The Origin and Development of the Quantum Theory

In this lecture I will endeavour to give a general account of the origin of the quantum theory, to sketch concisely its development up to the present, and to point out its immediate significance in physics.

Looking back over the last twenty years to the time when the conception and magnitude of the physical quantum of action first emerged from the mass of experimental facts, and looking back at the long and complicated path which finally led to an appreciation of its importance, the whole history of its development reminds me of the well-proved adage that "to err is human." And all the hard intellectual work of an industrious thinker must often appear vain and fruitless, but that striking occurrences sometimes provide him with an irrefutable proof of the fact that at the end of all his attempts, he does ultimately get one step nearer the truth. An indispensable hypothesis, though it does not guarantee a result, often arises from the pursuit of a definite object, the importance of which is not lessened by initial ill-success.

For me, such an object has, for a long time, been the solution of the problem of the distribution of energy in the normal spectrum of radiant heat. Gustav Kirchhoff showed that, in a space bounded by bodies at equal temperatures, but of arbitrary emissive and absorptive powers, the nature of the heat of radiation is completely independent of the nature of the bodies (1).* Later, a universal function was proved to exist, which depended only on temperature and wave-length, and was in no way related to the properties peculiar to any substance. The discovery of this remarkable function gave promise

* The numbers in parentheses refer to the notes at the end of the lecture.

of a deeper understanding of the relationship of energy to temperature, which forms the chief problem of thermo-dynamics, and, therefore, also of all molecular physics. There is no way at present available for obtaining this function but to select from all the various kinds of bodies occurring in Nature any one of known emission and absorption coefficients, and to calculate the heat radiation when the exchange of energy is stationary. According to Kirchhoff's theorem, this must be independent of the constitution of the body.

A body especially suited for this purpose appears to be Heinrich Hertz's oscillator, the laws of emission of which, for a given frequency, have recently been fully developed by Hertz (2). If a number of such oscillators be placed in a space enclosed by reflecting walls, they will exchange energy one with another by taking up or emitting electro-magnetic waves, analogous with a sound source and resonators, until finally stationary black radiation, so-called, obtains in the enclosure according to Kirchhoff's law. At one time I fostered the hope which seems to us rather naïve in these days, that the laws of classical electro-dynamics, if applied sufficiently generally, and extended by suitable hypotheses, would be sufficient to explain the essential points of the phenomenon looked for, and to lead to the desired goal. To this end, I first of all developed the laws of emission and absorption of a linear resonator in the widest possible way, in fact, by a roundabout way which I could have avoided by using H. A. Lorentz's electron theory then complete in all fundamental points. But since I did not then fully believe in the electron hypothesis, I preferred to consider the energy flowing across a spherical surface of a certain radius enclosing the resonator. This only deals with phenomena in vacuo, but the knowledge of these is enough to enable us to draw the necessary conclusions about the energy changes of the resonator.

The result of this long series of investigations was the establishment of a general relation between the energy of a resonator of given period and the radiant energy of the corresponding region of the spectrum in the surrounding field when the energy exchange is stationary (3). Some of these investigations could

be proved by comparison with available observations, particularly the damping measurements of V. Bjerknes, and this is a verification of the results (4). Thus the remarkable conclusion is reached that the relation does not depend on the nature of the resonator, in particular, not upon its damping coefficient—a very gratifying and welcome circumstance to me, since it allowed the whole problem to be simplified in so far that the energy of radiation could be replaced by the energy of the resonator. Thereby a system with one degree of freedom could be substituted for a complicated system with many degrees of freedom.

Indeed, this result was nothing but a step preparatory to starting on the real problem, which now appeared more formidable. The first attempt at solving the problem miscarried; for my original hope proved false, namely, that the radiation emitted from the resonator would, in some characteristic way, be distinct from the absorbed radiation and thus give a differential equation, by solving which it would be possible to derive a condition for the state of stationary radiation. The resonator only responded to the same rays as it emitted, and was not at all sensitive to neighbouring regions of the spectrum.

My assumption that the resonator could exert a one-sided, i.e. irreversible, effect on the energy of the surrounding field of radiation, was strongly contradicted by Ludwig Boltzmann (5). His mature experience led him to conclude that, according to the laws of classical mechanics, each phenomenon which I had considered, could operate in exactly the reverse direction. Thus, a spherical wave sent out from a resonator may be reversed and proceed in ever-diminishing concentric spheres until it shrinks up at the resonator and is absorbed by it, and causes again the energy previously absorbed to be emitted once more into space in the directions along which it had come. Even if, by introducing suitable limits, I could exclude from the hypothesis of "natural radiation" such singular phenomena as spherical waves travelling inwards, all these analyses show clearly that an essential connecting link is still missing for the complete understanding of the problem.

No other course remained open to me but to attack the prob-

lem from the opposite direction, namely, through thermodynamics, with which I felt more familiar. Here I was helped by my previous researches into the second law of thermodynamics, and I straightway conceived the idea of connecting the entropy and not the temperature of the resonator with the energy, indeed, not the entropy itself, but its second differential coefficient with respect to energy, since this has a direct physical meaning for the irreversibility of the exchange of energy between resonator and radiation. Since at that time I did not see my way clear to go any further into the dependence of entropy and probability, I could, first of all, only refer to results that had already been obtained. Now, in 1899, the most interesting result was the law of energy distribution which had just been discovered by W. Wien (6). The experimental proof of this was undertaken by F. Paschen at the *Hochschule*, Hanover, and by O. Lummer and E. Pringsheim at the *Reichsanstalt*, Charlottenburg. This law represents the dependence of the intensity of radiation on temperature by means of an exponential function. Using this law to calculate the relation between the entropy and energy of a resonator, the remarkable result is obtained, that R, the reciprocal of the differential coefficient referred to above, is proportional to the energy (7). This exceedingly simple relation is a complete and adequate expression of Wien's law of distribution of energy; for the dependence upon wave-length is always given immediately as well as the dependence upon energy by Wien's generally accepted law of displacements (8).

Since the whole problem deals with one of the universal laws of Nature, and since I believed then, as I do now, that the more general a natural law is, the simpler is its form (though it cannot always be said with certainty and finality which is the simpler form), I thought for a long time that the above relation, namely, that R is proportional to the energy, should be considered as the foundation of the law of distribution of energy (9). This idea soon proved to be untenable in the light of more recent results. While Wien's law was confirmed for small values of energy, i.e. for short waves, O. Lummer and E. Pringsheim found large deviations in the case of long waves (10). Finally,

the observations made by G. Rubens and F. Kurlbaum, with infra-red rays after transmission through fluorspar and rock salt (11), showed a totally different relation, which, under certain conditions, was still very simple. In this case, R is proportional, not to the energy, but to the square of the energy, and this relation is more accurate the larger the energies and wavelengths considered (12).

Thus, by direct experiment, two simple limits have been fixed for the function R, i.e. for small values of the energy it is proportional to the energy, for large values it is proportional to the square of the energy. It was obvious that in the general case the next step was to express R to the sum of two terms, one involving the first power, the other the second power of the energy, so that the first term was the predominating term for small values of the energy, the second term for large values. This gave a new formula for the radiation (13), which has stood the test of experiment fairly satisfactorily so far. No final exact experimental verification has yet been given and a new proof is badly needed (14).

If, however, the radiation formula should be shown to be absolutely exact, it would possess only a limited value, in the sense that it is a fortunate guess at an interpolation formula. Therefore, since it was first enunciated, I have been trying to give it a real physical meaning, and this problem led me to consider the relation between entropy and probability, along the lines of Boltzmann's ideas. After a few weeks of the most strenuous work of my life, the darkness lifted and an unexpected vista began to appear.

I will digress a little. According to Boltzmann, entropy is a measure of physical probability, and the essence of the second law of thermo-dynamics is that in Nature, the more often a condition occurs, the more probable it is. In Nature, entropy itself is never measured, but only the difference of entropy, and to this extent one cannot talk of absolute entropy without a certain arbitrariness. Yet, the introduction of an absolute magnitude of entropy, suitably defined, is allowed, since certain general theorems can be expressed very simply by doing so. As far as I can see, it is exactly the same with energy. Energy itself

cannot be measured, but only a difference of energy. Therefore, one did not previously deal with energy, but with work, and Ernst Mach, who was concerned to a great extent with the conservation of energy, but avoided all speculations outside the domain of observation, has always refrained from talking of energy itself. Similarly, at first in thermo-chemistry, one considered heat of reaction, i.e. difference of energy, until William Ostwald emphatically showed that many involved considerations could be very much simplified, if one dealt with energy itself instead of calorimetric values. The undetermined additive constant in the expression for energy was fixed later by the relativity theorem of the relation between energy and inertia (15).

As in the case of energy, we can define absolute value for entropy and consequently for physical probability, if the additive constant is fixed so that entropy and energy vanish simultaneously. (It would be better to substitute temperature for energy here.) On this basis a comparatively simple combinatory method was derived for calculating the physical probability of a certain distribution of energy in a system of resonators. This method leads to the same expression for entropy as was obtained from the radiation theory (16). As an offset against much disappointment, I derived much satisfaction from the fact that Ludwig Boltzmann, in a letter acknowledging my paper, gave me to understand that he was interested in, and fundamentally in agreement with, my ideas.

For numerical applications of this method of probability we require two universal constants, each of which has an independent physical significance. The supplementary calculation of these constants from the radiation theory shows whether the method is merely a numerical one or has an actual physical meaning. The first constant is of a more or less formal nature, it depends on the definition of temperature. The value of this constant is $\frac{2}{3}$ if temperature be defined as the mean kinetic energy of a molecule in an ideal gas, and is, therefore, a very small quantity (17). With the conventional measure of temperature, however, this constant has an extremely small value, which is naturally closely dependent upon the energy of a single

molecule, and an exact knowledge of it leads, therefore, to the calculation of the mass of a molecule and the quantities depending upon it. This constant is frequently called Boltzmann's constant, though Boltzmann himself, to my knowledge, never introduced it—a curious circumstance, explained by the fact that Boltzmann, as appears from various remarks by him (18), never thought of the practicability of measuring this constant exactly. Nothing can better illustrate the impetuous advance made in experimental methods in the last twenty years than the fact that since then, not one only, but a whole series of methods have been devised for measuring the mass of a single molecule with almost the same accuracy as that of a planet.

While, at the time that I carried out the corresponding calculations from the radiation theory, it was impossible to verify exactly the figure obtained, and all that could be achieved was to check the order of magnitude; shortly afterwards, E. Rutherford and H. Geiger (19), succeeded in determining the value of the elementary electric charge to be $4·65 \times 10^{-10}$ electro-static units, by directly counting a-particles. The agreement of this figure with that calculated by me, $4·69 \times 10^{-10}$, was a definite confirmation of the usefulness of my theory. Since then, more perfect methods have been developed by E. Regener, R. A. Millikan, and others (20), and have given a value slightly higher than this.

The interpretation of the second universal constant of the radiation formula was much less simple. I called it the elementary quantum of action, since it is a product of energy and time, and was calculated to be $6·55 \times 10^{-27}$ erg. sec. Though it was indispensable for obtaining the right expression for entropy— for it is only by the help of it that the magnitude of the standard element of probability could be fixed for the probability calculations (21)—it proved itself unwieldy and cumbrous in all attempts to make it fit in with classical theory in any form. So long as this constant could be considered infinitesimal, as when dealing with large energies or long periods of time, everything was in perfect agreement, but in the general case, a rift appeared, which became more and more pronounced the weaker and more rapid the oscillations considered. The failure of all

attempts to bridge this gap soon showed that undoubtedly one of two alternatives must obtain. Either the quantum of action was a fictitious quantity, in which case all the deductions from the radiation theory were largely illusory and were nothing more than mathematical juggling. Or the radiation theory is founded on actual physical ideas, and then the quantum of action must play a fundamental rôle in physics, and proclaims itself as something quite new and hitherto unheard of, forcing us to recast our physical ideas, which, since the foundation of the infinitesimal calculus by Leibniz and Newton, were built on the assumption of continuity of all causal relations.

Experience has decided for the second alternative. That this decision should be made so soon and so certainly is not due to the verification of the law of distribution of energy in heat radiation, much less to my special derivation of this law, but to the restless, ever-advancing labour of those workers who have made use of the quantum of action in their investigations.

The first advance in this work was made by A. Einstein, who proved, on the one hand, that the introduction of the energy quanta, required by the quantum of action, appeared suitable for deriving a simple explanation for a series of remarkable observations of light effects, such as Stokes's rule, emission of electrons, and ionization of gases (22). On the other hand, by identifying the energy of a system of resonators with the energy of a rigid body, he derived a formula for the specific heat of a rigid body, which gives again quite correctly the variation of specific heat, particularly its decrease with decrease of temperature (23). It is not my duty here to give even an approximately complete account of this work. I can only point out the most important characteristic stages in the progress of knowledge.

We will now consider problems in heat and chemistry. As far as the specific heat of a solid body is concerned, Einstein's method, based on the assumption of a single characteristic oscillation of the atom, has been extended by M. Born and Th. von Kármán to the case of various characteristic oscillations, more in agreement with practice (24). By greatly simplifying the assumptions regarding the nature of the oscillations, P. Debye obtained a comparatively simple formula for the specific

heat of a solid body (25). This not only corroborates, particularly for low temperatures, the experimental values obtained by W. Nernst and his school, but also is in good agreement with the elastic and optical properties of the body. Further, quantum effects are very noticeable when considering the specific heat of gases. W. Nernst had shown at an early stage (26) that the quantum of energy of an oscillation must correspond to the quantum of energy of a rotation, and accordingly expected that the energy of rotation of a gas molecule would decrease with temperature. A. Eucken's measurements of the specific heat of hydrogen verified this deduction (27), and the fact that the calculations of A. Einstein and O. Stern, P. Ehrenfest, and others have not yet been in satisfactory agreement can be ascribed to our incomplete knowledge of the form of the hydrogen molecule. The work of N. Bjerrum, E. v. Bahr, H. Rubens, and G. Hettner, etc., on absorption bands in the infrared rays, shows that there can be no doubt that the rotations of the gas molecules indicated by the quantum conditions do actually exist. However, no one has yet succeeded in giving a complete explanation of these remarkable rotations.

Since all the affinity of a substance is ultimately bound up with its entropy, the theoretical calculation of entropy by means of quanta gives a method of attacking all problems in chemical affinity. Nernst's chemical constant is a characteristic for the absolute value of the entropy of a gas. O. Sackur calculated this constant directly (28) by a combinatory method similar to my method with oscillators, while O. Stern and H. Tetrode, by careful examination of experimental data of evaporation, determined the difference of the entropies of gaseous and non-gaseous substances (29).

The cases considered so far deal with thermo-dynamical equilibrium, which only give statistical mean values for a number of particles and long periods of time. This observation of electronic impulses, however, leads directly to the dynamical details of the phenomena considered. The determination by J. Franck and G. Hertz of the so-called resonance potential, or that critical velocity, the minimum velocity which an electron must have to bring about the emission of a quantum of light by

collision with a neutral atom, is as direct a method of measuring the quantum of action as can be desired (30). Also, in the case of the characteristic radiation of the Röntgen spectrum discovered by C. G. Barkla, similar methods which gave very good results were developed by D. L. Webster, E. Wagner, and others.

The liberation of quanta of light by electronic impulses is the converse of the emission of electrons by projection of light, Röntgen or Gamma rays, and here, again, the quanta of energy determined from the quantum of action and the frequency of oscillations play a characteristic part in the same way as we have seen above, in that the velocity of the electrons emitted does not depend on the intensity of the radiation (31), but on the wavelength of the light emitted (32). From a quantitative point of view, also, Einstein's relations for light quanta mentioned above have been verified in every way, particularly by R. A. Millikan, who determined the initial velocities of the emitted electrons (33), while the significance of the light quantum in causing photo-chemical reactions has been made clear by E. Warburg (34).

The results quoted above, collected from the most varied branches of physics, present an overwhelming case for the existence of the quantum of action, and the quantum hypothesis was put on a very firm foundation by Niels Bohr's theory of the atom. This theory was destined, by means of the quantum of action, to open a door into the wonderland of spectroscopy, which had obstinately defied all investigators since the discovery of spectral analysis. Once the way was made clear, a mass of new knowledge was obtained concerning this branch of science, as well as allied branches of physics and chemistry. The first brilliant result was Balmer's series for hydrogen and helium, including the reduction of the universal Rydberg constants to pure numbers (35), by which the small difference between hydrogen and helium was found to be due to the slower motion of the heavier atomic core. This led immediately to the investigation of other series in the optical and Röntgen spectra by means of Ritz's useful combination principle, the fundamental meaning of which was now demonstrated for the first time.

In the face of these numerous verifications (which could be

considered as very strong proofs in view of the great accuracy of spectroscopic measurements), those who had looked on the problem as a game of chance were finally compelled to throw away all doubt when A. Sommerfeld showed that—by extending the laws of distribution of quanta to systems with several degrees of freedom (and bearing in mind the variability of mass according to the theory of relativity)—an elegant formula follows which must, so far as can be determined by the most delicate measurements now possible (those of F. Paschen (36)), solve the riddle of the structure of hydrogen and helium spectra (37). This is an accomplishment in every way comparable with the famous discovery of the planet Neptune, whose existence and position had been calculated by Leverrier before it had been seen by human eye. Proceeding further along the same lines, P. Epstein succeeded in giving a complete explanation of the Stark effect of the electrical separation of the spectral lines (38), and P. Debye in giving a simple meaning to the K-series of the Röntgen spectrum, investigated by Manne Siegbahn (39). Moreover, there followed a large number of wider investigations, which explained more or less successfully the mystery of the structure of the atom.

In view of all these results—a complete explanation would involve the inclusion of many more well-known names—an unbiased critic must recognize that the quantum of action is a universal physical constant, the value of which has been found from several very different phenomena to be 6.54×10^{-27} ergs. secs. (40). It must seem a curious coincidence that at the time when the idea of general relativity is making headway and leading to unexpected results, Nature has revealed, at a point where it could be least foreseen, an absolute invariable unit, by means of which the magnitude of the action in a time space element can be represented by a definite number, devoid of ambiguity, thus eliminating the hitherto relative character.

Yet no actual quantum theory has been formed by the introduction of the quantum of action. But perhaps this theory is not so far distant as the introduction of Maxwell's light theory was from the discovery of the velocity of light by Olaf Römer. The difficulties in the way of introducing the quantum of action into

classical theory from the beginning have been mentioned above. As years have elapsed, these difficulties have increased rather than diminished, and although the impetuous advance of research has dealt with some of them, yet the inevitable gaps remaining in any extension are all the more painful to the conscientious and systematic worker. That which serves as the foundation of the law of action in Bohr's theory is made up of certain hypotheses which were flatly rejected, without any question, a generation ago by physicists. That quite definite orbits determined by quanta are a special feature of the atom may be considered admissible, but it is less easy to assume that the electrons, moving in these paths with a definite acceleration, radiate no energy. But that the quite sharply defined frequency of an emitted light quantum should be different from the frequency of the emitted electrons must seem, at first sight, to a physicist educated in the classical school, an almost unreasonable demand on his imagination.

However, figures are decisive, and the conclusion is that things have been gradually reversed. At first a new foreign element was fitted into a structure, generally considered fixed, with as little change as possible; but now the intruder, after gaining a secure place for itself, has taken the offensive, and to-day it is almost certain that it will undermine the old structure in some way or other. The question is at what place and to what degree this will happen.

If a surmise be allowed as to the probable outcome of this struggle, everything seems to indicate that the great principles of thermo-dynamics, derived from the classical theory, will not only maintain their central position in the quantum theory, but will be greatly extended. The adiabatic hypothesis of P. Ehrenfest (41) plays the same part in the quantum theory as the original experiments played in the founding of classical thermodynamics. Just as R. Clausius introduced, as a basis for the measure of entropy, the theorem that any two conditions of a material system are transformable one to the other by reversible processes, so Bohr's new ideas showed the corresponding way to explore the problems opened up by him.

A question, from the complete answer to which we may

expect far-reaching explanations, is what becomes of the energy of a light quantum after perfect emission? Does it spread out, as it progresses, in all directions, as in Huygens's wave theory, and while covering an ever-larger amount of space, diminish without limit? Or does it travel along as in Newton's emanation theory like a projectile in one direction? In the first case the quantum could never concentrate its energy in a particular spot to enable it to liberate an electron from the atomic influences; in the second case we would have the complete triumph of Maxwell's theory, and the continuity between static and dynamic fields must be sacrificed, and with it the present complete explanation of interference phenomena, which have been investigated in all details. Both these alternatives would have very unpleasant consequences for the modern physicist.

In each case there can be no doubt that science will be able to overcome this serious dilemma, and that what seems now to be incompatible may later be regarded as most suitable on account of its harmony and simplicity. Until this goal is attained the problem of the quantum of action will not cease to stimulate research and to yield results, and the greater the difficulties opposed to its solution, the greater will be its significance for the extension and deepening of all our knowledge of physics.

Notes

(The Bibliography is by no means complete, but serves as an indication of the papers which bear on the subject.)

1. G. Kirchhoff. Über das Verhältnis zwischen dem Emissionsvermögen und dem Absorptionsvermögen der Körper für Wärme und Licht. Gesammelte Abhandlungen. Leipzig, J. A. Barth, 1882, p. 597 (§ 17).
2. H. Hertz. Ann. d. Phys., **36,** p. 1, 1889.
3. Sitz.-Ber. d. Preuss. Akad. d. Wiss., 18 May, 1899, p. 455.
4. Sitz.-Ber. d. Preuss. Akad. d. Wiss., 20 Feb., 1896. Also Ann. d. Phys., **60,** p. 577. 1897.
5. L. Boltzmann. Sitz.-Ber. d. Preuss. Akad. d. Wiss., 3 March, 1898, p. 182.
6. W. Wien. Ann. d. Phys., **58,** p. 662, 1896.
7. According to Wien's Law of Energy Distribution, the relation between the energy U of a resonator and the temperature is given by

$$U = ae^{-\frac{b}{T}}.$$

    If S denote the entropy, then

$$\frac{1}{T} = \frac{dS}{dU}$$

    and R of the text $= 1 \bigg/ \dfrac{d^2S}{dU^2} = -bU.$

8. Wien's law of displacements shows that the energy U of a resonator $= \nu f\left(\dfrac{T}{\nu}\right)$ where ν is the frequency of the oscillations.
9. Ann. d. Phys., **1,** p. 719, 1900.