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ON COLLISION PROBLEMS INVOLVING LARGE INTERACTIONS

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Abstract

Many collisions, particularly those in which there is an exchange of electronic energy from one atom or molecule to another, involve interactions between the colliding bodies, which (being treated as perturbations) are too large to be handled by the ordinary Born method. A method is given for the treatment of such problems. Two cases must be distinguished, that of good and that of poor resonance, resonance being good if the transition which takes place at the collision does not involve the transfer of much energy from internal energy to relative translational energy, or *vice versa*. The case of good resonance is handled by Dirac's perturbation method (variation of constants), and the probability that a transition take place at a collision of given distance of closest approach found in terms of the perturbation (interaction) matrix component for that collision. In the case of poor resonance, we first assume the two atoms or molecules are held at a fixed distance from each other, and apply the perturbation due to the interaction between them constructing potential energy curves as a function of the distance, as if the whole system were a large molecule. We then allow the translational motion to take place. This introduces further perturbations, which in the case of poor resonance are always small, so that relatively few transitions will occur. Since the amount of energy which we may have transferred from internal to translational, or *vice versa*, and still have the case of good resonance may be determined in special cases as a function of the distance of closest approach, we may tell in any special case how close the two molecules or atoms must come to each other in order for there to be a transition at the collision. Thus a radius of action can be found. In general it is concluded that if the transition is to take place with a large radius of action (compared with kinetic theory radii), then less energy can be transferred from internal to translational, or *vice versa*, than has hitherto been supposed.

§1. Introduction

Many collision problems, particularly those in which the transition at collision involves the exchange of electronic energy from one atom or molecule to another, bring in interactions between the atoms or molecules, which (being treated as perturbations in a wave-mechanical perturbation theory) are so large that the ordinary Born method for handling such problems breaks down.[1] The first attempt to treat a case of this kind was made by Kallmann and London.[2] As their treatment was not entirely free from objections, I made an attack on the problem in another way,[3] as did also Zener,[4] but these attempts still leave much to be desired.

It will be the object of this communication to describe a method which I believe may be made the basis for a satisfactory solution of the problem. I

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[1] Kallmann and London, Zeits. f. Physik **60**, 417 (1930).

[2] Kallmann and London, Zeits. f. phys. Chem. **2B**, 207 (1929).

[3] Rice, Proc. Nat. Acad. Sci. **17**, 34 (1931).

[4] Zener, Phys. Rev. **38**, 277 (1931).

have not as yet completed the application to any particular case, but certain conclusions of a rather general nature seem possible, and it appears desirable to describe the procedure in as simple and general a way as possible, without the encumbrance of the special notation necessary for a special problem. The results also have an application of general interest with respect to the question of distinguishing between adiabatic and nonadiabatic processes, which we will not enter into in detail, but which the reader may readily see for himself.

§2. Statement of the Problem

We suppose that we have two molecules or atoms. Neglecting at first any interaction between them, the state of this pair of molecules or atoms may be designated by an eigenfunction ψ which may be written in the form

$$\psi = XR \tag{1}$$

where R depends on r, the distance between the centers of gravity of the two molecules and X depends on all other coordinates, to be designated as the internal coordinates. We assume that there are two eigenfunctions X which need to be considered, X_1 and X_2. Taking the initial state of the system to be that designated by the subscript 1, we require the probability that on collision it should go over (due to the action of the mutual attractions or repulsions neglected in setting up (1)) to the state designated by subscript 2.

The assumption that there are only these two states X_1 and X_2 to be considered constitutes the chief limitation on our method, because we know that, on account of the rotational degeneracy, it is always necessary to consider many states at a time.[3] Nevertheless I believe that the general character of the results will not be altered, though this must be investigated in the treatment of special cases.

The physical meaning of the transition from the state 1 to the state 2 may be illustrated by a typical example, in which X_1 represents one of the atoms in an excited electronic state, the other atom being unexcited, while with X_2 it is reversed. The transition considered then represents an exchange from one atom to the other of electronic excitation energy.

Corresponding to the two states X_1 and X_2 are two internal energies E_1 and E_2, respectively. Corresponding to the initial and final translational eigenfunctions R_1 and R_2 we have the translational energies T_1 and T_2, respectively. The total energies we shall designate as W_1 and W_2. Naturally we must have

$$W_1 = W_2. \tag{2}$$

If

$$E_1 = E_2 \tag{3}$$

we speak of a condition of exact resonance. This corresponds to no change of translational into internal energy, or *vice versa*, at collision. If $E_1 \neq E_2$ and $E_2 - E_1$ is fairly great[4a] we say the resonance is poor. As is to be expected the

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[4a] When statements of the size of quantities are made we shall always have reference to their *absolute magnitudes*.

probability of transition at a collision depends greatly on whether the resonance is good or poor. We shall find it necessary to use two different methods of attack for "good" and "poor" resonance, and shall have occasion to define these terms more exactly later.

In either case our first step is to set up an unperturbed wave equation, neglecting any mutual interaction between the two atoms or molecules. ψ_1 and ψ_2 obey the wave equations,

$$\begin{aligned}(H - W_1)\psi_1 &= 0\\ (H - W_2)\psi_2 &= 0\end{aligned} \tag{4}$$

where H is the unperturbed Hamiltonian operator for the system. X_1 and X_2 obey the equations

$$\begin{aligned}(H_0 - E_1 - l_1(l_1 + 1)/\kappa^2 r^2)X_1 &= 0\\ (H_0 - E_2 - l_2(l_2 + 1)/\kappa^2 r^2)X_2 &= 0\end{aligned} \tag{5}$$

where H_0 is the part of the Hamiltonian operator which contains derivatives with respect to the internal coordinates; l_1 and l_2 are the quantum numbers which give the angular momentum which is connected with the free motion of the two atoms or molecules in the states 1 and 2 respectively; and $\kappa^2 = 8\pi^2 M/h^2$ where h is Planck's constant and M the reduced mass. The terms involving the l's enter into the equation in the ordinary process of separating the variables.[5]

R_1 and R_2 can be expressed in terms of quantities F_1 and F_2 defined in accord with the equation

$$R = F/r \tag{6}$$

the F's obeying the equation (subscripts 1 or 2 to be inserted)

$$d^2F/dr^2 + (\kappa^2 T - l(l + 1)/r^2)F = 0. \tag{7}$$

The quantity l_1 plays an important role in our calculations. For it is seen that F_1 decreases very rapidly for values of r less than r_0, where

$$r_0 = l_1(l_1 + 1)/\kappa^2 T_1. \tag{8}$$

This distance is the distance of closest approach (or at least what would be the closest approach if there were no forces between the atom or molecules) of two molecules or atoms with the given relative kinetic energy and angular momentum in the classical theory, and the same interpretation retains most of its significance in the quantum theory.

It is evident that in the transition l will be subject to selection rules, and we shall now assume

$$l_1 = l_2 \tag{9}$$

for only in this way can we remain consistent with our original assumption that only one final state exists which combines with the given state 1. This condition also demands certain selection rules among the other rotational quantum numbers. These we will not need, however, to consider further.

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[5] As in Frenkel, "Wellenmechanik," Springer, Berlin, 1929, pp. 245–6.

We now take into account the interaction between the two atoms or molecules, that is, the energy in excess of that they would have if they were an infinite distance apart. This can be expressed as a function, V, of the internal coordinates of the two atoms and the distance r. The problem is treated as a perturbation problem, with V the perturbation function. Corresponding to V will be a matrix

$$\begin{array}{cc} v_{11} & v_{12} \\ v_{21} & v_{22}. \end{array}$$

(In the matrix as written the exponential time factor is assumed not to be included.) First we shall consider the case where[6] $v_{11}=v_{22}=0$. The matrix must of course be Hermitian so that $v_{21}=v_{12}^*$, where the asterisk means conjugate complex.

v_{12} will be a function of r_0, E_1, and E_2-E_1, and it may readily be seen that it will be larger in absolute value the smaller[7] r_0 and $|E_2-E_1|$. The fact that large values of v_{12} are associated with small values of $|E_2-E_1|$ is due to the fact that when $|E_2-E_1|$ is small $|T_2-T_1|$ will be small also, since the total energy cannot change in the collision. If T_1 and T_2 are the same the eigenfunctions F_1 and F_2 of Eq. (7) will be the same, and the integral by which v_{12} is determined, the integrand of which contains the factor F_1F_2dr, will be large. But if F_1 and F_2 are different, and since they are oscillating functions of r, the factor F_1F_2 will then have positive and negative parts when considered as a function of r; in the integration these will tend to cancel, giving small values for the integral. The situation is not greatly different from that described by Condon in his well-known explanation of the intensities in band spectra.

§3. Case of Good Resonance

We shall at first assume that E_2-E_1 is so small that v_{12} is not less than, say, $\frac{1}{2}$ of the value it would have if $E_2-E_1=0$. We shall define this as "good" or "exact" resonance. We may then find the probability of transition per collision in terms of v_{12}. To simplify the notation we shall assume $v_{12}^*=v_{12}$. The results will hold if this is not the case.

We substitute $-(h/2\pi i)\partial/\partial t$ for W_1 or W_2 in Eq. (4), put in a more general function ψ, and bring in the mutual energy, so that

$$\left(H + V + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\psi = 0. \tag{10}$$

We proceed, according to the Dirac method of variation of constants,[8] to

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[6] This is true if the interaction is the dipole interaction described in my preliminary article. These are probably the only forces we need to consider if we merely wish to discover whether radii of action larger than kinetic theory radii can occur. (See Kallmann and London, reference 2.) And, of course, as soon as we have to consider radii of the order of kinetic theory radii we cannot neglect v_{11} and v_{22}.

[7] See, e.g., the calculation in reference 3. The maximum may not occur *exactly* at $E_2-E_1=0$, and some modification of the statement is necessary if Eq. (9) does not hold.

[8] Dirac, Proc. Roy. Soc. **112A**, 673–5 (1926).

find ψ in terms of the original eigenfunctions, which satisfy the equations of the type (4). In so doing it is of course to be noted that due to the free motion of the two atoms or molecules with respect to each other there will be a continuous series of eigenfunctions and eigenvalues for Eq. (4). It will therefore be necessary to integrate over the energy, though naturally only states in the immediate neighborhood of W_1 will make any appreciable contribution. For purposes of normalization it is most convenient to introduce a largest value, r_1, for r, the ψ's then being normalized so that, for example,

$$\int \psi_1^2 d\tau = 1 \tag{11}$$

where $d\tau$ is the volume element, and where the integration is taken over all allowable values of the coordinates (r goes from 0 to r_1). The introduction of the largest value, r_1, will cause the continuous set of eigenfunctions to become a very close-spaced set of discrete ones. We will designate the difference between successive eigenvalues as ϵ (ϵ_1 or ϵ_2 corresponding to the initial or final states, respectively). ϵ will be given in terms of r_1 and T by the following expression

$$\epsilon = hT^{1/2}/r_1(2M)^{1/2} = 2\pi T^{1/2}/r_1\kappa. \tag{12}$$

It is seen that there will be a group of eigenfunctions with the internal part X_1 and a group with the internal part X_2. Any one of the former group we designate as ψ_i, of the latter as ψ_f, the corresponding energy values will be E_i and E_f, W_i and W_f, T_i and T_f. The particular ψ's with energies W_1 and W_2 will still be ψ_1 and ψ_2.

We set

$$\psi = \Sigma_i a_i \psi_i \exp\,(-\,2\pi i W_i t/h) + \Sigma_f a_f \psi_f \exp\,(-\,2\pi i W_f t/h) \tag{13}$$

where the a's are coefficients which will be functions of the time, and follow Dirac by substituting ψ in Eq. (10), and using relations like (4):

$$\begin{aligned}(H - W_i)\psi_i &= 0\\ (H - W_f)\psi_f &= 0.\end{aligned} \tag{14}$$

we remember that[9] $v_{ff} = v_{ii} = 0$ getting thus the following equations:

$$-\,(h/2\pi i)da_f/dt = \Sigma_i a_i v_{fi} \exp\,\{2\pi i(W_f - W_i)t/h\} \tag{15}$$

$$-\,(h/2\pi i)da_i/dt = \Sigma_f a_f v_{fi} \exp\,\{2\pi i(W_i - W_f)t/h\}. \tag{16}$$

We begin with the system in a given state, which means that, at time $t=0$, all the a_f's are zero and all the a_i's are zero except a_1, which may be taken as 1. The solution which we get must be consistent with this condition. We start now by trying, as a solution,

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[9] This means, of course, that states with the same internal state do not interact with each other, and that the only transitions which occur directly are transitions which involve a change from one internal state to another. This, of course, considerably simplifies our problem, but the method of avoiding the difficulty which one runs into if this is not the case, has been given by Morse and Stueckelberg, reference 22. See §7.

$$a_f = k_f[1 - \exp\{2\pi i(W_f - W_1)t/h]/(W_f - W_1) \tag{17}$$

where k_f is a function of f. In the case in which the perturbation is small $k_f = v_{f1}$ as was shown by Dirac. We are interested in the case of large perturbations, but it will be seen later that k_f nevertheless remains proportional to v_{f1} if resonance is good. We proceed by substituting (17) into (16) and evaluating (16) by changing the sum into an integration. (This is done by simply replacing the summation sign by $\int dW_f/\epsilon_f$.) (16) then goes over, after a slight transformation, into the form:

$$-\frac{h}{2\pi i}\frac{da_i}{dt} \tag{18}$$
$$= \int_0^\infty \frac{k_f v_{fi}[\cos\{2\pi(W_1-W_f)t/h\} + i\sin\{2\pi(W_1-W_f)t/h\} - 1]e^{2\pi i(W_i-W_1)t/h}}{W_f - W_1}\frac{dW_f}{\epsilon_f}.$$

If t is large enough there is no contribution from the sine term in the integrand of (18) except in the immediate neighborhood of $W_f = W_1$; that part of the integral reduces practically to

$$-(ik_2 v_{2i}/\epsilon_2)\int_{-\infty}^{\infty} \frac{\sin(W_f - W_1)}{W_f - W_1}d(W_f - W_1),$$

a known form.[10] (k_2 is the value of k_f when $W_f = W_2 = W_1$) The contribution from the cosine term is negligible. (Any difficulty which might arise from the singularity at $W_f - W_1$ is automatically taken care of by the fact that the cosine term is equal to 1 at this point, hence the two terms cancel each other.) Eq. (18) thus reduces to

$$\frac{h}{2\pi i}\frac{da_i}{dt} = \left(\frac{i\pi k_2 v_{2i}}{\epsilon_2} + \int_0^\infty \frac{k_f v_{fi}}{W_f - W_1}\frac{dW_f}{\epsilon_f}\right)e^{2\pi i(W_i-W_1)t/h}. \tag{19}$$

The remaining integral in (19) can be evaluated roughly. v_{fi}, taken as a function of W_f, (holding i constant) may be expected in general to have a rather sharp maximum at or near the point where $T_f = T_i$. In the case of exact resonance this is also where $W_f = W_i$. In general we may designate the W_f which goes with $T_f = T_i$ as W_{f_i}. If W_{f_i} is not equal or nearly equal to W_1 the integral may be considered to have its greatest contribution in the neighborhood of $W_f = W_{f_i}$. It will be approximately

$$\int_0^\infty \frac{k_f v_{fi}}{W_f - W_1}\frac{dW_f}{\epsilon_f} = \frac{k_{f_i} v_{f_i i}}{W_{f_i} - W_1}\frac{\Delta W_{f_i}}{\epsilon_{f_i}} \tag{20}$$

where ΔW_{f_i} is such a quantity that

$$\int_0^\infty v_{fi}dW_f = v_{f_i i}\Delta W_{f_i}, \tag{21}$$

and may be called the effective width of the curve v_{fi} plotted against W_f. But as W_{f_i} approaches W_1 that is to say, putting the matter the other way

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[10] Peirce, "A Short Table of Integrals," Ginn and Co., Boston, 1910, Formula 484.

round, as W_i approaches W_{i_2} the value of the integral will eventually become zero at some point where the positive and negative parts cancel. It may be seen that roughly its value should not exceed such a value as would be obtained by putting $\Delta W_{f_i} = W_{f_i} - W_i$. Since ΔW_{f_i} will be small this means that W_{f_i} is nearly equal to W_1 which is equal to W_2, hence that we may substitute the subscript 2 for f_i. Then, putting the matter the other way round, we see that the i subscript will be roughly i_2. Thus

$$\text{Max} \int_0^\infty \frac{k_f v_{f_i}}{W_f - W_1} \frac{dW_f}{d\epsilon_f} \sim \frac{k_2 v_{2i_2}}{\epsilon_2}\,. \tag{22}$$

If now the state i_2 chances to be close to the state 1, that is, if T_2 is nearly equal to T_1 (the case of good resonance) the value of (22) becomes $k_2 v_{21}/\epsilon_2$ while for i near 1 in (19) it is seen that the right hand side of (19) will be of the order of its first term. If we assume as a first approximation that we may neglect the second term in (19) we may write (for W_i near W_1)

$$(h/2\pi i)da_i/dt = (i\pi k_2 v_{21}/\epsilon_2) \exp \left\{2\pi i(W_i - W_1)t/h\right\}. \tag{23}$$

The word "near" means: "Defined about as closely as good resonance is defined."

Eq. (23) will not hold unless we have good resonance, for when i is 1 the second term in the parentheses in (19) becomes by (20):

$$[k_{f_1} v_{f_1 1}/(W_{f_1} - W_1)]\Delta W_{f_1}/\epsilon_{f_1}. \tag{24}$$

This is to be compared with the first term, $i\pi k_2 v_{21}/\epsilon_2$. Now if resonance is not good v_{21} will be small compared with $v_{f_1 1}$ which is, of course, the maximum value of v_{f1}. Furthermore, we may in general expect that v_{f1} will fall off more rapidly than $1/(W_f - W_1)$ as $W_f - W_1$ becomes greater than ΔW_{f_1}. So the second term of (19) becomes then predominant unless k_{f_1} is sufficiently smaller than k_2 which it will not be (23) was derived on the assumption that the first term predominated. Since we shall base our subsequent deductions in this part of the paper on (23), they will hold roughly for the case of good resonance, that is T_2 must be near enough T_1 so v_{21} is within a factor of 2 or so of the maximum value.

Integrating (23) and making $a_i = 0$ at $t = 0$ we get (note $v_{21} = v_{12}$)

$$a_i = ik_2\pi v_{12}[\exp\{2\pi i(W_i - W_1)t/h\} - 1]/\epsilon_2(W_i - W_1). \tag{25}$$

We can substitute this into Eq. (15) and proceed in the same way that we have just done. We must note, however, that at $t = 0$ we have $a_1 = 1$. As $i \rightarrow 1$ the value of (25) becomes $-2\pi^2 k_2 v_{12} t/\epsilon_2 h$. It seems, therefore, entirely natural to set[11]

$$a_1 = 1 + \lim_{i \rightarrow 1} ik_2\pi v_{12}[\exp\left\{2\pi i(W_i - W_1)t/h\right\} - 1]/\epsilon_2(W_i - W_1). \tag{26}$$

When we evaluate (15) and integrate we get (for W_f near W_2)

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[11] It is necessary to retain a_1 in this form in order to get reasonable results in our subsequent calculations.

$$a_f = (v_{12} - k_2\pi^2 v_{12}^2/\epsilon_1\epsilon_2)[1 - \exp\{2\pi i(W_f - W_1)t/h\}]/(W_f - W_1). \tag{27}$$

But this must coincide with the expression (17) for a_f. Equating these two for a_2 we get an equation for k_2, which yields

$$k_2 = v_{12}/(1 + \pi^2 v_{12}^2/\epsilon_1\epsilon_2). \tag{28}$$

In order to find the total number of systems in the second state we must evaluate $\sum_f a_f a_f^*$. With the aid of (17) and (28) we find by turning the summation into an integration

$$\Sigma_f a_f a_f^* = 4\pi^2 v_{12}^2 t/h(1 + \pi^2 v_{12}^2/\epsilon_1\epsilon_2)^2\epsilon_2. \tag{29}$$

Thus the rate of transfer from the state 1 to all the states f, which rate we may call γ_{12} is given by

$$\gamma_{12} = 4\pi^2 v_{12}^2/h(1 + \pi^2 v_{12}^2/\epsilon_1\epsilon_2)^2\epsilon_2. \tag{30}$$

Now the eigenfunction ψ_1 represents a system in a certain internal condition with translational energy T_1, moving hence from r_0 to r_1 and back again with velocity $(2T_1/M)^{1/2}$. In unit time it will go from r_0 to r_1 and back again approximately $(2T_1/M)^{1/2}/2r_1$ times which may be taken as the number of collisions per unit time of a system in the state 1. This is equal to ϵ_1/h, by (12), hence the probability of transition per collision may be obtained by dividing (30) by ϵ_1/h and is given by [12]

$$N_{12} = 4\pi^2 v_{12}^2/(1 + \pi^2 v_{12}^2/\epsilon_1\epsilon_2)^2\epsilon_1\epsilon_2. \tag{31}$$

It is seen that N_{12} first increases then decreases as v_{12} increases and hence as r_0 the distance of closest approach, decreases. When

$$\pi^2 v_{12}^2/\epsilon_1\epsilon_2 = 1 \tag{32}$$

$N_{12} = 1$. It never becomes greater than this, as of course it must not. The value of r_0 for which (32) holds may be taken as a rough measure of the effective radius of action in any case of exact resonance, since v_{12} will usually increase very rapidly as r_0 increases. This gives a rough justification for the method used in my preliminary article, as far as that is concerned with exact resonance, and, therefore, a justification, except for a numerical factor, of Kallmann and London's result for that case. Eq. (31) is of course not an absolutely exact equation and depends on the validity of the approximations which have been made.

It may be remarked that the quantity on the left hand side of (32) is independent of r_1 as it must be. Since the parts of the integration at great distances r contribute nothing to v_{12}, the latter quantity will depend inversely on r_1, due to the normalization of ψ_1 and ψ_2, while the same dependence is true for ϵ_1 and ϵ_2, as is seen from (12).

Eq. (31) solves the transition problem for the case of exact resonance, whether the perturbation is large or small. It reduces, of course, to the usual result for small perturbations if $v_{12}^2 \ll \epsilon_1\epsilon_2$. It has been pointed out that there

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[12] Because we have the case of exact resonance, $\epsilon_1 = \epsilon_2$.

will be obstacles in the way of obtaining a similar result if the resonance is not exact. We might, however, expect that we could at least treat the cases where $v_{12}^2 \ll \epsilon_1\epsilon_2$ by the usual formula for small perturbations. Unfortunately this is not true, however. The difficulty arises from the fact that, in the case of poor resonance, v_{12} is not as large as v_{1f_1}, so that though v_{12}^2 is small compared to $\epsilon_1\epsilon_2$ it may not be true that $v_{1f_1}^2$ will be, so we really do not have the case of small perturbations after all. The criterion for small perturbations is that the second term of (13) should always and for all values of r, but particularly such values as are of importance in the integral which defines a perturbation matrix component, v_{if}, be small compared with the first term. At time $t=0$ the r-factor of the first term is simply F_1. The r-factor of the second term should never approach this in magnitude. To find the conditions under which this will be true, let us evaluate $\Sigma_f\, a_f F_f \exp(-2\pi i W_f t/h)$. Since if the perturbation is small we have $k_f = v_{f1}$ we shall simply substitute this value in (17) and use this expression. In a manner similar to that in which we obtained Eq. (19) we get (t large)

$$\Sigma_f a_f F_f (\exp(-2\pi i W_f t/h) = -\left(i\pi F_2 v_{21}/\epsilon_2 \right.$$
$$\left. + \int_0^\infty \frac{v_{f1}F_f}{W_f - W_1} \frac{dW_f}{\epsilon_f} \right) \exp(-2\pi i W_1 t/h).$$

It is seen that if v_{21}/ϵ_2 is small the first term will always be small, but we must evaluate the integral. Now the range of W_f over which v_{f1} has a large value is just that range over which F_f does not get appreciably out of phase in those regions (the important regions) of r which contribute to the integral giving v_{f1}. Thus we set $F_f = F_{f_1}$ for that region of r, and evaluate the integral as we did the integral in (19), obtaining as a rough value $v_{f_1 1}F_{f_1}\Delta W_{f_1}/\epsilon_{f_1}(W_{f_1} - W_1)$. If this is small we can use the small perturbation approximation. Since, if resonance is poor, $\Delta W_{f_1} \ll W_{f_1} - W_1$ it is always safe to use the approximation if $v_{f_1 1}/\epsilon_{f_1}$ is not greater than about 1. That is, we may surely use the approximation for small perturbations provided this approximation would be correct, even if we had exact resonance. Any attempt to carry the small perturbation case up toward the region where $v_{12}^2/\epsilon_1\epsilon_2$ itself is large, as was done in our preliminary article[3] will be inadmissible except for getting an upper limit, as, indeed, we stated to be the case at the time. (though, due to the rapid decrease of v_{12} as $|E_2 - E_1|$ increases, this may nevertheless turn out to be a pretty good approximation). The method of §5 allows us to show that in the case of poor resonance the transition probability at collision will always be small (except, perhaps, at the very boundary of good resonance, i.e. not very poor resonance). If we have to contrast this with cases where the probability of transition approaches unity, this is entirely satisfactory—transition probabilities, if resonance is poor, are negligible. In many cases, however, transition probabilities of the order of 1 never occur—we are interested in comparing very much smaller probabilities. Here the calculations for small perturbations hold, and no further analysis is required.

§4. Discussion of §3

Since in §3 we have really given only an outline of the derivation of (28), it may be well to discuss further some of the points involved, as well as give an interpretation of the results in terms of an incoming wave and outgoing waves of particles.

In the first place our deductions are based on the assumption that (for state f very far from 2)

$$k_2/k_f = v_{12}/v_{1f} \tag{33}$$

and more or less implicitly on the assumption that (for state i very far from 1)

$$k_1/k_i = v_{21}/v_{2i}. \tag{34}$$

But are these assumptions consistent with each other and with Eq. (19) and with the equation similar to (19) but involving da_f/dt instead of da_i/dt, for all values of i and f? The answer is yes. For Eq. (34) follows from (19) provided the first term on the right-hand side of (19) is large compared with the second, and this condition is fulfilled provided (33) is true. Using (33) we have to show that

$$\left| i\pi k_2 v_{2i}/\epsilon_2 \right| \gg \left| k_2 v_{1f_i} v_{f_i i} \Delta W_{f_i} / v_{12}(W_{f_i} - W_1)\epsilon_{f_i} \right|. \tag{35}$$

Since $v_{f_i i} \sim v_{12}$ and $v_{1f_i} \sim v_{2i}$ and $\epsilon_2 \sim \epsilon_{f_i}$ and $\Delta W_{f_i} \ll W_{f_i} - W_1$ this is seen to be true.[13] Similarly (33) follows from (19) and (34). They are therefore consistent, and so we have gone a step further in the construction of the complete consistent solution of the Dirac equations (15) and (16), at least within the limits which the approximations for i and f not far from 1 and 2, respectively, allow.

We may next consider the question of the constant of integration in the expressions for a_f and a_i. This has been chosen to make the quantities have the proper values, in general zero, at $t=0$. But it will have been noted that the evaluation of da_i/dt from (18) depends upon the assumption that t is great. Specifically it may be seen from (18) that it must be so great that exp $2\pi i \Delta W_{f_1} t/h$ has gone through a considerable number of periods. This being the case, the expression (19) for da_i/dt does not hold from the moment $t=0$, and the same may be said for the similar expression for da_f/dt. This will affect the constant of integration. However, if i is near enough to 1, it is obvious that exp $2\pi i(W_i - W_1)t/h$ will (because $|W_i - W_1| \ll \Delta W_{f_1}$) have gone through but a fraction of a period after the expression (19) has begun to hold. Therefore, the constant of integration must be approximately correct if i is near 1 (and similarly if f is near 2), which is all that is necessary. In fact, the exact value of the constant of integration is not important so long as it does not vary rapidly with i when i is in the neighborhood of 1 (or with f when f is in the neighborhood of 2), for it would not matter, for example, if the last term in (19) were multiplied by a factor, which might be complex, but in all events would of the order of 1 in absolute value.

One of the most satisfactory checks of the general correctness of the procedure in §3 will be afforded by the ability to express the results in terms of ingoing and outgoing waves of pairs of atoms or molecules. We may now consider how this may be done.

Consider first the eigenfunctions F_f. At great distances, they are of the form,

$$F_f = \sin \kappa T_f^{1/2} r \tag{36}$$

ignoring a possible phase constant and the normalization factor. The part of the complete eigenfunction with the final internal state which depends on r is given by

$$\Sigma_f a_f F_f e^{-2\pi i T_f t/h} = e^{-2\pi i T_2 t/h} \int_{-\infty}^{\infty} \frac{k_f(e^{-2\pi i (T_f - T_2)t/h} - 1)\sin(\kappa T_f^{1/2} r)}{T_f - T_2} \frac{d(T_f - T_2)}{\epsilon_f}. \tag{37}$$

We have substituted from (17) for a_f, since we have decided that (17) will hold if W_f is near enough to W_2 or W_1 and as we may see only such states contribute appreciably to the integral[14]

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[13] Actually some of our deductions are based on the assumption that T_1, T_2, and all T_i and T_f are of the same order of magnitude. This will include a range of values very much greater than such a difference $T_1 - T_2$ as would be necessary in order for resonance to be poor, and cannot invalidate our conclusions.

[14] Since this is true, it is permissible to take the limits from $-\infty$ to ∞, when we change over to the variable $T_f - T_2$ instead of T_f.

in (37). Also we have made the obviously correct substitution $T_f - T_2$ for $W_f - W_2$. We can also substitute $\sin\{\kappa T_2^{1/2}r + \kappa r(T_f - T_2)/2T_2^{1/2}\}$ for $\sin(\kappa T_f^{1/2}r)$ and then perform the integration. We obtain[15]

$$\Sigma_f a_f F_f e^{-2\pi i T_f t/h} = -\frac{\pi k_2}{\epsilon_2} e^{i\kappa T_2^{1/2}r} \quad \text{if} \quad \frac{\kappa r}{2T_2^{1/2}} < \frac{2\pi t}{h} \qquad (38)$$

$$= 0 \quad \text{if} \quad \frac{\kappa r}{2T_2^{1/2}} > \frac{2\pi t}{h}.$$

This represents a wave of pairs of particles traveling outward from each other with a relative particle velocity equal to $(2T_2/M)^{1/2}$ and with a definite wave front which moves out with the relative particle velocity. Now, in similar fashion, using (25) and (26), we find

$$\begin{aligned} &\Sigma_i a_i F_i \exp(-2\pi i T_i t/h) \\ &\quad = (i\pi^2 v_{12} k_2/\epsilon_1\epsilon_2)\exp(i\kappa T_1^{1/2}r) + \sin(\kappa T_1 r) \quad \text{if } \kappa r/2T_1^{1/2} < 2\pi t/h \\ &\quad = \sin(\kappa T_1 r) \quad \text{if } \kappa r/2T_1^{1/2} > 2\pi t/h. \end{aligned} \qquad (39)$$

This may be interpreted as the original stationary state with index 1, represented by the sine term, plus a *negative* wave of pairs of particles, with relative particle velocity equal to $(2T_1/M)^{1/2}$ and a definite wave front with the relative particle velocity, corresponding to those which have been removed and are going out in the wave represented by (38). To show that this is true note that $\sin(\kappa T_1^{1/2}r) = -\frac{1}{2}i\,[\exp(i\kappa T_1^{1/2}r) - \exp(-i\kappa T_1^{1/2}r)]$ so that the first equation of (39) becomes

$$\begin{aligned} &\Sigma_i a_i F_i \exp(-2\pi i T_i t/h) \\ &\quad = -i(\tfrac{1}{2} - \pi^2 v_{12} k_2/\epsilon_1\epsilon_2)\exp(i\kappa T_1^{1/2}r) + \tfrac{1}{2}i\exp(-i\kappa T_1^{1/2}r). \end{aligned} \qquad (40)$$

It may readily be shown (with the aid of (28)) that the square of the absolute value of the coefficient of $\exp(i\kappa T_1^{1/2}r)$ in (40) plus the square of the absolute value of the coefficient of $\exp(i\kappa T_2^{1/2}r)$ in (38) is equal to the square of the absolute value of the coefficient of $\exp(-i\kappa T_1^{1/2}r)$ in (40). Thus we see that our solution represents a groups of pairs of particles coming inward in the state represented by the index 1, and two groups of pairs of particles going outward (i.e., pairs of particles in which a collision has occurred), one of which groups represents pairs of particles in which the transition in which we are interested has occurred, the other pairs of particles in which the transition has not occurred, and that we have conservation of matter. We must remember that we are considering the case of exact resonance so $T_1 = T_2$, and $\epsilon_1 = \epsilon_2$.

§5. CASE OF POOR RESONANCE

For the case of poor resonance we shall need a different method of attack. In effect, we shall treat the two atoms as an unstable molecule. We first find the internal eigenfunctions when we hold r fixed but take the interaction between the two atoms into account. There will, of course, be two of these eigenfunctions, which we designate as χ_1 and χ_2. If we divide the Hamiltonian H into the two parts, H_0, which contains the derivatives with respect to all the internal coordinates, and H_r which contains the derivatives with respect to r then χ_1 and χ_2 will satisfy the equations[16]

$$\begin{aligned} (H_0 + V - U_1 - l_1(l_1+1)/\kappa^2 r^2)\chi_1 &= 0 \\ (H_0 + V - U_2 - l_1(l_1+1)/\kappa^2 r^2)\chi_2 &= 0 \end{aligned} \qquad (41)$$

where U_1 and U_2 are the eigenvalues (which will of course be functions of r).

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[15] We change the exponentials into the sine-cosine form, and expand the expression for $\sin\{\kappa T_2^{1/2}r + \kappa r(T_f - T_2)/2T_2^{1/2}\}$, using the formula for the sine of the sum of two angles. The integral finally reduces to integrals of the form of Formula 484 in Peirce, reference 10.

[16] See Eq. (9).

So by ordinary perturbation methods we can find χ_1 and χ_2 in terms of X_1 and X_2 (which obey Eqs. (5)) and U_1 and U_2 in terms of E_1 and E_2. We will have

$$\begin{aligned}\chi_1 &= a_{11}X_1 + a_{21}X_2 \\ \chi_2 &= a_{12}X_1 + a_{22}X_2\end{aligned} \tag{42}$$

where the coefficients a_{11}, a_{12}, a_{21} and a_{22} will be functions of r, though X_1 and X_2 are, of course, not. In setting up the perturbation matrix components (matrix components of V) for this problem we integrate with respect to all variables but r and the matrix components, which we call

$$\begin{matrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{matrix}$$

will be functions of r. We take $u_{11}=u_{22}=0$. (This is the only way, in general, that it is possible to have $v_{11}=v_{22}=0$). The solution of the perturbation problem gives us[17] (assuming $E_1>E_2$ and $U_1>U_2$)

$$\begin{aligned}U_1 &= (E_1 + E_2 + ((E_1 - E_2)^2 + 4u_{12}^2)^{1/2})/2 \\ U_2 &= (E_1 + E_2 - ((E_1 - E_2)^2 + 4u_{12}^2)^{1/2})/2\end{aligned} \tag{43}$$

$$-a_{21}/a_{11} = a_{12}/a_{22} = u_{12}/(E_2 - U_1) = u_{12}/(U_2 - E_1). \tag{44}$$

The actual values of the a's can be obtained from the normalization of the χ's but are not necessary for our purposes. It is only necessary to note (a) that the ratio in (44) changes from 0 to 1 as u_{12} becomes large, which means as r becomes small; and (b) that this change takes place in the neighborhood of such a value of r that $u_{12}\sim E_1-E_2$. On account of the normalization a_{11} and a_{22} change from 1 to $2^{1/2}$ and a_{12} and a_{21} from 0 to $2^{1/2}$.

Now in considering the result of a collision we are not really interested in what happens during the collision itself, but only in the difference in the condition of the system before and after the collision. Since for large r we see that χ_1 coincides with X_1 and χ_2 with X_2, a change from χ_1 to χ_2 is essentially the same thing as a change from X_1 to X_2, and if we can find the probability of such a change at a collision we have solved the problem.

Thus far we have not talked about the relative translational motion in this case. Now we can use the energies U_1 and U_2 as effective potential energies (the usual thing in the treatment of molecules) and set up wave equations of the form

$$\begin{aligned}(H_r + U_1 + l_1(l_1 + 1)/r^2 - W_1)S_1 &= 0 \\ (H_r + U_2 + l_1(l_1 + 1)/r^2 - W_2)S_2 &= 0\end{aligned} \tag{45}$$

where S_1 and S_2 are to be the translational eigenfunctions and W_1 and W_2 the total energies. Naturally, as before, $W_1=W_2$ and we must remember that the Eqs. (45) have continuous sets of eigenfunctions. As before we use the subscripts i and f to designate functions of the initial and final types.

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[17] This method of calculating energy curves was suggested by London, Zeits. f. phys. Chem. **11B**, 222 (1930). It was also suggested to me by Dr. Clarence Zener before the appearance of London's article. The subsequent handling of the transition problem is, as far as I am aware, new.

The procedure which is ordinarily used in the case of molecules, and which we follow here, is as follows. We try for eigenfunctions expressions of the form $\chi_1 S_1$ and $\chi_2 S_2$ and substitute them into the exact wave equation, which is of the form (4). Such functions do not fit the wave equation exactly, and we have certain terms left over which may be treated, following Slater,[18] as a perturbation. We have a perturbation matrix, which we write out:

$$\begin{matrix} p_{11} & p_{12} \\ p_{21} & p_{22}. \end{matrix}$$

We may now use these matrix components and attempt to solve with them the problem of the transition from state χ_1 to state χ_2 as we solved the problem of the transition from X_1 to X_2 in §3 by the use of the perturbation matrix components v_{12}, etc. One might expect to run into difficulties in this attempt, but we shall now show that in the case of poor resonance the matrix components must always be small, so that the possibility of transition can be entirely neglected.

As in analogous cases[19] we may write these matrix components (we take a general one which we call p_{mn}) as follows:

$$p_{mn} = -\kappa^{-2}\int (\chi_m G_m/r)\left[(G_n/r)(\partial^2\chi_n/\partial r^2) + (2/r)(dG_n/dr)(\partial\chi_n/\partial r)\right]d\tau' r^2 dr \quad (46)$$

where $G_m = rS_m$, etc., $d\tau'$ is the volume element, excluding dr, and the integration is taken over all allowed values of the coordinates. Now G_m will roughly be a sinusoidal function of the argument $\kappa T_m^{1/2} r$ (where T_m is the translational energy) and amplitude of $(2/r_1)^{1/2}$ (on account of the normalization), and similarly for G_n. The value of the derivatives of the χ's will depend upon the derivatives of the a's in terms of which the χ's are expressed (Eq. (42)). Now a_{11} will change practically from $2^{1/2}$ to 1 in some distance, equal, say to Δr with an average da_{11}/dr of roughly $1-2^{1/2}$, and similarly for the other a's. Then it is seen that the integral with respect to r need be carried over a region equal to only Δr. We can say roughly that

$$\begin{aligned} \chi_m &\lesssim X_1 \\ \partial\chi_n/\partial r &\lesssim X_1/\Delta r \\ \partial^2\chi_n/\partial r^2 &\lesssim X_1/(\Delta r)^2. \end{aligned} \quad (47)$$

(The choosing of the subscript 1 for these expressions rather than 2 is purely arbitrary—either would give the order of magnitude satisfactorily.)

Also we may write

$$dG_n/dr \sim \kappa T_n^{1/2} G_n' \quad (48)$$

where G_n' is the derivative of G_n with respect to its argument. Using (47) and (48) in (46) we see that[4a]

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[18] Slater, Proc. Nat. Acad. Sci. **13,** 423 (1927).

[19] See Rice, Phys. Rev. **35,** 1552 ff (1930).

$$p_{mn} \lesssim -\kappa^{-2}\int (X_1 G_m/r)\left[(G_n/r)(X_1/(\Delta r)^2) + (2/r)(\kappa T_n{}^{1/2} G_n')(X_1/\Delta r)\right] d\tau' r^2 dr$$

and noting that $\int X_1{}^2 d\tau' = 1$ we have

$$p_{mn} \lesssim -\kappa^{-2}\int (G_m G_n/(\Delta r)^2 + 2\kappa T_n{}^{1/2} G_m G_n'/\Delta r) dr. \tag{49}$$

If the two sinusoidal functions G_m and G_n (or G_m and G_n') are in phase p_{mn} will have its largest possible value. Remembering then what we have said about extending the integration with respect to r over a region equal to Δr and our statement about the amplitude of G_m of G_n we may write

$$p_{mn} \lesssim 1/\kappa^2 r_1 \Delta r + 2T_n{}^{1/2}/\kappa r_1. \tag{50}$$

Now if T_n is of the order of the translational energy of an atom or molecule at room temperature $1/T_n{}^{1/2}\kappa$ will be of the order of 10^{-9} cm. It is not to be expected that any interaction between the atoms will cause the a's to change appreciably in much less than this distance, so we may write $\Delta r > 10^{-9}$ cm, so the right hand side of (50) will be of the order of its second term. Thus we may write

$$p_{mn} \lesssim 2T_n{}^{1/2}/\kappa r_1. \tag{51}$$

By Eq. (12) we may write

$$p_{mn} \lesssim \epsilon_n/\pi. \tag{52}$$

Now this is just large enough, (assuming $\epsilon_1 \sim \epsilon_2$) so that if we substitute p_{12} for v_{12} in Eq. (31), N_{12} becomes of the order of 1. But the right hand side of (52) gives the maximum value that p_{mn} can take. In the case of poor resonance p_{mn} will be much less because then the sinusoidal functions in (49) will be out of phase[20] and have different periods, if $n \neq m$. We rapidly get into the regions of small perturbations and negligible transition probabilities (see end §3). This situation will be only accentuated by the original effect of the perturbation u_{12} on the potential energy between the atoms, as indicated in (43) inasmuch as it pushes the energy curves away from each other. We must also consider the case where $m = n$. It may be shown that the second term on the right of (46) is zero when integrated if[21] $m = n$—this leaves only the first term to consider. It may be taken into account by simply adding increments[22] to U_1 and U_2, and solving this new problem (that is, we use the new eigenfunctions for Eqs. (45). The cross terms of the matrix component will be changed, and the diagonal ones will then be zero). The increment to be added is the part of the integral which is integrated with respect to all variables except r, that is $-\kappa^{-2}\int \chi_m(\partial^2\chi_m/\partial r^2)d\tau'$. It may be shown to have the same

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[20] The fact that we have to deal with G_n' instead of G_n makes a little change in what we will define as good or exact resonance, but not enough to make much difference, especially for the rather rough considerations we have in mind.

[21] Similar to Rice, Phys. Rev. **35**, 1555 (1930).

[22] Morse and Stueckelberg, Ann. d. Physik **9**, 579 (1931).

value whether m is 1 or 2, by the use of (44) and the relations $a_{11}^2+a_{21}^2=a_{12}^2+a_{22}^2=1$. Since U_1 and U_2 are affected in the same way, the question of whether resonance occurs or not is not greatly affected, especially as the size of the term added to the U's will usually be small. It will be of the order $1/\kappa^2(\Delta r)^2$ at the value of r where it is greatest and even if the colliding atoms were hydrogen, for which κ is smallest Δr would have to be as small as 3×10^{-9} cm for the additional energy term to be equal to the average translational energy of an atom at room temperature.

The question may arise as to why it is that we can assume that poor resonance for the matrix components v_{11}, etc., is also poor resonance for the matrix components p_{11}, etc. This can be seen from the Eq. (44) and for the expression for p_{mn}, which is to be compared to the expression $v_{mn}=\int F_m F_n u_{mn} dr$. ($u_{mn}$ already contains the integration for all variables besides r.) If we go from large to small values of r, it will be seen from (44) that u_{mn} will at first have the same general characteristics as a function of r as the nonoscillating part of the integrand of (46), but the latter eventually approaches zero as r decreases (at the point where the a's become practically all equal) while u_{mn} continues to increase. If the nonoscillating part of the integrand of (46) decreases (as $r\rightarrow 0$) at a point $r<r_0$ (where r_0 is defined in (8) $-r_0$ gives the point where the oscillating part decreases) then it is obvious that the properties of p_{mn} will be similar to those of v_{mn}. If the decrease takes place at a greater value of r this means that the contributions to the integral for p_{mn} occur at greater values of r than those for v_{mn}, and consequently at a point where the integrand will be changing more gradually. Thus the relatively important contributions to p_{mn} will be spread over a relatively greater range of r than those of v_{mn} and this means that the two oscillating factors in the integration will more quickly get out of phase with each other in the case of p_{mn} than in the case of v_{mn}. Thus poor resonance for v_{mn} will certainly be poor resonance for p_{mn}.

One may also question why the method of this section could not be used for cases of exact resonance, as well. It might of course, theoretically at least, be used, but complications will arise. As may be seen from (43) and (44) the change in the values of the a's would take place at greater and greater values of r the less E_2-E_1 became.[4a] This would introduce great complications both in the calculation and its interpretation. It seems best, therefore, to stick to the easily worked out and easily interpreted method of §3.

§6. SUMMARY OF THE RESULTS

It thus appears that we may say that, if resonance is good, transitions will take place provided the atoms or molecules come roughly within a certain minimum distance of each other. Outside that distance no appreciable exchange of energy will take place.

But, exact resonance, as it is defined in §3, depends upon how closely the atoms do approach, because the matrix components depend on this. Hence, provided they approach within the maximum distance described in the above paragraph, we may say that they will or will not exchange energy, depending on how closely the energies E_1 and E_2 match. Conversely, we may say, given E_2-E_1, exchange of energy will take place provided the distance of approach is less than a certain critical distance. This distance may be found as a function of E_2-E_1. In general it will be greater the smaller[4a] E_2-E_1.

It is not my desire to enter into particular cases here. But it may not be amiss to mention that cases 2 and 3 of my preliminary article are roughly the cases of poor resonance. An unfortunate typographical error occurred in the definition of these cases.[23] In both instances the expression $(r_0\eta E_{k_1})^{-1/2}$ should have been $(r_0\eta E_{k_1}{}^{1/2})^{-1}$. The present result, if it may be applied directly to the case where many final and initial states are involved, says that practically no transfer of energy will take place if the resonance is poor. It would be difficult to imagine the possibility of radii of action larger than kinetic theory of radii if the resonance difference were greater than a millivolt, a case which practically does not occur unless the exchange is between identical atoms. As far as our results go they thus say that abnormally large radii of action do not occur. Zemansky has recently shown that, in the cases of interaction of mercury atoms with other atoms, many of the large radii of action formerly believed to exist are due to misinterpretation of the experimental data. A careful evaluation of the quantities involved, even if resonance is exact, shows that a reasonably favorable situation is required in order to give exceptionally large radii, and the present results at least strongly indicate that such an evaluation will usually be much too sanguine. I believe therefore, that all cases (except some in which resonance is exact) in which experimental results are reported which give large radii of action that they should be very carefully scrutinized. In many cases, I believe, it will be found that a reinterpretation of the data does away with the necessity of assuming that large radii of action actually exist.

§7. CASE OF NONZERO DIAGONAL MATRIX COMPONENTS

The case where the components u_{11} and u_{22} of the matrix of §5 and therefore v_{11} and v_{22} of the matrix of §3 are not zero may probably be dealt with by use of the two methods described above. u_{11} and u_{22} may simply be added in the Eq. (7) or (45) as potential energies[22] (u_{11} in the first equation in either case, u_{22} in the second). Then we proceed to take care of the cross terms in the matrix as above.

The corrected potential energy curves may have various complex forms. In particular the curves for the two states may cross. We may expect the case in which transitions may be probable to be that in which the relative translational energy in the initial state is such that the two atoms or molecules would just come to rest with respect to each other at the point where the curves cross. The results of this expectation have been discussed in a recent

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[23] Due to an error in V, the expression for r_c in Case 1 should be increased by about 40 percent a change which is, however, about canceled by the substitution of the expression in the Eq. (32) for that of Eq. (4) of the earlier article. The r_c's for cases 2 and 3 will also be slightly modified, but these results are no longer of so much interest being superceded by the present results.

note.[24] It is hoped, however, that it will be possible to take some definite, though hypothetical case, and work it through in some detail, so further discussion of this case will be left for a future communication.

As mentioned above in a footnote[6] the case of zero diagonal matrix components can hold only when the collisions which need to be considered have a distance or closest approach greater than kinetic theory radii. This means that either the radius of action is so large that such close collisions do not contribute an appreciable amount to the total number of transitions, or else we are only interested in seeing whether large radii of action occur or not. But in many cases the radii of action are of the order of kinetic theory radii, and this means that undoubtedly the interactions are too large to be considered by the ordinary Born collision method or the modifications of it which have thus far appeared. Such cases require the treatment indicated by the present section, and they probably occur more often than the cases where the diagonal matrix components can be neglected. The discussion in the previous sections of this paper, therefore, must be considered as illustrative of the type of thing one must expect where large interactions occur, and not as something to be compared directly with much of the experimental data which is at hand. It is, however, of particular interest, as indicating the entirely different treatment of the case of poor resonance necessary when the interactions are large, and the relatively low probabilities of transition in this case as compared with the probabilities when resonance is good.

§8. Discussion

It may be of interest to compare my results with those of the recent article by Zener,[4] in which the problem of inelastic collisions is attacked by a method based partly on classical theory and partly on quantum theory. While I feel that the correctness of his Eq. (1), on which his conclusions are based, is not entirely self-evident, I believe that it should give good results as long as the interactions are small. By this, I mean that the interaction (called here u_{12} and by Zener $V_{n'}{}^{n''}$) must everywhere be so small that the probability of energy exchange would be small if the resonance were exact, and this definition holds even in the case where resonance is poor (see end §3). I do not believe that Zener would concur in this definition, but I use it as the basis for discussion. If the interaction is small, then the probability of transition may be found by the Born or the Dirac method. This consists in the evaluation of Eq. (3) of my preliminary article,[3] and Zener has shown that this method gives essentially identical results in the particular case discussed in my article. The transition probabilities thus considered are always so small we would neglect them in the case of large interactions. In the case where the interaction is large Zener proposes to use and generalize the method I suggested,[3] except that he is going to substitute the probability he calculates by his method for the probability I calculate by mine. This can give only an upper limit, as it gave in my case; as stated above (end §3) this may

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[24] Rice, Phys. Rev. **37**, 1187, 1551 (1931); see also Jabłoński, Zeits. f. Physik **70**, 730 (1931).

be a good approximation, but it is harder to judge how good in Zener's treatment than in mine. The advantage of Zener's method, in those cases in which it can be applied, lies in the case with which the calculations can be made and the results envisioned.

The recent paper of Morse and Stueckelberg[22] does not attempt to treat the case of large interactions, but introduces a device which prevents large interactions from artificially appearing where they really do not belong. The general results obtained are very interesting, but before even the theory of small perturbations can be said to be in final form it will need very considerable modifications. Their theory bears the same relation to the true theory of small perturbations, as the main part of this paper bears to the more general problem outlined in §7.