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Physics. — “*The spectrum of a rotating molecule according to the theory of quanta.*” By J. M. BURGERS. (Communicated by Prof. H. A. LORENTZ).

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§ 1. *Introduction.*

N. BJERRUM has drawn attention to the fact that if a molecule which carries a vibrating resonator, rotates, this rotation exerts an influence upon the frequency of the light emitted ¹⁾. If the frequency of the resonator is ν_0 ²⁾, the angular velocity of the molecule being $\omega = 2\pi\nu'$, the frequencies: ν_0 , $\nu_0 + \nu'$, $\nu_0 - \nu'$ will be found in the light emitted by the system. Molecules of this kind will also absorb the frequencies ν_0 , $\nu_0 + \nu'$, $\nu_0 - \nu'$ from radiation which falls upon them. Starting from this principle BJERRUM has explained the structure of the bands which are found in the infra-red absorption spectra of certain gases. It was assumed that the velocity of rotation of the molecule is determined by a condition taken from the theory of quanta, so that ω can only have values which are an integral multiple of a certain quantity ω_0 . In the spectrum of such a gas a line of the frequency ν_0 will be accompanied by a set of equidistant satellites, given by the general formula:

$$\nu_l = \nu_0 + n \frac{\omega_0}{2\pi}.$$

The bands observed in the absorption spectra of water vapour and other gases actually have a structure that may be described by this formula ³⁾.

On the principles of the theory of quanta, however, one will be inclined to assume that a given spectral line is not emitted by a vibrating electron, but that it is emitted when the electron passes from a certain definite state of motion *discontinuously* to another

¹⁾ N. BJERRUM, Nernst-Festschrift p. 93 (1912). — Lord RAYLEIGH was the first to point out this influence of the rotation (Scientific Papers, IV, p. 17). — Compare also: W. C. MANDERSLOOT, De breedte van spektraallijnen (Diss. Utrecht 1914).

²⁾ In this paper “frequency” will always denote the number of vibrations per second.

³⁾ Cf. for instance: EVA VON BAHR, Verh. Deutsch.Phys. Ges. 15, p. 710, 1150, (1913); H. RUBENS & G. HETTNER, Sitz. Ber. Berl. Akad. p. 167, 1916.

definite state. If in the first state the energy of the electron is: α' , in the second state: α'' , then according to BOHR's hypothesis the difference $\alpha' - \alpha''$ will be emitted as light of the frequency:

$$\nu = \frac{\alpha' - \alpha''}{h}$$

On the other hand the electron can absorb light of the same frequency if it passes back from the second state to the first.

Now the following question arises: Suppose the electron to move in the field of a rotating molecule; does the rotation of the molecule exert an influence of the same kind on the frequency of the light emitted, as it does in BJERRUM's theory? The object of this communication is to show that following the lines of the theory of quanta, it is possible to deduce at least for certain rotating systems spectral formulae which show the same character as the one given by BJERRUM.

§ 2. General formulae for the motion of an electron in the field of a rotating molecule.

It will be assumed that the molecule has an unvariable form, and that it can rotate about an axis fixed in space. The position of the molecule is determined by the angle of rotation φ_2 . In the field of the molecule an electron moves; its position will be given by polar coordinates r, ϑ, φ_1 (the axis of the polar system of coordinates coincides with the axis of the molecule).

The potential energy of the system V is a function of the relative positions of the electron and the molecule, hence it depends on r, ϑ and $\varphi_1 - \varphi_2$ ¹⁾. If m be the mass of the electron, I the moment of inertia of the molecule about the axis of rotation, the Lagrangian function for the system is:

$$L = \frac{m}{2} (\dot{r}^2 + r^2 \dot{\vartheta}^2 + r^2 \sin^2 \vartheta \dot{\varphi}_1^2) + \frac{I}{2} \dot{\varphi}_2^2 - V(r, \vartheta, \varphi_1 - \varphi_2). \quad (1)$$

In this formula we shall put:

$$\varphi_1 - \varphi_2 = \psi_1; \quad \varphi_2 = \psi_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the momenta corresponding to the coordinates $r, \vartheta, \psi_1, \psi_2$ are calculated, the Hamiltonian function will be found to be:

$$H = \frac{1}{2m} \left(R^2 + \frac{\Theta^2}{r^2} + \frac{\Psi_1^2}{r^2 \sin^2 \vartheta} \right) + \frac{(\Psi_2 - \Psi_1)^2}{2I} + V(r, \vartheta, \psi_1). \quad (3)$$

ψ_2 being a cyclic coordinate, Ψ_2 is constant. Ψ_1 represents the

¹⁾ In V $\varphi_1 - \varphi_2$ necessarily occurs: otherwise the rotation of the molecule cannot exert any influence upon the motion of the electron. (This applies also to the theory of RAYLEIGH and BJERRUM, cf. W. C. MANDERSLOOT, l. c. II, § 3).

total moment of momentum of electron and molecule together; it determines the rotation of the system as a whole.

If $\Psi_2 = 0$, the motion of the electron is determined by the function:

$$H_0 = \frac{1}{2m} \left(R^2 + \frac{\Theta^2}{r^2} + \frac{\Psi_1^2}{r^2 \sin^2 \vartheta} \right) + \frac{\Psi_1^2}{2I} + V(r, \vartheta, \psi_1) \quad (4)$$

It will now be assumed that it is possible to find solutions of the problem characterized by the Ham. function (4) (in this problem there is no disturbing influence of the rotation), and that these solutions are of the following form: the coordinates and momenta can be expressed as periodic functions (with period 2π) of three variables q_1, q_2, q_3 , which depend linearly on the time (so-called "angular variables")¹⁾. If the canonical momenta p_1, p_2, p_3 , corresponding to these variables, are introduced²⁾, the original coordinates and momenta $r, \vartheta, \psi_1, R, \Theta, \Psi_1$ can be expressed as functions of $q_1, q_2, q_3, p_1, p_2, p_3$. This transformation of the variables possesses the property of conserving the canonical (HAMILTONIAN) form of the equations of motion.³⁾

To find solutions of the problem given by (3) ($\Psi_2 \neq 0$), it may be considered as a problem of disturbed motion, and instead of the original coordinates and momenta the p and q may be introduced as new variables. The equations of motion of the q and p then are the HAMILTONIAN equations, derived from the function $K(q, p)$, which is obtained if in (3) the original coordinates and momenta are replaced by their expressions as functions of the q and p . This function has the form:

$$\begin{aligned} K(q, p) &= H_0 - \frac{\Psi_1 \Psi_2}{I} + \frac{\Psi_2^2}{2I} = \\ &= A_0(p_1, p_2, p_3) + \frac{\Psi_2^2}{2I} - \frac{\Psi_{10}(p_1, p_2, p_3) \cdot \Psi_2}{I} - \\ &\quad - \frac{\Psi_2}{I} \sum' \left[\beta_{m_1 m_2 m_3}(p_1, p_2, p_3) \cdot \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (m_1 q_1 + m_2 q_2 + m_3 q_3) \right] \quad (5) \end{aligned}$$

¹⁾ Solutions of this kind are — as is known — of frequent use in Astronomy, especially for the treatment of problems of disturbed motion. In the most common cases they have the form of trigonometric expansions according to sines and cosines of combinations of the q . — (The expression found for ψ_1 has a slightly different form, as this variable can increase indefinitely; for instance ψ_1 may be found to be equal to q_3 plus a periodic function of q_1, q_2, q_3).

In the theory of quanta K. SCHWARZSCHILD was the first to introduce solutions of that nature (Sitz. Ber. Berl. Akad. p. 548, 1916) Compare also J. M. BURGERS, these Proceedings p. 163.

²⁾ These momenta p_1, p_2, p_3 are constant.

³⁾ Comp. WHITTAKER, Anal. Dynamics (Cambridge 1904) p. 297, 396.

⁴⁾ Σ' denotes a summation over all positive and negative values of the m , with the exception of simultaneous zero values.

(where Ψ_{10} represents the mean value of Ψ_1 (the moment of momentum of the electron).

It will be assumed :

1. that in $A_0(p_1, p_2, p_3)$ all the p occur, in such a way that between the three differential quotients $\partial A_0/\partial p_1, \partial A_0/\partial p_2, \partial A_0/\partial p_3$ there do not exist any rational relations;

2. that I is very large, and that the quantity Ψ_2/I is small as compared to the mean angular velocity of the electron, so that the second and higher powers of this quantity may be neglected.

It is then very easy to find solutions of the problem considered, following a method given by DELAUNAY and WHITTAKER¹⁾; if these solutions are restricted to the terms which contain Ψ_2/I to the powers 0 and 1, they are of the form :

$$\begin{aligned} p_1 &= P_1 + \frac{\Psi_2}{I} \cdot \sum' \left[\gamma_{m_1 m_2 m_3} (P_1, P_2, P_3) \cdot \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (m_1 Q_1 + m_2 Q_2 + m_3 Q_3) \right] \\ q_1 &= Q_1 + \frac{\Psi_2}{I} \cdot \sum' \left[\delta_{m_1 m_2 m_3} (P_1, P_2, P_3) \cdot \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (m_1 Q_1 + m_2 Q_2 + m_3 Q_3) \right] \end{aligned} \quad (6)$$

Here Q_1, Q_2, Q_3 are new angular variables; P_1, P_2, P_3 are the canonical momenta, corresponding to them.

The total energy of the system is found to be (to the same degree of approximation):

$$\alpha = A_0(P_1, P_2, P_3) - \frac{\Psi_2}{I} \cdot \Psi_{10}(P_1, P_2, P_3) + \frac{\Psi_2^2}{2I} \dots \quad (7)$$

§ 3. The Quantum formulae.

Following the ideas developed by SCHWARZSCHILD²⁾, the quantum formulae for the system may be introduced as follows :

the quantities P_1, P_2, P_3, Ψ_2 are put equal to integral multiples of $\frac{h}{2\pi}$:

$$P_1 = n_1 \frac{h}{2\pi}; \quad P_2 = n_2 \frac{h}{2\pi}; \quad P_3 = n_3 \frac{h}{2\pi}; \quad \Psi_2 = n_4 \frac{h}{2\pi} \quad \dots \quad (8)$$

The energy, when expressed as a function of the quantum numbers n_1, n_2, n_3, n_4 , becomes:

$$\alpha = \alpha_0(n_1, n_2, n_3) - n_4 \cdot \frac{\alpha_1(n_1, n_2, n_3) \cdot h}{2\pi I} + n_4^2 \frac{h^2}{8\pi^2 I} \quad \dots \quad (9)$$

¹⁾ Cf. WHITTAKER, l. c. p. 404.

²⁾ The three terms of this equation may be interpreted approximately as follows: A_0 is the energy of the electron; $\Psi_2^2/2I$ is the energy of rotation of the molecule; the term $-\frac{\Psi_2 \cdot \Psi_{10}}{I}$ is related to the CORIOLIS-reaction generated by the rotation.

³⁾ K. SCHWARZSCHILD, l. c.

If the electron passes from a state of motion characterized by the numbers $n_1' n_2' n_3' n_4'$ to another, characterized by $n_1'' n_2'' n_3'' n_4''$, the energy decreasing from α' to α'' , according to BOHR's hypothesis the system emits light of the frequency:

$$\nu = \frac{\alpha' - \alpha''}{h} \dots \dots \dots (10)$$

Hence the spectrum lines of the molecule under consideration are given by the formula:

$$\nu = \frac{\alpha_0' - \alpha_0''}{h} - \frac{n_4' \cdot \alpha_1' - n_4'' \cdot \alpha_1''}{2\pi I} + (n_4'^2 - n_4''^2) \frac{h}{8\pi^2 I} \dots \dots (11)$$

With the aid of this expression it is possible to show the influence of the rotation on the spectrum.

§ 4. Discussion of the spectrum.

The spectrum lines given by formula (11), which are characterized by 8 numbers, may be grouped in different ways. In order to show the influence of the rotation of the molecule as clearly as possible we will consider a definite change $n_1' n_2' n_3' \rightarrow n_1'' n_2'' n_3''$ (hence the values of $\alpha_0' \alpha_0'' \alpha_1' \alpha_1''$ are fixed); then by giving different values to the numbers n_4', n_4'' , different systems of lines are obtained.

A. First consider the case $n_4' = n_4'' = 0$ (in both states of motion the rotation of the molecule as a whole is zero); then the frequency is:

$$\nu_0 = \frac{\alpha_0' - \alpha_0''}{h} \dots \dots \dots (12)$$

B. If n_4' and n_4'' are equal, and different from zero, the frequency will be found to be:

$$\nu_I = \nu_0 - n_4' \frac{\alpha_1' - \alpha_1''}{2\pi I} \dots \dots \dots (13)$$

Hence the original line ν_0 appears to be accompanied on both sides by equidistant satellites, in the same way as in BJERRUM's theory. The distance of the satellites is equal to:

$$\Delta \nu = \frac{\alpha_1' - \alpha_1''}{2\pi I} \dots \dots \dots (14)$$

In general the value given by (14) is not the same as that given by BJERRUM's theory which is:

$$\Delta \nu = \frac{h}{4\pi^2 I} \dots \dots \dots (14a)$$

The expressions (14) and (14a) may give the same value if for

instance $\alpha_1 = n_3 \frac{h}{2\pi}$; for certain systems this may be approximately the case ¹⁾).

C. If $n_4' \neq n_4''$, so that the general formula (11) has to be retained, each line ν_0 appears to possess a double infinite system of satellites, the distances of which are given by a quadratic formula. This formula is of the same type as the one given by DESLANDRES and others for the band spectra ²⁾. A formula of this kind has been derived from the theory of quanta for the first time by SCHWARZSCHILD ³⁾; SCHWARZSCHILD has also pointed out that if the moment of inertia I is calculated from the coefficient of the term of the second degree, the values obtained are of the proper order of magnitude.

Other groups of lines.

D. If n_1', n_2', n_3' are equal to n_1'', n_2'', n_3'' , respectively, so that only n_4 changes in the transition from the first state of motion to the second, a set of lines is obtained, which may be denoted by the name of "rotation spectrum":

$$\nu_r = - (n_4' - n_4'') \frac{\alpha_1}{2\pi I} + (n_4'^2 - n_4''^2) \frac{h}{8\pi^2 I} \dots (15)$$

From the order of magnitude of the coefficients it may be inferred that these lines are to be found in the infra-red (they stretch out as far as $\nu = \infty$, $\lambda = \infty$).

E. RUBENS and HETTNER ⁴⁾ have observed in the absorption spectrum

¹⁾ The difference between formula (14) and (14a) becomes of importance if it is desired to calculate the value of the moment of inertia from the distance of the lines. (In BJERRUM's theory $\frac{h}{2\pi^2 I}$ is sometimes given for $\Delta\nu$ instead of the value (14a); cf. H. RUBENS and G. HETTNER, l. c. p. 168).

A more important difference between formula (14) and BJERRUM's theory is that the value given by (14) depends on $\alpha_1' - \alpha_1''$, and hence on the numbers $n_1' n_2' n_3' n_1'' n_2'' n_3''$. This makes the value of $\Delta\nu$ in general different for different lines ν_0 , whereas on BJERRUM's theory $\Delta\nu$ is independent of ν_0 .

Compare also the example given in § 5.

²⁾ Cf. H. M. KONEN, *Das Leuchten der Gase und Dämpfe*, (BRAUNSCHWEIG, 1913), p. 214, seq.

³⁾ K. SCHWARZSCHILD, l. c. p. 566. — SCHWARZSCHILD supposes that the rotation of the molecule and the motion of the electron do not exert any influence upon each other; the opposite supposition is essential to the theory given above. This is the cause of the term which is linear in n_4 and n_4'' being absent in SCHWARZSCHILD's formula.

⁴⁾ H. RUBENS and G. HETTNER, l. c.

of water vapour a system of lines which are related to the series given by (13) by the formula :

$$\nu_{II} = \nu_I - \nu_0 \quad (16)$$

These investigators, who explain the system ν_I on BJERRUM's theory ascribe the lines ν_{II} to the emission or absorption of the rotating molecules themselves¹⁾. The interpretation of the lines on the theory given above is more difficult, and less general. They may occur in special cases, if it is possible to find transitions $n_1' n_2' n_3' \rightarrow n_1'' n_2'' n_3''$, for which α_0 does *not* change, while the value of α_1 changes by the same amount as is given by the formula (13)²⁾. In general it will thus not be possible to find a system ν_{II} corresponding to each system of lines ν_0, ν_I . Compare also the example given in § 5³⁾.

§ 5. Example.

An illustration of the preceding theory is afforded by considering a system, which is characterized by the following expression for the potential energy of the electron in the field of the molecule :

$$V = -\frac{Ee}{r} + \frac{a}{r^2} + \frac{b + c \cos(\varphi_1 - \varphi_2)}{r^2 \sin^2 \vartheta} \quad (17)$$

(The form of V has been chosen in this way in order to make possible the integration of the equations of motion by means of the method of separation of the variables; cf. P. STACKEL, C.R. **116**, p. 485, 1893; **121**, p. 489, 1895).

The energy of the permissible motions of the electron, when expressed as a function of the quantum numbers, is found to be :

$$\begin{aligned} a &= -\frac{2\pi^2 m e^2 E^2}{h^2} \left(\frac{1}{n_1^2} - \frac{8\pi^2 m \cdot a}{n_1^3 \cdot n_2 \cdot h^2} - \frac{8\pi^2 m \cdot b}{n_1^3 \cdot |n_2| \cdot h^2} \right) + \frac{(n_3 - n_4)^2 \cdot h^2}{8\pi^2 I} = \\ &= \alpha_0 - \frac{n_3 \cdot n_4 \cdot h^2}{4\pi^2 I} + \frac{n_4^2 \cdot h^2}{8\pi^2 I} \quad (18) \end{aligned}$$

(in this formula terms of the 2nd and higher orders in a, b, c have been neglected).

The mean value \mathcal{W}_{10} of the moment of momentum of the electron is equal to :

¹⁾ Compare in connection with this: M. PLANCK, Ann. d. Phys. **52**, p. 491, 1917.

²⁾ In every case changes $n_1' n_2' n_3' \rightarrow n_1'' n_2'' n_3''$ must be possible for which only the sign of the moment of momentum of the electron changes (and hence the sign of α_1); α_0 then retains the same value. Cf. § 5.

³⁾ It may be remarked that formula (15) can also give a system of equidistant lines in the infra red, if $n_1' = -n_4''$ (the moment of momentum of the molecule changes sign, while the direction of rotation of the electron remains the same); the distance of the lines is equal to: $\alpha_1 / I\pi$.

$$\nu_{10} = n_3 \frac{h}{2\pi} + \dots$$

n_3 may be positive or negative; this depends on the direction of motion of the electron.

In the principal part α_0 of α only the absolute value $|n_3|$ occurs.

From (18) the spectral formula may be deduced in the same way as above. The following groups of lines (corresponding to those called **B** and **E** in § 4) are of special interest:

a). Take: $n_3' = -n_3'' = -n_3$; $n_4' = n_4'' = n_4$; the values of n_1, n_2 change in an arbitrary manner. The frequencies emitted then are.

$$\nu_I = \frac{2\pi^2 m e^2 E^2}{h^3} \left(\frac{1}{n_1''^2} - \frac{1}{n_1'^2} + \dots \text{etc.} \right) + \frac{2n_3 n_4 h}{4\pi^2 I} = \nu_0 + \frac{2n_3 n_4 h}{4\pi^2 I} \quad (I)$$

If n_3 has always the same value, different positive and negative values of n_4 give a set of equidistant lines, accompanying the line ν_0 ; the distance of two consecutive satellites will be:

$$\Delta \nu = \frac{2n_3 \cdot h}{4\pi^2 I}$$

b). Take: $n_3' = -n_3'' = -n_3$; $n_4' = n_4'' = n_4$ (as was done above under a); while the values of n_1 and n_2 do not change. In this case:

$$\alpha_0(n_1', n_2', n_3') = \alpha_0(n_1'', n_2'', n_3'');$$

hence the frequency emitted becomes:

$$\nu_{II} = + \frac{2n_3 n_4 \cdot h}{4\pi^2 I} = \nu_I - \nu_0 \dots \dots \dots (II)$$

The structure of these systems is in some respects analogous to that of the absorption bands of water vapour; (I) corresponds to the band observed near: $\lambda = 6,26\mu$; (II) to the lines in the far distant infra-red.

It must not be forgotten, however, that this example has been chosen arbitrarily, so that no great value can be attached to the absolute magnitude of $\Delta \nu$.

Summary.

An attempt is made to show that it is possible to deduce from the theory of quanta spectral formulae for rotating systems, which may explain the structure of the bands, observed in the infra-red absorption spectra of certain gases.

At the same time a formula has been found which might be useful in the explanation of the band spectra and which is an extension of one already given by SCHWARZSCHILD.

In order to simplify the problem it has been assumed that the system rotates about a fixed axis, hence the question arises whether it is not possible to give a more general treatment, in which account is taken of the precessional motion of the molecule.