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## CHARGE EXCHANGE WITH SMALL ENERGY TRANSFER

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A general formula is derived for electronic charge exchange when the change of the energy of the electron is small relative to the distances between nearest energy levels in both atomic systems.

The deduction of the formula is analogous to that of the semiclassical Bohr quantum conditions. For a special case a similar result was obtained earlier by Zener and Rosen. The Massey criterion which defines the position of the maximum of the cross section is examined more precisely. The oscillating character of the differential cross section, analogous to that of the resonance charge exchange, is established.

The results obtained can also be applied to a number of other processes, such as an excitation transfer in collisions between atoms or ions.

### 1. The formulation of the problem and qualitative considerations

If we suppose that nuclei are treated classically then in a two state approximation the process of the charge exchange can be described by a system of two equations:

$$\begin{aligned}i\dot{a} &= H_{11}a + H_{12}b \\i\dot{b} &= H_{21}a + H_{22}b\end{aligned}\tag{1}$$

where the coefficients  $H_{ik}$  are functions of the internuclear distance  $R$  which itself depends from the time  $t$ . The values  $a$  and  $b$  determine the probabilities  $\omega_1 = |a|^2$  and  $\omega_2 = |b|^2$  of the electron being near to the atom A or to the atom B in definite atomic states  $\Psi_A$  and  $\Psi_B$ . From the condition  $|a|^2 + |b|^2 = 1$  it follows that the matrix  $H_{ik}$  must be hermitian. We shall not consider here questions connected with the derivation of the system (1) in spite of some uncertainty connected with nonorthogonality of the functions  $\Psi_A$  and  $\Psi_B$  at finite distances  $R$ . The functions  $H_{11}$  and  $H_{22}$  tend to the constants at large  $R$  while next terms in their expansions at large  $R$  depend on the type of collision. For the simplest case, the collision  $A^+ + B$ , we have

$$H_{11} = -T_A - \alpha_A/R^4 + \dots, \quad H_{22} = -T_B - \alpha_B/R^4,$$

where  $\alpha$  are the polarisabilities and  $T$  the ionisation potentials of atoms A, B in states  $\Psi_A$  and  $\Psi_B$ . The exchange term  $H_{12}$  can be expressed as an

integral containing the functions  $\Psi_A$  and  $\Psi_B$  and therefore exponentially decreases at large  $R$ ; the exponent is  $-\sqrt{2TR}$ , where  $T$  is the smallest of the ionisation potentials of atoms A and B.

If we impose the initial conditions  $|a(-\infty)| = 1$ ,  $b(-\infty) = 0$  and integrate the system (1) then the probability of charge exchange is determined by value

$$\omega = |b(\infty)|^2.$$

For every value of  $R$  we can construct some linear combinations

$$c_1 \Psi_A + c_2 \Psi_B$$

which approximate the molecular functions  $\Phi_A$  and  $\Phi_B$  which tend at large  $R$  to the  $\Psi_A$  and  $\Psi_B$ . The coefficients can be found as solutions of the system

$$\begin{aligned} (H_{11} - \lambda)c_1 + H_{12}c_2 &= 0, \\ H_{21}c_1 + (H_{22} - \lambda)c_2 &= 0. \end{aligned} \quad (2)$$

It can be shown easily that the type of the solutions essentially depends on the relation between the quantities  $\Delta = H_{11} - H_{22}$  and  $H_{12}$ .

If  $|H_{12}| \ll |\Delta|$  then  $c_1 \approx 1$ ,  $c_2 \approx 0$ ,  $\lambda \approx H_{11}$  or  $c_1 \approx 0$ ,  $c_2 \approx 1$ ,  $\lambda \approx H_{22}$ . If however  $|H_{12}| \gg |\Delta|$  then  $\lambda \approx \frac{1}{2}(H_{11} + H_{22}) \pm |H_{12}|$ ,  $c_1 = 2^{-\frac{1}{2}}$ ,  $c_2 = \pm 2^{-\frac{1}{2}}$ , and the situation is analogous to that of the resonance charge exchange<sup>1,2</sup>, when the molecular functions can be approximately expressed as symmetrical and antisymmetrical combinations of atomic ones. In the resonance case  $H_{11} = H_{22} = 0$ ,  $H_{12}$  is real and the equation (1) can be solved exactly<sup>1,2</sup>.

Let us consider now the case when  $\Delta_\infty = (H_{11} - H_{22})_{R \rightarrow \infty} = T_B - T_A$  is small and the exchange integral  $H_{12}$  becomes equal to  $\Delta$  at some  $R_0$  which is large relative to the size of atoms.

In this region the exchange integral decreases already exponentially and therefore the interval  $\delta R$  where the moduli of  $H_{12}$  and  $\Delta$  are comparable is approximately equal to  $(2T)^{-\frac{1}{2}}$ .

In this region the shape of molecular functions changes from being localised and similar to the atomic ones  $\Psi_A$ ,  $\Psi_B$  at  $R > R_0$  to the symmetrical and antisymmetrical combinations  $2^{-\frac{1}{2}}(\Psi_A \pm \Psi_B)$  at  $R < R_0$ . Therefore we can suppose the nonadiabatic transitions take place only in this region and in other regions the system develops adiabatically.

If the system passes the region  $\delta R$  during the time  $\delta t$  which is large relative to the period of oscillations corresponding to the exchange frequency  $H_{12} \approx \Delta$  i.e. if  $\delta t \cdot \Delta \gg 1$ , then the probability of charge exchange is exponentially small. On the other hand if  $\delta t \cdot \Delta \ll 1$ , then the change of molecular

functions will be of an occasional character and we must simply reexpand the previous function  $\Psi_A$  in the form of the superposition of  $\Psi_A + \Psi_B$ ,  $\Psi_A - \Psi_B$  i.e. we have the case of resonant charge exchange, and the probability changes rapidly and oscillates between zero and unity.

## 2. The formula for the probability of charge exchange

To obtain quantitative results let us divide the whole interval  $-\infty < t < \infty$  into 5 regions: (I)  $R > R_0$ , (II)  $R \sim R_0$ , (III)  $R < R_0$ , (IV)  $R \sim R_0$ , (V)  $R > R_0$ . The motion is symmetrical relative to the inversion of time and therefore the solutions of equations (1) in regions I, V and II, IV are similar. We shall suppose that in regions I, III and V there are no non-adiabatic transitions and therefore the solution can be written at once. If we solve the problem in regions II and IV we can join the solutions in all regions and obtain  $\omega$ .

Such consideration is analogous to the semiclassical method for determination of the wave function and of the energy of a particle in a one dimensional potential (or the coefficient of transition through a potential barrier). The role of the coordinate is played here by the time, and the regions II, IV are analogous to the turning points where the semiclassical (adiabatical) approximation is not applicable and therefore they demand special consideration.

Just as in the case of turning points we can approximate the functions  $H_{ik}$  in regions II, IV by simple functions for which the equations (1) have an exact solution. In this case it is natural to make the assumption that  $H_{11}$ ,  $H_{22}$  are constants and  $H_{12}$  exponentially decreases.

We have then a system of equations

$$\begin{aligned} i\dot{a} &= \alpha a + \beta e^{\gamma t} b \\ i\dot{b} &= -\alpha b + \beta e^{\gamma t} a \end{aligned} \quad (3)$$

(by a phase transformation it is easy to make  $H_{11} + H_{22} = 0$ ). The solution of these equations which has the correct form in the region I i.e. satisfies the conditions  $|a(-\infty)| = 1$ ,  $b(-\infty) = 0$ , can be obtained easily:

$$\begin{aligned} a &= \left( \frac{\pi\beta}{2\gamma} \operatorname{sech} \frac{\pi\alpha}{2\gamma} \right)^{\frac{1}{2}} e^{\frac{1}{2}\gamma t} J_{-\frac{1}{2} - i\alpha/\gamma} \left( \frac{\beta}{\gamma} e^{\gamma t} \right), \\ b &= -i \left( \frac{\pi\beta}{2\gamma} \operatorname{sech} \frac{\pi\alpha}{2\gamma} \right)^{\frac{1}{2}} e^{\frac{1}{2}\gamma t} J_{\frac{1}{2} - i\alpha/\gamma} \left( \frac{\beta}{\gamma} e^{\gamma t} \right). \end{aligned} \quad (4)$$

At large positive values of the argument of the Bessel functions we can use the asymptotic formulas which are applicable in the region III:

$$\begin{aligned}
 a &\sim \left(\operatorname{sech} \frac{\pi\alpha}{2\gamma}\right)^{\frac{1}{2}} \cos \left(\frac{\beta}{\gamma} e^{\gamma t} + i \frac{\pi\alpha}{2\gamma}\right), \\
 b &\sim -i \left(\operatorname{sech} \frac{\pi\alpha}{2\gamma}\right)^{\frac{1}{2}} \sin \left(\frac{\beta}{\gamma} e^{\gamma t} + i \frac{\pi\alpha}{2\gamma}\right).
 \end{aligned}
 \tag{5}$$

In the region III we can write also the usual adiabatical solution neglecting the term  $\Delta = H_{11} - H_{22}$

$$\begin{aligned}
 a &= A \cos \left(\int H_{12} dt + \varphi\right), \\
 b &= -iA \sin \left(\int H_{12} dt + \varphi\right).
 \end{aligned}
 \tag{6}$$

The comparison of (5) and (6) enables us to choose the right amplitude  $A$  and phase  $\varphi$ . We have then for the region III:

$$\begin{aligned}
 a &= \left(\operatorname{sech} \frac{\pi\alpha}{2\gamma}\right)^{\frac{1}{2}} \cos \left(\int_{-\infty}^t H_{12} dt + i \frac{\pi\alpha}{2\gamma}\right), \\
 b &= -i \left(\operatorname{sech} \frac{\pi\alpha}{2\gamma}\right)^{\frac{1}{2}} \sin \left(\int_{-\infty}^t H_{12} dt + i \frac{\pi\alpha}{2\gamma}\right).
 \end{aligned}
 \tag{7}$$

In region IV we have to solve the system

$$\begin{aligned}
 i\dot{a} &= \alpha a + \beta e^{-\gamma t'} b, \\
 i\dot{b} &= -\alpha b + \beta e^{-\gamma t'} a,
 \end{aligned}
 \tag{8}$$

where  $t'$  differs from  $t$  only by a constant.

Further we must join the obtained solution with (7) in the region III and obtain the value  $|\omega|$  at  $t \rightarrow \infty$ . We have then

$$\omega = \left(\operatorname{sech} \frac{\pi\alpha}{2\gamma}\right)^2 \cdot \left(\sin \int_{-\infty}^{+\infty} H_{12} dt\right)^2.
 \tag{9}$$

The meaning of parameters  $\alpha$  and  $\gamma$  is obvious:  $\alpha = \frac{1}{2}\Delta$  and  $\gamma t = (2T)^{\frac{1}{2}}R$ . If we expand  $R(t)$  in powers of  $t$  in vicinity of  $R_0$  and keep only two terms, we have

$$\gamma = (2T)^{\frac{1}{2}}(dR/dt)_{R_0}.
 \tag{10}$$

Using arbitrary units and these expressions for  $\alpha$  and  $\gamma$  we have finally

$$\omega = \left[ \operatorname{sech} \left\{ \frac{\pi\Delta}{2\sqrt{2mT}} \left(\frac{dR}{dt}\right)_{R_0}^{-1} \right\} \sin \left( \frac{1}{h} \int_{-\infty}^{+\infty} H_{12} dt \right) \right]^2.
 \tag{11}$$

Let us estimate the limits of applicability of this formula.

They follow first from the assumption we made that  $\Delta = H_{11} - H_{22}$  remains approximately constant in the region where  $H_{12}$  changes exponentially from values appreciably larger than  $\Delta$  to the values appreciably smaller than it. The exponential decrease of  $H_{12}$  begins at some distance not very much larger than the sum of the atomic radii.

Let us estimate now the size of critical region. The splitting of energy terms from one side of interval must be determined by the value of  $\Delta$  and, from the other side by the value of  $H_{12}$ . If we assume that at the ends of interval these values differ at most by two then the largest one already gives 90 % of the whole splitting. Therefore we can practically assume the region  $\delta R$  is of the order  $(2T)^{-\frac{1}{2}}$  i.e. is comparable with the size of the atoms. If we take into account the oscillation of the electronic wave functions,  $(2T)^{-\frac{1}{2}}$  and consequently  $\delta R$  can be even less than the size of the atom. Further, the region where  $\Delta$  is practically constant can be estimated if we assume that the deviation of integrals  $H_{11}$ ,  $H_{12}$  from constant values is determined by electrostatic interactions between nucleus and electronic clouds and neglect the slow varying polarisation term (collisions of type  $A^+ + B$ ). Such interaction decreases more rapidly ( $\exp(-2\sqrt{2TR})$ ) than the exchange term and therefore this condition gives no additional limitations.

So we see that the values  $R_0$  must be more than  $2 \sim 2.5$  times larger than the atomic size. This corresponds to the energy transfer of about  $\frac{1}{3}$  or less of the ionisation potential. There is another limitation. Namely, we assumed that  $dR/dt$  is constant in the critical region  $\delta R$ . The validity of this assumption can be easily estimated from geometrical considerations. At sufficiently small impact parameter  $\rho$  it is always satisfied (except at very small velocities). If  $\rho$  approaches  $R_0$  the situation becomes worse, but at these values of  $\rho$  the probability is small and brings in only small contribution in the cross section.

So the effective small parameters of the theory are the relative change of the values  $\Delta$  and  $dR/dt$  in the region  $\delta R$ . Finally some limitations arise from the two-level approximation itself. It is evident that we must take into account all processes which can go with appreciable probability. Therefore the energy transfer must be at least several time less than the distance from the nearest terms of the same symmetry. This limitation exceeds all others and therefore controls the validity of formula (11).

There remain of course the usual limitations connected with the classical consideration of nuclei (for low velocities), with the momentum transfer by electron from one atom to another (at high velocities) etc.

### 3. Discussion

The formula derived enables us to make some preliminary remarks.

1. At  $\Delta = 0$  it passes into well known formula for symmetrical charge exchange. We obtain the same formula if the impact parameter  $\rho$  is less than  $R_0$  and the parameter  $s = \pi\Delta/(2mT)^{1/2}v$  is small. Then the cross section can be estimated by formula  $\sigma = \frac{1}{2}\pi R_1^2$  where  $R_1$  is the value of the impact parameter at which  $(1/h)\int_{-\infty}^{+\infty} H_{12} dt$  is comparable with unity. The cross section cannot exceed however the quantity  $\frac{1}{2}\pi R_0^2$ , this quantity gives the order of the maximum of the cross section.

2. At low velocities, when the cross section decreases with velocity, a rough estimation gives an asymptotic formula which is valid at  $s > 2$

$$\sigma \approx 4\pi R_0^2 s^{-1} e^{-s}.$$

We replaced here  $\sin^2$  by  $\frac{1}{2}$  and  $(dR/dt)_{R_0}$  was obtained from geometrical considerations. The cross section exponentially decreases with velocity, so the qualitative considerations of section 1 are confirmed.

3. The characteristic parameter  $s = \pi\Delta/\sqrt{2T}v$  determines the behavior of the cross section at low velocities and (less accurately) the position of the maximum of the cross section ( $s \sim 1$ ). This parameter coincides with the parameter which is used in the well known Massey criterion<sup>3,4</sup> for the same purpose

$$\Delta_\infty l/hv \sim 1, \quad (13)$$

where  $l$  is some parameter comparable with the atomic size. It is seen from comparison that for small  $\Delta$ ,  $l$  is equal to  $\pi(2T)^{-1/2}$ .

It is interesting that the parameter  $s$  does not contain the Planck constant  $h$  and the Massey criterion is in this case, in fact, a classical criterion.

4. At low velocities the cross section is small, but the probability decreases slowly as the impact parameter increases: the process takes place at small angle scattering and we have (so to say) a very transparent target of large dimensions — about  $\pi R_0^2$ . On the contrary at high velocities after the cross section reaches its maximum it decreases as in the resonance case.

5. If we take into account the curvature of trajectories and do not smooth the  $\sin^2$  we can calculate oscillations of the differential cross section like those which were predicted<sup>1,2</sup> and observed<sup>5</sup> for symmetrical charge exchange. There is a difference from the symmetrical case; namely the probability oscillates between zero and some value less than unity. These oscillations are the most characteristic feature of that theory and show that the nonadiabatic transitions take place only in a relatively small region, and beyond this region the molecular states interfere. No doubt the oscillations

of the differential cross section observed in <sup>5</sup> (for example the  $H^+ + He$  case) are due to such interference.

6. In region III, during the approach of the atoms the values  $H_{12}$  and  $\Delta$  can become comparable again, so we must replace [in the formula (11)] the integrand  $H_{12}$  by  $\sqrt{H_{12}^2 + \Delta^2}$  i.e. we can use in region III the real energy terms.

7. It can happen that the real terms approach very closely in region III; then we have an additional nonadiabatic region which must be treated with the use of the Landau-Zener formula <sup>6,7</sup>. The nonadiabatic region also can arise at very small  $R$  near the point of closest approach.

8. In the derivation of the Landau-Zener formula we suppose that in the nonadiabatic region the exchange integral  $H_{12}$  is constant and the difference  $\Delta$  varies rapidly and depends linearly on  $t$ . In the derivation of formula (11), on the contrary, we suppose that  $\Delta$  is constant, but  $H_{12}$  varies rapidly and so we consider an opposite limiting case.

9. The changes of the values  $H_{11}$ ,  $H_{22}$  at  $R > R_0$  which are connected with polarisation, Coulomb interaction etc. (i.e. with nonexchange processes) do not directly influence the probability of charge exchange. They can change only the value of  $\Delta$  at  $R \neq R_0$ . So even at exact accidental resonance when  $H_{11} = H_{22}$  at  $R = \infty$ ,  $\Delta(R_0)$  will be different from zero. For the process  $A^+ + B \rightarrow A + B^+$  for instance,  $\Delta$  and  $R_0$  can be found in such case from the equation

$$\Delta = |\alpha_A - \alpha_B|/R_0^4 = |H_{12}(R_0)|. \quad (14)$$

10. It can happen that  $H_{12}$  increases at small  $R$  so rapidly that the equation  $H_{12} = \Delta$  is satisfied at  $R_0$  which is smaller than the atomic size, or is never satisfied at all. Then the formula is not applicable. This consideration is especially valid if we have "charge-asymmetrical" collision, for example  $He^{++} + H \rightarrow H^+ + He$  (2s, 2p).

11. The formula is not applicable at high velocities of colliding particles ( $v \rightarrow 1$ ) when we must take into account the transfer of momentum by electrons and multiply  $\Psi_A$ ,  $\Psi_B$  by the factor  $e^{i\mathbf{v} \cdot \mathbf{r}}$  which causes a decrease of the cross section.

12. For a special case, when  $H_{11} = -H_{22} = \alpha$  and  $H_{12} = \beta \operatorname{sech} \gamma t$  the system (I) was integrated exactly by Zener and Rosen<sup>8</sup>. Formula (10) is in this case an exact one. The advantage of our derivation consists in that we make a minimum of assumptions about the behavior of  $H_{ik}$  beyond the regions II, IV, and it can be clearly seen that the transitions are connected only with the behavior of  $H_{ik}$  in these critical regions. From the Zener-Rosen model these conclusions cannot be seen directly.



13. To obtain parameter  $R_0$  we must know  $H_{12}$  as a function of  $R$  for large  $R$ . Sometimes this function can be estimated (i.e. from the binding energy of the molecular ion  $AB^+$ ) sometimes it can be calculated, but as a rule we know only the order of magnitude of  $H_{12}$ , which corresponds to the error about  $\delta R$  in determination of  $R_0$ . So  $R_0$  is in fact an adjustable parameter. Perhaps the formula (11) can be used to obtain  $H_{12}$  from the experimental data for charge exchange.

14. We do not make any assumption about the analyticity. However this feature is important if we consider the asymptotic behavior of probability at  $v \rightarrow 0$ . The jumps in  $H_{ik}$  or in their derivatives imply that  $\omega$  is proportional to some power of  $v$  at small  $v$ . The smoother the functions  $H_{ik}$  the further in the region of small  $v$  we can apply formulae of type (11) or the Landau-Zener formula.

15. The system (1) and the assumptions made about  $H_{ik}$  are of very general character, and therefore the results obtained can be applied to various problems when a transition between two close energy states takes place due to a smooth perturbation which depends on time and exponentially decreases as  $t \rightarrow \pm \infty$ . Examples are the transfer of excitation between s-states in a collision between atoms, experiments of Stern-Gerlach type<sup>8</sup>, the transition between fs or hfs levels etc.

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