The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science

Series 6

ISSN: 1941-5982 (Print) 1941-5990 (Online) Journal homepage: https://www.tandfonline.com/loi/tphm17

LXXXIII. *The quantum-theory of radiation and line spectra*

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IN his able report on Radiation and the Quantum-Theory Prof. Jeans †, dealing with theories of line spectra, remarks that Bohr's assumption is "not inconsistent with the quantum-theory and is closely related to it." The possibility therefore of deducing the results of Planck and Bohr from a single form of quantum-theory naturally suggests itself. Such a theory is developed in the present paper, and it will be seen that it contains that of Planck (in one of its forms) as a special case and, while formally distinct from Bohr's theory, leads to the same results when applied to the Rutherford type of atom in which an electron travels in a circular orbit round a positively charged nucleus.

This theory is based on the following hypotheses:—

(1) Interchanges of energy between dynamical systems and the æther, or between one dynamical system and another, are "catastrophic" or discontinuous in character. That is to say, each system behaves as a conservative one during certain intervals, and between these intervals are relatively very short ones during which definite amounts of energy may be emitted or absorbed.

(2) The motion of a system in the intervals between such discontinuous energy exchanges is determined by Hamiltonian dynamics as applied to conservative systems. It will be convenient to speak of a system, during such an interval, as being in one of its steady states.

(3) Let $q_1, q_2, \ldots p_1, p_2, \ldots$ be the Hamiltonian positional and impulse coordinates of a system in one of its steady states, and let L be its kinetic energy, expressed as a function of $\dot{q}_1, \dot{q}_2, \ldots$ and $q_1, q_2, \ldots$. This function is homogeneous and of the second degree in $\dot{q}_1, \dot{q}_2, \ldots$. If L contains products $\dot{q}_r \dot{q}_s$ $(r \neq s)$, we shall suppose them to have been removed by a substitution of the form:

$$\dot{q}_r = \alpha_{1r}\dot{q}_1' + \alpha_{2r}\dot{q}_2' + \ldots + \alpha_{nr}\dot{q}_n',$$

and we have therefore

$$L = \tfrac{1}{2}A_1\dot{q}_1^2 + \tfrac{1}{2}A_2\dot{q}_2^2 + \ldots + \tfrac{1}{2}A_n\dot{q}_n^2,$$

* Communicated by Prof. J. W. Nicholson.

† J. H. Jeans, Phys. Soc. Report on Radiation and the Quantum-Theory, p. 51 (1914).

and further

$$2L = \dot{q}_1 \frac{\partial L}{\partial \dot{q}_1} + \dot{q}_2 \frac{\partial L}{\partial \dot{q}_2} + \ldots + \dot{q}_n \frac{\partial L}{\partial \dot{q}_n},$$

and consequently

$$\left.\begin{array}{l} 2L_1 = \dot{q}_1 p_1 \\ 2L_2 = \dot{q}_2 p_2 \\ \cdots\cdots \\ 2L_n = \dot{q}_n p_n \end{array}\right\} \quad \ldots\ldots \quad (1)$$

where $L_1 = \frac{1}{2} A_1 \dot{q}_1^2$, $L_2 = \frac{1}{2} A_2 \dot{q}_2^2$, &c.

We assume that the system in one of its steady states has a period $\frac{1}{\nu_1}$ corresponding to $\dot{q}_1$, $\frac{1}{\nu_2}$ corresponding to $\dot{q}_2$, and so on. From the equations (1) we get

$$2\int L_1 dt = \int p_1 dq_1$$

and similar equations containing L_2, L_3, &c. Our third hypothesis can now be stated as follows:—The discontinuous energy exchanges always occur in such a way that the steady motions satisfy the equations:

$$\left.\begin{array}{l} \int p_1 dq_1 = \rho h \\ \int p_2 dq_2 = \sigma h \\ \int p_3 dq_3 = \tau h \\ \cdots\cdots\cdots \end{array}\right\} \quad \ldots\ldots \quad (2)$$

where ρ, σ, τ, ... are positive integers (including zero) and the integrations are extended over the values p_s and q_s corresponding to the period $\frac{1}{\nu_s}$. The factor h is Planck's universal constant. It will be convenient to denote these integrals by H_1, H_2, ... respectively.

We shall now consider the statistical equilibrium of a collection of N similar systems of the type specified above. Let $N_{\rho\sigma\tau\ldots}$ be the nnmber of systems for which $H_1 = \rho h$, $H_2 = \sigma h$, $H_3 = \tau h$, and so on; and $N_{\rho'\sigma'\tau'\ldots}$ the number of systems for which $H_1 = \rho' h$, $H_2 = \sigma' h$, $H_3 = \tau' h \ldots$. Let us further write

$$f_{\rho\sigma\tau\ldots} = \frac{N_{\rho\sigma\tau\ldots}}{N} \quad \ldots\ldots \quad (3)$$

so that we have

$$\sum_{\rho=0}^{\rho=\infty} \sum_{\sigma=0}^{\sigma=\infty} \sum_{\tau=0}^{\tau=\infty} \ldots f_{\rho\sigma\tau\ldots} = 1. \quad . \quad . \quad . \quad (4)$$

For the sake of brevity we shall say that $N_{\rho\sigma\tau\ldots}$ systems are on the locus $(\rho\sigma\tau\ldots)$, $N_{\rho'\sigma'\tau'\ldots}$ on the locus $(\rho'\sigma'\tau'\ldots)$, and so on. We have for the energy of the whole collection of systems the following expression:—

$$E = N \sum_{\rho=0}^{\rho=\infty} \sum_{\sigma=0}^{\sigma=\infty} \sum_{\tau=0}^{\tau=\infty} \ldots E_{\rho\sigma\tau\ldots} f_{\rho\sigma\tau\ldots} \quad . \quad (5)$$

where $E_{\rho\sigma\tau\ldots}$ is the energy of a system on the locus $(\rho\sigma\tau\ldots)$. If P is the number of ways in which N systems can be distributed, so that $N_{\rho\sigma\tau\ldots}$ lie on the locus $(\rho\sigma\tau\ldots)$, $N_{\rho'\sigma'\tau'\ldots}$ on the locus $(\rho'\sigma'\tau'\ldots)$, and so on, we have

$$P = \frac{N!}{(N_{\rho\sigma\tau\ldots})!\,(N_{\rho'\sigma'\tau'\ldots})!\ldots} \quad . \quad . \quad . \quad (6)$$

We shall call P (after Planck) the "thermodynamic probability" of the distribution in question, and identify the quantity

$$\phi = k \log P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

with the *entropy* of the assemblage of systems; the quantity k is the entropy constant. We may assume $N_{\rho\sigma\tau\ldots}$, $N_{\rho'\sigma'\tau'\ldots}$, and *a fortiori* N to be individually very large numbers, and therefore, by Stirling's theorem,

$$P = \frac{N^N}{\left(N_{\rho\sigma\tau\ldots}^{N_{\rho\sigma\tau\ldots}}\right)\left(N_{\rho'\sigma'\tau'\ldots}^{N_{\rho'\sigma'\tau'\ldots}}\right)\ldots}$$

This last equation, together with (3) and (7), leads to the following expression for the entropy of the collection of systems:—

$$\phi = -kN \sum_0^\infty \sum_0^\infty \sum_0^\infty \ldots f_{\rho\sigma\tau\ldots} \log f_{\rho\sigma\tau\ldots} \quad . \quad . \quad (8)$$

The condition for statistical equilibrium is expressed by

$$\delta\phi = 0,$$

where the variation is subject to the total energy being constant, and also to equation (4). We easily obtain, by the usual variational method,

$$1 + \log f_{\rho\sigma\tau\ldots} + \beta E_{\rho\sigma\tau\ldots} + \gamma = 0$$

$$\text{or} \quad f_{\rho\sigma\tau\ldots} = A e^{-\beta E_{\rho\sigma\tau\ldots}} \quad . \quad . \quad . \quad . \quad (9)$$

The value of A is determined by equation (4). The quantity β can be shown to be equal to $\frac{1}{kT}$, where T is the absolute temperature of the collection of systems. From (8) and (9) we find

$$\phi = -kN \sum_0^\infty \sum_0^\infty \sum_0^\infty \ldots A e^{-\beta E_{\rho\sigma\tau\ldots}} (\log A - \beta E_{\rho\sigma\tau\ldots})$$

or $$\phi = -kN \log A + k\beta N \sum_0^\infty \sum_0^\infty \sum_0^\infty \ldots A E_{\rho\sigma\tau\ldots} e^{-\beta E_{\rho\sigma\tau\ldots}},$$

and therefore by (5) and (9)

$$\phi = -kN \log A + k\beta E. \quad . \quad . \quad . \quad . \quad (10)$$

On differentiating with respect to β we get

$$\frac{d\phi}{d\beta} = -kN \frac{d \log A}{d\beta} + kE + k\beta \frac{dE}{d\beta}, \quad . \quad . \quad (11)$$

and since

$$1 = A \sum_0^\infty \sum_0^\infty \sum_0^\infty \ldots e^{-\beta E_{\rho\sigma\tau\ldots}}$$

we have

$$0 = \frac{dA}{d\beta} \cdot \frac{1}{A} - A \sum_0^\infty \sum_0^\infty \sum_0^\infty \ldots E_{\rho\sigma\tau\ldots} e^{-\beta E_{\rho\sigma\tau\ldots}},$$

or $$\frac{d \log A}{d\beta} = \frac{E}{N}.$$

Substituting this in equation (11) we see that

$$\frac{d\phi}{d\beta} = k\beta \frac{dE}{d\beta}$$

or $$\frac{d\phi}{dE} = k\beta.$$

Therefore $k\beta = \frac{1}{T}$. The law of distribution of the systems among the different loci is therefore expressed by

$$f_{\rho\sigma\tau\ldots}=\frac{e^{-\frac{E_{\rho\sigma\tau\ldots}}{kT}}}{\sum\limits_0^\infty\sum\limits_0^\infty\sum\limits_0^\infty\ldots e^{-\frac{E_{\rho\sigma\tau\ldots}}{kT}}} \quad . \quad . \quad . \quad (12)$$

when equilibrium has been attained.

Equations (5) and (12) give us, for the average energy of a system,

$$\overline{E}=\frac{\sum\limits_0^\infty\sum\limits_0^\infty\sum\limits_0^\infty\ldots E_{\rho\sigma\tau\ldots}e^{-\frac{E_{\rho\sigma\tau\ldots}}{kT}}}{\sum\limits_0^\infty\sum\limits_0^\infty\sum\limits_0^\infty\ldots e^{-\frac{E_{\rho\sigma\tau\ldots}}{kT}}} \quad . \quad . \quad . \quad (13)$$

Theory of Radiation.

The foregoing results are very general. We shall show that they include Planck's theory (one form of it at any rate) as a special case. We may write the equation of motion of one of Planck's oscillators, when in a steady state, in the form

$$m\frac{d^2q}{dt^2}+Kq=0.$$

The most convenient form of solution for our purpose is

$$q=R\cos(2\pi\nu t-\theta), \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where R and θ are the constants of integration, and therefore

$$p=-2\pi\nu mR\sin(2\pi\nu t-\theta). \quad . \quad . \quad . \quad (15)$$

The energy of such an oscillator is easily shown to be

$$2\pi^2\nu^2mR^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Now we have, from (14) and (15),

$$\int_t^{t+\frac{1}{\nu}}pdq=4\pi^2\nu^2mR^2\int_t^{t+\frac{1}{\nu}}\sin^2(2\pi\nu t-\theta)dt,$$

and consequently

$$\rho h=2\pi^2\nu mR^2,$$

and therefore, by (16),

$$E_\rho=\rho h\nu. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

On substituting this value of E_ρ in (12) we find that

$$f_\rho = \left(1 - e^{-\frac{h\nu}{kT}}\right) e^{-\frac{\rho h\nu}{kT}}. \quad . \quad . \quad . \quad . \quad (18)$$

Therefore the law of distribution of the oscillators among the different loci is precisely that given by Planck *.

From (13) and (17) we deduce for the average energy of an oscillator

$$\overrightarrow{E} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

a well known result in Planck's theory. It may therefore be said that the proposed theory includes that of Planck (at least in one of its forms).

We may regard the æther as a collection of oscillators which, through the medium of matter, exchange energy with one another. The number of these, per unit volume, in the frequency range between ν and $\nu + d\nu$, has been shown by Jeans and others † to be

$$\frac{8\pi\nu^2 d\nu}{c^3},$$

where c is the velocity of radiation in the æther. The most probable distribution of these oscillators among the loci mentioned above, *i. e.* the distribution corresponding to maximum entropy, is one which makes their average energy

$$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1},$$

and therefore we get for the energy within the frequency range ν to $\nu + d\nu$,

$$U_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{d\nu}{e^{\frac{h\nu}{kT}} - 1},$$

which is Planck's radiation formula.

Theory of Line Spectra.

We shall now show that Bohr's ‡ assumptions, in so far at any rate as we restrict ourselves to the type of atom or

* M. Planck, 'Theorie d. Wärmestrahlung,' p. 139, equations (220) and (227), second edition.

† J. H. Jeans, Phil. Mag. x. p. 91 (1905); M. Planck, *loc. cit.* p. 175.

‡ N. Bohr, Phil. Mag. xxvi. p. 1 (1913).

emitting system to which Bohr's theory has been applied with some measure of success, can be immediately deduced from the theory outlined above. The systems which he assumes to emit the hydrogen, helium, and other spectra are characterized, in their steady states, by constant kinetic energy, and by one positional coordinate q. The hypothesis expressed by equations (2) takes, for such systems, the form

$$2\mathrm{L}\int_{t}^{t+\frac{1}{\nu}} dt=\rho h$$

or

$$\mathrm{L}=\frac{\rho h\nu}{2}, \quad \ldots \ldots \quad (20)$$

and, since L in these systems is numerically the same as Bohr's * W, we see that (20) expresses Bohr's principal hypothesis. A further assumption made by Bohr is that the energy emitted by an atom, in passing from one steady state to another, is exactly equal to $h\nu_1$, where ν_1 is the frequency of the emitted radiation. Now according to the foregoing theory, since the energy of the æther vibrations of frequency ν must be equal to $rh\nu$ (equation (17)), where r is a positive integer or zero, it follows that the energy emitted by an atom (like those assumed by Bohr) must be equated to

$$r_1h\nu_1+r_2h\nu_2+\ldots, \quad \ldots \quad (21)$$

where the r's are integers, not necessarily all positive, and ν_1, $\nu_2 \ldots$ are the frequencies of the corresponding æther vibrations. The present theory therefore includes this second assumption of Bohr's as a special case.

The conclusion that energy emissions to the æther are represented by an expression of the form (21), and are not necessarily monochromatic in all cases, receives some support from Prof. Barkla's experimental work on X-radiation †. It is noteworthy that Barkla finds that the energy absorbed from the primary radiation, during the production of the "fluorescent" radiations, is equal to

$$\tfrac{1}{2}mv^2+h\nu_{\mathrm{K}}+h\nu_{\mathrm{L}}$$

per electron emitted, the first term representing the kinetic energy of the emitted electron and ν_{K}, ν_{L} the frequencies of the "fluorescent" radiations.

* N. Bohr, *loc. cit.*
† C. G. Barkla, 'Nature,' 4th Mar. 1915.

The main object of this paper is to show that the form of quantum-theory which seems necessary to account for line spectra is not really distinct from that originally proposed by Planck, and the subject of its further application to line spectra and other phenomena may be left for a future publication.

In conclusion I wish to express my thanks to Professors J. W. Nicholson and O. W. Richardson for their advice and criticisms.

Wheatstone Laboratory, King's College,
March 1915.

LXXXIV. *Negative Thermionic Currents from Tungsten.*

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Introduction.

THE emission of negative electricity from an incandescent metal or carbon filament has been the subject of several investigations †. The number of electrons carried from the filament to a neighbouring positively charged electrode increases very rapidly with the temperature. The exact quantitative relation between the number of electrons emitted and the temperature of the filament was established by Richardson, and has been verified by the experiments of others. It was assumed that the emission is determined simply by the number of electrons whose kinetic energy is sufficient to overcome the forces tending to prevent their escape from the metal.

This relation is expressed by the formula

$$i = a\mathrm{T}^{\frac{1}{2}}e^{-\frac{b}{\mathrm{T}}},$$

where i is the saturation (maximum) current in amperes per square cm. and T is the absolute temperature. The quantities a and b are constants, the latter being proportional to the work done by an electron in escaping from the metallic surface. On this view, a pure metal in a perfect vacuum would give a thermionic current which would be a function of its physical properties only. In any actual case the presence of traces of impurities or gases would presumably

* Communicated by Prof. O. W. Richardson, F.R.S.

† Richardson, Camb. Phil. Proc. vol. xi. p. 286 (1901); Phil. Trans. A, vol. cci. p. 497 (1903); H. A. Wilson, Phil. Trans. A, vol. ccii. p. 243 (1903); Deininger, *Ann. d. Phys.* xxv. p. 304 (1908).