
THE QUANTUM THEORY OF THE ATOM

CHAPTER I

THE ORIGIN OF THE QUANTUM THEORY; PLANCK'S RADIATION FORMULA

1. *The origin of the quantum theory.* During the last fifteen years of the nineteenth century, the problem of the distribution of energy in the spectrum of a black body had actively exercised the minds of the ablest mathematical physicists, and had resisted all attempts to find a theoretical formula, based upon the mechanical principles of Newton and the electro-dynamical theory of Maxwell, which would agree with the known experimental evidence.

The difficulties culminated in the proof by Jeans¹ in 1909 of a formula, established for all wave lengths, which was generally accepted as the only result to which the laws of Newton and Maxwell by themselves could lead. This formula was flatly in conflict with the results of experiment.

But for some time before this decisive result had been obtained, it had become more and more apparent that the classical theory (of Newton and Maxwell) was incapable, alone, of accounting for the absorption and emission of radiation by atoms; some new axiom was required.

The new theory was given in 1900 by Planck² who had devoted himself for many years to the application of thermodynamical principles to electro-dynamics; in the course of this work the need for some form of *discontinuity* in atomic processes had become apparent.

He supposed that the oscillating electrons of the radiating

¹ J. H. JEANS, *Phil. Mag.* **17**, p. 229, 1909.

² M. PLANCK, *Verhandl. d. Deutschen Phys. Ges.* **2**, p. 202, 1900.

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body do not radiate or absorb energy continuously, as required by the ordinary electrodynamics, but on the contrary radiate and absorb discontinuously. The energy of the 'oscillator' (oscillating electron) was supposed to be a whole multiple of a 'quantum' of energy of magnitude $h\nu$, where h is a constant (Planck's constant) and ν is the frequency of the oscillator (the number of oscillations per second). Thus the oscillator can only emit or absorb energy in whole multiples of the quantum $h\nu$; or, interchanges of energy between matter and radiation can only occur discontinuously in quanta.

The new theory, 'the quantum theory,' led to a formula for the distribution of energy in the spectrum in remarkable agreement with the results of experiment.

The quantum theory soon led to new advances. The first was due to Einstein, who readily explained the photo-electric effect¹, which had hitherto defied explanation in terms of the classical theory, and also found a formula which accounted for the decrease of the specific heat of solid bodies with falling temperature². Einstein's view, which depended upon the assumption of a single free period for the atoms, was extended by Born and Karman³ to the case of several free periods; while Debye⁴ by a simplification of the assumptions as to the nature of the free periods found a formula for the specific heat of solid bodies which more closely represents its values, especially for the low temperatures obtained by Nernst⁵ and his pupils, and which was in striking agreement with the elastic and optical properties of such bodies.

Again, Nernst⁶ pointed out that to an energy quantum of vibration, such as that of Planck, there must correspond an energy quantum of rotation, and that it was to be expected that the rotational energy of gas molecules would vanish at

¹ A. EINSTEIN, *Ann. d. Phys.* **17**, p. 132, 1905.

² A. EINSTEIN, *Ann. d. Phys.* **22**, p. 180, 1907.

³ M. BORN and TH. VON KARMAN, *Phys. Zeitschr.* **14**, p. 15, 1913.

⁴ P. DEBYE, *Ann. d. Phys.* **39**, p. 789, 1912.

⁵ W. NERNST, *Zeitschr. für Elektrochem.* p. 818, 1911.

⁶ W. NERNST, *Phys. Zeitschr.* **13**, p. 1064, 1912.

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very low temperatures. This conclusion was verified by Eucken's¹ measurements of the specific heat of hydrogen.

These and other results obtained in the most diverse regions of physics formed in themselves almost overwhelming proof of the existence of the quantum of energy, but it was not until 1913, when Niels Bohr² with brilliant success derived the Balmer formula for the spectral lines of hydrogen, and the Rydberg constant in terms of known physical magnitudes, that the quantum theory met with real recognition.

2. *Radiation.* Electromagnetic waves are known of a wide range of wave length—electric waves, infra-red rays, light, ultra-violet rays, X-rays, and γ -rays—a sequence of wave lengths diminishing from hundreds of metres for electric waves to lengths of order 10^{-10} cm. for γ rays. Denoting by Å., the Ångström unit of 10^{-8} cm. and by X, the X-ray unit of 10^{-11} cm., the visible spectrum extends from about wave length $\lambda = 7000$ Å. (red) to $\lambda = 4000$ Å. (violet). The longer infra-red rays have been observed up to lengths of order 100μ , where $\mu = 1000$ Å.; the shorter ultra-violet rays have been observed down to a few hundred Å. and these are the same as the very 'soft' X-rays of the lighter elements; the sequence of X-rays continues with decreasing wave length until the 'hard' X-rays of the heavier elements merge into the γ -rays. The ordinary range of X-rays is from $10,000X$ to $2000X$; the γ -rays have been observed down to $70X$.

If a body is kept at a given temperature and steadily emits radiation without structural change the radiation is 'pure temperature radiation.' Lamp black is a substance which can emit or absorb almost all wave lengths of temperature radiation; an ideal body which can emit or absorb all wave lengths is called a 'black body.'

Consider a hollow metal globe with a small hole in it. Any radiation entering the hole from outside would be partly absorbed by the walls and partly reflected. The chance of the reflected radiation ever emerging from the hole is very small

¹ A. EUCKEN, *Sitzungsber. d. Preuss. Akad. Wiss.* p. 141, 1912.

² N. BOHR, *Phil. Mag.* 26, pp. 1, 476, 857, 1913.

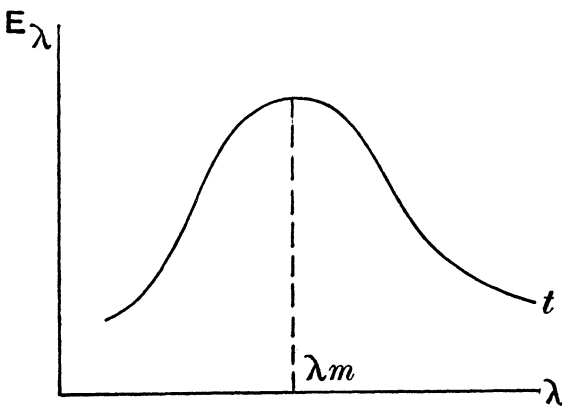
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indeed, and such minute portion as did so would have undergone so many reflections that its intensity would be very small. It may therefore be said that a small hole in a hollow body is a perfect absorber of heat, that is, is the experimental realisation of the perfect black body.

Hence if a small hole be made in the wall of a hollow metal vessel heated to some given temperature, the radiation from the hole will be that of the 'ideal' black body at that temperature.

By the use of a prism of fluorspar 'black-body' radiation can be dispersed into a spectrum. If the energy of the part of the spectrum corresponding to wave lengths between λ and $\lambda + d\lambda$, where $d\lambda$ is a small definite range of wave length, is measured by a bolometer and is $E_\lambda \cdot d\lambda$, E_λ can be plotted as ordinate with λ as abscissa for all the wave lengths of the spectrum. The distribution of energy amongst the different wave lengths is thus known by experiment. The form of this curve was determined by the experiments of Lummer and Pringsheim¹ for a range of temperatures 620° to 1646° (Thomson degrees).

The form of the curve was



¹ O. LUMMER and E. PRINGSHEIM, *Verhandl. d. Deutschen Phys. Ges.* 1, pp. 23 and 215, 1899.

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There is a wave length (λ_m) for which E_λ is a maximum at any given temperature.

3. *Wien's law.* The researches of Kirchhoff¹ on the emission and absorption of radiation, of Boltzmann² and of Wien³, who applied the general principles of thermodynamics to radiation, led to the theoretical deduction of Wien's law that $E_\lambda = \frac{1}{\lambda^5} f(\lambda t)$, where f is a function entirely independent of the nature of the particular substance emitting or absorbing the radiation, and t is the temperature.

The maximum of the experimental curve would correspond to the equation

$$\frac{d}{d\lambda} \left[\frac{1}{\lambda^5} f(\lambda t) \right] = 0,$$

or

$$\lambda t f'(\lambda t) = 5f(\lambda t).$$

This is a numerical equation for λt , and if c is the root, $\lambda_m t = c$; thus as the temperature rises λ_m diminishes, or, the maximum moves to shorter and shorter wave lengths as t increases. This is the 'displacement law' of Wien. The constant c was found by Lummer and Pringsheim to be $\cdot 294$ cm.-deg.

For the sun, Langley found $\lambda_m = 5000 \text{ \AA.} = 5 \times 10^{-5} \text{ cm.}$, so that

$$t = \frac{\cdot 294}{5 \times 10^{-5}} = 5880; \text{ or, } t \text{ is about } 6000^\circ.$$

For the high temperatures in the interior of the stars of the order of 10^6 degrees, the corresponding λ_m would be of order $\cdot 294 \times 10^{-6}$ or 3×10^{-8} or $3000X$ and the maximum of the energy of the radiation would be of an average X-ray type.

¹ G. KIRCHHOFF, 'Gesammelte Abhandlungen,' Leipzig, p. 597, 1882.

² L. BOLTZMANN, Ann. Phys. Chem. 22, p. 291, 1884.

³ W. WIEN, Sitzungsber. Akad. Wiss. Berlin, p. 55, 1893. A full account of the deduction of this law is given by M. PLANCK in his book 'Wärmestrahlung' (fünfte Auflage), Leipzig, pp. 59-88, 1923, and by H. A. LORENTZ in his 'Theory of Electrons' (English translation), chap. II, 1909. Also 'Principles of Thermodynamics' by G. BIRTWISTLE, pp. 152-157, Cambridge, 1925.

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4. *The function f .* It has been seen that the principles of thermodynamics lead to the formula $E_\lambda = \lambda^{-5} f(\lambda t)$, but they do not suffice to determine the analytical form of the function f . Further progress can only be made by the use of some hypothesis as to the nature of the emission and absorption of energy by the vibrating electrons ('oscillators').

The earliest attempt to deduce a form for f was published by Wien¹ in 1896. He assumed that the length λ of the waves emitted by a molecule is a function of its velocity v and that E_λ is proportional to the number of molecules having velocities between v and $v + dv$. This led to an exponential form for the function f .

Wien found that $f(x) = ae^{-\frac{b}{x}}$, so that

$$E_\lambda = \lambda^{-5} f(\lambda t) = a\lambda^{-5} e^{-b/\lambda t},$$

where a, b are constants.

In 1899 Lummer and Pringsheim (loc. cit.) had tested this formula by experiment, and in 1900 Rubens and Kurlbaum², using infra-red rays of much greater wave length, extended the test. Wien's formula was found to hold for values of λt below a certain value, but to fail for long wave lengths.

At about this time, Rayleigh³ found the form $f(x) = cx$ for large wave lengths, where c is a constant, so that

$$E_\lambda = \lambda^{-5} f(\lambda t) = ct/\lambda^4,$$

for large wave lengths. This formula agreed well with experiment for long wave lengths.

Thus at this time (1900) there were two formulae,

$$E_\lambda = a\lambda^{-5}e^{-b/\lambda t} \text{ (Wien) and } E_\lambda = ct\lambda^{-4} \text{ (Rayleigh),}$$

the former holding for small wave lengths and the latter for large wave lengths, each in agreement with experiment for a certain range of λ .

5. *The discovery of Planck's formula.* For some years before 1900, Planck had endeavoured to determine f by some

¹ W. WIEN, Ann. d. Phys. 58, p. 662, 1896.

² H. RUBENS and F. KURLBAUM, Sitzungsber. Akad. Wiss. Berlin, p. 929, 1900.

³ RAYLEIGH, Phil. Mag. 49, p. 539, 1900; 'Coll. Papers,' vol. 4, p. 483.

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new assumption as to the nature of the interaction between the 'oscillators' and the radiation. He considered the possibility of the oscillator being able to exert an 'irreversible' action on the radiation, to the consternation of his thermodynamical mentor Boltzmann¹. In the course of his work he had used a function S , the reciprocal of $\frac{d^2\phi}{dE^2}$, where ϕ is the entropy and E the energy, S having a direct physical significance in connection with the irreversibility of the energy exchanges between the oscillators and the radiation.

He calculated S for each of the formulae of Wien and Rayleigh. Wien's formula is

$$E = ae^{-\beta/t}, \text{ where } \alpha = a\lambda^{-5}, \beta = b\lambda^{-1}.$$

$$\text{But } d\phi = \frac{dE}{t}, \quad \therefore \frac{d\phi}{dE} = \frac{1}{t} \text{ and } \frac{d^2\phi}{dE^2} = -\frac{1}{t^2} \frac{dt}{dE}.$$

$$\text{But } \log E = -\frac{\beta}{t} + \text{constant.}$$

$$\therefore \frac{dE}{E} = \frac{\beta dt}{t^2},$$

$$\text{so that } \frac{dt}{dE} = \frac{t^2}{E\beta},$$

$$\therefore \frac{d^2\phi}{dE^2} = -\frac{1}{E\beta},$$

$$\therefore S = 1 / \frac{d^2\phi}{dE^2} = -E\beta.$$

Rayleigh's formula is $E = \gamma t$, where $\gamma = c\lambda^{-4}$,

$$\therefore \frac{dt}{dE} = \frac{1}{\gamma},$$

$$\text{and } \frac{d^2\phi}{dE^2} = -\frac{1}{t^2} \frac{dt}{dE} = -\frac{1}{\gamma t^2} = -\frac{\gamma}{E^2},$$

$$\therefore S = -E^2/\gamma.$$

Thus the function S for small wave lengths was proportional to E and for large wave lengths to E^2 . Planck therefore tried

¹ L. BOLTZMANN, Sitzungsber. d. Preuss. Akad. Wiss. p. 455, 1899.

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$S = -\beta E - \frac{E^2}{\gamma}$ as a possibility in general, the first term being important for small energies and the second for large energies.

This assumption led to

$$\begin{aligned}\frac{d^2\phi}{dE^2} &= \frac{1}{S} = -\frac{\gamma}{\beta\gamma E + E^2} \\ &= \frac{1}{\beta} \left[\frac{1}{\beta\gamma + E} - \frac{1}{E} \right], \\ \therefore \frac{d\phi}{dE} &= \frac{1}{\beta} \log \left(\frac{\beta\gamma + E}{E} \right).\end{aligned}$$

Also since

$$\begin{aligned}\frac{1}{t} &= \frac{d\phi}{dE}, \\ \frac{\beta}{t} &= \log \left(\frac{\beta\gamma + E}{E} \right), \\ \therefore \frac{\beta\gamma}{E} + 1 &= e^{\frac{\beta}{t}},\end{aligned}$$

or

$$E = \frac{\beta\gamma}{e^{\frac{\beta}{t}} - 1}.$$

Inserting the values of β , γ , namely, $\beta = b\lambda^{-1}$, $\gamma = c\lambda^{-4}$,

$$E_\lambda = \frac{bc\lambda^{-5}}{e^{b/\lambda t} - 1},$$

where b , c are constants.

This new radiation formula¹, which was so far 'only an interpolation formula found by happy guesswork,' to use Planck's own phrase, was found to agree closely with experiment for all values of λ .

For large values of λt , it becomes

$$E_\lambda = \frac{bc\lambda^{-5}}{b} = \frac{ct}{\lambda^4},$$

the formula of Rayleigh, and for small values of λt , it becomes

$$E_\lambda = \frac{bc\lambda^{-5}}{e^{\frac{b}{\lambda t}}} = \frac{bc}{\lambda^5} e^{-\frac{b}{\lambda t}},$$

the formula of Wien.

¹ M. PLANCK, Verhandl. d. Deutschen Phys. Ges. p. 202, 1900.

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From this time onward Planck was occupied with the task of giving this formula a real physical basis; he turned to Boltzmann's line of thought that entropy is a measure of physical probability.

6. *Entropy and probability.* In the thermodynamical theory of a gas, the state of the gas is defined by a small number of parameters, such as the temperature and pressure. In the kinetic theory of a gas, the state of the gas is defined by a large number of parameters, the coordinates and velocities of its molecules. The temperature and pressure are the mean values of certain functions of the parameters of the kinetic theory, so that a given thermodynamical state may correspond to a large number of different kinetic states ('complexions' as Gibbs termed them) for which the aforesaid mean values are the same. Boltzmann considered that a given thermodynamical state was the more likely to occur the greater the number of 'complexions' by which it could be realised, and he took this number (W) to be the measure of the probability of its occurrence.

7. *The equation $\phi = R \log W$.* Let ϕ be the entropy of a system in some given state and W the probability of its occurrence. Boltzmann took the view that Clausius' principle that a system tends to pass towards states of greater entropy is also the principle that systems tend to pass towards states of greater probability of occurrence, and wrote $\phi = f(W)$.

Consider two independent systems in respective states 1 and 2 for which the probabilities are W_1, W_2 . Then if the two are considered as forming one system, the probability W for the system is equal to $W_1 W_2$, as any pair of 'complexions' of the separate systems taken together forms a 'complexion' of the whole.

But the entropy ϕ of the system is $\phi_1 + \phi_2$.

Therefore since $\phi_1 = f(W_1), \phi_2 = f(W_2)$ and $\phi = f(W)$,

$$f(W_1) + f(W_2) = f(W) = f(W_1 W_2) \dots\dots(1).$$

Differentiating both sides with respect to W_1 , keeping W_2

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constant, it follows that $f'(W_1) = W_2 f'(W_1 W_2)$, and differentiating this with respect to W_2 , keeping W_1 constant,

$$0 = f'(W_1 W_2) + W_2 W_1 f''(W_1 W_2),$$

or $0 = f'(W) + W f''(W)$.

Hence $\log f'(W) + \log W = \text{constant}$,

$$\therefore f'(W) = \frac{k}{W},$$

$$\therefore f(W) = k \log W + C.$$

Substituting in (1),

$$k \log W_1 + C + k \log W_2 + C = k \log (W_1 W_2) + C,$$

$$\therefore C = 0,$$

and $\phi = k \log W$.

This general result was first found for a perfect gas by Boltzmann¹.

Since $dE = t d\phi$, where t is the temperature,

$$dE = t d(k \log W),$$

$$\therefore \frac{1}{kt} = \frac{d}{dE} (\log W).$$

The right-hand side can be calculated² for a perfect gas and is found to be equal to $\frac{1}{Rt}$, where R is the gas constant per molecule = 13.8×10^{-17} , so that $k = R$, and $\frac{1}{Rt} = \frac{d}{dE} (\log W)$, in general.

8. Planck's oscillator. It has been mentioned above that the mechanism of emission and absorption of radiation by any substance is on the electron theory supposed to be a very large number of 'oscillators' each having its own period and contained in the radiating body. On account of Kirchhoff's laws that the nature of black-body radiation is independent of the substance which emits or absorbs it, the nature of the oscillator is immaterial; Planck chose the simplest form of oscillator, namely, a linear one whose kinetic and potential

¹ L. BOLTZMANN, 'Vorlesungen über Gastheorie,' 1, § 6.

² J. H. JEANS, 'The dynamical theory of gases,' chap. v.