PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES

Volume 10 AUGUST 15, 1924 Number 8

ON THE SIMULTANEOUS JUMPING OF TWO ELECTRONS IN BOHR'S MODEL

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Communicated, June 11, 1924

1. Messrs. H. N. Russell and F. A. Saunders recently discovered in the arc spectrum of calcium a new series[1] ($1p-mp'$) which they attribute to the simultaneous jumping of two electrons. It must be conceded that the evidence in favor of such a hypothesis is very strong. There cannot be the slightest doubt that the lines in question really constitute a series, because Russell and Saunders have divided them into groups showing the regular triplet structure, each group containing the same spacings (105.9 and 52.3) due to the three levels of the first term. This term is, therefore, identified as ($1p$) of the triplet system ($1p_1 = 33988.7$, $1p_2 = 34094.6$, $1p_3 = 34146.9$).[2] Beginning with the third group of the series the second terms then turn out to be negative.[3] This means that the energy available for emission is larger than that corresponding to a jump of an electron from infinity to the $1p$-level. It is hard to see how the excess of energy could be supplied, unless it is due to the jumping of a second electron. Moreover, such a conclusion is strongly supported by quantitative relations. If we consider the limiting value of the second term corresponding to the limit of the series or to the removal of the first electron into infinity, this whole value must be due to the energy of the second electron. At the same time the atom has now the constitution of an ionized atom, so that the above limiting value must correspond to one of the possible energy differences in that state of the atom or, in other words, to one of the frequencies of the spark spectrum. This is in fact the case: as Russell and Saunders pointed out, the extrapolated limiting value falls within 1/200 volt from the energy difference $1\delta-1\pi$ in the spark spectrum, or within the limits of the error of extrapolation. We have, therefore, to regard the occurrence of such double jumps as an established experimental fact and to look for a theoretical explanation of it.

2. At first sight it seems that it is not easy to reconcile the conditions

sketched in the preceding section with the principle of correspondence. However, it will be shown that a closer study of the problem leads to the conclusion that there is no difficulty: on the contrary, the phenomenon in question, far from contradicting the principle of correspondence, flows from it as its natural consequence and is *due to the coupling of the electrons within the atom.* To make this clear we shall use a very much simplified model of an atom containing two electrons which, however, retains all the essential features of a real atom with regard to the question we are going to study.

3. Let our model be constituted of two electrons attached by forces proportional to the distance to two positions of rest O_1 and O_2 and able to move only in the straight line O_1O_2. Let the distance between O_1 and O_2 be denoted by a and the displacements of the electrons from their respective positions of rest by x_1 and x_2. We assume that these displacements are small compared with a, and that a is small compared with the wave length of the emitted radiation. The distance between the two electrons is, therefore, equal to $a + x_2 - x_1$ and the force of their mutual interaction to $e^2/(a + x_2 - x_1)^2$, if e means the charge of an electron. Denoting the coefficients of the elastic forces of attachment to the two positions of rest by $-m\omega_1^2$ and $-m\omega_2^2$ (m being the mass of the electron), we finally get the equations of motion in the form

$$\ddot{x}_1 + \omega_1^2 x_1 = -e^2/m(a + x_2 - x_1)^2, \qquad \ddot{x}_2 + \omega_2^2 x_2 = e^2/m(a + x_2 - x_1)^2 \quad (1)$$

4. We are going to discuss first the case when the distance a is so large that the force of coupling is negligible compared to the forces of attachment. Equations (1) assume then the simple form

$$\ddot{x}_1 + \omega_1^2 x_1 = 0, \qquad \ddot{x}_2 + \omega_2^2 x_2 = 0 \quad (2)$$

defining the harmonic oscillations

$$x_1 = A_1 \cos(\omega_1 t + \delta_1), \qquad x_2 = A_2 \cos(\omega_2 t + \delta_2) \quad (3)$$

Our system represents the totality of two linear resonators. Subjecting the motion of these resonators to quantum restrictions, we obtain for the energy of the stationary orbits the well known expression of Planck[4] $n_1\omega_1 h/2\pi$ for the first electron and $n_2\omega_2 h/2\pi$ for the second, where n_1 and n_2 represent quantic integers. The total energy of the system is, therefore

$$E = h(n_1\omega_1 + n_2\omega_2)/2\pi \quad (4)$$

According to Bohr's theory light is emitted by our system if its motion changes from the stationary state characterized by the numbers n_1', n_2' to the state corresponding to n_1, n_2, the frequency ν_Q being determined by the difference of energies divided by

$$\nu_Q = [(n_1' - n_1)\omega_1 + (n_2' - n_2)\omega_2]/2\pi \quad (5)$$

5. The question is now, which of the possible differences $n_1' - n_1$, $n_2' - n_2$ do actually occur. And this question is answered by Bohr's principle of correspondence, which is based on the study of the emission of light which the same system would have in the classical theory. The amplitude of the emitted waves is according to the classical theory proportional to the total acceleration of electric charges taking place in the system, that is, to $\ddot{x}_1 + \ddot{x}_2$ (provided that the size of the system is small compared with the wave length). For a system of two degrees of freedom with a double periodicity characterized by the two angular velocities ω_1 and ω_2 the general expression of the acceleration is the two-fold Fourier series

$$\ddot{x}_1 + \ddot{x}_2 = \sum_0^\infty \sum_0^\infty A_{\tau_1\tau_2} \cos [(\tau_1\omega_1 + \tau_2\omega_2)t + \delta_{\tau_1\tau_2}] \qquad (6)$$

where τ_1 and τ_2 denote whole numbers. The possible frequencies are, therefore, given in the classical theory by the arguments of all the terms of the Fourier series

$$\nu_c = (\tau_1\omega_1 + \tau_2\omega_2)/2\pi \qquad (7)$$

We see that expressions (5) and (7) become identical if we put

$$n_1' - n_1 = \tau_1, \quad n_2' - n_2 = \tau_2 \qquad (8)$$

so that to every possible frequency in the quantum theory there corresponds a possible classical frequency. However, in the classical case a large part of the frequencies contained in formula (7) will not actually occur, because many of the coefficients $A_{\tau_1\tau_2}$ will turn out to be equal to zero. For instance, if we compute $\ddot{x}_1 + \ddot{x}_2$ for our model, we have from (3)

$$\ddot{x}_1 + \ddot{x}_2 = -\omega_1^2 A_1 \cos(\omega_1 t + \delta_1) - \omega_2^2 A_2 \cos(\omega_2 t + \delta_2) \qquad (9)$$

so that the double sum (6) is reduced to only two terms and our of the possible cases (7) only those two will be realized in which $\tau_1 = 1$, $\tau_2 = 0$, and $\tau_1 = 0$, $\tau_2 = 1$.

The principle of correspondence can be briefly stated as the hypothesis that light of any frequency ν_Q in the theory of quanta has the same intensity as the corresponding frequency ν_c computed on the basis of the classical theory. It follows from this and relations (8) that out of the totality of possible jumps represented by formula (5) only two will actually occur, namely

$$1.\ n_1' - n_1 = 1,\ n_2' - n_2 = 0; \qquad 2.\ n_1' - n_1 = 0,\ n_2' - n_2 = 1 \qquad (10)$$

These relations give the *selection principle* for our model: the quantic numbers can change only by zero or by unity, and only one of the electrons can jump at a time.

6. Turning to the general case, when the coupling cannot be neglected, we make use of our assumption that x_1 and x_2 are small compared with a. We can then expand the right side of equations (1) in powers of $(x_2-x_1)/a$

$$\frac{e^2}{m(x_2-x_1+a)^2} = \frac{e^2}{ma^2} - \frac{2e^2}{ma^3}(x_2-x_1) + \frac{3e^2}{ma^4}(x_2-x_1)^2 + \ldots$$

The change in the motion of our electrons which the two first terms of this series will produce is well known. The constant term produces only a displacement of the positions of rest, the linear term a slight change in the frequency of the oscillations. Neither of these effects is of any interest to us. We may, therefore, treat the problem as if these two terms were absent and restrict ourselves to the discussion of the third quadratic term. With the abbreviation $3e^2/ma^4 = 2s$ equations (1) assume the form

$$\ddot{x}_1 + \omega_1^2 x_1 = -2s(x_2-x_1)^2; \qquad \ddot{x}_2 + \omega_2^2 x_2 = 2s(x_2-x_1)^2 \qquad (11)$$

The term on the right side is a small correction term. We get, therefore, the first approximation if we substitute into this term the approximate values (3) for x_1 and x_2:

$$\begin{aligned}\ddot{x}_1 + \omega_1^2 x_1 = {} & -s(A_1^2 + A_2^2) + 2sA_1A_2 \cos[(\omega_1+\omega_2)t + \delta_1 + \delta_2] + \\ & + 2sA_1A_2 \cos[(\omega_1-\omega_2)t + \delta_1 - \delta_2] + sA_1^2 \cos(2\omega_1 t + 2\delta_1) + \\ & + sA_2^2 \cos(2\omega_2 t + 2\delta_2)\end{aligned} \qquad (12)$$

Owing to the inhomogeneous terms on the right, we must, in order to get a solution of this equation add to the integral (9) the particular integral of this equation which is composed just of the same cosine terms that occur in the equation only with different coefficients. In this way we find for the acceleration

$$\begin{aligned}\ddot{x}_1 + \ddot{x}_2 = {} & -\omega_1^2 A_1 \cos(\omega_1 t + \delta_1) - \omega_2^2 A_2 \cos(\omega_2 t + \delta_2) + \\ & + A_{11} \cos(2\omega_1 t + \delta_{11}) + A_{12} \cos[(\omega_1+\omega_2)t + \delta_{12}] + \\ & + A_{21} \cos[(\omega_1-\omega_2)t + \delta_{21}] + A_{22} \cos(2\omega_2 t + \delta_{22})\end{aligned} \qquad (13)$$

We have written the coefficients of the additional terms in an abbreviated form instead of giving their expressions in terms of A_1, A_2, ω_1, ω_2. It is sufficient for our purpose to notice that they do not vanish and that they are, in general, all of the same order of magnitude. With our new equations (11) the energy expression (4) will no longer be strictly valid. We are, however, interested not in the exact values of the resulting frequencies, but in the permissible combinations of quantic numbers. The correction, is, therefore, of no avail for our purpose and we may continue to use formula (5) in its old shape. The same reasoning as in section 5 leads to expect, on account of the principle of correspondence, the following additional combinations:

3. $n_1'-n_1 = 2$, $n_2'-n_2 = 0$, 4. $n_1'-n_1 = 1$, $n_2'-n_2 = 1$,
5. $n_1'-n_1 = \pm 1$, $n_2'-n_2 = \mp 1$, 6. $n_1'-n_1 = 0$, $n_2'-n_2 = 2$.

We see that the selection principle (10) breaks down in two respects. Besides the change of a quantic number by *one* or *zero* there appears a change by *two* units. Moreover, both quantic numbers may change by unity at the same time, and *these last combinations correspond to the simultaneous jumping of both electrons*. It is obvious that by discussing the cubic term of our expansion and taking a model with three electrons we would obtain the possibility of three electrons jumping at the same time. However, the corresponding lines must have a much lower intensity.

6. If we regard instead of our simplified model the actual conditions in an atom, the results will not change essentially. The selection principle as stated by Bohr and Rubinowicz is that the azimutal quantum number k for a jumping electron can change only by unity: $k'-k = \pm 1$. If we neglect in an atom containing several electrons their mutual interactions we will, as in section 4, get the additional restriction that only one electron can jump at a time. On the other hand, the coupling of the electrons will cause this selection principle to break down and new combinations, including the simultaneous jumping of two electrons, to become permissible. In fact, it is not so hard to calculate the perturbations in question as to present the calculations in a concise form. The first new combinations to appear are $k'-k = \pm 2$, $k'-k = 0$ and the simultaneous jumping of two electrons ($k'-k = \pm 1$ for each of them). The combination $k'-k = 0$ has a simple geometrical meaning. The absence of it is due to the orbit being a plane one. When the coupling forces become so strong that the motion of the electron can no longer be regarded as plane even for the short time of its period, the combination $k'-k = 0$ assumes an appreciable probability.

Which of the three new combinations appears first with increasing coupling depends on the size, shape and relative orientation of the two orbits and can hardly be predicted in a general way. It is, however, interesting to note that the double jump discovered by Russell and Saunders appears in the spectra of metals of the second group where the Bohr-Rubinowicz selection principle just begins to break down, and the combinations $k'-k = \pm 2$ and $k'-k = 0$ begin to become a regular feature of the spectrum, especially in the singlet system. It may be expected, therefore, that in the spectra of the groups of higher order, where the selection principle breaks down completely, jumps of this type will become much more common.

[1] H. N. Russell and F. A. Saunders (to be published).

[2] The first two groups of this series were found by R. Götze (*Ann. Physik, Leipzig*, **66**, p. 291, 1921.)

[3] Negative terms occur also in another series of the calcium spectrum $1d-md'$. The first group was given by Götze (*loc. cit.*). Russell and Saunders succeeded in finding the second group in which the terms $2d'$ are negative. It is most probable that the $1p-1p'$ series of strontium is produced in quite the same way as the analogous series of calcium, but only the first two groups of the strontium series are known.

[4] As $\omega_1/2\pi = \nu_1$, the expression may be written $n_1 h\nu_1$. Compare: M. Planck, *Wärmestrahlung*, section 137. Leipzig, 1921.

THE COMPTON AND DUANE EFFECTS

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Communicated June 19, 1924

Late in 1922, Professor A. H. Compton[2] developed a quantum theory for the scattering of X-rays by collisions with electrons. According to this theory when radiation of wave-length λ falls on a scattering substance the scattered wave-length increases by an amount given by the formula

$$\Delta\lambda = \frac{2h}{mc}\sin^2\frac{\theta}{2} = 0.0484\sin^2\frac{\theta}{2} \qquad (1)$$

where θ is the angle between the direction of the incident and emergent beams. We shall call this the Compton shift.

Compton, using an ionization spectrometer with low dispersion, actually found the wave-length shifted by the predicted amount. P. A. Ross[3] at Stanford University repeated the experiment using a photographic plate to detect the radiation and fairly high resolving power. He not only found the correct Compton shift but also an unshifted line, which is most likely due to collisions of the radiation with massive nuclear systems. On repeating his experiment, Compton also found this unshifted line which in some cases is more intense than the shifted one.

Bergen Davis at Columbia University also reported finding these two lines but according to him the Compton shift depends slightly on the atomic number of the scattering substance.

Since then the Compton shift has been verified also in England in the Davy-Faraday Laboratory by Muller. He used the K α-rays of silver, molybdenum, and copper scattered by paraffin, glass, and aluminum. All together these workers have verified the Compton shift as given by formula (1) for incident wave-lengths ranging from 0.2 to 1.5 Å. with scattering substances well spread over the periodic table and for various angles.