NOTE ON RADIATIONLESS TRANSITIONS INVOLVING THREE-BODY COLLISIONS

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When an electron makes a transition from a continuous state to a bound state, for example in the case of neutralization of a positive ion or formation of a negative ion, its excess energy must be disposed of in some way. It is usually given off as radiation. In the case of neutralization of positive ions the radiation forms the well-known continuous spectrum. No such spectrum due to the direct formation of negative ions has, however, been observed. This process has been fully discussed in a recent paper by Massey and Smith†. It is shown that in this case the spectrum would be difficult to observe.

The excess energy may, however, be released without radiation if we have a three-body collision, between two electrons and an atom, or between two atoms and an electron, the third body taking up the excess as kinetic energy. It has been suggested that negative ions may be formed in regions of high electron concentration in discharges by this process, and accordingly no continuous spectrum would be emitted. It is therefore of interest to estimate the probability of such processes.

Three-body collisions have not been much studied by means of wave mechanics. We first give an approximate treatment of the collision of two electrons with an atom in the case when one is captured into a bound state. We treat the atom as a fixed field of force, considering only the motion of the two electrons. The problem of the formation of negative ions presents the simplest case. The field of force due to the neutral atom is limited to a small region and plane waves may be used to represent the free motion of the electrons in the atomic field‡. We wish to calculate the probability that one electron will make a transition from a state of positive energy to a bound state while the other goes to the appropriate continuous state of higher energy.

Let $\mathbf{r}_1, \mathbf{r}_2$ represent the distances of the two electrons from the centre of the atom. The wave equation describing their motion is then

$$\left[\nabla_1^2+\nabla_2^2+\frac{8\pi^2 m}{h^2}\left(E-V(r_1)-V(r_2)+\frac{e^2}{|r_1-r_2|}\right)\right]\Psi=0, \qquad (1)$$

$V(r)$ being the potential energy of an electron in the atomic field. For large

† *Proc. Roy. Soc.* A (in the Press).
‡ See Massey and Smith, *loc. cit.*

distances from the atom the wave function for the initial motion will have the form

$$\exp\left[ik_1(\mathbf{n}_1.\mathbf{r}_1)+ik_2(\mathbf{n}_2.\mathbf{r}_2)\right],$$

the velocities of the two electrons being

$$\mathbf{v}_1=hk_1\mathbf{n}_1/2\pi m, \quad \mathbf{v}_2=hk_2\mathbf{n}_2/2\pi m.$$

If we use this wave function as an approximation, the mutual repulsion of the electrons will not be taken into account. This is important, since it prevents both electrons from being near the atom at the same time when both are moving slowly. We may allow in some measure for this effect as follows. The wave function for the two electrons may be separated into two parts, a plane wave representing the motion of their centre of gravity and a Coulomb wave function representing their relative motion. If the accurate Coulomb wave function is used, the analysis becomes very complicated. We therefore use an approximation, valid for small distances of approach when the relative velocity is small and tending to the ordinary plane wave when the relative velocity is large. We take for the relative motion†

$$\Psi_{\text{rel}}=e^{-\frac{1}{2}\pi\alpha}\,\Gamma(1+i\alpha)\,e^{ik_R(\mathbf{N}.\mathbf{r}_1-\mathbf{r}_2)}$$

where $1/\alpha=k_Ra_0$. This leads to an approximate initial wave function

$$e^{-\frac{1}{2}\pi\alpha}\,\Gamma(1+i\alpha)\,e^{ik_1(\mathbf{n}_1.\mathbf{r}_1)+ik_2(\mathbf{n}_2.\mathbf{r}_2)}. \tag{2}$$

For the wave function of the final state we take the form

$$e^{ik'(\mathbf{n}'.\mathbf{r}_1)}\psi_0(r_2), \tag{3}$$

where $hk'\mathbf{n}'/(2\pi m)$ is the velocity of the escaping electron and $\psi_0(r_2)$ is the wave function for the motion of the bound electron in the atomic field.

A treatment corresponding to Born's approximation represents the degree of accuracy which we may hope to obtain without considerable elaboration. This approximation is known to give too large transition probabilities for low velocity collisions. However, we shall obtain an upper limit which will be sufficient for the purpose in hand.

Again one ought to allow for exchange by taking into account the symmetry properties of the electrons. It appears however that the most important terms arise from the transition of a slow electron into the bound state under the perturbation of one which is moving considerably faster, and the simple wave functions give the important contribution to the transition probability.

If we normalize so that the "k_1" electrons correspond to unit current, and the "k_2" electrons to unit density the transition probability as given by Born's approximation is

$$\frac{v'}{v_1}\,|F(k_1, k_2)|^2\,d\omega, \tag{4}$$

† Cf. Mott and Massey, *Theory of atomic collisions*, Chapter III.

when the free electron escapes into a solid angle $d\omega$. $F(k_1, k_2)$ is the expression†

$$\frac{2\pi me^2 C}{h^2}\iint \psi_0^*(r_2)\left[\frac{1}{|r_1-r_2|}-\frac{1}{r_1}\right]\exp\{ik_1(\mathbf{n}_1.\mathbf{r}_1)+ik_2(\mathbf{n}_2.\mathbf{r}_2)-ik'(\mathbf{n}'.\mathbf{r}_1)\}\,d\mathbf{r}_1 d\mathbf{r}_2, \tag{5}$$

where C is written for $e^{-\frac{1}{2}\pi\alpha}\Gamma(1+i\alpha)$.

To get the total transition probability we must integrate (4) over all angles and also average over the angle between the initial directions of motion of the electrons. The largest contribution comes from values of $\mathbf{n}_1$ near $-\mathbf{n}_2$. As an approximation we therefore take $1/(k_1+k_2)a_0$ for the value of α in C.

To evaluate $F(k_1, k_2)$ we first integrate with respect to $\mathbf{r}_1$ using the integral

$$\int e^{ik(\mathbf{n}.\mathbf{r})}/|r_1-r|\,d\mathbf{r}=\frac{4\pi}{k^2}e^{ik(\mathbf{n}.\mathbf{r}_1)}.$$

This gives
$$F(k_1, k_2)=\frac{8\pi^2 me^2 C}{p^2K^2}\int\psi_0(r_2)\,[e^{ikr_2\cos\theta}-e^{ik_2r_2\cos\theta}]\,d\mathbf{r}_2, \tag{6}$$

where $kr_2\cos\theta=(k_1\mathbf{n}_1+k_2\mathbf{n}_2-k'n', r)$ and $K=|k_1\mathbf{n}_1-k'n'|$. We take for ψ_0 the form‡ $N_0e^{-\alpha r}$. Expanding $e^{ikr\cos\theta}$ in the series

$$e^{ikr\cos\theta}=\frac{\pi^{\frac{1}{2}}}{(2kr)^{\frac{1}{2}}}\sum_0^\infty(2n+1)\,i^nJ_{n+\frac{1}{2}}(kr)\,P_n(\cos\theta)$$

we find that only the zero order harmonic gives a contribution. The integration may then be performed, giving

$$F(k_1, k_2)=\frac{64\pi^3 me^2N_0\alpha}{K^2}\left[\frac{1}{(\alpha^2+k^2)^2}-\frac{1}{(\alpha^2+k_2^2)^2}\right].$$

To average over the initial directions of incidence, and perform the angular integration it is convenient to transform to "momentum coordinates" and integrate with respect to k and K. We find for the total transitions probability

$$Q_3=\frac{\pi v'}{2k_1k_2k'v_1}\int_{k'-k_1}^{k'+k_1}dK\int_{K-k_2}^{K+k_2}|F(k_1, k_2)|^2\,dk.$$

The integration with respect to k may be carried out analytically, but that with respect to K is better done numerically. The final result of the calculation is shown in the figure, values of Q_3 being given for different values of k_1 in the case when $k_1 \gg k_2$. This case is found to be the most important, Q_3 being much smaller when k_1 and k_2 are both large or both small. In the case of three-body collisions we cannot regard Q_3 as a "cross-section", its dimensions being L^5. However, we may regard the quantity N_eQ_3, where N_e is the number of slow electrons per unit volume, as a cross-section, and we may compare it with Q_R, the cross-section for radiative transitions, in order to estimate the relative importance of the two

† Cf. Mott and Massey, *Theory of atomic collisions*, p. 98.
‡ See Massey and Smith, *loc. cit.*

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processes. Since Q_R is of the order of 10^{-22} cm.^{2}† we see that an electron density of 10^{18} per c.c. would be necessary before the three-body process would be of equal importance. This value is much larger than that obtained in discharges.

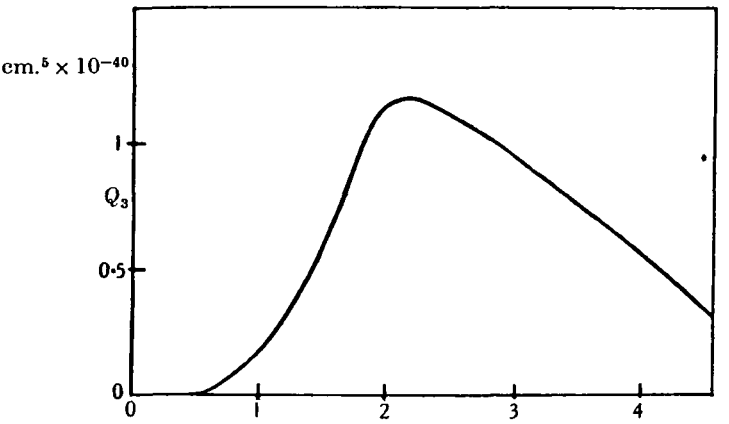

Fig. 1. k_1 (atomic units). Transition probability Q_3 for case $k_2 \ll k_1$.

In the case of a collision between two atoms and an electron we may expect a still smaller probability that the electron should jump from a continuous to a bound state, the two atoms carrying off the excess energy between them. This is so because of the difficulty in transferring kinetic energy to the heavy particles (Frank-Condon Principle). It therefore appears that at the pressures common in discharges this process is also of little importance.

† Massey and Smith, *loc. cit.*

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