On the Theory of Quantum Mechanics.

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§ 1. *Introduction and Summary.*

The new mechanics of the atom introduced by Heisenberg[*] may be based on the assumption that the variables that describe a dynamical system do not obey the commutative law of multiplication, but satisfy instead certain quantum conditions. One can build up a theory without knowing anything about the dynamical variables except the algebraic laws that they are subject to, and can show that they may be represented by matrices whenever a set of uniformising variables for the dynamical system exists.[†] It may be shown, however (see § 3), that there is no set of uniformising variables for a system containing more than one electron, so that the theory cannot progress very far on these lines.

A new development of the theory has recently been given by Schrödinger.[‡] Starting from the idea that an atomic system cannot be represented by a trajectory, *i.e.*, by a point moving through the co-ordinate space, but must be represented by a wave in this space, Schrödinger obtains from a variation principle a differential equation which the wave function ψ must satisfy. This differential equation turns out to be very closely connected with the Hamiltonian equation which specifies the system, namely, if

$$H(q_r, p_r) - W = 0$$

is the Hamiltonian equation of the system, where the q_r, p_r are canonical variables, then the wave equation for ψ is

$$\left\{H\left(q_r, ih\frac{\partial}{\partial q_r}\right) - W\right\}\psi = 0, \tag{1}$$

where h is $(2\pi)^{-1}$ times the usual Planck's constant. Each momentum p_r in H is replaced by the operator $ih\,\partial/\partial q_r$, and is supposed to operate on all that exists on its right-hand side in the term in which it occurs. Schrödinger takes the values of the parameter W for which there exists a ψ satisfying (1) that is

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[*] See various papers by Born, Heisenberg and Jordan, 'Zeits. f. Phys.,' vol. 33 onwards.

[†] 'Roy. Soc. Proc.,' A, vol. 110, p. 561 (1926).

[‡] See various papers in the 'Ann. d. Phys.,' beginning with vol. 79, p. 361 (1926).

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continuous, single-valued and bounded throughout the whole of q-space to be the energy levels of the system, and shows that when the general solution of (1) is known, matrices to represent the p_r and q_r may easily be obtained, satisfying all the conditions that they have to satisfy according to Heisenberg's matrix mechanics, and consistent with the energy levels previously found. The mathematical equivalence of the theories is thus established.

In the present paper, Schrödinger's theory is considered in § 2 from a slightly more general point of view, in which the time t and its conjugate momentum $-W$ are treated from the beginning on the same footing as the other variables. A more general method, requiring only elementary symbolic algebra, of obtaining matrix representations of the dynamical variables is given.

In § 3 the problem is considered of a system containing several similar particles, such as an atom with several electrons. If the positions of two of the electrons are interchanged, the new state of the atom is physically indistinguishable from the original one. In such a case one would expect only symmetrical functions of the co-ordinates of all the electrons to be capable of being represented by matrices. It is found that this allows one to obtain two solutions of the problem satisfying all the necessary conditions, and the theory is incapable of deciding which is the correct one. One of the solutions leads to Pauli's principle that not more than one electron can be in any given orbit, and the other, when applied to the analogous problem of the ideal gas, leads to the Einstein-Bose statistical mechanics.

The effect of an arbitrarily varying perturbation on an atomic system is worked out in § 5 with the help of a new assumption. The theory is applied to the absorption and stimulated emission of radiation by an atom. A generalisation of the description of the phenomena by Einstein's B coefficients is obtained, in which the phases play their proper parts. This method cannot be applied to spontaneous emission.

§ 2. *General Theory.*

According to the new point of view introduced by Schrödinger, we no longer leave unspecified the nature of the dynamical variables that describe an atomic system, but count the q's and t as ordinary mathematical variables (this being permissible since they commute with one another) and take the p's and W to be the differential operators

$$p_r = -ih\frac{\partial}{\partial q_r}, \qquad -\mathrm{W} = -ih\frac{\partial}{\partial t}. \tag{2}$$

Whenever a p_r or W occurs in a term of an equation, it must be considered as meaning the corresponding differential operator operating on all that occurs on its

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right-hand side in the term in question. Thus, by carrying out the operations, one can reduce any function of the p's, q's, W and t to a function of the q's and t only.

The relations (2) require two obvious modifications to be made in the algebra governing the dynamical variables. Firstly, only rational integral functions of the p's and W have a meaning, and, secondly, *one can multiply up an equation by a factor* (*integral in the p's and* W) *on the left-hand side, but one cannot, in general, multiply up by factor on the right-hand side.* Thus, if one is given the equation $a = b$, one can infer from it that $\mathrm{X}a = \mathrm{X}b$, where X is arbitrary, but one cannot in general infer that $a\mathrm{X} = b\mathrm{X}$.

There are, however, certain equations $a = b$ for which it is true that $a\mathrm{X} = b\mathrm{X}$ for any X, and these equations we call identities. The quantum conditions

$$q_r p_s - p_s q_r = ih\delta_{rs}, \qquad p_r p_s - p_s p_r = 0,$$

with the similar relations involving $-\mathrm{W}$ and t, are identities, as it can easily be verified (and has been verified by Schrödinger) that the relations

$$(q_r p_s - p_s q_r)\,\mathrm{X} = ih\delta_{rs}\mathrm{X},$$

etc., hold for any X. These relations form the main justification for the assumptions (2).

If $a = b$ is an identity, we can deduce, since $a\mathrm{X} = b\mathrm{X}$ and $\mathrm{X}a = \mathrm{X}b$, that

$$a\mathrm{X} - \mathrm{X}a = b\mathrm{X} - \mathrm{X}b,$$

or

$$[a, \mathrm{X}] = [b, \mathrm{X}].$$

Thus we can equate the Poisson bracket of either side of an identity with an arbitrary quantity, and so our quantum identity is the analogue of an identity on the classical theory. We assume the general equation $xy - yx = ih[x, y]$ and the equations of motion of a dynamical system to be identities.

A dynamical system is specified by a Hamiltonian equation between the variables

$$\mathrm{H}(q_r, p_r, t) - \mathrm{W} = 0, \tag{3}$$

or more generally

$$\mathrm{F}(q_r, p_r, t, \mathrm{W}) = 0, \tag{4}$$

and the equations of motion are

$$dx/ds = [x, \mathrm{F}],$$

where x is any function of the dynamical variables, and s is a variable which depends on the form in which (4) is written, and, in particular, is just t if (4) is written in the form (3). On the new theory we consider the equation

$$\mathrm{F}\psi = 0, \tag{5}$$

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which, if we take ψ to be a function of the q's and t only, is an ordinary differential equation for ψ. From the general solution of this differential equation the matrices that form the solution of the mechanical problem may be very easily obtained.

Since (5) is linear in ψ, its general solution is of the form

$$\psi = \Sigma c_n \psi_n, \tag{6}$$

where the c_n's are arbitrary constants and the ψ_n's are a set of independent solutions, which may be called eigenfunctions. Only solutions that are continuous, single-valued and bounded throughout the whole domain of the q's and t are recognised by the theory. Instead of a discreet set of eigenfunctions ψ_n there may be a continuous set $\psi(\alpha)$, depending on a parameter α, and satisfying the differential equation for all values of α in a certain range, in which case the sum in (6) must be replaced by an integral $\int c_\alpha \psi(\alpha)\, d\alpha$,* or both a discreet set and a continuous set may occur together. For definiteness, however, we shall write down explicitly only the discreet sum in the following work.

We shall now show that any constant of integration of the dynamical system (either a first integral or a second integral) can be represented by a matrix whose elements are constants, there being one row and column of the matrix corresponding to each eigenfunction ψ_n. Let a be a constant of integration of the system, *i.e.*, a function of the dynamical variables such that $[a, \mathrm{F}] = 0$ identically. We have the relation

$$\mathrm{F}a = a\mathrm{F},$$

which, being an identity, we can multiply by ψ_n on the right-hand side. We thus obtain

$$\mathrm{F}a\psi_n = a\mathrm{F}\psi_n = 0,$$

since $\mathrm{F}\psi_n = 0$ (although not identically). Hence $a\psi_n$ is a solution of the differential equation (5), so that it can be expanded in the form (6), *i.e.*,

$$a\psi_n = \Sigma_m \psi_m a_{mn},$$

where the a_{mn}'s are constants. We take the quantities a_{mn} to be the elements of the matrix that represents a. The matrix rule of multiplication evidently holds, since, if b is another constant of integration of the system, we have

$$ab\psi_n = a\Sigma_m \psi_m b_{mn} = \Sigma_{mk} \psi_k a_{km} b_{mn},$$

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* The general solution may contain quantities, such as ψ_a and $\partial\psi_a/\partial a$, which satisfy the differential equation (5), but which cannot strictly be put in the form $\int c_a \psi_a da$, although they may be regarded as the limits of series of quantities which are of this form.

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and also

$$ab\psi_n = \Sigma_k \psi_k (ab)_{kn},$$

so that

$$(ab)_{kn} = \Sigma_m a_{km} b_{mn}.$$

As an example of a constant of integration of the dynamical system, we may take the value $x(t_0)$ that an arbitrary function x of the p's, q's, W and t has at a specified time $t = t_0$. The matrix that represents $x(t_0)$ will consist of elements each of which is a function of t_0. Writing t for t_0, we see that an arbitrary function of the dynamical variables, $x(t)$, or simply x, can be represented by a matrix whose elements are functions of t only.

The matrix representation we have obtained is not unique, since any set of independent eigenfunctions ψ_n will do. To obtain the matrices of Heisenberg's original quantum mechanics, we must choose the ψ_n's in a particular way. We can always, by a linear transformation, obtain a set of ψ_n's which makes the matrix representing any given constant of integration of the dynamical system a diagonal matrix. Suppose now that the Hamiltonian F does not contain the time explicitly, so that W is a constant of the system, and is the energy, and we choose the ψ_n's so as to make the matrix representing W a diagonal matrix, *i.e.*, so as to make

$$\mathrm{W}\psi_n = \mathrm{W}_n \psi_n, \tag{7}$$

where W_n is a numerical constant. Let x be any function of the dynamical variables *that does not involve the time explicitly*, and put

$$x\psi_n = \Sigma_m x_{mn} \psi_m,$$

where the x_{mn}'s are functions of the time only. We shall now show that the x_{mn}'s are of the form

$$x_{mn} = a_{mn} e^{i(\mathrm{W}_m - \mathrm{W}_n)t/h}, \tag{8}$$

where the a_{mn}'s are constants, as on Heisenberg's theory. We have

$$\begin{aligned} \mathrm{W}x\psi_n &= \Sigma_m \mathrm{W} x_{mn} \psi_m \\ &= \Sigma_m (\mathrm{W}x_{mn} - x_{mn}\mathrm{W})\,\psi_m + \Sigma_m x_{mn} \mathrm{W}\psi_m \\ &= \Sigma_m ih\dot{x}_{mn}\psi_m + \Sigma_m x_{mn} \mathrm{W}_m \psi_m. \end{aligned} \tag{9}$$

Also, since x does not contain t explicitly,

$$\begin{aligned} \mathrm{W}x\psi_n = x\mathrm{W}\psi_n = x\mathrm{W}_n\psi_n &= \mathrm{W}_n x\psi_n \\ &= \mathrm{W}_n \Sigma_m x_{mn} \psi_m. \end{aligned} \tag{10}$$

Equating the coefficients of ψ_m in (9) and (10), we obtain

$$ih\dot{x}_{mn} = x_{mn}(\mathrm{W}_n - \mathrm{W}_m),$$

which shows that x_{mn} is of the form (8).

We have thus shown that with the ψ_n's chosen in this way the matrices satisfy all the conditions of Heisenberg's matrix mechanics, except the condition that the matrices that represent real quantities are Hermitic (*i.e.*, have their *mn* and *nm* elements conjugate imaginaries). There does not seem to be any simple general proof that this is the case, as the proof would have to make use of the fact that the ψ_n's are bounded. It is easy to prove the particular case that the matrix representing W is Hermitic, *i.e.*, that the W_n's are real, since from (7) ψ_n must be of the form

$$\psi_n = u_n e^{-iW_n t/h},$$

where u_n is independent of t, and if W_n contains an imaginary part, ψ_n would not remain bounded as t becomes infinite. In general, the matrices representing real quantities could be Hermitic only if the arbitrary numerical constants by which the ψ_n's may be multiplied are chosen in a particular way.

We may regard an eigenfunction ψ_n as being associated with definite numerical values for some of the constants of integration of the system. Thus, if we find constants of integration $a, b, \ldots$ such that

$$a\psi_n = a_n\psi_n, \qquad b\psi_n = b_n\psi_n, \ldots \tag{11}$$

where $a_n, b_n, \ldots$ are numerical constants, we can say that ψ_n represents a state of the system in which $a, b, \ldots$ have the numerical values $a_n, b_n, \ldots$ (Note that $a, b, \ldots$ must commute for (11) to be possible.) In this way we can have eigenfunctions representing stationary states of an atomic system with definite values for the energy, angular momentum, and other constants of integration.

It should be noticed that the choice of the time t as the variable that occurs in the elements of the matrices representing variable quantities is quite arbitrary, and any function of t and the q's that increases steadily would do. To determine accurately the radiation emitted by the system in the direction of the x-axis, one would have to use $(t - x/c)$ instead of t.* It is probable that the representation of a constant of integration of the system by a matrix of constant elements is more fundamental than the representation of a variable quantity by a matrix whose elements are functions of some variable such as t or $(t - x/c)$. It would appear to be possible to build up an electromagnetic theory in which the potentials of the field at a specified point x_0, y_0, z_0, t_0 in space-time are represented by matrices of constant elements that are functions of x_0, y_0, z_0, t_0.

§ 3. *Systems containing Several Similar Particles.*

In Heisenberg's matrix mechanics it is assumed that the elements of the matrices that represent the dynamical variables determine the frequencies and

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* 'Roy. Soc. Proc.,' A, vol. 111, p. 405 (1926).

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intensities of the components of radiation emitted. The theory thus enables one to calculate just those quantities that are of physical importance, and gives no information about quantities such as orbital frequencies that one can never hope to measure experimentally. We should expect this very satisfactory characteristic to persist in all future developments of the theory.

Consider now a system that contains two or more similar particles, say, for definiteness, an atom with two electrons. Denote by (mn) that state of the atom in which one electron is in an orbit labelled m, and the other in the orbit n. The question arises whether the two states (mn) and (nm), which are physically indistinguishable as they differ only by the interchange of the two electrons, are to be counted as two different states or as only one state, *i.e.*, do they give rise to two rows and columns in the matrices or to only one? If the first alternative is right, then the theory would enable one to calculate the intensities due to the two transitions $(mn) \to (m'n')$ and $(mn) \to (n'm')$ separately, as the amplitude corresponding to either would be given by a definite element in the matrix representing the total polarisation. The two transitions are, however, physically indistinguishable, and only the sum of the intensities for the two together could be determined experimentally. Hence, in order to keep the essential characteristic of the theory that it shall enable one to calculate only observable quantities, one must adopt the second alternative that (mn) and (nm) count as only one state.

This alternative, though, also leads to difficulties. The symmetry between the two electrons requires that the amplitude associated with the transition $(mn) \to (m'n')$ of x_1, a co-ordinate of one of the electrons, shall equal the amplitude associated with the transition $(nm) \to (n'm')$ of x_2, the corresponding co-ordinate of the other electron, *i.e.*,

$$x_1(mn\,;\ m'n') = x_2(nm\,;\ n'm'). \tag{12}$$

If we now count (mn) and (nm) as both defining the same row and column of the matrices, and similarly for $(m'n')$ and $(n'm')$, equation (12) shows that each element of the matrix x_1 equals the corresponding element of the matrix x_2, so that we should have the matrix equation

$$x_1 = x_2.$$

This relation is obviously impossible, as, amongst other things, it is inconsistent with the quantum conditions. We must infer that unsymmetrical functions of the co-ordinates (and momenta) of the two electrons cannot be represented by matrices. Symmetrical functions, such as the total polarisation of the atom, can be considered to be represented by matrices without inconsistency,

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and these matrices are by themselves sufficient to determine all the physical properties of the system.

One consequence of these considerations is that the theory of uniformising variables introduced by the author can no longer apply. This is because, corresponding to any transition $(mn) \rightarrow (m'n')$, there would be a term $e^{i(\alpha w)}$ in the Fourier expansions, and we should require there to be a unique state, $(m''n'')$, say, such that the same term $e^{i(\alpha w)}$ corresponds to the transition $(m'n') \rightarrow (m''n'')$, and $e^{2i(\alpha w)}$ corresponds to $(mn) \rightarrow (m''n'')$. If the m's and n's are quantum numbers, and we take the case of one quantum number per electron for definiteness, we should have to have

$$m'' - m' = m' - m, \qquad n'' - n' = n' - n.$$

Since, however, the state $(m'n')$ may equally well be called the state $(n'm')$, we may equally well take

$$m'' - n' = n' - m, \qquad n'' - m' = m' - n,$$

which would give a different state $(m''n'')$. There is thus no unique state $(m''n'')$ that the theory of uniformising variables demands.

If we neglect the interaction between the two electrons, then we can obtain the eigenfunctions for the whole atom simply by multiplying the eigenfunctions for one electron when it exists alone in the atom by the eigenfunctions for the other electron alone, and taking the same time variable for each.* Thus if $\psi_n(x, y, z, t)$ is the eigenfunction for a single electron in the orbit n, then the eigenfunction for the whole atom in the state (mn) is

$$\psi_m(x_1, y_1, z_1, t)\, \psi_n(x_2, y_2, z_2, t) = \psi_m(1)\, \psi_n(2),$$

say, where x_1, y_1, z_1 and x_2, y_2, z_2 are the co-ordinates of the two electrons, and $\psi(r)$ means $\psi(x_r, y_r, z_r, t)$. The eigenfunction $\psi_m(2)\, \psi_n(1)$, however, also corresponds to the same state of the atom if we count the (mn) and (nm) states as identical. But two independent eigenfunctions must give rise to two rows and columns in the matrices. If we are to have only one row and column in the matrices corresponding to both (mn) and (nm), we must find a set of eigenfunctions ψ_{mn} of the form

$$\psi_{mn} = a_{mn}\psi_m(1)\, \psi_n(2) + b_{mn}\psi_m(2)\, \psi_n(1),$$

where the a_{mn}'s and b_{mn}'s are constants, which set must contain only one ψ_{mn} corresponding to both (mn) and (nm), and must be sufficient to enable one to

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* The same time variable t must be taken in each owing to the fact that we write the Hamiltonian equation for the whole system : $\mathrm{H}(1) + \mathrm{H}(2) - \mathrm{W} = 0$, where $\mathrm{H}(1)$ and $\mathrm{H}(2)$ are the Hamiltonians for the two electrons separately, so that there is a common time t conjugate to minus the total energy W.

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obtain the matrix representing any symmetrical function A of the two electrons. This means the ψ_{mn}'s must be chosen such that A times any chosen ψ_{mn} can be expanded in terms of the chosen ψ_{mn}'s in the form

$$A\psi_{mn} = \Sigma_{m'n'}\psi_{m'n'}A_{m'n',\,mn}, \tag{13}$$

where the $A_{m'n',\,mn}$'s are constants or functions of the time only.

There are two ways of choosing the set of ψ_{mn}'s to satisfy the conditions. We may either take $a_{mn} = b_{mn}$, which makes each ψ_{mn} a symmetrical function of the two electrons, so that the left-hand side of (13) is symmetrical and only symmetrical eigenfunctions will be required for its expansion, or we may take $a_{mn} = -b_{mn}$, which makes ψ_{mn} antisymmetrical, so that the left-hand side of (13) is antisymmetrical and only antisymmetrical eigenfunctions will be required for its expansion. Thus the symmetrical eigenfunctions alone or the antisymmetrical eigenfunctions alone give a complete solution of the problem. The theory at present is incapable of deciding which solution is the correct one. We are able to get complete solutions of the problem which make use of less than the total number of possible eigenfunctions at the expense of being able to represent only symmetrical functions of the two electrons by matrices.

These results may evidently be extended to any number of electrons. For r non-interacting electrons with co-ordinates $x_1, y_1, z_1 \ldots, x_r, y_r, z_r$, the symmetrical eigenfunctions are

$$\Sigma_{\alpha_1\ldots\alpha_r}\psi_{n_1}(\alpha_1)\,\psi_{n_2}(\alpha_2)\ldots\psi_{n_r}(\alpha_r), \tag{14}$$

where $\alpha_1, \alpha_2 \ldots \alpha_r$ are any permutation of the integers $1, 2 \ldots r$, while the antisymmetrical ones may be written in the determinantal form

$$\begin{vmatrix} \psi_{n_1}(1), & \psi_{n_1}(2) & \ldots\ \psi_{n_1}(r) \\ \psi_{n_2}(1), & \psi_{n_2}(2) & \ldots\ \psi_{n_2}(r) \\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot \\ \psi_{n_r}(1), & \psi_{n_r}(2) & \ldots\ \psi_{n_r}(r) \end{vmatrix}. \tag{15}$$

If there is interaction between the electrons, there will still be symmetrical and antisymmetrical eigenfunctions, although they can no longer be put in these simple forms. In any case the symmetrical ones alone or the antisymmetrical ones alone give a complete solution of the problem.

An antisymmetrical eigenfunction vanishes identically when two of the electrons are in the same orbit. This means that in the solution of the problem with antisymmetrical eigenfunctions there can be no stationary states with

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two or more electrons in the same orbit, which is just Pauli's exclusion principle.* The solution with symmetrical eigenfunctions, on the other hand, allows any number of electrons to be in the same orbit, so that this solution cannot be the correct one for the problem of electrons in an atom.†

§ 4. *Theory of the Ideal Gas.*

The results of the preceding section apply to any system containing several similar particles, in particular to an assembly of gas molecules. There will be two solutions of the problem, in one of which the eigenfunctions are symmetrical functions of the co-ordinates of all the molecules, and in the other antisymmetrical.

The wave equation for a single molecule of rest-mass m moving in free space is

$$\{p_x^2 + p_y^2 + p_z^2 - W^2/c^2 + m^2c^2\}\,\psi = 0$$

$$\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{h^2}\right\}\psi = 0,$$

and its solution is of the form

$$\psi_{\alpha_1\alpha_2\alpha_3} = \exp.\, i\,(\alpha_1 x + \alpha_2 y + \alpha_3 z - \mathrm{E}t)/h, \tag{16}$$

where α_1, α_2, α_3 and E are constants satisfying

$$\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - \mathrm{E}^2/c^2 + m^2c^2 = 0.$$

The eigenfunction (16) represents an atom having the momentum components α_1, α_2, α_3 and the energy E.

We must now obtain some restriction on the possible eigenfunctions due to the presence of boundary walls. It is usually assumed that the eigenfunction, or wave function associated with a molecule, vanishes at the boundary, but we should expect to be able to deduce this, if it is true, from the general theory. We assume, as a natural generalisation of the methods of the preceding section, that there must be only just sufficient eigenfunctions for one to be able to represent by a matrix any function of the co-ordinates that has a physical meaning. Suppose for definiteness that each molecule is confined between two boundaries at $x = 0$ and $x = 2\pi$. Then only those functions of x that are defined only for $0 < x < 2\pi$ have a physical meaning and must be capable of being represented by matrices. (This will require fewer eigenfunctions than if every

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* Pauli, 'Zeits. f. Phys.,' vol. 31, p. 765 (1925).

† Prof. Born has informed me that Heisenberg has independently obtained results equivalent to these. (Added in proof)—see Heisenberg, 'Zeit. fur Phys.,' vol. 38, p. 411 (1926).

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function of x had to be capable of being represented by a matrix.) These functions $f(x)$ can always be expanded as Fourier series of the form

$$f(x) = \Sigma_n a_n e^{inx}, \tag{17}$$

where the a_n's are constants and the n's integers. If we choose from the eigenfunctions (16) those for which α_1/h is an integer, then $f(x)$ times any chosen eigenfunction can be expanded as a series in the chosen eigenfunctions whose coefficients are functions of t only, and hence $f(x)$ can be represented by a matrix. Thus these chosen eigenfunctions are sufficient, and are easily seen to be only just sufficient, for the matrix representation of any function of x of the form (17). Instead of choosing those eigenfunctions with integral values for α_1/h, we could equally well take those with α_1/h equal to half an odd integer, or more generally with $\alpha_1/h = n + \varepsilon$, where n is an integer and ε is any real number. The theory is incapable of deciding which are the correct ones. For statistical problems, though, they all lead to the same results.

When y and z are also bounded by $0 < y < 2\pi$, $0 < z < 2\pi$, we find for the number of waves associated with molecules whose energies lie between E and E + dE the value

$$\frac{4\pi}{c^3 h^3}(\mathrm{E}^2 - m^2c^4)^{\frac{1}{2}}\,\mathrm{E}\,d\mathrm{E}.$$

This value is in agreement with the ordinary assumption that the wave function vanishes at the boundary. It reduces, when one neglects relativity mechanics, to the familiar expression

$$\frac{2\pi}{h^3}(2m)^{\frac{3}{2}}\,\mathrm{E}_1^{\frac{1}{2}}d\mathrm{E}_1, \tag{18}$$

where $\mathrm{E}_1 = \mathrm{E} - mc^2$ is the kinetic energy. For an arbitrary volume of gas V the expression must be multiplied by $\mathrm{V}/(2\pi)^3$.

To pass to the eigenfunctions for the assembly of molecules, between which there is assumed to be no interaction, we multiply the eigenfunctions for the separate molecules, and then take either the symmetrical eigenfunctions, of the form (14), or the antisymmetrical ones, of the form (15). We must now make the new assumption that all stationary states of the assembly (each represented by one eigenfunction) have the same *a priori* probability. If now we adopt the solution of the problem that involves symmetrical eigenfunctions, we should find that all values for the number of molecules associated with any wave have the same *a priori* probability, which gives just the Einstein-Bose statistical mechanics.* On the other hand, we should obtain a different

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* Bose, 'Zeits. f. Phys.,' vol. 26, p. 178 (1924); Einstein, 'Sitzungsb. d. Preuss. Ac.,' p. 261 (1924) and p. 3 (1925).

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statistical mechanics if we adopted the solution with antisymmetrical eigenfunctions, as we should then have either 0 or 1 molecule associated with each wave. The solution with symmetrical eigenfunctions must be the correct one when applied to light quanta, since it is known that the Einstein-Bose statistical mechanics leads to Planck's law of black-body radiation. The solution with antisymmetrical eigenfunctions, though, is probably the correct one for gas molecules, since it is known to be the correct one for electrons in an atom, and one would expect molecules to resemble electrons more closely than light-quanta.

We shall now work out, according to well-known principles, the equation of state of the gas on the assumption that the solution with antisymmetrical eigenfunctions is the correct one, so that not more than one molecule can be associated with each wave. Divide the waves into a number of sets such that the waves in each set are associated with molecules of about the same energy. Let A_s be the number of waves in the sth set, and let E_s be the kinetic energy of a molecule associated with one of them. Then the probability of a distribution (or the number of antisymmetrical eigenfunctions corresponding to distributions) in which N_s molecules are associated with waves in the sth set is

$$W = \Pi_s \frac{A_s!}{N_s!\,(A_s - N_s)!},$$

giving for the entropy

$$S = k \log W = k\Sigma_s \{A_s(\log A_s - 1) - N_s(\log N_s - 1) - (A_s - N_s)[\log(A_s - N_s) - 1]\}.$$

This is to be a maximum, so that

$$0 = \delta S = k\Sigma_s\{-\log N_s + \log(A_s - N_s)\}\,\delta N_s$$
$$= k\Sigma_s \log(A_s/N_s - 1)\,.\,\delta N_s,$$

for all variations δN_s that leave the total number of molecules $N = \Sigma_s N_s$ and the total energy $E = \Sigma_s E_s N_s$ unaltered, so that

$$\Sigma_s \delta N_s = 0, \qquad \Sigma_s E_s \delta N_s = 0.$$

We thus obtain

$$\log(A_s/N_s - 1) = \alpha + \beta E_s,$$

where α and β are constants, which gives

$$N_s = \frac{A_s}{e^{\alpha + \beta E_s} + 1}. \tag{19}$$

By making a variation in the total energy E and putting $\delta E/\delta S = T$, the temperature, we readily find that $\beta = 1/kT$, so that (19) becomes

$$N_s = \frac{A_s}{e^{\alpha + E_s/kT} + 1}.$$

This formula gives the distribution in energy of the molecules. On the Einstein-Bose theory the corresponding formula is

$$N_s = \frac{A_s}{e^{\alpha + E_s/kT} - 1}.$$

If the sth set of waves consists of those associated with molecules whose energies lie between E_s and $E_s + dE_s$, we have from (18) [where E_s now means the E_1 of equation (18)],

$$A_s = 2\pi V\,(2m)^{\frac{3}{2}}\,E_s^{\frac{1}{2}}\,dE_s/(2\pi h)^3,$$

where V is the volume of the gas. This gives

$$N = \Sigma N_s = \frac{2\pi V\,(2m)^{\frac{3}{2}}}{(2\pi h)^3}\int_0^\infty \frac{E_s^{\frac{1}{2}}dE_s}{e^{\alpha + E_s/kT} + 1}$$

and

$$E = \Sigma E_s N_s = \frac{2\pi V\,(2m)^{\frac{3}{2}}}{(2\pi h)^3}\int_0^\infty \frac{E_s^{\frac{3}{2}}dE_s}{e^{\alpha + E_s/kT} + 1}.$$

By eliminating α from these two equations and using the formula $PV = \frac{2}{3}E$, where P is the pressure, which holds for any statistical mechanics, the equation of state may be obtained.

The saturation phenomenon of the Einstein-Bose theory does not occur in the present theory. The specific heat can easily be shown to tend steadily to zero as $T \to 0$, instead of first increasing until the saturation point is reached and then decreasing, as in the Einstein-Bose theory.

§ 5. *Theory of Arbitrary Perturbations.*

In this section we shall consider the problem of an atomic system subjected to a perturbation from outside (*e.g.*, an incident electromagnetic field) which can vary with the time in an arbitrary manner. Let the wave equation for the undisturbed system be

$$(H - W)\psi = 0, \tag{20}$$

where H is a function of the p's and q's only. Its general solution is of the form

$$\psi = \Sigma_n c_n \psi_n, \tag{21}$$

where the c_n's are constants. We shall suppose the ψ_n's to be chosen so that one is associated with each stationary state of the atom, and to be multiplied

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by the proper constants to make the matrices that represent real quantities Hermitic.

Now suppose a perturbation to be applied, beginning at the time $t = 0$. The wave equation for the disturbed system will be of the form

$$(\mathrm{H} - \mathrm{W} + \mathrm{A})\,\psi = 0, \tag{22}$$

where A is a function of the p's, q's and t, and is real. It will be shown that we can obtain a solution of this equation of the form

$$\psi = \Sigma_n a_n \psi_n, \tag{23}$$

where the a_n's are functions of t only, which may have the arbitrary values c_n at the time $t = 0$. We shall consider the general solution (21) of equation (20) to represent an assembly of the undisturbed atoms in which $|c_n|^2$ is the number of atoms in the nth state, and shall assume that (23) represents in the same way an assembly of the disturbed atoms, $|a_n(t)|^2$ being the number in the nth state at any time t. We take $|a_n|^2$ instead of any other function of a_n because, as will be shown later, this makes the total number of atoms remain constant.

The condition that ψ defined by equation (23) shall satisfy equation (22) is

$$\begin{aligned} 0 &= \Sigma_n (\mathrm{H} - \mathrm{W} + \mathrm{A})\, a_n \psi_n \\ &= \Sigma_n a_n (\mathrm{H} - \mathrm{W} + \mathrm{A})\, \psi_n - ih\Sigma_n \dot{a}_n \psi_n, \end{aligned} \tag{24}$$

since H and A commute with a_n,† while $\mathrm{W}a_n - a_n\mathrm{W} = ih\dot{a}_n$ identically. Suppose $\mathrm{A}\psi_n$ to be expanded in the form

$$\mathrm{A}\psi_n = \Sigma_m \mathrm{A}_{mn} \psi_m,$$

where the coefficients A_{mn} are functions of t only, and satisfy $\mathrm{A}_{mn}{}^* = \mathrm{A}_{nm}$, where the * denotes the conjugate imaginary. Equation (24) now becomes, since $(\mathrm{H} - \mathrm{W})\,\psi_n = 0$,

$$\Sigma_{mn} a_n \mathrm{A}_{mn} \psi_m - ih\Sigma_m \dot{a}_m \psi_m = 0.$$

Taking out the coefficient of ψ_m, we find

$$ih\dot{a}_m = \Sigma_n a_n \mathrm{A}_{mn}, \tag{25}$$

which is a simple differential equation showing how the a_m's vary with the time.

Taking conjugate imaginaries, we find

$$-ih\dot{a}_m{}^* = \Sigma_n a_n{}^* \mathrm{A}_{mn}{}^* = \Sigma_n a_n{}^* \mathrm{A}_{nm}.$$

Hence, if $\mathrm{N}_m = a_m a_m{}^*$ is the number of atoms in the mth state, we have

$$\begin{aligned} ih\dot{\mathrm{N}}_m &= ih\,(\dot{a}_m a_m{}^* + \dot{a}_m{}^* a_m) \\ &= \Sigma_n\,(a_n \mathrm{A}_{mn} a_m{}^* - a_n{}^* \mathrm{A}_{nm} a_m). \end{aligned}$$

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† The statement a commutes with b means $ab = ba$ identically.

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This gives

$$ih\Sigma_m \dot{N}_m = \Sigma_{nm} (a_m{}^* A_{mn} a_n - a_n{}^* A_{nm} a_m) = 0,$$

as required.

If the perturbation consists of incident electromagnetic radiation moving in the direction of the x-axis and plane polarised with its electric vector in the direction of the y-axis, the perturbing term A in the Hamiltonian is, with neglect of relativity mechanics, $\kappa/c \,.\, \dot{\eta}$,† where η is the total polarisation in the direction of the y-axis and O, κ, O, O are the components of the potential of the incident radiation. We can expand $\eta\psi_n$ and $\dot{\eta}\psi_n$ in the form

$$\eta\psi_n = \Sigma_m \eta_{mn} e^{i(W_m - W_n)t/h} \psi_m,$$

$$\dot{\eta}\psi_n = \Sigma_m \dot{\eta}_{mn} e^{i(W_m - W_n)t/h} \psi_m,$$

where the η_{mn}'s and $\dot{\eta}_{mn}$'s are constants, and $\dot{\eta}_{mn} = i(W_m - W_n)/h \,.\, \eta_{mn}$. Our previous A_{mn} is now $\kappa/c \,.\, \dot{\eta}_{mn} e^{i(W_m - W_n)t/h}$, and equation (25) becomes

$$ihc\dot{a}_m = \Sigma_n a_n \kappa \dot{\eta}_{mn} e^{i(W_m - W_n)t/h}. \tag{26}$$

We can integrate this equation to the first order in κ by replacing the a_n's on the right-hand side by their values c_n at the time $t = 0$. This gives

$$a_m = c_m + 1/ihc \,.\, \Sigma_n c_n \dot{\eta}_{mn} \int_0^t \kappa(s)\, e^{i(W_m - W_n)s/h}\, ds. \tag{27}$$

To obtain a second approximation, we write for the a_n's on the right-hand side of (26) their values given by (27). We thus find for the value of a_m at the time T,

$$\begin{aligned} a_m = c_m &+ 1/ihc \,.\, \Sigma_n c_n \dot{\eta}_{mn} \int_0^T \kappa(t)\, e^{i(W_m - W_n)t/h}\, dt \\ &- 1/h^2c^2 \,.\, \Sigma_{nk} c_k \dot{\eta}_{nk} \dot{\eta}_{mn} \int_0^T \kappa(t)\, e^{i(W_m - W_n)t/h}\, dt \int_0^t \kappa(s)\, e^{i(W_n - W_k)s/h}\, ds \qquad (28) \\ = c_m &+ c_m{}' + c_m{}'', \end{aligned}$$

say, where $c_m{}'$ and $c_m{}''$ denote the first- and second-order terms respectively.

This gives for the number of atoms in the state m at the time T

$$N_m = a_m a_m{}^* = c_m c_m{}^* + c_m{}' c_m{}^* + c_m c_m{}'^* + c_m{}' c_m{}'^* + c_m{}'' c_m{}^* + c_m c_m{}''^*.$$

If we wish to obtain effects that are independent of the initial phases of the atoms, we must substitute $c_m \exp.\, i\gamma_m$ for c_m and average over all values of γ_m

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† We have neglected a term involving κ^2. This approximation is legitimate, even though we later evaluate the number of transitions that occur in a time T to the order κ^2, provided T is large compared with the periods of the atom.

from 0 to 2π. This makes the first-order terms in N_m, namely, $c_m' c_m{}^*$ and $c_m c_m{}'^*$, vanish, while the second-order terms give

$$1/h^2c^2 \,.\, \Sigma_n c_n c_n{}^* \dot{\eta}_{mn} \dot{\eta}_{mn}{}^* \int_0^T \kappa(t)\, e^{i(W_m - W_n)t/h}\, dt \,.\, \int_0^T \kappa(t)\, e^{-i(W_m - W_n)t/h}\, dt$$

$$-1/h^2c^2 \,.\, \Sigma_n c_m c_m{}^* \dot{\eta}_{nm} \dot{\eta}_{mn} \int_0^T \kappa(t)\, e^{i(W_m - W_n)t/h}\, dt \int_0^t \kappa(s)\, e^{i(W_n - W_m)s/h}\, ds$$

$$-1/h^2c^2 \,.\, \Sigma_n c_m c_m{}^* \dot{\eta}_{nm}{}^* \dot{\eta}_{mn}{}^* \int_0^T \kappa(t)\, e^{-i(W_m - W_n)t/h}\, dt \int_0^t \kappa(s)\, e^{i(W_m - W_n)s/h}\, ds,$$

which reduces to

$$1/h^2c^2 \,.\, \Sigma_n \{ |c_n|^2 - |c_m|^2 \} |\dot{\eta}_{nm}|^2 \left| \int_0^T \kappa(t)\, e^{i(W_m - W_n)t/h}\, dt \right|^2. \qquad (29)$$

This gives ΔN_m, the increase in the number of atoms in the state m from the time $t = 0$ to the time $t = T$. The term in the summation that has the suffix n may be regarded as due to transitions between the state m and the state n.

If we resolve the radiation from the time $t = 0$ to the time $t = T$ into its harmonic components, we find for the intensity of frequency ν per unit frequency range the value

$$I_\nu = 2\pi\nu^2 c^{-1} \left| \int_0^T \kappa(t)\, e^{2\pi i\nu t}\, dt \right|^2.$$

Hence the term in expression (29) for ΔN_m due to transitions between state m and state n may be written

$$1/2\pi h^2 \nu^2 c \,.\, \{ |c_n|^2 - |c_m|^2 \} |\dot{\eta}_{nm}|^2 I_\nu,$$

where

$$2\pi\nu = (W_m - W_n)/h,$$

or

$$2\pi/h^2 c \,.\, \{ |c_n|^2 - |c_m|^2 \} |\eta_{nm}|^2 I_\nu.$$

If one averages over all directions and states of polarisation of the incident radiation, this becomes

$$2\pi/3h^2 c \,.\, \{ |c_n|^2 - |c_m|^2 \} |P_{nm}|^2 I_\nu,$$

where

$$|P_{nm}|^2 = |\xi_{nm}|^2 + |\eta_{nm}|^2 + |\zeta_{nm}|^2,$$

ξ, η and ζ being the three components of total polarisation. Thus one can say that the radiation has caused $2\pi/3h^2c \,.\, |c_n|^2 |P_{nm}|^2 I_\nu$ transitions from state n to state m, and $2\pi/3h^2c \,.\, |c_m|^2 |P_{nm}|^2 I_\nu$ transitions from state m to state n, the probability coefficient for either process being

$$B_{n \to m} = B_{m \to n} = 2\pi/3h^2 c \,.\, |P_{nm}|^2,$$

in agreement with the ordinary Einstein theory.

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The present theory thus accounts for the absorption and stimulated emission of radiation, and shows that the elements of the matrices representing the total polarisation determine the transition probabilities. One cannot take spontaneous emission into account without a more elaborate theory involving the positions of the various atoms and the interference of their individual emissions, as the effects will depend upon whether the atoms are distributed at random, or arranged in a crystal lattice, or all confined in a volume small compared with a wave-length. The last alternative mentioned, which is of no practical interest, appears to be the simplest theoretically.

It should be observed that we get the simple Einstein results only because we have averaged over all initial phases of the atoms. The following argument shows, however, that the initial phases are of real physical importance, and that in consequence the Einstein coefficients are inadequate to describe the phenomena except in special cases. If initially all the atoms are in the normal state, then it is easily seen that the expression (29) for ΔN_m holds without the averaging process, so that in this case the Einstein coefficients are adequate. If we now consider the case when some of the atoms are initially in an excited state, we may suppose that they were brought into this state by radiation incident on the atoms before the time $t = 0$. The effect of the subsequent incident radiation must then depend on its phase relationships with the earlier incident radiation, since a correct way of treating the problem would be to resolve both incident radiations into a single Fourier integral. If we do not wish the earlier radiation to appear explicitly in the calculation, we must suppose that it impresses certain phases on the atoms it excites, and that these phases are important for determining the effect of the subsequent radiation. It would thus not be permissible to average over these phases, but one would have to work directly from equation (28).

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