

The Quantum Theory of the Emission and Absorption of Radiation.

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§ 1. Introduction and Summary.

The new quantum theory, based on the assumption that the dynamical variables do not obey the commutative law of multiplication, has by now been developed sufficiently to form a fairly complete theory of dynamics. One can treat mathematically the problem of any dynamical system composed of a number of particles with instantaneous forces acting between them, provided it is describable by a Hamiltonian function, and one can interpret the mathematics physically by a quite definite general method. On the other hand, hardly anything has been done up to the present on quantum electrodynamics. The questions of the correct treatment of a system in which the forces are propagated with the velocity of light instead of instantaneously, of the production of an electromagnetic field by a moving electron, and of the reaction of this field on the electron have not yet been touched. In addition, there is a serious difficulty in making the theory satisfy all the requirements of the restricted principle of relativity, since a Hamiltonian, function can no longer be used. This relativity question is, of course, connected with the previous ones, and it will be impossible to answer any one question completely without at the same time answering them all. However, it appears to be possible to build up a fairly satisfactory theory of the emission of radiation and of the reaction of the radiation field on the emitting system on the basis of a kinematics and dynamics which

are not strictly relativistic. This is the main object of the present paper. The theory is non-relativistic only on account of the time being counted throughout as a c -number, instead of being treated symmetrically with the space coordinates. The relativity variation of mass with velocity is taken into account without difficulty.

The underlying ideas of the theory are very simple. Consider an atom interacting with a field of radiation, which we may suppose for definiteness to be confined in an enclosure so as to have only a discrete set of degrees of freedom. Resolving the radiation into its Fourier components, we can consider the energy and phase of each of the components to be dynamical variables describing the radiation field. Thus if E_r , is the energy of a component labelled r and Θ_r is the corresponding phase (defined as the time since the wave was in a standard phase), we can suppose each E_r and Θ_r to form a pair of canonically conjugate variables. In the absence of any interaction between the field and the atom, the whole system of field plus atom will be describable by the Hamiltonian

$$H = \sum_r E_r + H_0 \quad (1)$$

equal to the total energy, H_0 being the Hamiltonian for the atom alone, since the variables E_r, Θ_r obviously satisfy their canonical equations of motion

$$\dot{E}_r = -\frac{\partial H}{\partial \Theta_r} = 0, \quad \dot{\Theta}_r = \frac{\partial H}{\partial E_r} = 1.$$

When there is interaction between the field and the atom, it could be taken into account on the classical theory by the addition of an interaction term to the Hamiltonian (1), which would be a function of the variables of the atom and of the variables E_r, Θ_r that describe the field. This interaction term would give the effect of the radiation on the atom, and also the reaction of the atom on the radiation field.

In order that an analogous method may be used on the quantum theory, it is necessary to assume that the variables E_r, Θ_r are q -numbers satisfying the standard quantum conditions $\Theta_r E_r - E_r \Theta_r = ih$, etc., where h is $(2\pi)^{-1}$ times the usual Planck's constant, like the other dynamical variables of the problem. This assumption immediately gives light-quantum properties to the radiation.¹ For if ν_r is the frequency of the component r , $2\pi\nu_r\Theta_r$ is an

¹Similar assumptions have been used by Born and Jordan ["Z. f. Physik," vol. 34, p. 886 (1925)] for the purpose of taking over the classical formula for the emission of radiation by a dipole into the quantum theory, and by Born, Heisenberg and Jordan ["Z. f. Physik," vol. 35, p. 606 (1925)] for calculating the energy fluctuations in a field of black-body radiation.

angle variable, so that its canonical conjugate $E_r/2\pi\nu$ can only assume a discrete set of values differing by multiples of h , which means that E_r can change only by integral multiples of the quantum $(2\pi h)\nu_r$. If we now add an interaction term (taken over from the classical theory) to the Hamiltonian (1), the problem can be solved according to the rules of quantum mechanics, and we would expect to obtain the correct results for the action of the radiation and the atom on one another. It will be shown that we actually get the correct laws for the emission and absorption of radiation, and the correct values for Einstein's A's and B's. In the author's previous theory,² where the energies and phases of the components of radiation were c -numbers, only the B 's could be obtained, and the reaction of the atom on the radiation could not be taken into account.

It will also be shown that the Hamiltonian which describes the interaction of the atom and the electromagnetic waves can be made identical with the Hamiltonian for the problem of the interaction of the atom with an assembly of particles moving with the velocity of light and satisfying the Einstein-Bose statistics, by a suitable choice of the interaction energy for the particles. The number of particles having any specified direction of motion and energy, which can be used as a dynamical variable in the Hamiltonian for the particles, is equal to the number of quanta of energy in the corresponding wave in the Hamiltonian for the waves. There is thus a complete harmony between the wave and light-quantum descriptions of the interaction. We shall actually build up the theory from the light-quantum point of view, and show that the Hamiltonian transforms naturally into a form which resembles that for the waves.

The mathematical development of the theory has been made possible by the author's general transformation theory of the quantum matrices.³ Owing to the fact that we count the time as a c -number, we are allowed to use the notion of the value of any dynamical variable at any instant of time. This value is a q -number, capable of being represented by a generalised "matrix" according to many different matrix schemes, some of which may have continuous ranges of rows and columns, and may require the matrix elements to involve certain kinds of infinities (of the type given by the δ functions⁴). A matrix scheme can be found in which any desired set of

²"Roy. Soc. Proc.," A, vol. 112, p. 661, § 5 (1926). This is quoted later by, *loc. cit.*, I.

³"Roy. Soc. Proc.," A, vol. 113, p. 621 (1927). This is quoted later by *loc. cit.*, II. An essentially equivalent theory has been obtained independently by Jordan ["Z. f. Physik," vol. 40, p. 809 (1927)]. See also, F. London, "Z. f. Physik," vol. 40, p. 193 (1926).

⁴*Loc. cit.* II, § 2.

constants of integration of the dynamical system that commute are represented by diagonal matrices, or in which a set of variables that commute are represented by matrices that are diagonal at a specified time.⁵ The values of the diagonal elements of a diagonal matrix representing any q -number are the characteristic values of that q -number. A Cartesian coordinate or momentum will in general have all characteristic values from $-\infty$ to $+\infty$ while an action variable has only a discrete set of characteristic values. (We shall make it a rule to use unprimed letters to denote the dynamical variables or q -numbers, and the same letters primed or multiply primed to denote their characteristic values. Transformation functions or eigenfunctions are functions of the characteristic values and not of the q -numbers themselves, so they should always be written in terms of primed variables.)

If $f(\xi, \eta)$ is any function of the canonical variables ξ_k, η_k , the matrix representing f at any time t in the matrix scheme in which the ξ_k at time t are diagonal matrices may be written down without any trouble, since the matrices representing the ξ_k and η_k themselves at time t are known, namely

$$\left. \begin{aligned} \xi_k(\xi' \xi'') &= \xi'_k \delta(\xi' \xi''), \\ \eta_k(\xi' \xi'') &= -ih \delta(\xi'_1 - \xi''_1) \dots \delta(\xi'_{k-1} - \xi''_{k-1}) \delta'(\xi'_k - \xi''_k) \delta(\xi'_{k+1} - \xi''_{k+1}) \dots \end{aligned} \right\} \quad (2)$$

Thus if the Hamiltonian H is given as a function of the ξ_k and η_k , we can at once write down the matrix $H(\xi' \xi'')$. We can then obtain the transformation function, (ξ' / α') which transforms to a matrix scheme (α) in which the Hamiltonian is a diagonal matrix, as (ξ' / α') must satisfy the integral equation

$$\int H(\xi' \xi'') d\xi'' (\xi'' / \alpha') = W(\alpha') \cdot (\xi' / \alpha'), \quad (3)$$

of which the characteristic values $W(\alpha')$ are the energy levels. This equation is just Schrödinger's wave equation for the eigenfunctions (ξ' / α') , which becomes an ordinary differential equation when H is a simple algebraic function of the ξ_k and η_k on account of the special equations (2) for the matrices representing ξ_k and η_k . Equation (3) may be written in the more general

⁵One can have a matrix scheme in which a set of variables that commute are at all times represented by diagonal matrices if one will sacrifice the condition that the matrices must satisfy the equations of motion. The transformation function from such a scheme to one in which the equations of motion are satisfied will involve the time explicitly. See p. 628 in loc. cit. II.

form

$$\int H(\xi'\xi'')d\xi''(\xi''/\alpha') = i\hbar\partial(\xi'/\alpha')/\partial t, \quad (3')$$

in which it can be applied to systems for which the Hamiltonian involves the time explicitly.

One may have a dynamical system specified by a Hamiltonian H which cannot be expressed as an algebraic function of any set of canonical variables, but which can all the same be represented by a matrix $H(\xi'\xi'')$. Such a problem can still be solved by the present method, since one can still use equation (3) to obtain the energy levels and eigenfunctions. We shall find that the Hamiltonian which describes the interaction of a light-quantum and an atomic system is of this more general type, so that the interaction can be treated mathematically, although one cannot talk about an interaction potential energy in the usual sense.

It should be observed that there is a difference between a light-wave and the de Broglie or Schrödinger wave associated with the light-quanta. Firstly, the light-wave is always real, while the de Broglie wave associated with a light-quantum moving in a definite direction must be taken to involve an imaginary exponential. A more important difference is that their intensities are to be interpreted in different ways. The number of light-quanta per unit volume associated with a monochromatic light-wave equals the energy per unit volume of the wave divided by the energy $(2\pi\hbar)\nu$ of a single light-quantum. On the other hand a monochromatic de Broglie wave of amplitude a (multiplied into the imaginary exponential factor) must be interpreted as representing a^2 light-quanta per unit volume for all frequencies. This is a special case of the general rule for interpreting the matrix analysis,⁶ according to which, if (ξ'/α') or $\psi_{\alpha'}(\xi'_k)$ is the eigenfunction in the variables ξ_k of the state α' of an atomic system (or simple particle), $|\psi_{\alpha'}(\xi'_k)|^2$ is the probability of each ξ_k having the value ξ'_k , [or $|\psi_{\alpha'}(\xi'_k)|^2 d\xi'_1 d\xi'_2 \dots$ is the probability of each ξ_k lying between the values ξ'_k and $\xi'_k + d\xi'_k$, when the ξ_k have continuous ranges of characteristic values] on the assumption that all phases of the system are equally probable. The wave whose intensity is to be interpreted in the first of these two ways appears in the theory only when one is dealing with an assembly of the associated particles satisfying the Einstein-Bose statistics. There is thus no such wave associated with electrons.

⁶Loc. cit., II, §§ 6,7.

§ 2. The Perturbation of an Assembly of Independent Systems.

We shall now consider the transitions produced in an atomic system by an arbitrary perturbation. The method we shall adopt will be that previously given by the author,⁷ which leads in a simple way to equations which determine the probability of the system being in any stationary state of the unperturbed system at any time⁸ This, of course, gives immediately the probable number of systems in that state at that time for an assembly of the systems that are independent of one another and are all perturbed in the same way. The object of the present section is to show that the equations for the rates of change of these probable numbers can be put in the Hamiltonian form in a simple manner, which will enable further developments in the theory to be made.

Let H_0 be the Hamiltonian for the unperturbed system and V the perturbing energy, which can be an arbitrary function of the dynamical variables and may or may not involve the time explicitly, so that the Hamiltonian for the perturbed system is $H = H_0 + V$. The eigenfunctions for the perturbed system must satisfy the wave equation

$$i\hbar\partial\psi/\partial t = (H_0 + V)\psi,$$

where $(H_0 + V)$ is an operator. If $\psi = \sum_r a_r \psi_r$ is the solution of this equation that satisfies the proper initial conditions, where the ψ_r 's are the eigenfunctions for the unperturbed system, each associated with one stationary state labelled by the suffix r , and the a_r 's are functions of the time only, then $|a_r|^2$ is the probability of the system being in the state r at any time. The a_r 's must be normalised initially, and will then always remain normalised. The theory will apply directly to an assembly of N similar independent systems if we multiply each of these a_r 's by $n^{1/2}$ so as to make $\sum_r |a_r|^2 = 1$. We shall now have that $|a_r|^2$ is the probable number of systems in the state r .

The equation that determines the rate of change of the a_r 's is⁹

$$i\hbar\dot{a}_r = \sum_s V_{rs} a_s, \tag{4}$$

⁷Loc. cit., I.

⁸The theory has recently been extended by Born ["Z. f. Physik," vol. 40, p. 167 (1926)] so as to take into account the adiabatic changes in the stationary states that may be produced by the perturbation as well as the transitions. This extension is not used in the present paper.

⁹Loc. cit., I, equation (25).

where the V_{rs} 's are the elements of the matrix representing V . The conjugate imaginary equation is

$$-i\hbar\dot{a}_r^* = \sum_s V_{rs}^* a_s^* = \sum_s a_s^* V_{sr}. \quad (4')$$

If we regard a_r and $i\hbar a_r^*$ as canonical conjugates, equations (4) and (4') take the Hamiltonian form with the Hamiltonian function $F_1 = \sum_{rs} a_r^* V_{rs} a_s$, namely,

$$\frac{da_r}{dt} = \frac{1}{i\hbar} \frac{\partial F_1}{\partial a_r^*}, \quad i\hbar \frac{\partial a_r^*}{dt} = -\frac{\partial F_1}{\partial a_r}.$$

We can transform to the canonical variables N_r, ϕ_r by the contact transformation

$$a_r = N_r^{1/2} e^{-i\phi_r/\hbar}, \quad a_r^* = N_r^{1/2} e^{i\phi_r/\hbar}.$$

This transformation makes the new variables N_r and ϕ_r real, N_r being equal to $a_r a_r^* = |a_r|^2$, the probable number of systems in the state r , and ϕ_r/\hbar being the phase of the eigenfunction that represents them. The Hamiltonian F_1 now becomes

$$F_1 = \sum_{rs} V_{rs} N_r^{1/2} N_s^{1/2} e^{i(\phi_r - \phi_s)/\hbar},$$

and the equations that determine the rate at which transitions occur have the canonical form

$$\dot{N}_r = -\frac{\partial F_1}{\partial \phi_r}, \quad \dot{\phi}_r = \frac{\partial F_1}{\partial N_r}.$$

A more convenient way of putting the transition equations in the Hamiltonian form may be obtained with the help of the quantities

$$b_r = a_r e^{-iW_r t/\hbar}, \quad b_r^* = a_r^* e^{iW_r t/\hbar},$$

W_r being the energy of the state r . We have $|b_r|^2$ equal to $|a_r|^2$ the probable number of systems in the state r . For b_r we find

$$\begin{aligned} i\hbar \dot{b}_r &= W_r b_r + i\hbar \dot{a}_r e^{-iW_r t/\hbar} \\ &= W_r b_r + \sum_s V_{rs} b_s e^{i(W_s - W_r)t/\hbar} \end{aligned}$$

with the help of (4). If we put $V_{rs} = c_{rs} e^{i(W_r - W_s)t/\hbar}$, so that v_{rs} is a constant when V does not involve the time explicitly, this reduces to

$$\begin{aligned} i\hbar \dot{b}_r &= W_r b_r + \sum_s v_{rs} b_s \\ &= \sum_s H_{rs} b_s, \end{aligned} \quad (5)$$

where $H_{rs} = W_r \delta_{rs} + v_{rs}$, which is a matrix element of the total Hamiltonian $H = H_0 + V$ with the time factor $e^{i(W_r - W_s)t/\hbar}$ removed, so that H_{rs} is a constant when H does not involve the time explicitly. Equation (5) is of the same form as equation (4), and may be put in the Hamiltonian form in the same way.

It should be noticed that equation (5) is obtained directly if one writes down the Schrödinger equation in a set of variables that specify the stationary states of the unperturbed system. If these variables are ξ_h , and if $H(\xi'\xi'')$ denotes a matrix element of the total Hamiltonian H in the (ξ) scheme, this Schrödinger equation would be

$$i\hbar \partial \Phi(\xi') / \partial t = \Sigma_{\xi''} H(\xi'\xi'') \psi(\xi''), \quad (6)$$

like equation (3'). This differs from the previous equation (5) only in the notation, a single suffix r being there used to denote a stationary state instead of a set of numerical values ξ'_k for the variables ξ_k , and b_r being used instead of $\psi(\xi')$. Equation (6), and therefore also equation (5), can still be used when the Hamiltonian is of the more general type which cannot be expressed as an algebraic function of a set of canonical variables, but can still be represented by a matrix $H(\xi'\xi'')$ or H_{rs} .

We now take b_r and $i\hbar b_r^*$ to be canonically conjugate variables instead of a_r and $i\hbar a_r^*$. The equation (5) and its conjugate imaginary equation will now take the Hamiltonian form with the Hamiltonian function

$$F = \Sigma_{rs} b_r^* H_{rs} b_s. \quad (7)$$

Proceeding as before, we make the contact transformation

$$b_r = N_r^{1/2} e^{-i\Theta_r/\hbar}, \quad b_r^* = N_r^{1/2} e^{i\Theta_r/\hbar}, \quad (8)$$

to the new canonical variables N_r, Θ_r , where N_r is, as before, the probable number of systems in the state r , and Θ_r is a new phase. The Hamiltonian F will now become

$$F = \Sigma_{rs} H_{rs} N_r^{1/2} N_s^{1/2} e^{i(\Theta_r - \Theta_s)/\hbar},$$

and the equations for the rates of change of N_r and Θ_r will take the canonical form

$$\dot{N}_r = -\frac{\partial F}{\partial \Theta_r}, \quad \dot{\Theta}_r = \frac{\partial F}{\partial N_r}.$$

The Hamiltonian may be written

$$F = \Sigma_r W_r N_r + \Sigma_{rs} v_{rs} N_r^{1/2} N_s^{1/2} e^{i(\Theta_r - \Theta_s)/\hbar}. \quad (9)$$

The first term $\sum_r W_r N_r$ is the total proper energy of the assembly, and the second may be regarded as the additional energy due to the perturbation. If the perturbation is zero, the phases Θ_r would increase linearly with the time, while the previous phases ϕ_r would in this case be constants.

§ 3. The Perturbation of an Assembly satisfying the Einstein-Bose Statistics.

According to the preceding section we can describe the effect of a perturbation on an assembly of independent systems by means of canonical variables and Hamiltonian equations of motion. The development of the theory which naturally suggests itself is to make these canonical variables q -numbers satisfying the usual quantum conditions instead of c -numbers, so that their Hamiltonian equations of motion become true quantum equations. The Hamiltonian function will now provide a Schrödinger wave equation, which must be solved and interpreted in the usual manner. The interpretation will give not merely the probable number of systems in any state, but the probability of any given distribution of the systems among the various states, this probability being, in fact, equal to the square of the modulus of the normalised solution of the wave equation that satisfies the appropriate initial conditions. We could, of course, calculate directly from elementary considerations the probability of any given distribution when the systems are independent, as we know the probability of each system being in any particular state. We shall find that the probability calculated directly in this way does not agree with that obtained from the wave equation except in the special case when there is only one system in the assembly. In the general case it will be shown that the wave equation leads to the correct value for the probability of any given distribution when the systems obey the Einstein-Bose statistics instead of being independent.

We assume the variables $b_r, i\hbar b_r^*$ of § 2 to be canonical q -numbers satisfying the quantum conditions

$$b_r \cdot i\hbar b_r^* - i\hbar b_r^* \cdot b_r = i\hbar$$

or

$$b_r b_r^* - b_r^* b_r = 1,$$

and

$$\begin{aligned} b_r b_s - b_s b_r &= 0, & b_r^* b_s^* - b_s^* b_r^* &= 0, \\ b_r b_s^* - b_s^* b_r &= 0 & (s \neq r). \end{aligned}$$

The transformation equations (8) must now be written in the quantum form

$$\left. \begin{aligned} b_r &= (N_r + 1)^{1/2} e^{i\Theta_r/h} = e^{-i\Theta_r/h} N_r^{1/2} \\ b_r^* &= N_r^{1/2} e^{i\Theta_r/h} = e^{i\Theta_r/h} (N_r + 1)^{1/2}, \end{aligned} \right\} \quad (10)$$

in order that the N_r, Θ_r may also be canonical variables. These equations show that the N_r can have only integral characteristic values not less than zero,¹⁰ which provides us with a justification for the assumption that the variables are q -numbers in the way we have chosen. The numbers of systems in the different states are now ordinary quantum numbers.

The Hamiltonian (7) now becomes

$$\begin{aligned} F &= \sum_{rs} b_r^* H_{rs} b_s = \sum_{rs} N_r^{1/2} e^{i\Theta_r/h} H_{rs} (N_s + 1)^{1/2} e^{-i\Theta_s/h} \\ &= \sum_{rs} H_{rs} N_r^{1/2} (N_s + 1 - \delta_{rs})^{1/2} e^{i(\Theta_r - \Theta_s)/h} \end{aligned} \quad (11)$$

in which the H_{rs} are still c -numbers. We may write this F in the form corresponding to (9)

$$F = \sum_r W_r N_r + \sum_{rs} v_{rs} N_r^{1/2} (N_s + 1 - \delta_{rs})^{1/2} e^{i(\Theta_r - \Theta_s)/h} \quad (11')$$

in which it is again composed of a proper energy term $\sum_r W_r N_r$ and an interaction energy term.

The wave equation written in terms of the variables N_r is¹¹

$$i\hbar \frac{\partial}{\partial t} \psi(n'_1, N'_2, N'_3 \dots) = F \psi(N'_1, N'_2, N'_3 \dots), \quad (12)$$

where F is an operator, each Θ_r occurring in F being interpreted to mean $i\hbar \partial / \partial N'_r$. If we apply the operator $e^{\pm i\Theta_r/h}$ to any function $f(N'_1, N'_2, N'_3, \dots)$ of the variables N'_1, N'_2, \dots the result is

$$\begin{aligned} e^{\pm i\Theta_r/h} f(N'_1, N'_2, \dots, N'_r, \dots) &= e^{\pm \partial / \partial N'_r} f(N'_1, N'_2, \dots, N'_r \dots) \\ &= f(N'_1, N'_2, \dots, N'_r \mp 1, \dots). \end{aligned}$$

¹⁰See § 8 of the author's paper "Roy. Soc. Proc.," A, vol. III, p. 281 (1926). What are there called the c -number values that a q -number can take are here given the more precise name of the characteristic values of that q -number.

¹¹We are supposing for definiteness that the label r of the stationary states takes the values 1, 2, 3...

If we use this rule in equation (12) and use the expression (11) for F we obtain¹²

$$\begin{aligned} & ih \frac{\partial}{\partial t} \psi(N'_1, N'_2, N'_3 \dots) \\ &= \sum_r H_{rs} N_r'^{1/2} (N'_s + 1 - \delta_{rs})^{1/2} \psi(N'_1, N'_2, \dots, N'_r - 1, \dots, N'_s + 1, \dots). \end{aligned} \quad (13)$$

We see from the right-hand side of this equation that in the matrix representing F , the term in F involving $e^{i(\Theta_r - \Theta_s)/h}$ will contribute only to those matrix elements that refer to transitions in which N_r decreases by unity and N_s increases by unity, i.e., to matrix elements of the type $F(N'_1, N'_2, \dots, N'_r \dots N'_s; N'_1, N'_2 \dots N'_r - 1 \dots N'_s + 1 \dots)$. If we find a solution $\psi(N'_1, N'_2 \dots)$ of equation (13) that is normalised [*i.e.*, one for which $\sum_{N'_1, N'_2 \dots} |\psi(N'_1, N'_2 \dots)|^2 = 1$] and that satisfies the proper initial conditions, then $|\psi(N'_1, N'_2 \dots)|^2$ will be the probability of that distribution in which N'_1 systems are in state 1, N'_2 in state 2, \dots at any time.

Consider first the case when there is only one system in the assembly. The probability of its being in the state q is determined by the eigenfunction $\psi(N'_1, N'_2, \dots)$ in which all the N' 's are put equal to zero except N'_q , which is put equal to unity. This eigenfunction we shall denote by $\psi\{q\}$. When it is substituted in the left-hand side of (13), all the terms in the summation on the right-hand side vanish except those for which $r = q$, and we are left with

$$ih \frac{\partial}{\partial t} \psi\{q\} = \sum_r H_{qs} \psi\{s\},$$

which is the same equation as (5) with $\psi\{q\}$ playing the part of b_q . This establishes the fact that the present theory is equivalent to that of the preceding section when there is only one system in the assembly.

Now take the general case of an arbitrary number of systems in the assembly, and assume that they obey the Einstein-Bose statistical mechanics. This requires that, in the ordinary treatment of the problem, only those eigenfunctions that are symmetrical between all the systems must be taken into account, these eigenfunctions being by themselves sufficient to give a complete quantum solution of the problem.¹³ We shall now obtain the equation for the rate of change of one of these symmetrical eigenfunctions, and show that it is identical with equation (13).

If we label each system with a number n , then the Hamiltonian for the assembly will be $H_A = \sum_n H(n)$, where $H(n)$ is the H of § 2 (equal to $H_0 + V$) expressed in terms of the variables of the n th system. A stationary state of

¹²When $s = r$, $\psi(N'_1, N'_2, N'_r - 1 \dots N'_s)$ is to be taken to mean $\psi(N'_1, N'_2, \dots, N'_r \dots)$.

¹³Loc. cit., I, § 3.

the assembly is defined by the numbers $r_1, r_2 \dots r_n \dots$ which are the labels of the stationary states in which the separate systems lie. The Schrödinger equation for the assembly in a set of variables that specify the stationary states will be of the form (6) [with H_A instead of H], and we can write it in the notation of equation (5) thus: –

$$i\hbar \dot{b}(r_1 r_2 \dots) = \sum_{s_1, s_2 \dots} H_A(r_1 r_2 \dots; s_1 s_2 \dots) b(s_1 s_2 \dots), \quad (14)$$

where $H_A(r_1 r_2 \dots; s_1 s_2 \dots)$ is the general matrix element of H_A [with the time factor removed]. This matrix element vanishes when more than one s_n differs from the corresponding r_n ; equals $H_{r_m s_m}$ when s_m differs from r_m and every other s_n equals r_n ; and equals $\sum_n H_{r_n r_n}$ when every s_n equals r_n . Substituting these values in (14), we obtain

$$i\hbar \dot{b}(r_1 r_2 \dots) = \sum_m \sum_{s_m \neq r_m} H_{r_m s_m} b(r_1 r_2 \dots r_{m-1} s_m r_{m+1} \dots) + \sum_n H_{r_n r_n} b(r_1 r_2 \dots). \quad (15)$$

We must now restrict $b(r_1 r_2 \dots)$ to be a symmetrical function of the variables $r_1, r_2 \dots$ in order to obtain the Einstein-Bose statistics. This is permissible since if $b(r_1 r_2 \dots)$ is symmetrical at any time, then equation (15) shows that $\dot{b}(r_1 r_2 \dots)$ is also symmetrical at that time, so that $b(r_1 r_2 \dots)$ will remain symmetrical.

Let N_r denote the number of systems in the state r . Then a stationary state of the assembly describable by a symmetrical eigenfunction may be specified by the numbers $N_1, N_2 \dots N_r \dots$ just as well as by the numbers $r_1, r_2 \dots r_n \dots$, and we shall be able to transform equation (15) to the variables $N_1, N_2 \dots$. We cannot actually take the new eigenfunction $b(N_1, N_2 \dots)$ equal to the previous one $b(r_1 r_2 \dots)$ but must take one to be a numerical multiple of the other in order that each may be correctly normalised with respect to its respective variables. We must have, in fact,

$$\sum_{r_1, r_2 \dots} |b(r_1 r_2 \dots)|^2 = 1 = \sum_{N_1, N_2 \dots} |b(N_1, N_2 \dots)|^2,$$

and hence we must take $|b(N_1, N_2 \dots)|^2$ equal to the sum of $|b(r_1 r_2 \dots)|^2$ for all values of the numbers $r_1 r_2 \dots$ such that there are N_1 of them equal to 1, N_2 equal to 2, etc. There are $N!/N_1!N_2! \dots$ terms in this sum, where $N = \sum_r N_r$ is the total number of systems, and they are all equal, since $b(r_1 r_2 \dots)$ is a symmetrical function of its variables $r_1, r_2 \dots$. Hence we must have

$$b(N_1, N_2 \dots) = (N!/N_1!N_2! \dots)^{1/2} b(r_1 r_2 \dots).$$

If we make this substitution in equation (15), the left-hand side will become $ih(N_1!N_2!\dots/N!)^{1/2}\dot{b}(N_1, N_2\dots)$. The term $H_{r_ms_m}b(r_1r_2\dots r_{m-1}s_mr_{m+1}\dots)$ in the first summation on the right-hand side will become

$$\begin{aligned} & [N_1!N_2!\dots(N_r-1)!\dots(N_s+1)!\dots/N!]^{1/2} \\ & H_{rs}b(N_1, N_2\dots N_r-1\dots N_s+1\dots), \end{aligned} \quad (16)$$

where we have written r for r_m and s for s_m . This term must be summed for all values of s except r , and must then be summed for r taking each of the values $r_1, r_2\dots$. Thus each term (16) gets repeated by the summation process until it occurs a total of N_r times, so that it contributes

$$\begin{aligned} & N_r[N_1!N_2!\dots(N_r-1)!\dots(N_s+1)!\dots/N!]^{1/2}H_{rs} \\ & b(N_1, N_2\dots N_r-1\dots N_s+1\dots) \\ & = N_r^{1/2}(N_s+1)^{1/2}(N_1!N_2!\dots/N!)^{1/2}H_{rs}b(N_1, N_2\dots N_r-1\dots N_s+1\dots) \end{aligned}$$

to the right-hand side of (15). Finally, the term $\Sigma_n H_{r_nr_n}b(r_1, r_2\dots)$ becomes

$$\Sigma_r N_r H_{rr} \cdot b(r_1r_2\dots) = \Sigma_r N_r H_{rr} \cdot (N_1!N_2!\dots/N!)^{1/2}b(N_1, N_2\dots).$$

Hence equation (15) becomes, with the removal of the factor $(N_1!N_2!\dots/N!)^{1/2}$,

$$\begin{aligned} & ih\dot{b}(N_1, N_2\dots) = \Sigma_r \Sigma_{s \neq r} N_r^{1/2}(N_s+1)^{1/2} \\ & H_{rs}b(N_1, N_2\dots N_r-1\dots N_s+1\dots) + \Sigma_r N_r H_{rr}b(N_1, N_2\dots), \end{aligned} \quad (17)$$

which is identical with (13) [except for the fact that in (17) the primes have been omitted from the N 's, which is permissible when we do not require to refer to the N 's as q -numbers]. We have thus established that the Hamiltonian (11) describes the effect of a perturbation on an assembly satisfying the Einstein-Bose statistics.

§ 4. The Reaction of the Assembly on the Perturbing System.

Up to the present we have considered only perturbations that can be represented by a perturbing energy V added to the Hamiltonian of the perturbed system, V being a function only of the dynamical variables of that system and perhaps of the time. The theory may readily be extended to the case when the perturbation consists of interaction with a perturbing dynamical system, the reaction of the perturbed system on the perturbing

system being taken into account. (The distinction between the perturbing system and the perturbed system is, of course, not real, but it will be kept up for convenience.)

We now consider a perturbing system, described, say, by the canonical variables J_k, ω_k , the J 's being its first integrals when it is alone, interacting with an assembly of perturbed systems with no mutual interaction, that satisfy the Einstein-Bose statistics. The total Hamiltonian will be of the form

$$H_T = H_P(J) + \sum_n H(n),$$

where H_P is the Hamiltonian of the perturbing system (a function of the J 's only) and $H(n)$ is equal to the proper energy $H_0(n)$ plus the perturbation energy $V(n)$ of the n th system of the assembly. $H(n)$ is a function only of the variables of the n th system of the assembly and of the J 's and ω 's, and does not involve the time explicitly.

The Schrödinger equation corresponding to equation (14) is now

$$i\hbar \dot{b}(J', r_1 r_2 \dots) = \sum_{J''} \sum_{s_1, s_2} \dots H_r(J', r_1 r_2 \dots; J'' s_1 s_2 \dots) b(J'', s_1 s_2 \dots),$$

in which the eigenfunction b involves the additional variables J'_k . The matrix element $H_T(J', r_1 r_2 \dots; J'', s_1 s_2 \dots)$ is now always a constant. As before, it vanishes when more than one s_n differs from the corresponding r_n . When s_m differs from r_m and every other s_n equals r_n , it reduces to $H(J' r_m; J'' s_m)$, which is the $(J', r_m; J'' s_m)$, matrix element (with the time factor removed) of $H = H_0 + V$, the proper energy plus the perturbation energy of a single system of the assembly; while when every s_n equals r_n it has the value $H_P(J') \delta_{J' J''} + \sum_n H(J' r_n; J'' r_n)$. If, as before, we restrict the eigenfunctions to be symmetrical in the variables $r_1, r_2 \dots$ we can again transform to the variables $N_1, N_2 \dots$, which will lead, as before, to the result

$$i\hbar \dot{b}(J', N'_1, N'_2 \dots) = H_P(J') b(J', N'_1, N'_2 \dots) + \sum_{J''} \sum_{r,s} N_r^{1/2} (N'_s + 1 - \delta_{rs})^{1/2} H(J' r; J'' s) b(J'', N'_1, N'_2 \dots N'_r - 1 \dots N'_s + 1 \dots) \quad (18)$$

This is the Schrödinger equation corresponding to the Hamiltonian function

$$F = H_P(J) + \sum_{r,s} H_{rs} N_r^{1/2} (N_s + 1 - \delta_{rs})^{1/2} e^{i(\Theta_1 - \Theta_2)/\hbar}, \quad (19)$$

in which H_{rs} is now a function of the J 's and ω 's, being such that when represented by a matrix in the (J) scheme its $(J' J'')$ element is $H(J' r; J'' s)$. (It should be noticed that H_{rs} still commutes with the N 's and Θ 's.)

Thus the interaction of a perturbing system and an assembly satisfying the Einstein-Bose statistics can be described by a Hamiltonian of the form

(19). We can put it in the form corresponding to (11') by observing that the matrix element $H(J'r; J''s)$ is composed of the sum of two parts, a part that comes from the proper energy H_0 which equals W_r when $J_k'' = J_k'$ and $s = r$ and vanishes otherwise, and a part that comes from the interaction energy V which may be denoted by $v(J'r; J''s)$. Thus we shall have

$$H_{rs} = W_r \delta_{rs} + v_{rs},$$

where v_{rs} is that function of the J 's and ω 's which is represented by the matrix whose $(J'J'')$ element is $v(J'r; J''s)$, and so (19) becomes

$$F = H_P(J) + \Sigma_r W_r N_r + \Sigma_{r,s} v_{rs} N_r^{1/2} (N_s + 1 - \delta_{rs})^{1/2} e^{i(\Theta_r - \Theta_s)/h}. \quad (20)$$

The Hamiltonian is thus the sum of the proper energy of the perturbing system $H_P(J)$ the proper energy of the perturbed systems $\Sigma_r W_r N_r$ and the perturbation energy $\Sigma_{r,s} v_{rs} N_r^{1/2} (N_s + 1 - \delta_{rs})^{1/2} e^{i(\Theta_r - \Theta_s)/h}$.

§ 5. Theory of Transitions in a System from One State to Others of the Same Energy.

Before applying the results of the preceding sections to light-quanta, we shall consider the solution of the problem presented by a Hamiltonian of the type (19). The essential feature of the problem is that it refers to a dynamical system which can, under the influence of a perturbation energy which does not involve the time explicitly, make transitions from one state to others of the same energy. The problem of collisions between an atomic system and an electron, which has been treated by Born,¹⁴ is a special case of this type. Born's method is to find a periodic solution of the wave equation which consists, in so far as it involves the coordinates of the colliding electron, of plane waves, representing the incident electron, approaching the atomic system, which are scattered or diffracted in all directions. The square of the amplitude of the waves scattered in any direction with any frequency is then assumed by Born to be the probability of the electron being scattered in that direction with the corresponding energy.

This method does not appear to be capable of extension in any simple manner to the general problem of systems that make transitions from one state to others of the same energy. Also there is at present no very direct and certain way of interpreting a periodic solution of a wave equation to

¹⁴Born, "Z. t. Physik," vol. 38, p. 803 (1926).

apply to a non-periodic physical phenomenon such as a collision. (The more definite method that will now be given shows that Born's assumption is not quite right, it being necessary to multiply the square of the amplitude by a certain factor.)

An alternative method of solving a collision problem is to find a *non-periodic* solution of the wave equation which consists initially simply of plane waves moving over the whole of space in the necessary direction with the necessary frequency to represent the incident electron. In course of time waves moving in other directions must appear in order that the wave equation may remain satisfied. The probability of the electron being scattered in any direction with any energy will then be determined by the rate of growth of the corresponding harmonic component of these waves. The way the mathematics is to be interpreted is by this method quite definite, being the same as that of the beginning of § 2.

We shall apply this method to the general problem of a system which makes transitions from one state to others of the same energy under the action of a perturbation. Let H_0 be the Hamiltonian of the unperturbed system and V the perturbing energy, which must not involve the time explicitly. If we take the case of a continuous range of stationary states, specified by the first integrals, α_k say, of the unperturbed motion, then, following the method of § 2, we obtain

$$i\hbar \dot{a}(\alpha') = \int V(\alpha' \alpha'') d\alpha'' \cdot a(\alpha''), \quad (21)$$

corresponding to equation (4). The probability of the system being in a state for which each α_k lies between $\alpha_{k'}$ and $\alpha_{k'} + d\alpha_{k'}$ at any time is $|a(\alpha')|^2 d\alpha_1 \cdot d\alpha_2 \dots$ when a $a(\alpha')$ is properly normalised and satisfies the proper initial conditions. If initially the system is in the state α^0 we must take the initial value of $a(\alpha')$ to be of the form $a^0 \cdot \delta(\alpha' - \alpha^0)$. We shall keep a^0 arbitrary, as it would be inconvenient to normalise $a(\alpha')$ in the present case. For a first approximation we may substitute for $a(\alpha'')$ in the right-hand side of (21) its initial value. This gives

$$i\hbar \dot{a}(\alpha') = a^0 V(\alpha' \alpha^0) = \alpha^0 v(\alpha' \alpha^0) e^{i[W(\alpha') - W(\alpha^0)]t/\hbar},$$

where $v(\alpha' \alpha^0)$ is a constant and $W(\alpha')$ is the energy of the state α' . Hence

$$i\hbar a(\alpha') = a^0 \delta(\alpha' - \alpha^0) + \alpha^0 v(\alpha' \alpha^0) \frac{e^{i[W(\alpha') - W(\alpha^0)]t/\hbar} - 1}{i[W(\alpha') - W(\alpha^0)]/\hbar}. \quad (22)$$

For values of the α'_k such that $W(\alpha')$ differs appreciably from $W(\alpha^0)$, $a(\alpha')$ is a periodic function of the time whose amplitude is small when the perturbing energy V is small, so that the eigenfunctions corresponding to these stationary states are not excited to any appreciable extent. On the other hand, for values of the α'_k such that $W(\alpha') = W(\alpha^0)$ and $\alpha'_k \neq \alpha_k^0$ for some k , $a(\alpha')$ increases uniformly with respect to the time, so that the probability of the system being in the state α' at any time increases proportionally with the square of the time. Physically, the probability of the system being in a state with exactly the same proper energy as the initial proper energy $W(\alpha^0)$ is of no importance, being infinitesimal. We are interested only in the integral of the probability through a small range of proper energy values about the initial proper energy, which, as we shall find, increases linearly with the time, in agreement with the ordinary probability laws.

We transform from the variables $\alpha_1, \alpha_2 \dots \alpha_u$ to a set of variables that are arbitrary independent functions of the α 's such that one of them is the proper energy W , say, the variables $W, \gamma_1, \gamma_2, \dots \gamma_{u-1}$. The probability at any time of the system lying in a stationary state for which each γ_k lies between γ'_k and $\gamma'_k + d\gamma'_k$ is now (apart from the normalising factor) equal to

$$d\gamma'_1 \cdot d\gamma'_2 \dots d\gamma'_{u-1} \int |a(\alpha')|^2 \frac{\partial(\alpha'_1, \alpha'_2 \dots \alpha'_u)}{\partial(W', \gamma'_1 \dots \gamma'_{u-1})}. \quad (23)$$

For a time that is large compared with the periods of the system we shall find that practically the whole of the integral in (23) is contributed by values of W' very close to $W^0 = W(\alpha^0)$. Put

$$a(\alpha') = a(W', \gamma') \quad \text{and} \quad \partial(\alpha'_1, \alpha'_2 \dots \alpha'_u) / \partial(W', \gamma'_1 \dots \gamma'_{u-1}) = J(W', \gamma').$$

Then for the integral in (23) we find, with the help of (22) (provided $\gamma'_k \neq \gamma_k^0$ for some k)

$$\begin{aligned} \int |a(W', \gamma')|^2 J(W', \gamma') dW' &= |a^0|^2 \int |v(W', \gamma'; W^0, \gamma^0)|^2 J(W', \gamma') \\ &\quad \frac{[e^{i(W'-W^0)t/h} - 1][e^{-i(W'-W^0)t/h} - 1]}{(W' - W^0)^2} dW' \\ &= \frac{2|a^0|^2 \int |v(W', \gamma'; W^0, \gamma^0)|^2 J(W', \gamma') [1 - \cos(W' - W^0)t/h]}{(W' - W^0)^2 \cdot dW'} \\ &= \frac{2|a^0|^2 t/h \cdot \int |v(W^0 + hx/t, \gamma'; W^0, \gamma^0)|^2 J(W^0 + hx/t, \gamma') (1 - \cos x)}{x^2 \cdot dx}, \end{aligned}$$

if one makes the substitution $(W' - W^0)t/h = x$. For large values of t this reduces to

$$\begin{aligned} & 2|a^0|^2 t/h \cdot |v(W^0, \gamma'; W^0, \gamma^0)|^2 J(W^0, \gamma') \int_{-\infty}^{\infty} (1 - \cos x)/x^2 \cdot dx \\ & = 2\pi |a^0|^2 t/h \cdot |v(W^0, \gamma'; W^0, \gamma^0)|^2 J(W^0, \gamma'). \end{aligned}$$

The probability per unit time of a transition to a state for which each γ_k lies between γ'_k and $\gamma'_k + d\gamma'_k$ is thus (apart from the normalising factor)

$$2\pi |a^0|^2 /h \cdot |v(W^0, \gamma'; W^0, \gamma^0)|^2 J(W^0, \gamma') d\gamma'_1 \cdot d\gamma'_2 \dots d\gamma'_{u-1}, \quad (24)$$

which is proportional to the square of the matrix element associated with that transition of the perturbing energy.

To apply this result to a simple collision problem, we take the α 's to be the components of momentum p_x, p_y, p_z of the colliding electron and the γ 's to be Θ and ϕ , the angles which determine its direction of motion. If, taking the relativity change of mass with velocity into account, we let P denote the resultant momentum, equal to $(p_x^2 + p_y^2 + p_z^2)^{1/2}$, and E the energy, equal to $(m^2 c^4 + P^2 c^2)^{1/2}$, of the electron, m being its rest-mass, we find for the Jacobian

$$J = \frac{\partial(p_x, p_y, p_z)}{\partial(E, \Theta, \phi)} = \frac{EP}{c^2} \sin \Theta.$$

Thus the $J(W^0, \gamma')$ of the expression (24) has the value

$$J(W^0, \gamma') = E' P' \sin \Theta / c^2, \quad (25)$$

where E' and P' refer to that value for the energy of the scattered electron which makes the total energy equal the initial energy W^0 (i.e., to that value required by the conservation of energy).

We must now interpret the initial value of $a(\alpha')$, namely, $a^0 \delta(\alpha' - \alpha^0)$, which we did not normalise. According to § 2 the wave function in terms of the variables α_k is $b(\alpha') = a(\alpha') e^{iW't/h}$, so that its initial value is

$$a^0 \delta(\alpha' - \alpha^0) e^{-iW't/h} = a^0 \delta(p'_x - p_x^0) \delta(p'_y - p_y^0) \delta(p'_z - p_z^0) e^{-iW't/h}.$$

If we use the transformation function¹⁵

$$(x'/p') = (2\pi h)^{-3/2} e^{i\Sigma_{xyz} p'_x x'/h},$$

¹⁵The symbol x is used for brevity to denote x, y, z .

and the transformation rule

$$\psi(x') = \int (x'/p') \psi(p') dp'_x dp'_y dp'_z,$$

we obtain for the initial wave function in the coordinates x, y, z the value

$$a^0 (2\pi h)^{-3/2} e^{i\Sigma_{xyz} p_x^0 x'/h} e^{-W't/h}.$$

This corresponds to an initial distribution of $|a^0|^2 (2\pi h)^{-3}$ electrons per unit volume. Since their velocity is $P^0 c^2/E^0$, the number per unit time striking a unit surface at right-angles to their direction of motion is $|a^0|^2 P^0 c^2/(2\pi h)^3$. Dividing this into the expression (24) we obtain, with the help of (25),

$$4\pi^2 (2\pi h)^2 \frac{E'E^0}{c^4} |v(p'; p^0)|^2 \frac{P'}{p^0} \sin \Theta' d\Theta' d\phi'. \quad (26)$$

This is the effective area that must be hit by an electron in order that it shall be scattered in the solid angle $\sin \Theta' d\Theta' d\phi'$ with the energy E' . This result differs by the factor $(2\pi h)^2/2mE' \cdot P'/P^0$ from Born's.¹⁶ The necessity for the factor P'/p^0 in (26) could have been predicted from the principle of detailed balancing, as the factor $|v(p'; p^0)|^2$ is symmetrical between the direct and reverse processes.¹⁷

§ 6. Application to Light-Quanta.

We shall now apply the theory of § 4 to the case when the systems of the assembly are light-quanta, the theory being applicable to this case since light-quanta obey the Einstein-Bose statistics and have no mutual interaction. A light-quantum is in a stationary state when it is moving with constant momentum in a straight line. Thus a stationary state r is fixed by the three components of momentum of the light-quantum and a variable that specifies its state of polarisation. We shall work on the assumption that there are a finite number of these stationary states, lying very close to one another, as it would be inconvenient to use continuous ranges. The interaction of the light-quanta with an atomic system will be described by a Hamiltonian of the form (20), in which $H_P(J)$ is the Hamiltonian for the

¹⁶In a more recent paper ("Nachr. Gesell. d. Wiss.," Gottingen, p. 146 (1926)) Born has obtained a result in agreement with that of the present paper for non-relativity mechanics, by using an interpretation of the analysis based on the conservation theorems. I am indebted to Prof. N. Bohr for seeing an advance copy of this work.

¹⁷See Klein and Rosseland, "Z. f. Physik," vol. 4, p. 46, equation (4) (1921).

atomic system alone, and the coefficients v_{rs} are for the present unknown. We shall show that this form for the Hamiltonian, with the v_{rs} arbitrary, leads to Einstein's laws for the emission and absorption of radiation.

The light-quantum has the peculiarity that it apparently ceases to exist when it is in one of its stationary states, namely, the zero state, in which its momentum, and therefore also its energy, are zero. When a light-quantum is absorbed it can be considered to jump into this zero state, and when one is emitted it can be considered to jump from the zero state to one in which it is physically in evidence, so that it appears to have been created. Since there is no limit to the number of light-quanta that may be created in this way, we must suppose that there are an infinite number of light-quanta in the zero state, so that the N_0 of the Hamiltonian (20) is infinite. We must now have Θ_0 the variable canonically conjugate to N_0 a constant, since

$$\dot{\Theta}_0 = \partial F / \partial N_0 = W_0 + \text{terms involving } N_0^{-1/2} \text{ or } (N_0 + 1)^{-1/2}$$

and W_0 is zero. In order that the Hamiltonian (20) may remain finite it is necessary for the coefficients v_{r0}, v_{0r} to be infinitely small. We shall suppose that they are infinitely small in such a way as to make $v_{r0}N_0^{1/2}$ and $v_{0r}N_0^{1/2}$ finite, in order that the transition probability coefficients may be finite. Thus we put

$$v_{r0}(N_0 + 1)^{1/2}e^{-i\Theta_0/h} = v_r, \quad v_{0r}N_0^{1/2}e^{i\Theta_0/h} = v_r^*,$$

where v_r and v_r^* are finite and conjugate imaginaries. We may consider the v_r and v_r^* to be functions only of the J 's and ω 's of the atomic system, since their factors $(N_0 + 1)^{1/2}e^{i\Theta_0/h}$ and $N_0^{1/2}e^{i\Theta_0/h}$ are practically constants, the rate of change of N_0 being very small compared with N_0 . The Hamiltonian (20) now becomes

$$\begin{aligned} F = H_P(J) + \sum_r W_r N_r &+ \sum_{r \neq 0} [v_r N_r^{1/2} e^{i\Theta_r/h} + v_r^* (N_r + 1)^{1/2} e^{-i\Theta_r/h}] \\ &+ \sum_{r \neq 0} \sum_{s \neq 0} v_{rs} N_r^{1/2} (N_s + 1 - \delta_{rs})^{1/2} e^{i(\Theta_r - \Theta_s)/h}. \end{aligned} \quad (27)$$

The probability of a transition in which a light-quantum in the state r is absorbed is proportional to the square of the modulus of that matrix element of the Hamiltonian which refers to this transition. This matrix element must come from the term $v_r N_r^{1/2} e^{i\Theta_r/h}$ in the Hamiltonian, and must therefore be proportional to $N_r'^{1/2}$ where N_r' is the number of light-quanta in state r before the process. The probability of the absorption process is thus proportional to N_r' . In the same way the probability of a light-quantum in state r being emitted is proportional to $(N_r' + 1)$, and the probability of

a light-quantum in state r being scattered into state s is proportional to $N'_r(N'_s + 1)$. Radiative processes of the more general type considered by Einstein and Ehrenfest,¹⁸ in which more than one light-quantum take part simultaneously, are not allowed on the present theory.

To establish a connection between the number of light-quanta per stationary state and the intensity of the radiation, we consider an enclosure of finite volume, A say, containing the radiation. The number of stationary states for light-quanta of a given type of polarisation whose frequency lies in the range ν_r to $\nu_r + d\nu_r$ and whose direction of motion lies in the solid angle $d\omega$ about the direction of motion for state r will now be $A\nu_r^2 d\nu_r d\omega_r / c^3$. The energy of the light-quanta in these stationary states is thus $N'_r \cdot 2\pi h \nu_r \cdot A\nu_r^2 d\nu_r - r d\omega_r / c^3$. This must equal $Ac^{-1} I_r d\nu_r d\omega_r$ where I_r is the intensity per unit frequency range of the radiation about the state r . Hence

$$I_r = N'_r (2\pi h) \nu_r^3 / c^2, \quad (28)$$

so that N'_r is proportional to I_r and $(N'_r + 1)$ is proportional to $N'_r + (2\pi h) \nu_r^3 / c^2$. We thus obtain that the probability of an absorption process is proportional to I_r the incident intensity per unit frequency range, and that of an emission process is proportional to $I_r + (2\pi h) \nu_r^3 / c^2$, which are just Einstein's laws.¹⁹ In the same way the probability of a process in which a light-quantum is scattered from a state r to a state s is proportional to $I_r [I_s + (2\pi h) \nu_s^3 / c^2]$, which is Pauli's law for the scattering of radiation by an electron.²⁰

§ 7. The Probability Coefficients for Emission and, Absorption.

We shall now consider the interaction of an atom and radiation from the wave point of view. We resolve the radiation into its Fourier components, and suppose that their number is very large but finite. Let each component be labelled by a suffix r , and suppose there are i_s components associated with the radiation of a definite type of polarisation per unit solid angle per

¹⁸ "Z. f. Physik," vol. 19, p. 301 (1923).

¹⁹ The ratio of stimulated to spontaneous emission in the present theory is just twice its value in Einstein's. This is because in the present theory either polarised component of the incident radiation can stimulate only radiation polarised in the same way, while in Einstein's the two polarised components are treated together. This remark applies also to the scattering process.

²⁰ Pauli, "Z. f. Physik," vol. 18, p. 272 (1923).

unit frequency range about the component r . Each component r can be described by a vector potential k_r chosen so as to make the scalar potential zero. The perturbation term to be added to the Hamiltonian will now be, according to the classical theory with neglect of relativity mechanics, $c^{-1}\Sigma_r k_r X_r$, where X_r is the component of the total polarisation of the atom in the direction of k_r , which is the direction of the electric vector of the component r .

We can, as explained in § 1, suppose the field to be described by the canonical variables N_r, Θ_r , of which N_r is the number of quanta of energy of the component r , and Θ_r is its canonically conjugate phase, equal to $2\pi h\nu_r$ times the Θ_r of § 1. We shall now have $k_r = a_r \cos \Theta_r/h$, where a_r is the amplitude of k_r which can be connected with N_r as follows: – The flow of energy per unit area per unit time for the component r is $\frac{1}{2}\pi c^{-1}a_r^2\nu_r^2$. Hence the intensity per unit frequency range of the radiation in the neighbourhood of the component r is $I_r = \frac{1}{2}\pi c^{-1}a_r^2\nu_r^2\sigma_r$. Comparing this with equation (28), we obtain $a_r = 2(h\nu_r/c\sigma_r)^{1/2}$, and hence

$$k_r = 2(h\nu_r/c\sigma_r)^{1/2}N_r^{1/2}\cos\Theta_r/h.$$

The Hamiltonian for the whole system of atom plus radiation would now be, according to the classical theory,

$$F = H_P(J) + \Sigma_r(2\pi h\nu_r)N_r + 2c^{-1}\Sigma_r(h\nu_r/c\sigma_r)^{1/2}\dot{X}_r N_r^{1/2}\cos\Theta_r/h, \quad (29)$$

where $H_P(J)$ is the Hamiltonian for the atom alone. On the quantum theory we must make the variables N_r and Θ_r canonical q -numbers like the variables J_k, ω_k that describe the atom. We must now replace the $N_r^{1/2}\cos\Theta_r/h$ in (29) by the real q -number

$$\frac{1}{2}\left\{N_r^{1/2}e^{i\Theta_r/h} + e^{-i\Theta_r/h}N_r^{1/2}\right\} = \frac{1}{2}\left\{N_r^{1/2}e^{i\Theta_r/h} + (N_r + 1)^{1/2}e^{-i\Theta_r/h}\right\}$$

so that the Hamiltonian (29) becomes

$$F = H_P(J) + \Sigma_r(2\pi h\nu_r)N_r + h^{1/2}c^{-3/2}\Sigma_r(\nu_r/\sigma_r)^{1/2}X_r\left\{N_r^{1/2}e^{i\Theta_r/h} + (N_r + 1)^{1/2}e^{-i\Theta_r/h}\right\}. \quad (30)$$

This is of the form (27), with

$$v_r = v_r^* = h^{1/2}c^{-3/2}(\nu_r/\sigma_r)^{1/2}\dot{X}_r \quad (31)$$

and

$$v_{rs} = 0 \quad (r, s \neq 0).$$

The wave point of view is thus consistent with the light-quantum point of view and gives values for the unknown interaction coefficient v_{rs} in the light-quantum theory. These values are not such as would enable one to express the interaction energy as an algebraic function of canonical variables. Since the wave theory gives $v_{rs} = 0$ for $s \neq 0$, it would seem to show that there are no direct scattering processes, but this may be due to an incompleteness in the present wave theory.

We shall now show that the Hamiltonian (30) leads to the correct expressions for Einstein's A 's and B 's. We must first modify slightly the analysis of § 5 so as to apply to the case when the system has a large number of discrete stationary states instead of a continuous range. Instead of equation (21) we shall now have

$$i\hbar\dot{a}(\alpha') = \sum_{\alpha''} V(\alpha'\alpha'')a(\alpha'').$$

If the system is initially in the state α^0 we must take the initial value of $a(\alpha')$ to be $\delta_{\alpha'\alpha^0}$, which is now correctly normalised. This gives for a first approximation

$$i\hbar\dot{a}(\alpha') = V(\alpha'\alpha^0) = v(\alpha'\alpha^0)e^{i[W(\alpha')-W(\alpha^0)]t/\hbar},$$

which leads to

$$i\hbar a(\alpha') = \delta_{\alpha'\alpha^0} + v(\alpha'\alpha^0) \frac{e^{i[W(\alpha')-W(\alpha^0)]t/\hbar} - 1}{i[W(\alpha') - W(\alpha^0)]/\hbar},$$

corresponding to (22). If, as before, we transform to the variables $W, \gamma_1, \gamma_2 \dots \gamma_{u-1}$, we obtain (when $\gamma' \neq \gamma^0$)

$$a(W'\gamma') = v(W', \gamma'; W^0, \gamma^0)[1 - e^{i(W'-W^0)t/\hbar}]/(W' - W^0).$$

The probability of the system being in a state for which each γ_k equals γ'_k is $\sum_{W'} |a(W'\gamma')|^2$. If the stationary states lie close together and if the time t is not too great, we can replace this sum by the integral $(\Delta W)^{-1} \int |a(W'\gamma')|^2 dW'$, where ΔW is the separation between the energy levels. Evaluating this integral as before, we obtain for the probability per unit time of a transition to a state for which each $\gamma_k = \gamma'_k$

$$2\pi/\hbar \Delta W \cdot |v(W^0, \gamma'; W^0, \gamma^0)|^2. \quad (32)$$

In applying this result we can take the γ 's to be any set of variables that are independent of the total proper energy W and that together with W define a stationary state.

We now return to the problem defined by the Hamiltonian (30) and consider an absorption process in which the atom jumps from the state J^0 to the state J' with the absorption of a light-quantum from state r . We take the variables γ' to be the variables J' of the atom together with variables that define the direction of motion and state of polarisation of the absorbed quantum, but not its energy. The matrix element $v(W^0, \gamma'; W^0, \gamma^0)$ is now

$$h^{1/2} c^{-3/2} (\nu_r / \sigma_r)^{1/2} \dot{X}_r(J^0 J') N_r^0,$$

where $\dot{X}_r(J^0 J')$ is the ordinary $(J^0 J')$ matrix element of \dot{X}_r . Hence from (32) the probability per unit time of the absorption process is

$$\frac{2\pi}{h\Delta W} \cdot \frac{h\nu_r}{c^3\sigma - r} \left| \dot{X}_r(J^0 J') \right|^2 N_r^0.$$

To obtain the probability for the process when the light-quantum comes from any direction in a solid angle $d\omega$ we must multiply this expression by the number of possible directions for the light-quantum in the solid angle $d\omega$ which is $d\omega\sigma_r\Delta W/2\pi h$. This gives

$$d\omega \frac{\nu_r}{hc^3} \left| \dot{X}_r(J^0 J') \right|^2 N_r^0 = d\omega \frac{1}{2\pi h^2 c \nu_r^2} \left| \dot{X}_r(J^0 J') \right|^2 I_r$$

with the help of (28). Hence the probability coefficient for the absorption process is $1/2\pi h^2 c \nu_r^2 \cdot |\dot{X}_r(J^0 J')|^2$ in agreement with the usual value for Einstein's absorption coefficient in the matrix mechanics. The agreement for the emission coefficients may be verified in the same manner.

The present theory, since it gives a proper account of spontaneous emission, must presumably give the effect of radiation reaction on the emitting system, and enable one to calculate the natural breadths of spectral lines, if one can overcome the mathematical difficulties involved in the general solution of the wave problem corresponding to the Hamiltonian (30). Also the theory enables one to understand how it comes about that there is no violation of the law of the conservation of energy when, say, a photo-electron is emitted from an atom under the action of extremely weak incident radiation. The energy of interaction of the atom and the radiation is a q -number that does not commute with the first integrals of the motion of the atom alone or with the intensity of the radiation. Thus one cannot specify this energy by a

c -number at the same time that one specifies the stationary state of the atom and the intensity of the radiation by c -numbers. In particular, one cannot say that the interaction energy tends to zero as the intensity of the incident radiation tends to zero. There is thus always an unspecifiable amount of interaction energy which can supply the energy for the photo-electron.

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Summary.

The problem is treated of an assembly of similar systems satisfying the Einstein-Bose statistical mechanics, which interact with another different system, a Hamiltonian function being obtained to describe the motion. The theory is applied to the interaction of an assembly of light-quanta with an ordinary atom, and it is shown that it gives Einstein's laws for the emission and absorption of radiation.

The interaction of an atom with electromagnetic waves is then considered, and it is shown that if one takes the energies and phases of the waves to be q -numbers satisfying the proper quantum conditions instead of c -numbers, the Hamiltonian function takes the same form as in the light-quantum treatment. The theory leads to the correct expressions for Einstein's A 's and B 's.