Angular Momentum and Electron Impact. By P. M. S. BLACKETT, King's College.

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1. There seems to be little doubt that the detailed mechanism of ionisation or excitation by electron impact will not admit of description, even to a first approximation, by the system of classical mechanics. However the experimental work of Franck and Horton and their collaborators, has shown that, within the limits of the error of experiment, an electron is able to impart the whole or part of its kinetic energy to the atom it excites. When its initial energy is greater than the excitation energy, the electron, instead of being brought to rest, retains the excess as kinetic energy.

This shows that the total energy of the system, consisting of one atom and one impacting electron, is, within the limits of the experimental error, the same before and after the collision. In this paper an investigation will be made of the assumption that there is exact conservation of both energy and linear and angular momentum. It will be shown that it is possible to derive from this assumption an upper limit to the probability of excitation by electron impact, for electron energies just greater than the excitation energy. One other assumption only will be made. This concerns certain necessary limitations on the nature of the resultant field of the atom. The effect of the quantum orientation of the atoms in a magnetic field will be shown to impose important restrictions on the conditions for excitation. The predicted probabilities are shown to be in rough agreement with some results of Franck.

2. We will first investigate the conditions under which an electron of velocity v_0 and energy E_0 can switch an atom from a stationary state of energy W_1 to another of energy W_2, when $E_0 = W_2 - W_1$. Here the small kinetic energy of the atom after the collision is ignored.

The process is supposed to take place without emission or absorption of radiation and in a space free from electric or magnetic fields. The atom itself is to have no resultant charge, so that its field may fall off rapidly with the distance. In order to simplify the discussion it will be assumed that the force between the atom and an electron vanishes entirely at a radial distance greater than some arbitrary distance d_0. Clearly d_0 must be taken to be of the order of, but somewhat larger than, the kinetic theory radius of the atom.

The Quantum Theory demands that each stationary state must be characterised by an integral, or half integral, number j, defining the total angular momentum $jh/2\pi$ of the atom.

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The atom, of mass M, is supposed to be initially at rest with its centre of gravity at the origin of a set of rectangular coordinates x, y, z (Fig. 1). The total angular momentum of the atom is $jh/2\pi$ before collision and $j'h/2\pi$ after collision. The direction cosines of the initial and final axes of angular momentum are p, q, r and p', q', r'. Then without loss of generality the electron, of mass m, can move initially along the line $y = \rho, x = 0$, so that the y and z components of its angular momentum are both zero. The distance from the centre of the atom on to the initial path of the electron, which will be called the striking radius, is therefore ρ. After the collision the electron is at rest relative to the atom at a distance from the atom greater than d_0, while the atom and electron together will be in motion with total momentum mv_0 parallel to Oz. Since the atom must in general be expected to be displaced from the origin

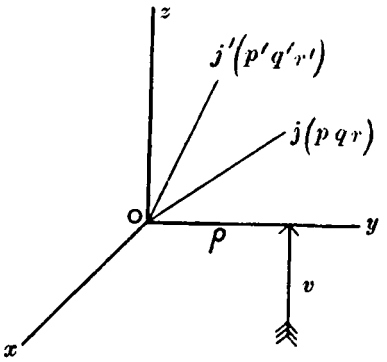


Fig. 1

during the collision, its linear momentum will have a moment about the origin. In view of the small value of the ratio m/M and the assumption of a maximum radius d_0 of the atomic field, it is easy to see that this moment can be neglected in the analysis that follows.

As we are here dealing with the limiting case of an electron of initial velocity v_0, we will attach the suffix 0 to the quantities p', q', r' and ρ. Later when we consider a more general case we will drop this suffix.

The expressions for the energy and angular momentum, neglecting terms of the order of m/M compared with unity, are

$$mv_0^2 + 2(W_2 - W_1) = 0 \qquad \text{.....(1).}$$

$$mv_0\rho_0 + (jp - j'p_0')\, h/2\pi = 0 \qquad \text{.....(2),}$$

$$\left.\begin{aligned} jq &= j'q_0' \\ jr &= j'r_0' \end{aligned}\right\} \qquad \text{.....(3).}$$

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From (3) and the geometrical relations between the direction cosines we have

$$p_0' = \pm \left[1 - \frac{j^2}{j'^2}(1 - p^2)\right]^{\frac{1}{2}} \qquad \ldots\ldots(4).$$

From (2) and (4) we obtain

$$\rho_0 = \frac{h}{2\pi m v_0}[-jp \pm \{j'^2 - j^2(1 - p^2)\}^{\frac{1}{2}}] \qquad \ldots\ldots(5).$$

Equations (3) and (4) give the final direction of the axis of the atom in terms of the initial direction and the initial and final quantum numbers. The corresponding and unique values of ρ_0 for which excitation can occur are given by (5). The probability of such excitation is clearly zero.

It will be noticed that ρ_0 depends only on that component of the initial angular momentum of the atom which is parallel to that of the electron.

When $j' > j$, p_0' is real for all values of p. For any initial orientation there is therefore always some value ρ_0 for which excitation can occur. But when $j' < j$, p_0' is only real when $p \geqslant 1 - (j'/j)^2$. Only atoms whose initial orientation satisfies this relation can then be excited. This case will only arise when the atom is not initially in its normal state, or when, if such atoms exist, the normal state has a value of j greater than that of some other possible state.

3. We will now show that when electrons of energy greater than E_0 are considered, the probability of excitation is no longer zero. Suppose that the electron has a velocity v slightly greater than v_0, and that we represent its energy by

$$E = E_0(1 + \alpha^2),$$

where α^2 is a fraction small compared with unity, yet large compared with m/M. Since the energy lost on collision is still E_0, the final velocity of the electron instead of being zero is now αv_0.

Consider the resulting change in the angular momentum relations. The initial x component will now be $mv\rho$; the other components remain zero. If d is the perpendicular distance from the origin on to the final path of the electron, the final angular momentum of the electron is $\alpha m v_0 d$. Let the direction cosines of this angular momentum be p'', q'', r''. Then instead of (2) and (3) we have to the same approximation,

$$mv\rho + (jp - j'p')\,h/2\pi - \alpha m v_0 p'' d = 0 \qquad \ldots\ldots(6),$$

$$\left.\begin{aligned}(jq - j'q')\,h/2\pi - \alpha m v_0 q'' d = 0\\ (jr - j'r')\,h/2\pi - \alpha m v_0 r'' d = 0\end{aligned}\right\} \qquad \ldots\ldots(7).$$

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The final orientation of the atom is now denoted by p', q', r' instead of p_0', q_0', r_0', to distinguish this new case in which $\alpha \neq 0$.

From (7), introducing p_0' from (4), and neglecting terms containing α^2, we get

$$p'^2 = p_0'^2 + \alpha \,.\, 4\pi m v_0 d\,(q'q'' + r'r'')/hj'.$$

Provided $p_0'^2 \rangle\rangle \alpha \,.\, 4\pi m v_0 d/hj'$, we can expand in ascending powers of α, and then neglect in the result terms containing its square and higher powers. Thus we find

$$p' = p_0' + \alpha \,.\, 2\pi m v_0 d\,(q'q'' + r'r'')/hp_0'j' \qquad \ldots\ldots(8).$$

Using this result in (6) and introducing ρ_0 from (5) we find, to the same approximation,

$$\rho = \rho_0 + \alpha\epsilon d/p_0'.$$

In this ϵ has been written for $(p_0'p'' + q'q'' + r'r'')$. Since p_0' and p' cannot differ greatly, we can see that ϵ is approximately equal to the cosine of the angle ζ between the final angular momenta of the atom and the electron. We must therefore have $-1 < \epsilon < +1$. Though d like ζ is undetermined, both depending on the unknown detailed mechanism of collision, we know that $d \not> d_0$. Thus ρ must lie between the values ρ' and ρ'' given by the positive and negative signs in the equation

$$\rho = \rho_0 \pm \alpha d_0/p_0' \qquad \ldots\ldots(9).$$

Defining $\delta\rho$ as the possible range $|\,\rho' - \rho''\,|$ of ρ we get

$$\delta\rho = |\,2\alpha d_0/p_0'\,| \qquad \ldots\ldots(10).$$

For a non-zero value of α there is therefore a *range* of values of ρ for which excitation can occur. A non-zero probability of excitation is thus obtained. The part of the atomic disc which will be effective as an excitation target will be an annular ring of mean radius ρ_0 and radial breadth $\delta\rho$.

When $p_0'^2 \not> \alpha \,.\, 4\pi m v_0 d/hj'$ the analysis must be altered. It is not worth while to consider this case, except to mention that when p_0' is very small, it can be shown that ρ is then of the order $d_0\alpha^{\frac{1}{2}}$. We will, however, calculate the probability of excitation as if (9) were valid for all values of p_0', since doing so will not introduce an appreciable error. It may be pointed out that $p_0'^2$ is always greater than $1 - (j/j')^2$ so that it can only become small when $j = j'$.

4. In order to calculate the area of the excitation target, it is convenient to refer the system to a new set of axes X, Y, Z (Fig. 2). The centre of the atom is again at the origin but its initial axis OC is fixed in the ZY plane, making an angle ψ with OZ. An electron

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whose initial path is parallel to OZ and whose striking radius ρ makes an angle ϕ with OX, will excite an atom if ρ lies between ρ' and ρ''. If we denote by θ the angle between OC and a line OB in the XZ plane at right angles to the striking radius, we have

$$p = \cos\theta = -\sin\psi\cos\phi.$$

The area of the target which will be denoted by $G(\alpha)$ is

$$\int_0^{2\pi} |\rho_0| \delta\rho d\phi,$$

which gives on introducing the values of ρ_0 and $\delta\rho$, and integrating,

$$G(\alpha) = 2\alpha d_0 j' h/mv_0 \qquad \ldots\ldots(11).$$

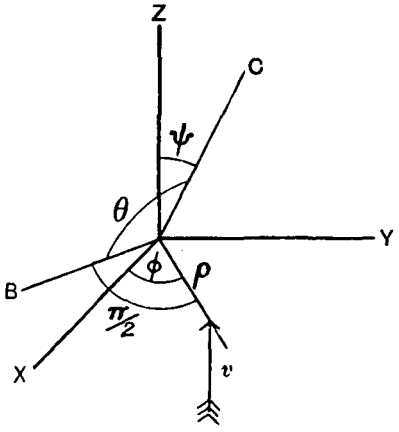


Fig. 2

The target area is therefore independent of the orientation ψ of the atom, relative to the initial path of the electron; it is therefore the same for all atoms. Expressing this area as a fraction $F(\alpha)$* of the whole atomic disc $\pi\sigma^2$ we obtain

$$F(\alpha) = 2\alpha d_0 hj'/\pi mv_0\sigma^2 \qquad \ldots\ldots(12).$$

No actual measurements of this quantity appear to have been made, but it is possible to make a rough comparison with experiment by proceeding as follows:

* This fraction $F(\alpha)$ has been called by Hertz the Efficiency of Inelastic Collision (*Proc. Amst. Acad.* March 25, 1922). Klein and Rosseland (*Zeit. für Phys.*, 4, p. 46, 1921) defined a quantity $S_1^2(\epsilon)$ so that the probability that an atom would be switched in unit time from a state 1 to a state 2, is equal to $S_1^2(\epsilon)$ multiplied by the number of atoms in state 1 and by the number of electrons of energy ϵ. Since $G(\alpha)$ is merely an upper limit, we have the relation

$$S_1^2(\epsilon) < vG(\alpha),$$

in which v is the velocity of the electron of energy $\epsilon = E_0(1+\alpha^2)$.

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We put F in (12) equal to unity and so obtain the value α_m for which the whole area of the atom becomes effective. Then $\alpha_m^2 E_0$ will be the smallest increase of electron energy, above the excitation point, necessary to give the maximum excitation,—that is, so that every collision may be effective.

Consider the excitation of the normal helium atom. The two resonance potentials 19·7 and 20·5 volts correspond to the switch of an atom from the normal $1S$ state to the ortho-state $2s$ and the par-state $2S$, respectively. The quantum numbers* j to be attributed to the three states are 1, 2 and 1. We will take σ to be $1{\cdot}1 \times 10^{-8}$ cms. and d_0 to be 2σ. This last assumption is arbitrary but will serve as a first approximation. Then for the $1S \rightarrow 2s$ switch we have $j' = 2$, whence $\alpha_m = 0{\cdot}15$. For the $1S \rightarrow 2S$ switch, $j' = 1$, and $\alpha_m = 0{\cdot}31$. The corresponding values of the energy range $\alpha_m^2 E_0$ are 0·5 and 1·9 volts.

If we turn to the curves given by Franck† and Knipping of the photo-electric current produced by the radiation resulting from the excitation of the $1S \rightarrow 2S$ and $1S \rightarrow 2s$ transitions of helium, we find that the main rise of current for the latter occurs within a range of electron energy of less than a volt. Thus the value predicted by the theory seems to be of the right order; this is all that could be expected in view of the uncertainty of the data and the extrapolation of (12) to such large values of α. It would be tempting to compare the greater range of voltage predicted for the former switch with the slower rise of the experimental curves above 20·5 volts. It is however doubtful now far this is legitimate since the number of electrons available for the excitation of this switch will not be independent of the frequency of occurrence of the lower voltage switch.

Again, in the curves given by Franck‡ and Einsporn, the whole rise of current due to the excitation of the mercury 1850 line, $1S - 2P$, occurs within a range of less than half a volt. If we put $\sigma = 2{\cdot}5 \times 10^{-8}$ cms., $d_0 = 2\sigma$, and $j' = 2$, which is the value attributed by Bohr to the singlet P terms, we get $\alpha_m = 0{\cdot}20$ and $\alpha_m^2 E_0 = 0{\cdot}28$ volts. This again is in rough agreement with the measured value. It is possible, however, that the rise of current is controlled chiefly by the electron velocity distribution. If this is so the agreement shown above must be discounted.

Emphasis must again be laid on the fact that equation (12) applies only when α^2 is small compared with unity, and therefore refers strictly only to the slope of the curve measuring the degree of excitation *immediately* above the excitation point.

It is of interest to note that the form of the annular target of

* Bohr, *Ann. der Physik*, 71, p. 286, 1923.
† Franck and Knipping, *Zeit. für Phys.*, 1, p. 321, 1920.
‡ Franck and Einsporn, *Zeit. für Phys.*, 2, p. 18, 1920.

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an atom in a given orientation is a circle not in general concentric with the atom. For (5) can be written in the form

$$\rho_0 = c\cos\phi \pm [(a^2 - c^2) + c^2\cos^2\phi]^{\frac{1}{2}},$$

where $$a = (j'^2 - j^2\cos^2\psi)^{\frac{1}{2}}\, h/2\pi m v_0,$$

and $$c = hj\sin\psi/2\pi m v_0.$$

This is the polar equation of a circle of radius a and whose centre is at a distance c from the atomic centre. When $a > 0$ the target is therefore a circular ring of varying radial width $\delta\rho$. Some of these circles are shown in Fig. 3, for the $1S \rightarrow 2s$ switch of helium for which j and j' are equal to 1 and 2 respectively. The numbers against the circles are the values of ψ to which the circle corresponds. The line OL is the projection of the initial axis on the plane of the disc. The dotted circle has a radius, equal on the same scale, to the kinetic theory radius of the atom. It is possible that the outer parts of the target are not actually effective. Especially will this be the case when j' is large.

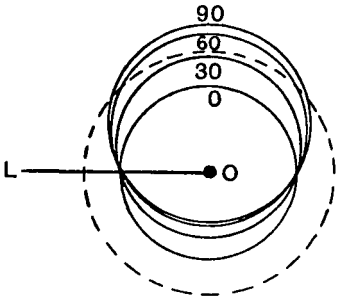


Fig. 3

5. We will now return to a more detailed consideration of the meaning of d_0. To do this we have to consider how the electron leaves the field of the atom after the collision. Suppose that $\alpha = 0$, and that the atomic field can be considered as central and represented by a force μr^{-s} on the electron. The electron will then leave the atom in a "critical" orbit of zero total energy. If χ is the angle between its velocity u and the radius vector r, its orbit will be defined by the two equations

$$mu^2 + 2\int_{\infty}^{r} \mu r^{-s}\, dr = 0,$$

and $$mur\sin\chi = H,$$

where H is the constant angular momentum of the electron about the centre of force. Provided $s \neq 1$ these give

$$r^{3-s} = \frac{1}{2m}\frac{H^2}{\sin^2\chi}\frac{s-1}{\mu} \qquad \text{.....(13).}$$

When $s = 2$ (or more generally $s < 3$) the orbit extends to infinity for any value of H. The maximum value H_2 that H can take is given by putting $\chi = \pi/2$ when r has its initial value r_0, which must be taken to be of the order of the atomic radius. Taking the intensity of the field as that of a singly charged ion at a distance

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r_0, we find for this case of $s = 2$, that the maximum value H_2 is of the order of the whole angular momentum of an atom ($h/2\pi$). This means that in a field varying as the inverse square of the distance, an electron receding to infinity with a velocity tending to zero, retains an angular momentum comparable with that of the atom. This is why the foregoing analysis will not apply to the case of ionisation. Equations (2) and (3) do not hold and there appears to be no reason to suppose, from this point of view of angular momentum alone, that there are any necessary restrictions on the values of ρ_0. The whole area of the disc may become effective immediately the electron energy reaches the ionisation value.

When excitation is considered the field falls off very rapidly with the distance. Possibly s may have a value as great as 8. From (13) when $s > 3$, r can only become large when H is small. An electron will certainly escape from an atom if its orbit extends to a distance R comparable with the mean distances apart of the atoms. For $r > R$ we must have $H_s^2 < 2\mu m R^{3-s}/(s-1)$. If this field, varying as r^{-s}, has the same intensity at r_0 as the inverse square field already discussed, we have

$$\frac{H_s}{H_2} < \frac{1}{(s-1)^{\frac{1}{2}}} \left(\frac{r_0}{R}\right)^{\frac{s-3}{2}}$$

Since at all pressures in use $R \rangle\rangle r_0$, H_s will be negligibly small compared with the angular momentum of the atom, provided s is greater than about 4. In cases of excitation of neutral atoms we are therefore entitled to neglect the final moment of momentum of the impacting electron, when its energy is zero.

When its energy is not zero, the orbit is not a critical one and cannot apparently be simply calculated for s greater than 3. But it does seem clear that even now there will be a definite maximum to the possible final angular momentum of an electron of given final energy. The simple assumption that has been made in section 2, to the effect that the field stops abruptly at a distance d_0 from the atom, expresses this expectation. For outside this distance, the path of the electron will be straight and its maximum moment of momentum will be amv_0d_0. If the calculation could be performed d_0 could be evaluated in terms of μ, s, r_0, R and the total energy a^2E_0 of the orbit. In this paper it has been taken arbitrarily as a constant equal to twice the kinetic theory radius of the atom.

6. So far we have been concerned with the excitation of atoms in a field free space. The study of the Zeeman effect has shown that to an atom in a magnetic field must be attributed a fourth quantum number defining the projection of the total angular momentum on the direction of the field. If λ be the angle between

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the j axis of the atom and the field direction we have a relation of the type

$$\cos\lambda = m/j \qquad \text{.....(14).}$$

There seems to be some difference of opinion as to which of the $2j + 1$ values of m allowed by (14) actually occur in a given type of atom. However, neglecting such restrictions there will be $2j + 1$ cones*, having the field direction as axis, on which both the initial and final axes of the atoms must lie. A switch by electron impact from one orientation to another is then only possible when the final orientation specified by (3) and (4) is such as to fulfil one of these conditions.

We cannot however retain any of the analysis of section 2 by which these equations were obtained unless we can consider the system of atom and electron as a closed system. This will not be so when there is an external field. Strictly it is only within the whole system of atom, electron, and field generating bodies, that momentum will be conserved. But if the period of the Larmor rotation due to the field is very large compared with the time of collision, which will be satisfied in fields of moderate strength, it is then legitimate to neglect to a first approximation the influence of the field during the collision. We can thus apply directly the conditions already found for the excitation radius, with the additional restrictions as to the initial and final orientations. No attempt will be made to work out fully the probability of excitation in a field of force, owing to the somewhat complicated nature of the problem; but a discussion will be given which will illustrate the nature of the procedure.

7. If a unit sphere is drawn with its centre at the origin of the original axes x, y, z, then the initial and final orientations can be represented by two points P and P' on its surface. (Fig. 4.) Then when $\alpha = 0$ we see from (3) that P_0' must lie on the great circle through P and Ox: further, the ratio of the sines of the arcs xP and xP_0' must be j'/j. The point P_0' will have another possible position corresponding to the negative sign for p_0' in (4), but with the same values of q_0' and r_0'. If another point M on the surface of the sphere represents the direction of the field, we must also have P and P_0' lying on one or other of the set of small circles, whose common pole is M, and whose radii are given by the possible values of $\sin\lambda$. Only in exceptional circumstances can these conditions be satisfied.

When $\alpha > 0$, equations (7) take the place of (3). The condition for P' now is that it must lie within a small area about the point P_0', the extent of which is defined by the magnitude of the terms in (7) containing α. In general the effective target of an atom will

* The line ($m = j$) and the plane ($m = 0$) are included as limiting cases of cones.

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reduce to certain isolated parts of that annular ring which was obtained in section 2 by placing no restrictions on the possible final orientations.

As an example of the singular spatial relations that are necessary for excitation, the switch $1S \rightarrow 2s$ of the helium atom will be studied. The initial and final quantum numbers are again 1 and 2. The diamagnetism of helium requires the initial axis to be at right angles to the field ($m = 0$). It is probable that ortho-helium is paramagnetic and so allows m to take non-zero values. As our purpose is only to illustrate the phenomenon, remembering the doubt already mentioned as to the exact values to be ascribed to m, we will assume that m can take the values ± 1 and ± 2. Then

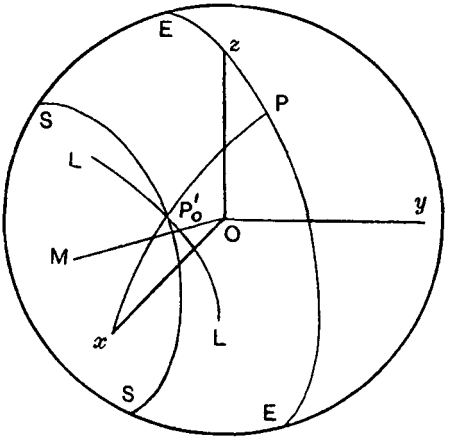


Fig. 4

in Fig. 4, P must lie on the equator EE of M: while P_0' must lie either at M, or on one of the two concentric small circles SS of latitude 30°. Equations (3) restrict P_0' also to that curve LL, which is such that sine (arc xP) divided by sine (arc xP_0') is equal to j'/j. The point where this locus passes through M or cuts one of the small circles SS (of which one only is drawn), will give the final orientations of the only possible switches.

Such considerations as these suggest that the effect of a magnetic field will not only influence the excitation of any switch but will influence different types in different ways. No attempt will be made to discuss the question of the strength of field in which the phenomenon should occur. While it is difficult to see how the results for the field free space can be in error, it is quite conceivable that the spatial quantum conditions have been interpreted too literally. The probabilities that have been calculated in section 3 have been for a field free space, but it is questionable whether the

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normal conditions inside such an apparatus as was used by Franck can be considered as such. It is hoped to settle by experiment this and other conclusions that can be derived from this analysis.

8. The principles of the conservation of angular momentum and energy have been assumed to hold during excitation by electron impact. For excitation to occur under these conditions the undeflected path of an electron, whose energy is only slightly greater than the excitation energy, must cross the atomic disc within a certain limited target. The area of this target is a function of the velocity, and expresses the upper limit to the probability of excitation. This area will be very drastically restricted if the atoms are orientated in a magnetic field both before and after collision.

These limitations on the type of a successful electron impact are in an important sense analogous to the limitations on the type of spontaneous emission of radiation found by Rubinowicz*, since they are derived from the same assumption of conservation of energy and angular momentum. Just as Rubinowicz's Selection Principle falls within the wider scope of Bohr's Correspondence Principle, so it may be anticipated that the limitations imposed on the excitation conditions, and the probabilities obtained from them, must be derivable from any generalised form of the Correspondence Principle that may yet be formulated to cover the process of excitation by electron impact.

I wish to express my gratitude to Mr R. H. Fowler of Trinity College for his valuable criticism and advice during this work.

* Rubinowicz, *Phys. Zeit.*, 19, p. 441, 1918.

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