-\infty}^{\infty} \varepsilon_{12}(t) e^{\frac{2\pi i}{h} \Delta E t} dt}{\int_{-\infty}^{\infty} \varepsilon_{12}(t) dt} \right|^2$$

A more instructive form is obtained by introducing the variable $\xi = t/\tau$, where τ is the time of collision defined by

$$\tau \varepsilon_{12}(0) = \int_{-\infty}^{\infty} \varepsilon_{12}(t) dt.$$

Then

$$P \leq \left| \frac{\int_{-\infty}^{\infty} \varepsilon_{12}(\xi) e^{\frac{2\pi i}{h} \tau \Delta E \xi} d\xi}{\int_{-\infty}^{\infty} \varepsilon_{12}(\xi) d\xi} \right|^2. \quad (7)$$

When $\tau \Delta E/h > 1$, P is much smaller when ε_{12} is an analytic function than of the type of curve b , fig. 2. The question arises, would this difference in the two P 's be eliminated merely by rounding off the corners of curve b , or must all

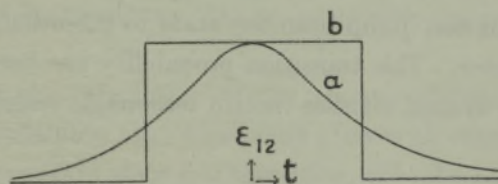


FIG. 3.— ε_{12} when $\varepsilon_1 - \varepsilon_2 = \text{a constant}$.

derivatives of ε_{12} be continuous? We find the answer when we integrate the numerator of (7) by parts. Since ε_{12} vanishes at $\xi = \pm \infty$, an expansion of P in inverse powers of $(2\pi\tau\Delta E/h)$ is seen to start with the $-2n$ 'th power, where n is the order of the first discontinuous derivative of ε_{12} .†

The second case has been solved in the preceding section. The problem is illustrated in fig. 2.

It was found that the transition probability P was

$$P = e^{-\frac{\pi^2}{h} \Delta^2} \left| \frac{d}{dt} (\varepsilon_1 - \varepsilon_2) \right|$$

* N. Rosen and C. Zener, 'Phys. Rev.', vol. 40, p. 502 (1932).

† The author is indebted to Professor Norbert Wiener for pointing out this relation.

where $\Delta = 2\varepsilon_{12}(0)$ = closest distance between the adiabatic eigenwerte E_1 , E_2 of the system.

In both cases P depends upon the relative velocity v in nearly the same manner, namely

$$P \sim e^{-v_0/v}.$$

In collisions one measures an effective cross section Q . Let the transitional region occur about the interatomic distance R_0 , then since v refers to the component of the relative velocity along the internuclear line, Q will be given by approximately

$$\begin{aligned} Q &= \pi R_0^2 \int_0^{\pi/2} e^{-v_0/v \cos \theta} \sin \theta \, d\theta \\ &= \pi R_0^2 \left\{ e^{-v_0/v} + \frac{v_0}{v} \text{Ei}(-v_0/v) \right\}. \end{aligned}$$

Summary.

When a single parameter is varied adiabatically, two eigenwerte of a system may approach each other, and then recede, the corresponding eigenfunctions having exchanged their characters. If the parameter is varied with a finite velocity, the system may jump from one state to the other, thus not suffering a change of character. This transition probability has been rigorously calculated provided the system satisfies certain reasonable restrictions.