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CHARGE TRANSFER AT SMALL RESONANCE DEFECTS

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A general formula is obtained for the probability of electronic charge transfer in cases in which the change of the electron's energy in the transition is small in comparison with the distance to the nearest levels in the two atomic systems. The derivation of the formula is analogous to the derivation of the Bohr quantum conditions in the semiclassical method. For a special case an analogous result has been obtained earlier by Zener and Rosen. The Massey criterion, which determines the position of the maximum of the effective cross section, is given a more precise meaning, and it is shown that the differential cross section has an oscillating behavior, analogous to that in the case of resonance charge transfer. The results can also be applied to a number of other processes, for example to the transfer of excitation between s states in collisions of atoms or ions.

1. STATEMENT OF PROBLEM AND QUALITATIVE EXAMINATION OF THE PROCESS

WE consider the problem of charge transfer in collisions of atoms or ions—that is, of processes of the types $A + B^+ \rightarrow A^+ + B$, $A + B^- \rightarrow A^- + B$, and so on—when the speed of motion of the atoms is much smaller than the speed of motion of the outer electrons, and their kinetic energies are much larger than those of the electrons. The charge-transfer cross section depends essentially on the resonance defect—the difference of the energies of the electron in the initial and final states—and increases sharply as this quantity goes to zero (resonance charge transfer[1,2]). Here we shall consider small resonance defects, and shall study the transition from the resonance case to the nonresonance case.

We shall assume that the nuclei move along classical trajectories, and write the wave function of the system in the approximate form

$$\Psi = a(t)\Psi_A + b(t)\Psi_B,$$

where Ψ_A, Ψ_B are the wave functions of the electron in the states near atoms A and B which are of interest to us. In this "two-level" approximation we get a system of equations for a, b in the usual way:

$$i\dot{a} = H_{11}a + H_{12}b, \qquad i\dot{b} = H_{21}a + H_{22}b, \tag{1}$$

where the coefficients H_{ik} are functions of the internuclear distance R, which in turn depends on the time. The unknown quantities a(t) and b(t) determine the probabilities $w_1 = |a|^2$ and $w_2 = |b|^2$ for the electron to be found near atom A or near atom B. The condition $|a|^2 + |b|^2 = 1$ means that the matrix H_{ik} is Hermitian. We shall not deal here with questions connected with the derivation of the system (1), although in this also there is some ambiguity, owing to the nonorthogonality of the atomic functions Ψ_A and Ψ_B for finite R.

The functions $H_{11}(R)$ and $H_{22}(R)$ approach constant values for $R \rightarrow \infty$; the successively smaller terms in the expansions of H_{11} and H_{22} are determined by the character of the collision. For the simplest case—collision of the atom A with the ion B^+—we have

$$H_{11} = -I_A - \alpha_A/R^4 + \ldots, \quad H_{22} = -I_B - \alpha_B/R^4 + \ldots,$$

where the α's are the polarizabilities and the I's are the ionization potentials of the atoms A and B in the states in which we are interested. The exchange term H_{12} is expressed in terms of an integral containing the functions Ψ_A and Ψ_B, and consequently falls off exponentially for $R \rightarrow \infty$; the argument of the exponential is $-(2I)^{1/2}R$, where I is the smaller of the ionization potentials of the atoms A and B.

If we fix the initial conditions $|a(-\infty)|^2 = 1$, $b(-\infty) = 0$ and integrate the system (1), the probability of charge transfer is $w = |b(\infty)|^2$.

For each value of R one can form certain linear combinations $c_1\Psi_A + c_2\Psi_B$ which roughly approximate the molecular functions Φ_A and Φ_B which go over into Ψ_A and Ψ_B for $R \rightarrow \infty$. The coefficients c_1 and c_2 can be found by solving the system of equations

$$(H_{11} - \lambda)\, c_1 + H_{12} c_2 = 0, \qquad H_{21} c_1 + (H_{22} - \lambda)\, c_2 = 0. \tag{2}$$

It is easily verified that the character of the solution depends essentially on the ratio of the quantities $\Delta = H_{11} - H_{22}$ and H_{12}. If $|H_{12}|$ is much smaller than $|\Delta|$, then either $c_1 \approx 1$, $c_2 \approx 0$, $\lambda \approx H_{11}$, or $c_2 \approx 1$, $c_1 \approx 0$, $\lambda \approx H_{22}$. If, on the other hand, $|H_{12}| \gg |\Delta|$, then $\lambda \approx \frac{1}{2}(H_{11} + H_{22}) \pm |H_{12}|$, $c_1 \approx 2^{-1/2}$, $c_2 \approx \pm 2^{-1/2}$, and the situation is analogous to the case of resonance or symmetrical charge transfer, for which the molecular functions can be represented as symmetric and antisymmetric combinations of the atomic functions. In this case $\Delta = 0$, H_{12} is real, and the equations (1) can be solved exactly.[1,2]

Let us now consider the case in which $\Delta_\infty = (H_{11} - H_{22})_{R \to \infty}$ is a small quantity and the exchange integral H_{12} becomes equal to Δ at a value R_0 which is much larger than the dimensions of the atoms. In this region the exchange integral is already decreasing exponentially, and consequently the range δR in which H_{12} and Δ are comparable in absolute value is about $(2I)^{-1/2}$. In this range there occurs the change of character of the molecular wave functions from the functions Ψ_A and Ψ_B, localized and close to the atoms, for $R > R_0$, to the symmetric and antisymmetric combinations $(\Psi_A \pm \Psi_B)/2^{1/2}$ for $R < R_0$. Therefore we can assume that it is in this region that the nonadiabatic transitions occur, and that outside it the system evolves in an adiabatic manner. If the system passes through the range δR in a time δt which is large in comparison with the period of vibrations with the exchange frequency $H_{12} \sim \Delta$ —that is, if $\Delta \delta t \gg 1$ —then the probability of charge transfer is small. In the opposite case, with $\Delta \delta t \ll 1$, the change of the molecular functions will be a sudden one, and we have only to expand the old function Ψ_A in terms of the new functions $(\Psi_A \pm \Psi_B)/2^{1/2}$; that is, we arrive at the case of symmetrical charge transfer, and the probability will vary rapidly, oscillating between zero and unity.

2. DERIVATION OF THE FORMULAS FOR THE TRANSITION PROBABILITY

In order to get qualitative results, we break up the whole range $-\infty < t < +\infty$ into five parts: 1) $R(t) > R_0$, 2) $R(t) \sim R_0$, 3) $R(t) < R_0$, 4) $R(t) \sim R_0$, 5) $R(t) > R_0$. It is obvious that the motion is symmetrical in time and that the solutions in the regions 1) and 5) and those in the regions 2) and 4) are of the same characters. We shall assume that in the regions 1), 3), and 5) there are no nonadiabatic transitions, and consequently the solution in these regions can be written at once. By solving the problem in regions 2) and 4) we can join the functions in all the regions and determine w.

This treatment is analogous to the semiclassical method for determining the wave function and energy of a particle in a one-dimensional potential well (or the transmission coefficient for a particle striking a potential barrier). Here the time plays the part of the coordinate, and the regions 2) and 4) are analogous to the turning points, at which the semiclassical (adiabatic) approximation is not valid and special treatment is required. Just as in the case of the turning points, we can approximate the functions H_{ik} in the regions 2) and 4) with simple functions in such a way that the equations can be solved exactly. In the present case it is natural to assume that in these regions H_{11} and H_{22} are constant, and H_{12} decreases exponentially. We get the system

$$i\dot{a} = \alpha a + \beta e^{\gamma t} b, \qquad i\dot{b} = -\alpha b + \beta e^{\gamma t} a \tag{3}$$

(it is easy to make $H_{11} + H_{22} = 0$ with a phase transformation).

The solution of these equations which has the correct form in region 1)—i.e., satisfies the conditions $|a(-\infty)| = 1$, $b(-\infty) = 0$ —is

$$a = \left(\frac{\pi\beta}{2\gamma} \operatorname{sech} \frac{\pi\alpha}{\gamma}\right)^{1/2} e^{\gamma t/2} J_{-1/2 - i\alpha/\gamma}\left(\frac{\beta}{\gamma} e^{\gamma t}\right),$$

$$b = -i\left(\frac{\pi\beta}{2\gamma} \operatorname{sech} \frac{\pi\alpha}{\gamma}\right)^{1/2} e^{\gamma t/2} J_{1/2 - i\alpha/\gamma}\left(\frac{\beta}{\gamma} e^{\gamma t}\right). \tag{4}$$

For large positive values of the argument of the Bessel functions we get asymptotic formulas valid in region 3):

$$a \sim \left(\operatorname{sech} \frac{\pi\alpha}{\gamma}\right)^{1/2} \cos\left(\frac{\beta}{\gamma} e^{\gamma t} + i \frac{\pi\alpha}{2\gamma}\right),$$

$$b \sim -i\left(\operatorname{sech} \frac{\pi\alpha}{\gamma}\right)^{1/2} \sin\left(\frac{\beta}{\gamma} e^{\gamma t} + i \frac{\pi\alpha}{2\gamma}\right). \tag{5}$$

In region 3) we can also write down the usual adiabatic solution, neglecting $H_{11} - H_{22}$:

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

By comparing Eqs. (5) and (6) we can choose the correct amplitude A and phase φ. In this way we get for the region 3)

$$a = \left(\operatorname{sech} \frac{\pi\alpha}{\gamma}\right)^{1/2} \cos\left(\int_{-\infty}^{t} H_{12} dt + i \frac{\pi\alpha}{2\gamma}\right),$$

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

In region 4) we must solve the system of equations

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

where t′ differs from t by the choice of the origin. We must then join the solution to the solution (7) in the region 3) and find the value of b for $t \to \infty$. We get

$$w = |b(\infty)|^2 = \operatorname{sech}^2 \frac{\pi\alpha}{\gamma} \sin^2 \int\limits_{-\infty}^{+\infty} H_{12} dt. \tag{9}$$

The meaning of the parameters α and γ is obvious: $\alpha = \Delta/2$, $\gamma t = (2I)^{1/2} R$. Expanding the right member of this last equation in powers of t in the neighborhood of the point R_0 and keeping only the linear term, we have

$$\gamma = \sqrt{2I}\,|dR/dt|_{R_0}. \tag{10}$$

We now insert the expressions for α and γ and go over to arbitrary units. We get finally

$$w = \operatorname{sech}^2 \left(\frac{\pi\Delta}{2\sqrt{2mI}} \left| \frac{dR}{dt} \right|^{-1}_{R_0} \right) \sin^2 \left(\frac{1}{h} \int\limits_{-\infty}^{+\infty} H_{12} dt \right). \tag{11}$$

Let us estimate the limits of validity of this formula. They come mainly from the assumption made in the derivation, that the difference $\Delta = H_{11} - H_{22}$ is approximately constant in the region where H_{12} is changing exponentially from values much smaller than this difference to values much larger. The exponential behavior of H_{12} begins almost immediately beyond the limits of the atom, i.e., for $R > a_0$.

Let us first estimate the size of the critical region δR. What we need is for it to be a good enough approximation to replace the solution (4) obtained in region 2) by the first term of the series expansion of the Bessel function in region 1), and also by its asymptotic expansion in region 3). Simple estimates show that if we do not demand great accuracy (10 to 20 percent), then for the function J_1, for example, this region is in the range 0.7—3.0; that is, it corresponds to a change of the argument by not more than a factor five. From this we get for δR the estimated value $1.5 \times (2I)^{-1/2}$, i.e., a quantity close to the dimensions of an atom.[1] It must be noted that an attempt to decrease the error leads to a rather rapid increase of δR and thus to poorer limits of applicability of the formulas, so that for practical purposes, when we allow for the two passages through the region δR, we must estimate the accuracy of the formulas as 30 percent [in comparison with the exact solution of the system (1)].

Furthermore, we can set a bound on the side of small R to the region in which the difference Δ is already practically constant, by assuming that the deviations of the integrals H_{11}, H_{22} from constant values are caused by the electrostatic interactions of the electron clouds and the nuclei, and neglecting the slowly varying polarization terms (collisions of type $A^+ + B$). This interaction falls off much faster than the exchange term [as $\exp\{-2(2I)^{1/2} R\}$], and consequently the quantity R_0 can be only a little larger—by a factor of two and a half—than the dimensions of the colliding atoms, corresponding to a resonance defect of a fifth or a sixth of the ionization potential.

Another limitation is that we have assumed the quantity dR/dt constant in the critical region δR. The degree of justification for this assumption can be found easily from geometrical arguments. It is always true for sufficiently small values of the impact parameter ρ. Things are worse when ρ gets close to R_0, but then the probability for charge transfer is extremely small and does not contribute much to the effective cross section.

Thus in effect the small parameters of the theory are the fractional changes of the quantities $H_{11} - H_{22}$ and dR/dt in the region δR.

Finally, the close approach of the two levels is itself a limitation. Obviously we should really include all processes which can occur with appreciable probability. This means that the resonance defect must be only a fraction of the distance to the nearest levels of the same symmetry. This condition takes precedence over the foregoing ones and is thus the main limitation on the applicability of our formulas.

In addition there are of course the usual restrictions associated with the classical approximation for the nuclei (on the side of small velocities), and with the transfer of the momentum from one atom to the other by the electron (at large velocities), and so on.

3. DISCUSSION

On the basis of our formula we can make the following preliminary remarks.

1. For $\Delta = 0$ this formula goes over into the well known formula for symmetrical charge transfer. The same formula is obtained for impact parameters smaller than R_0 if the parameter $s = \pi\Delta(2mI)^{-1/2} v^{-1}$ is small. Then the cross section is given by the formula $\sigma = \pi R_1/2$, where R_1

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[1] If we allow for the oscillation of the electronic functions inside the atom, then $(2I)^{-1/2}$, and consequently also δR, can be even smaller than the dimensions of the atom.

is the value of the impact parameter for which $h^{-1}\int H_{12}\,dt$ is of the order of unity. The cross section cannot, however, be larger than the value $\pi R_0^2/2$, which fixes the order of magnitude of the charge-transfer cross section.

2. At small velocities, for which the cross section decreases with the velocity, a rough estimate gives an asymptotic formula valid for $s > 2$:

$$\sigma \approx 4\pi R_0^2 s^{-1} e^{-s}. \tag{12}$$

Here we have replaced the square of the sine by one-half, and have determined $|dR/dt|_{R_0}$ from geometrical considerations. The cross section falls off exponentially as the velocity decreases. Thus the qualitative arguments of Sec. 1 are confirmed.

3. The characteristic parameter $s = \pi\Delta \times (2mI)^{-1/2} v^{-1}$, which determines the behavior of the cross section (12) for small velocities and (less rigorously) determines the position of the maximum of the cross section ($s \sim 1$), coincides with the parameter used for the same purpose in the so-called Massey criterion[3,4]:

$$\Delta_\infty l/hv = \Delta_\infty/pv \sim 1, \tag{13}$$

where l is a parameter of the order of the dimensions of the atoms and p is a characteristic momentum (the momentum transfer[4]). It can be seen from a comparison that for small values of Δ_∞, l is the radius $h(2mI)^{-1/2}$ of the outer electron shell (because of power-law factors l is somewhat smaller than this radius), and p is the average momentum of the least tightly bound electron. It is interesting that in this case the parameter s does not contain Planck's constant, and the Massey criterion is essentially a classical criterion.

4. Though at small velocities the cross section is small, the charge-transfer probability decreases slowly with increase of the impact parameter, the process occurs mainly in scattering through small angles, and we have, as it were, a "very transparent" target of large size $\sim \pi R_0^2$. At large velocities, on the other hand, after the maximum of the cross section, the decrease is mainly due to a decrease of the effective size of the target, just as for symmetrical charge transfer.

5. If we take into account the distortion of the trajectories and do not average the square of the sine in Eq. (11), then we can calculate oscillations of the effective cross section similar to those that have been predicted[1,2] and observed[5] for the symmetrical charge transfer. The oscillations, unlike those of the symmetrical charge transfer probability, go between zero and a quantity less than unity. The presence of these oscillations is one of the most characteristic features of this theory, which asserts that nonadiabatic transitions occur only in a comparatively narrow interval, while outside it interference of the molecular states occurs. The observations in a paper by Ziemba and others,[5] which show that there are oscillations of the effective cross section in many nonresonance processes, are undoubtedly to be explained by such interferences.

6. If, as the atoms are brought still closer together in region 3), the quantities Δ and H_{12} again become comparable in magnitude, then in Eq. (11) we must replace H_{12} by $(H_{12}^2 + \Delta^2)^{1/2}$ in the integrand; that is, in region 3) we can use the actual terms, since there are no nonadiabatic processes in this region.

7. If in region 3) the actual terms again come very close together, there is a new nonadiabatic region, in which we must use the formula of Landau and Zener,[6,7] and this complicates the treatment.

8. In the derivation of the Landau-Zener formula it is assumed that the exchange integral H_{12} is constant in the nonadiabatic region and that the difference Δ changes rapidly and depends linearly on t. In the derivation of Eq. (11), on the other hand, it is assumed that Δ is constant and H_{12} changes rapidly, and thus this is the opposite limiting case.

9. The changes of the quantities H_{11} and H_{22} for $R > R_0$ which are due to polarization, Coulomb interaction, and so on, i.e., to nonexchange processes, do not directly affect the charge-transfer probability. They can only change the value of Δ, which must be calculated not for $R = \infty$ (Δ_∞), but for $R = R_0$. Therefore even at exact "accidental" resonance, when with different atoms $H_{11} = H_{22}$ for $R \to \infty$, the quantity Δ will be different from zero. For example, for the process $A + B^+ \to A^+ + B$, Δ will in this case be given by the equation

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

10. It may happen that Δ increases so rapidly that the equality $\Delta = |H_{12}|$ is reached for an R_0 smaller than the dimensions of the atoms, or even is not reached anywhere at all. Then the theory cannot be applied. In particular this is true of the case in which the collisions are not "charge symmetric," for example $H + He^{++} \to H^+ + He^+(2s, 2p)$.

11. The formula cannot be applied for large speeds of the colliding particles ($v \gtrsim 1$), at which one must take into account the momentum transfer by the electron and replace the functions Ψ by Ψe^{ivr}, which leads to a decrease of the effective cross section.

12. For the case $H_{12} = \beta \operatorname{sech} \gamma t$, $H_{11} = -H_{22} = \alpha$, the system (1) has been integrated exactly by Zener and Rosen.[8] It is easily verified that in this case Eq. (9) is the exact answer. The virtue of the derivation given here is that the number of assumptions made about H_{ik} outside regions 2) and 4) is a minimum, and it is clearly seen that the transitions are caused only by the behavior of the functions in these regions. These conclusions do not follow directly from a consideration of the Rosen-Zener model.

13. In order to determine the parameter R_0 one must know the value of the exchange integral H_{12} as a function of R for R larger than the dimensions of the atoms. Sometimes this value can be estimated (for example, from the binding energy of the molecular ion AB^+), and sometimes it can be calculated, but as a rule both calculations and estimates give only the order of magnitude, which means that R_0 is determined only to within an amount of the order of δR. By fixing R_0 more exactly, we can use it as an adjustable parameter, and perhaps also as a quantity allowing us to determine H_{12} from experimental data on charge transfer.

14. In the derivation no assumptions were ever made about analyticity of $H_{ik}(t)$ or $H_{ik}(R)$. Such an assumption is actually necessary, however, for the treatment of the asymptotic behavior of the probability for $v \rightarrow 0$. The presence of discontinuities of the $H_{ik}(R)$ and their derivatives inevitably leads to a power-law dependence of w on v for small v. The smoother the functions $H_{ik}(R)$, the farther into the region of small v one can use formulas of the type of Eq. (11) or the Landau-Zener formula.

15. In conclusion we point out that the system (1) and the assumptions we have made about H_{ik} are very general, and therefore our results can be applied to a wide variety of problems in which there are transitions between two states of nearly equal energies under the action of a smooth perturbation which depends on the time and falls off exponentially for $t \rightarrow \pm\infty$. Examples are the transfer of excitation between S states of atoms, experiments of the Stern-Gerlach type,[8] transitions between fine-structure and hyperfine-structure levels under the action of nonstationary electromagnetic fields, and so on.

We propose next to make a detailed analysis of the experimental data on charge transfer in slow collisions from the point of view of the results obtained here.

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