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Author(s): D. R. Bates
Source: *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 257, No. 1288 (Aug. 23, 1960), pp. 22-31
Published by: Royal Society
Stable URL: https://www.jstor.org/stable/2413796
Accessed: 06-11-2018 12:58 UTC

Collisions involving the crossing of potential energy curves

By D. R. Bates, F.R.S.

Department of Applied Mathematics, The Queen's University of Belfast

(*Received* 11 *March* 1960)

The Landau–Zener formula for the transition probability at a crossing of potential energy curves is discussed. It is pointed out that the model used in the derivation has defects which make the range of validity of the formula much more restricted than is commonly supposed.

1. Introduction

Inelastic encounters between atomic systems are inherently very complicated to describe mathematically. It is therefore not surprising that little progress has been made towards developing methods for carrying out detailed calculations on collision cross-sections except at high velocities of relative motion. Indeed, the only relevant formula which can be evaluated at all readily is one pertaining to curve-crossing. This formula was derived independently by Landau (1932) and by Zener (1932), after whom it is named, and by Stueckelberg (1932). It has been used in a number of computations and because of its attractive simplicity it is introduced in many text-books on quantum mechanics. The object of the present note is to point out that it is in fact invalid over much of the energy range for which it seemingly was designed, and certainly has been employed, the restriction on the range being especially severe if the atomic orbitals involved are not spherically symmetrical.

2. Landau–Zener formula

To facilitate the subsequent discussion of the limitations of the Landau–Zener formula we shall here recall the essential features of its derivation.

Consider the transfer of an electron from state n of an atomic system A to state m of an atomic system B,

$$(A+e)_n + B \rightarrow A + (B+e)_m. \tag{1}$$

Let $\mathbf{R}$ be the relative position vector of the nuclei (which will be treated as classical particles) and let $\mathbf{r}$ be the position vector of the active electron with respect to the (fixed) mid-point of the internuclear line. Take $\psi_n(\mathbf{r}|\mathbf{R})$ and $E_n(R)$ to be the exact electronic eigenfunction and eigenenergy of the quasi-molecule formed when the systems on the left of (1) approach adiabatically from infinity and take $\psi_m(\mathbf{r}|\mathbf{R})$ and $E_m(R)$ to be the corresponding eigenfunction and eigenenergy associated with the systems on the right. It is supposed that at some internuclear distance R_c there is a pseudo-crossing of the curves, $E_n(R)$ and $E_m(R)$, with a related change in the forms of the eigenfunctions, so that whereas for $R \gg R_c$, $\psi_n(\mathbf{r}|\mathbf{R})$ and $\psi_m(\mathbf{r}|\mathbf{R})$ describe $(A+e)_n + B$ and $A + (B+e)_m$, respectively, for $R \ll R_c$ they describe $A + (B+e)_m$ and $(A+e)_n + B$, respectively. Two orthogonal linear combinations of $\psi_n(\mathbf{r}|\mathbf{R})$ and $\psi_m(\mathbf{r}|\mathbf{R})$ may be found such that for *any* internuclear distance one, $\phi_n(\mathbf{r}|\mathbf{R})$,

describes $(A+e)_n+B$ and the other, $\phi_m(\mathbf{r}|\mathbf{R})$, describes $A+(B+e)_m$. These satisfy the equations

$$\mathscr{H}\phi_n(\mathbf{r}|\mathbf{R}) = \hbar_{nn}(R)\,\phi_n(\mathbf{r}|\mathbf{R})+\hbar_{mn}(R)\,\phi_m(\mathbf{r}|\mathbf{R}) \tag{2}$$

and

$$\mathscr{H}\phi_m(\mathbf{r}|\mathbf{R}) = \hbar_{nm}(R)\,\phi_n(\mathbf{r}|\mathbf{R})+\hbar_{mm}(R)\,\phi_m(\mathbf{r}|\mathbf{R}), \tag{3}$$

where $\mathscr{H}$ is the Hamiltonian operator and where

$$\hbar_{pq}(R) = \int \phi_p^*(\mathbf{r}|\mathbf{R})\,\mathscr{H}\phi_q(\mathbf{r}|\mathbf{R})\,\mathrm{d}\mathbf{r}. \tag{4}$$

By definition, R_c is the internuclear distance at which the curves $\hbar_{nn}(R)$ and $\hbar_{mm}(R)$ cross. Attention is confined to encounters for which the energy of relative motion at the crossing is very much greater than the difference between the exact eigenenergies there, that is to encounters for which

$$\mathscr{E} \gg 2\,|\hbar_{nm}(R_c)|. \tag{5}$$

If terms not involving the initial and final states may be ignored the electronic wave function of the colliding systems may be expressed approximately in the form

$$\mathrm{X} = c_n(t)\Phi_n+c_m(t)\,\Phi_m, \tag{6}$$

where the c's are coefficients dependent on the impact parameter ρ as well as on the time t and where

$$\Phi_n = \phi_n(\mathbf{r}|\mathbf{R})\exp\left\{-\tfrac{1}{2}\mathrm{i}kz-\frac{\mathrm{i}}{\hbar}\int^t[\hbar_{nn}(R)+\tfrac{1}{8}mv^2]\,\mathrm{d}t\right\} \tag{7}$$

and

$$\Phi_m = \phi_m(\mathbf{r}|\mathbf{R})\exp\left\{\tfrac{1}{2}\mathrm{i}kz-\frac{\mathrm{i}}{\hbar}\int^t[\hbar_{mm}(R)+\tfrac{1}{8}mv^2]\,\mathrm{d}t\right\}, \tag{8}$$

with

$$k = mv/\hbar, \tag{9}$$

$$z = \mathbf{r}.\hat{\mathbf{v}}, \tag{10}$$

$\mathbf{v}$ being the relative velocity of the nuclei which as far as the determination of the transition probability is concerned† is taken to be constant and to equal the value at the crossing. With the aid of (2) and (3) it may be proved that

$$\left\{\mathscr{H}-\mathrm{i}\hbar\frac{\partial}{\partial t}\right\}\Phi_n = \left[\hbar_{mn}\phi_m-\mathrm{i}\hbar v\frac{\partial}{\partial Z_{\mathbf{r}_1}}\phi_n\right]\exp\left\{-\tfrac{1}{2}\mathrm{i}kz-\frac{\mathrm{i}}{\hbar}\int^t(\hbar_{nn}+\tfrac{1}{8}mv^2)\,\mathrm{d}t\right\} \tag{11}$$

and

$$\left\{\mathscr{H}-\mathrm{i}\hbar\frac{\partial}{\partial t}\right\}\Phi_m = \left[\hbar_{nm}\phi_n-\mathrm{i}\hbar v\frac{\partial}{\partial Z_{\mathbf{r}_2}}\phi_m\right]\exp\left\{\tfrac{1}{2}\mathrm{i}kz-\frac{\mathrm{i}}{\hbar}\int^t(\hbar_{mm}+\tfrac{1}{8}mv^2)\,\mathrm{d}t\right\}, \tag{12}$$

where

$$Z = \mathbf{R}.\hat{\mathbf{v}} = vt, \tag{13}$$

and where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the active electron with respect to the nuclei of A and B.

The assumption is made that the encounter is so slow that

(i) the $\exp(\pm\frac{1}{2}\mathrm{i}kz)$ factors may throughout be replaced by unity;

(ii) the second term in each of the square brackets on the right of the above equations may be neglected.

† In calculating the associated cross-section allowance is made for the variation of $\mathbf{v}$ along the classical orbit.

Substituting (6) in the Schrödinger equation and using the simplified versions of (11) and (12) it may be shown that

$$i\hbar v \frac{\partial c_n(Z)}{\partial Z} = \hbar_{nm} c_m(Z) \exp\left\{\frac{-i}{v\hbar}\int^Z (\hbar_{mm} - \hbar_{nn})\, dZ\right\} \tag{14}$$

and

$$i\hbar v \frac{\partial c_m(Z)}{\partial Z} = \hbar_{mn} c_n(Z) \exp\left\{\frac{-i}{v\hbar}\int^Z (\hbar_{nn} - \hbar_{mm})\, dZ\right\}. \tag{15}$$

Boundary conditions appropriate to the process being investigated are

$$c_n(-\infty) = 1, \quad c_m(-\infty) = 0. \tag{16}$$

A plausible model for which (14) and (15) may be treated analytically is now introduced. It is supposed that transitions only occur to an appreciable extent in a very narrow zone around the crossing. Within such a zone it is certainly permissible to take

$$\hbar_{nn} - \hbar_{mm} = (Z - Z_c)\alpha \tag{17}$$

and

$$\hbar_{nm} = \hbar_{mn} = \beta, \tag{18}$$

where

$$Z_c = \mathbf{R}_c . \hat{\mathbf{v}} \tag{19}$$

and α and β are constants. If relatively few transitions occur without, there is no reason why these relations, in spite of being invalid without, should not be adapted everywhere. The asymptotic amplitudes of the required solutions of (14) and (15) may then be obtained using the properties of the Weber function (Zener 1932). Their moduli are found to be given by

$$|c_n(\infty)|^2 = P \tag{20}$$

and

$$|c_m(\infty)|^2 = 1 - P, \tag{21}$$

with

$$P = \exp(-w), \tag{22}$$

where

$$w = \frac{2\pi}{\hbar}\hbar_{nm}^2 \Big/ v(\hbar'_{nn} - \hbar'_{mm}), \tag{23}$$

the primes indicating differentiation with respect to Z and all quantities being evaluated at the crossing, at internuclear distance R_c of the approximate potentials. Clearly P is the probability that in traversing the crossing the systems remain on the $\hbar_{nn}(R)$ curve (or, viewed in another way, that they jump from the $E_n(R)$ curve to the $E_m(R)$ curve); and $1-P$ is the probability that they jump from the $\hbar_{nn}(R)$ curve to the $\hbar_{mm}(R)$ curve (or, viewed in another way, that they remain on the $E_n(R)$ curve). Noting that in the case of a collision a crossing must be traversed twice, we can see that the probability that systems which initially approach in state n should finally recede in state m is

$$\mathscr{P} = 2P(1-P). \tag{24}$$

This is the Landau–Zener formula.

3. Nature of defects

3·1. Critical examination reveals that part of the basis of the Landau–Zener formula is incorrect in that, contrary to what is assumed, transitions may readily occur well away from the crossing.

The transition zone is the ill-defined zone around the crossing where the oscillations of the exponential functions on the right of (14) and (15) are not unduly rapid and therefore do not lead to pronounced cancellation when the equations are integrated. Treating the interaction matrix element $\hbar_{nm}$ as approximately constant, it may be seen that the width ΔZ of the transition zone is such that

$$\frac{1}{v\hbar}\left|\int_{Z_c-\frac{1}{2}\Delta Z}^{Z_c}(\hbar_{mm}-\hbar_{nn})\,\mathrm{d}Z+\int_{Z_c}^{Z_c+\frac{1}{2}\Delta Z}(\hbar_{nn}-\hbar_{mm})\,\mathrm{d}Z\right|=s\pi, \tag{25}$$

s being a dimensionless quantity somewhat greater than unity. Substitution from (17) yields

$$\Delta Z = (4\pi v\hbar s/\alpha)^{\frac{1}{2}}. \tag{26}$$

The width of the transition zone in the case of the model is thus proportional to the square root of the velocity of relative motion and is unbounded.

Since the difference between the Z-co-ordinates of the two crossings which arise in a collision is naturally finite, the failure of the model to set up an upper limit to ΔZ is unsatisfactory. It is responsible for the prediction by the Landau–Zener formula that if the velocity of relative motion v is increased, keeping the impact parameter fixed, the probability of charge transfer ultimately decreases as v^{-1} instead of as v^{-2} as, of course, it should.† This may readily be demonstrated. If v is sufficiently high $c_n(Z)$ does not differ significantly from unity. We see from (15) that $|c_m(\infty)|$ is then proportional to $\Delta Z/v$; from which we see also that the probability $|c_m(\infty)|^2$ is proportional to v^{-1} if ΔZ increases indefinitely as $v^{\frac{1}{2}}$ as it does in the model, but that $|c_m(\infty)|^2$ is proportional to v^{-2} if ΔZ is bounded as it is in fact. Proceeding instead purely analytically we have from (15) that

$$|c_m(\infty)| \sim \left|\frac{2\hbar_{mn}(R_c)}{\hbar v}\cdot\int_0^\infty \exp\frac{-\mathrm{i}\alpha Z^2}{2\hbar v}\,\mathrm{d}Z\right| \sim \left|\left(\frac{2\pi}{\hbar v\alpha}\right)^{\frac{1}{2}}\hbar_{mn}(R_c)\right| \tag{27}$$

in the case of the model. The correct asymptotic dependence on v would obviously ensue if the limits in the integral were finite.

Fallacious results are obtained not only when v is high. Though normally a rapidly decreasing function of Z, $|\hbar_{nm}|$ is taken to be constant in the derivation of the Landau–Zener formula. However, as will be demonstrated, ΔZ is in general too large for this procedure to be justified even when v is but moderate in magnitude.

Consider a representative collision in which to a sufficient approximation

$$\hbar_{nn}(R)-\hbar_{mm}(R) = \pm e^2/R+\hbar_{nn}(\infty)-\hbar_{mm}(\infty) \tag{28}$$

near the crossing, e being the electronic charge. Taking the impact parameter to be zero for simplicity, we have that

$$|\alpha| = e^2/Z_c^2. \tag{29}$$

Hence (26) may be written

$$\Delta Z = Z_c(4\pi\hbar sv/e^2)^{\frac{1}{2}} \simeq 0{\cdot}28Z_c s^{\frac{1}{2}}(\mathscr{E}/M)^{\frac{1}{4}}, \tag{30}$$

in which $\mathscr{E}$, the energy of relative motion at the crossing, is in eV and M, the reduced mass of the colliding atoms, is on the chemical (^{16}O) scale. Remembering that s

† The effect of the change in the translational motion of the active electron is here ignored.

is somewhat greater than unity,† we see from (30) that ΔZ may actually be comparable with Z_c even when $\mathscr{E}/M$ is not very large.

It is apparent from (22) that the probability $\mathscr{P}$ introduced in (24) is a maximum when w is 0·69‡ and therefore when $\mathscr{E}$ has the value $\mathscr{E}_a$ such that

$$(\mathscr{E}_a/M)^{\frac{1}{2}} \simeq 1{\cdot}4\,|\hbar_{nm}(R_c)|\,Z_c, \tag{31}$$

$\hbar_{nm}$ being in electron volts and Z_c in atomic units. Substituting in (30) we find that at the maximum the width of the transition zone is

$$\Delta Z_a \simeq 0{\cdot}49\,|\hbar_{nm}(R_c)|\,Z_c^2. \tag{32}$$

If the interaction is strong this width may be considerable.

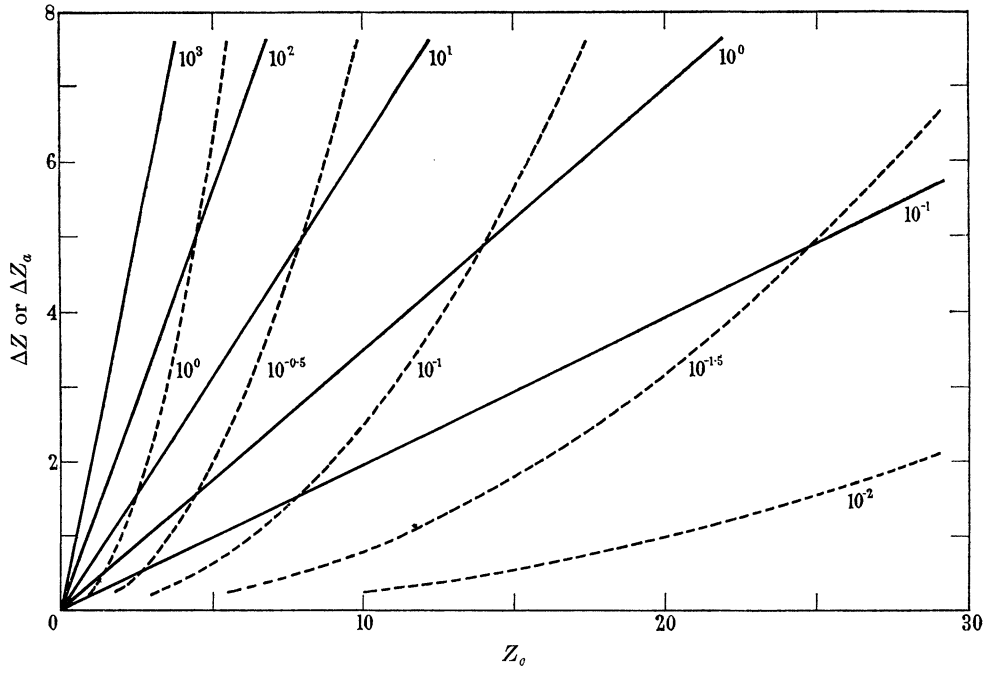

FIGURE 1. Width of transition zone. ———, ΔZ for value of $\mathscr{E}/M$ indicated; – – – –, ΔZ_a at maximum of $\mathscr{P}$ for value of $2|\hbar_{nm}|$ indicated. ($\mathscr{E}$ and $2|\hbar_{nm}|$ are in eV, M is on the chemical scale and ΔZ, ΔZ_a and Z_c are in atomic units.)

An indication of the behaviour when $\mathscr{E}$ greatly exceeds $\mathscr{E}_a$ may be obtained by expanding $\hbar_{nm}$ in a Taylor series about the crossing-point and proceeding otherwise as before. This yields

$$\mathscr{P} \sim 2w(1+\Gamma), \tag{33}$$

where w is as defined in (23) and the correction to the Landau–Zener formula due to the terms of the Taylor series after the first is

$$\Gamma = \left\{\frac{(\hbar''_{nm})^2 - \hbar_{nm}\hbar^{\mathrm{iv}}_{nm}}{(\hbar_{nm})^2}\right\}_{R=R_c} \gamma + \ldots, \tag{34}$$

with

$$\gamma = \left\{\frac{\hbar v}{2\,|\hbar'_{nn} - \hbar'_{mm}|}\right\}^2_{R=R_c} \tag{35}$$

† To be definite we shall in future arbitrarily replace 0·28 $s^{\frac{1}{2}}$ by 0·35.

‡ The position of the maximum cross-section is of course somewhat different—it occurs when w is 0·42 (cf. Boyd & Moiseiwitsch 1957).

From (28) it may be seen that (35) becomes

$$\gamma \doteq 1 \times 10^{-5} Z_c^4 \mathscr{E}/M, \tag{36}$$

in which the units are as specified in the preceding paragraph. The correction can give rise to a second maximum in the $\mathscr{P}$–$\mathscr{E}$ curve.

To enable the position to be readily assessed graphs of ΔZ against Z_c for selected values of $\mathscr{E}/M$ together with graphs of ΔZ_a against Z_c for selected values of $2|\hbar_{nm}|$ are presented in figure 1; and the calculated values of the relevant basic parameters for a number of charge-transfer processes are given in table 1. It is observed that for a particular type of process $2|\hbar_{nm}|$ tends to decrease rapidly as Z_c is increased.

TABLE 1. INFORMATION ON SOME PROCESSES INVOLVING CURVE-CROSSING (HEAD-ON COLLISIONS)

process	inter-nuclear distance at crossing Z_c (atomic units)	difference between exact energies at crossing $2\|\hbar_{nm}\|$ (eV)	energy of relative motion when probability $\mathscr{P}$ is maximum† $\mathscr{E}_a$ (eV)	width of corre-sponding transition zone† ΔZ_a (atomic units)
type‡ $He + X^{3+} \rightarrow He^+ + X^{2+}$				
with $X^{2+} = Be^{2+}(^3S)$	5·0 [a]	$9{\cdot}6 \times 10^{-1}$ [a]	$3{\cdot}7 \times 10^{2}$	4·4
$Be^{2+}(^3P)$	7·3 [a]	$9{\cdot}0 \times 10^{-2}$ [a]	$(1{\cdot}2 \times 10^{-1})$	(0·8)
$Be^{2+}(^1P)$	9·6 [a]	$4{\cdot}3 \times 10^{-3}$ [a]	$(2{\cdot}0 \times 10^{-6})$	(0·1)
type $H + X^{2+} \rightarrow H^+ + X^+$				
with $X^+ = Al^+(^1S)$	5·2 [b]	1·5 [b]	$1{\cdot}0 \times 10^{3}$	10·8
$Si^+(^2P)$	·9·6 [c]	$1{\cdot}0 \times 10^{-1}$ [c]	$(2{\cdot}3 \times 10^{-1})$	(2·4)
$B^+(^1P)$	11·1 [b]	$5{\cdot}7 \times 10^{-3}$ [b]	$(3{\cdot}4 \times 10^{-6})$	(0·2)
type $H^- + X^+ \rightarrow H + X$				
with $X = Li(2s)$	7·5 [d]	$6{\cdot}1 \times 10^{-1}$ [d]	$9{\cdot}0 \times 10^{1}$	8·6
$Na(3d)$	35·2 [d]	$4{\cdot}9 \times 10^{-3}$ [d]	$(2{\cdot}0 \times 10^{-4})$	(1·5)
$K(5p)$	51·4 [d]	$3{\cdot}8 \times 10^{-4}$ [d]	$(3{\cdot}4 \times 10^{-8})$	(0·3)

[a] Boyd & Moiseiwitsch (1957); [b] Dalgarno (1954);
[c] Bates & Moiseiwitsch (1954); [d] Bates & Boyd (1956).

† The brackets around certain of the entries indicates that $\mathscr{E}_a$ is not high enough for (5) to be satisfied.

‡ For this type of process, (29), (30), (32) and (36) must be multiplied on the right by 2, $2^{-\frac{1}{2}}$, $2^{-\frac{1}{2}}$ and 2^{-2}, respectively.

3·2. For reasons which will be obvious later (§3·3) we shall in this sub-section confine our attention to encounters involving only spherically symmetrical atomic orbitals.

Consider a charge-transfer process for which Z_c is sufficiently large (cf. table 1) to make $\mathscr{E}_a$ as given by (31), about the same as or less than $2|\hbar_{nm}|$ so that requirement (5) is not satisfied. The $\mathscr{P}$–$\mathscr{E}$ curve of Landau and Zener, obtained from (22) to (24) is inaccurate at least in the region up to and somewhat beyond its peak, the value of $\mathscr{E}$ at which a given value of $\mathscr{P}$ is predicted to occur being too low. When $\mathscr{E}$ is such that (5) is first satisfied ΔZ may still be small enough for the solutions of

(14) and (15) proposed by Landau and Zener to be valid; and these solutions may remain valid while $\mathscr{E}$ is increased by a considerable factor. However, when $\mathscr{E}$ is moderate in magnitude ΔZ becomes so large that failure to take account of the variation of the interaction energies with nuclear separation leads to serious error. In this region the value of $\mathscr{P}$ obtained from the Landau–Zener formula may be very

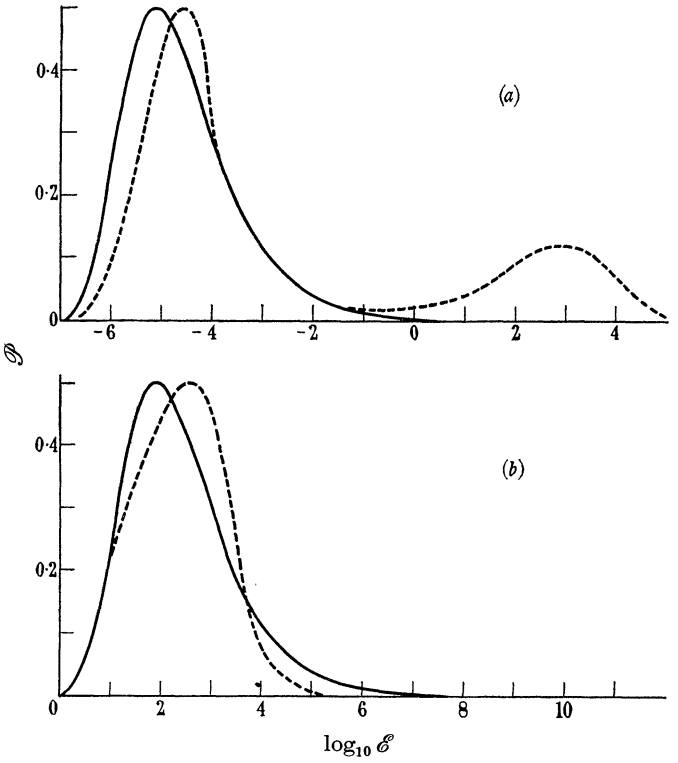

FIGURE 2. Probability $\mathscr{P}$ of charge transfer for s-s transitions; ———, calculated from Landau–Zener formula; – – – –, qualitatively corrected result. In (*a*) Z_c is large and in (*b*) Z_c is moderate or small in sense described in text. (The units for $\mathscr{E}$ are here arbitrary but in representative cases might be eV.)

much less than the value corresponding to the exact solutions of (14) and (15) which may be taken to be

$$\mathscr{P} = 2\left|\frac{1}{\hbar v}\int_{-\infty}^{\infty} h_{nm}\exp\left\{\frac{-\mathrm{i}}{\hbar v}\int_0^Z (h_{nn}-h_{mm})\,\mathrm{d}Z\right\}\mathrm{d}Z\right|^2 \tag{37}$$

and which may rise with increase in $\mathscr{E}$ and pass through a second maximum. As already explained the Landau–Zener $\mathscr{P}$–$\mathscr{E}$ curve falls off much too slowly asymptotically. Consequently the true $\mathscr{P}$–$\mathscr{E}$ curve eventually drops below it. Figure 2*a* compares the forms of the two $\mathscr{P}$–$\mathscr{E}$ curves schematically. A similar comparison is made in figure 2*b* for the case of a charge-transfer process having R_c moderate or small so that $\mathscr{E}_a$ is much greater than $2\,|h_{nm}(R_c)|$ and so that in addition ΔZ_a is large enough to invalidate the simple treatment even before the maximum is reached.

3·3. Equations (14) and (15) are not of course themselves exact: they depend on assumptions (i) and (ii) of §2; on assumption (iii) that the wave function X may be

written as in (6); and on assumption (iv) that the energy of relative motion is such that inequality (5) is satisfied.

Assumption (i) corresponds to ignoring any effect due to the change in the translational motion of the active electron when transferred from one system to the other. It is unjustified at velocities of relative motion greater than that at which

$$1/k(\equiv \hbar/mv) \simeq l, \tag{38}$$

where l is a measure of the linear extent of the more compact of the two atomic eigenfunctions involved; that is, it is unjustified if $\mathscr{E}$ exceeds

$$\mathscr{E}_T \simeq (2{\cdot}5\times 10^4 M/l^2)\,\mathrm{eV}, \tag{39}$$

in which M is on the chemical scale and l is in atomic units. As $\mathscr{E}$ is increased above $\mathscr{E}_T$ which is in general quite high, $\mathscr{P}$ falls off very rapidly because of the cancellation within the matrix element.

Serious error is likely to arise from assumptions (ii) and (iii) unless the eigenfunctions ϕ_n and ϕ_m are spherically symmetrical or unless the velocity of relative motion is low. Consider, for example, a charge-transfer process in which the electron is initially in an s state and finally in a p state. As will be seen shortly it is necessary to take account not only of the p state with angular eigenfunction $(3/4\pi)^{\frac{1}{2}}\cos\theta$ but also of that with angular eigenfunction $(3/4\pi)^{\frac{1}{2}}\sin\theta\sin\phi$, where θ is the polar angle with respect to the internuclear axis and ϕ is the azimuthal angle. Consequently (6) is modified to

$$\mathrm{X} = c_s(t)\,\Phi_s + c_{p_0}(t)\,\Phi_{p_0} + c_{p_1}(t)\,\Phi_{p_1}, \tag{40}$$

in which the original identifying subscripts n and m have, for clarity, been replaced by s and p_0, respectively, and the extra identifying subscript p_1 refers to the additional state introduced. The matrix elements connecting this state to the other two states naturally vanish,

$$\mathscr{H}_{sp_1} = \mathscr{H}_{p_0p_1} = 0,$$

and the equation, corresponding to (12) which is satisfied by Φ_{p_1}, is

$$\left\{\mathscr{H} - \mathrm{i}\hbar\frac{\partial}{\partial t}\right\}\Phi_{p_1} = \left[-\mathrm{i}\hbar v\frac{\partial}{\partial Z_{\mathbf{r}_2}}\phi_{p_1}\right]\exp\left\{\tfrac{1}{2}\mathrm{i}kz - \frac{\mathrm{i}}{\hbar}\int^t(\mathscr{H}_{p_1p_1} + \tfrac{1}{8}mv^2)\,\mathrm{d}t\right\}. \tag{41}$$

Taking cognisance of the rotation of the internuclear axis but ignoring any changes in the forms of the ϕ's it may be seen from equations (11) and (12) of Bates (1957) that

$$\frac{\partial}{\partial Z_{\mathbf{r}_1}}\phi_s = 0, \quad \frac{\partial}{\partial Z_{\mathbf{r}_2}}\phi_{p_0} = \frac{\rho\phi_{p_1}}{Z^2+\rho^2}, \quad \frac{\partial}{\partial Z_{\mathbf{r}_2}}\phi_{p_1} = \frac{-\rho\phi_{p_0}}{Z^2+\rho^2}. \tag{42}$$

Proceeding as before it may hence be shown that instead of being described by equations (14) and (15) the encounter is described by

$$\mathrm{i}\hbar v\frac{\partial c_s}{\partial Z} = \mathscr{H}_{sp_0}c_{p_0}\exp\left\{\frac{-\mathrm{i}}{\hbar v}\int^Z(\mathscr{H}_{p_0p_0} - \mathscr{H}_{ss})\,\mathrm{d}Z\right\}, \tag{43}$$

$$\begin{aligned}\mathrm{i}\hbar v\frac{\partial c_{p_0}}{\partial Z} = {}& \mathscr{H}_{p_0s}c_s\exp\left\{\frac{-\mathrm{i}}{\hbar v}\int^Z(\mathscr{H}_{ss} - \mathscr{H}_{p_0p_0})\,\mathrm{d}Z\right\}\\ &+\left[\frac{\mathrm{i}\hbar v\rho}{Z^2+\rho^2}c_{p_1}\exp\left\{\frac{-\mathrm{i}}{\hbar v}\int^Z(\mathscr{H}_{p_1p_1} - \mathscr{H}_{p_0p_0})\,\mathrm{d}Z\right\}\right],\end{aligned} \tag{44}$$

$$\mathrm{i}\hbar v\frac{\partial c_{p_1}}{\partial Z} = -\left[\frac{\mathrm{i}\hbar v\rho}{Z^2+\rho^2}c_{p_0}\exp\left\{\frac{-\mathrm{i}}{\hbar v}\int^Z(\mathscr{H}_{p_0p_0} - \mathscr{H}_{p_1p_1})\,\mathrm{d}Z\right\}\right], \tag{45}$$

in which terms not allowed for in the derivation of the Landau–Zener formula are enclosed in square brackets. Clearly the neglect of these *rotation* terms is unjustified if v is high. The value of v above which the neglect causes serious error is unfortunately difficult to estimate. It depends on the values of several quantities including $(\hbar_{ss}-\hbar_{p_0p_0})/\hbar v$, $(\hbar_{p_1p_1}-\hbar_{p_0p_0})/\hbar v$ and the ratio r of the modulus of the coefficient of c_{p_1} in (44) to that of c_s which ratio is given by

$$r = 0{\cdot}17\rho\mathscr{E}^{\frac{1}{2}}/M^{\frac{1}{2}}\hbar_{p_0s}(Z^2+\rho^2), \tag{46}$$

where $\mathscr{E}$ and $\hbar_{p_0s}$ are in eV, M is on the chemical scale and ρ and Z are in atomic units as usual. A sufficient condition for the rotational terms to be unimportant is that r should be much less than unity within the transition zone. In the case of head-on collisions r in fact vanishes. If ρ is approximately equal to Z_c the condition is satisfied at the crossing point if

$$\mathscr{E} \ll 140MZ_c^2|\hbar_{p_0s}(R_c)|^2\,\text{eV}. \tag{47}$$

As may be seen from table 1 the restriction is severe.

The rotation terms can have a profound effect on the $\mathscr{P}$–$\mathscr{E}$ curve. In particular they can make $\mathscr{P}$ become appreciable at lower $\mathscr{E}$ than it otherwise would. Take, for example, the charge-transfer process which equations (43) to (45) describe. Initially $|c_s|$ is unity. If $\mathscr{E}$ is low enough then according to the Landau–Zener formula $\mathscr{P}$ is small, $|c_{p_0}|$ becoming almost unity after the crossing is traversed for the first time but $|c_s|$ becoming almost unity again after the crossing is retraversed. The rotation terms give rise to the possibility that $|c_{p_1}|$ grows at the expense of $|c_{p_0}|$, in which event $|c_s|$ would *not* almost regain its initial value in the retraversal of the crossing and hence $\mathscr{P}$ would not be small. Detailed calculations are needed.

Assumption (5) only causes difficulties when $\mathscr{E}$ is very low (cf. table 1).

4. Concluding remarks

In spite of its defects the Landau–Zener formula is very useful at least for s-s transitions in that it provides a description of how curve-crossing influences collisions between atomic systems which in many instances is quantitative over some energy range. Moreover, the error to which it may lead is limited by the fact that it automatically ensures that the maximum probability of a given process occurring in an encounter is one-half.

The Landau–Zener formula is least satisfactory if other than s orbitals are involved. For s-s transitions the most pronounced failure is likely to occur in cases where the internuclear distance at the crossing is large (as in figure 2a); thus in such cases the position of the first peak in the probability versus energy curve may not be predicted correctly and, much more important, the existence of the second peak which often arises is not predicted at all. If the internuclear distance at the crossing is moderate or small (as in figure 2b), then apart from its asymptotic rate of fall-off being too slow the curve of Landau–Zener probability against energy may differ from the curve of true probability against energy mainly by being displaced. Should this also be true for other than $s-s$ transitions it would explain the partial success achieved by Boyd & Moiseiwitsch (1957) in fitting curves of cross-section against

energy derived from the Landau–Zener formula to experimental data, since they had at their disposal the parameter which determines the position of the maximum.

Since the course of a collision in general depends on interactions other than at the crossing, a simple treatment of wide applicability cannot be expected. When the Landau–Zener formula fails it may often be possible to use (37) modified if necessary to allow for the effect of the change in the translational motion of the active electron; when this rather laborious alternative also fails it may be difficult to make progress without solving the appropriate coupled equations numerically.

The research reported has been sponsored by the Air Force Cambridge Research Centre, Geophysics Research Directorate, of the Air Research and Development Command U.S. Air Force, through its European Office, under Contract No. AE 61(052)-131. It is a pleasure to thank Dr A. Dalgarno and Dr B. L. Moiseiwitsch for their comments on the original manuscript.

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