Four Lectures on Wave Mechanics

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Wave Mechanics

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*Dedicated
to the memory of
Fritz Hasenöhrl*

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FIRST LECTURE

1. Derivation of the fundamental idea of wave mechanics from Hamilton's analogy between ordinary mechanics and geometrical optics.

When a *mass-point m* moves in a conservative field of force, described by the potential energy $V(x, y, z)$, then, if you let it start from a given point A with a given velocity, i.e. with a given energy E, you will be able to get it into another arbitrarily chosen point B by suitably "aiming", i.e. by letting it start in a quite definitely chosen *direction*. There is in general *one* definite dynamical orbit which leads from A to B *with a given energy*. This orbit possesses the property that

$$\delta \int_A^B 2T\,dt = 0, \qquad \cdot \quad \cdot \quad \cdot \quad (1)$$

and is defined by this property (Hamilton's principle in the form given to it by Maupertuis). Here T means the

kinetic energy of the mass-point, and the equation means: consider the manifold of *all* orbits leading from A to B and subject to the law of conservation of energy $(T + V = E)$; among them the actual dynamical orbit is distinguished by the fact that, *for it* and for all infinitely adjacent orbits of the manifold, the $\int_A^B$ has the *same* value up to small quantities of the *second* order (the words "infinitely adjacent" being taken to define the *first* order of smallness). Calling $w = \dfrac{ds}{dt}$ the velocity of the mass-point, we have

$$2T = mw^2 = m\left(\frac{ds}{dt}\right)^2 = 2(E - V) = \frac{ds}{dt}\sqrt{2m(E - V)},$$

by means of which equation (1) can be transformed into

$$\delta \int_A^B \sqrt{2m(E - V)}\, ds = 0. \qquad . \quad . \quad (2)$$

This form has the advantage that the variational principle is applied to a purely geometrical integral, which does not contain the time-variable, and further, that the condition of constant energy is automatically taken care of.

Hamilton found it useful to compare equation (2) with *Fermat's* principle, which tells us that in an optically non-homogeneous medium the actual light rays, i.e. the tracks along which energy is propagated, are determined by the "law of minimum time" (as it is usually called). Let fig. 1 *now* refer to an optical medium of arbitrary non-homogeneity, e.g. the earth's atmosphere; then, if you have a searchlight at A, furnishing a well-defined beam, it will in general be possible to illuminate an arbitrarily chosen point B by suitably *aiming* at it with the searchlight. There is one definite light-path leading

from A to B, which obeys, and is uniquely defined by, the law

$$\delta \int_A^B \frac{ds}{u} = 0. \quad \cdots \quad (3)$$

Here ds, as before, means the element of the path, and u is the velocity of light, a function of the co-ordinates x, y, z.

The two laws contained in equations (2) and (3) respectively become *identical*, if we postulate that

$$u = \frac{C}{\sqrt{2m(E-V)}}, \quad \cdots \quad (4)$$

where C must be independent of x, y, z but may depend on E. Thus we have made a mental picture of an optical medium, in which the manifold of possible light-rays coincides with the manifold of dynamical orbits of a mass-point m moving *with given energy E* in a field of force $V(x, y, z)$. The fact that u, the velocity of light, depends not only on the co-ordinates but also on E, the total energy of the mass-point, is of the utmost importance.

This fact enables us to push the analogy a step farther by picturing the dependence on E as dispersion, i.e. as a dependence on *frequency*. For this purpose we must attribute to our light-rays a definite frequency ν, depending on E. We will (arbitrarily) put

$$E = h\nu \quad \cdots \quad (5)$$

(h being Planck's constant), without dwelling much on this assumption, which is very suggestive to modern physicists. Then this non-homogeneous and dispersive medium provides in its *rays* a picture of *all* the dynamical orbits of our particle. Now we can proceed a stage farther, putting the question: can we make a small

" point-like " *light-signal* move *exactly* like our mass-point? (Hitherto we have only secured the geometrical identity of *orbits*, quite neglecting the question of time-rate.) At first sight this seems impossible, since the velocity of the mass-point,

$$w = \frac{1}{m}\sqrt{2m(E-V)}, \quad \dots \quad (6)$$

is (along the path, i.e. with constant E) *inversely* proportional to the light-velocity u (see equation (4); C depends on E only). But we must remember that u is of course the ordinary *phase*-velocity, whereas a small light-signal moves with the so-called *group*-velocity, say g, which is given by

$$\frac{1}{g} = \frac{d}{d\nu}\left(\frac{\nu}{u}\right),$$

or, in our case, following equation (5), by

$$\frac{1}{g} = \frac{d}{dE}\left(\frac{E}{u}\right). \quad \dots \quad (7)$$

We will try to make $g = w$. The only means we have at our disposal for this purpose is a suitable choice of C, the arbitrary function of E that appeared in equation (4). From (4), (6), and (7), the postulate $g = w$ becomes

$$\frac{d}{dE}\left(\frac{E\sqrt{2m(E-V)}}{C}\right)$$
$$= \frac{m}{\sqrt{2m(E-V)}} \equiv \frac{d}{dE}\left(\sqrt{2m(E-V)}\right);$$

hence

$$\left(\frac{E}{C}-1\right)\sqrt{2m(E-V)}$$

is constant with respect to E. Since V contains the co-ordinates and C must be a function of E only, this

relation can obviously be secured in a general way only by making the first factor vanish. Hence

$$\frac{E}{C} - 1 = 0, \quad \text{or} \quad C = E,$$

which gives equation (4) the special form

$$u = \frac{E}{\sqrt{2m(E - V)}}. \quad \cdots \quad (8)$$

This assumption about phase-velocity is the only one which will secure absolute coincidence between the dynamical laws of motion of the mass-point and the optical laws of motion of light-signals in our imagined light-propagation. It is worth while mentioning that, according to (8),

$$u = \frac{\text{energy}}{\text{momentum}}. \quad \cdots \quad (8')$$

There is still *one* arbitrariness in the definition of u, viz.: E may obviously be changed by an arbitrary additive constant, if the same constant is added to $V(x, y, z)$. This arbitrariness cannot be overcome in the non-relativistic treatment and we are not going to deal with the relativistic one in the present lectures.

Now the fundamental idea of wave-mechanics is the following. The phenomenon, of which we believed we had given an adequate description in the old mechanics by describing the motion of a mass-point, i.e. by giving its co-ordinates x, y, z as functions of the time variable t, is to be described correctly—according to the new ideas—by describing a definite wave-motion, which takes place among waves of the type considered, i.e. of the definite frequency and velocity (and hence of the definite wave-length) which we ascribed to what we called " light " in

the preceding. The mathematical description of a wave-motion will be furnished not by a limited number of functions of the one variable t, but by a continuous manifold, so to speak, of such functions, viz. by a function (or possibly by several functions) of x, y, z, and t. These functions will be subject to a *partial* differential equation, viz. to some sort of *wave equation*.

The statement that what *really* happens is correctly described by describing a wave-motion does not necessarily mean exactly the same thing as: what really *exists* is the wave-motion. We shall see later on that in generalizing to an *arbitrary* mechanical system we are led to describe what really happens in such a system by a wave-motion in the generalized space of its co-ordinates (q-space). Though the latter has quite a definite physical meaning, it cannot very well be said to " exist "; hence a wave-motion in this space cannot be said to " exist " in the ordinary sense of the word either. It is merely an adequate mathematical description of what happens. It may be that also in the case of one single mass-point, with which we are now dealing, the wave-motion must not be taken to " exist " in *too* literal a sense, although the configuration space happens to coincide with ordinary space in this particularly simple case.

2. Ordinary mechanics only an approximation, which no longer holds for very small systems.

In replacing the ordinary mechanical description by a wave-mechanical description our object is to obtain a theory which comprises both ordinary mechanical phenomena, in which quantum conditions play no appreciable part, and, on the other hand, typical quantum phenomena. The hope of reaching this object resides in the following

analogy. Hamilton's wave-picture, worked out in the way discussed above, contains *something* that corresponds to ordinary mechanics, viz. the *rays* correspond to the mechanical *paths*, and *signals* move like *mass-points*. But the description of a wave-motion in terms of *rays* is merely an approximation (called " geometrical optics " in the case of light-waves). It only holds if the structure of the wave phenomenon that we happen to be dealing with is coarse compared with the wave-length, and as long as we are only interested in its " coarse structure ". The detailed fine structure of a wave phenomenon can never be revealed by a treatment in terms of rays (" geometrical optics "), and there always exist wave-phenomena which are altogether so minute that the ray-method is of no use and furnishes no information whatever. Hence in replacing ordinary mechanics by wave mechanics we may hope on the one hand to retain ordinary mechanics as an approximation which is valid for the coarse " macro-mechanical " phenomena, and on the other hand to get an explanation of those minute " micro-mechanical " phenomena (motion of the electrons in the atom), about which ordinary mechanics was quite unable to give any information. At least it was unable to do so without making very artificial accessory assumptions, which really formed a much more important part of the theory than the mechanical treatment itself.*

* To give an example: the actual application of the rules for quantization to the several-electron problem was, strange to say, not hindered by the fact that nobody in the world ever knew how to *enunciate* them for a non-conditionally periodic system! We simply *took* the problem of several bodies to be conditionally periodic, though it was perfectly well known that it was not. This shows, I think, that ordinary mechanics was not made use of in a very serious manner, otherwise the said application would have been as impossible as the application of penal law to the motion of the planets.

The step which leads from ordinary mechanics to wave mechanics is an advance similar in kind to Huygens' theory of light, which replaced Newton's theory. We might form the symbolic proportion:

Ordinary mechanics : Wave mechanics
= Geometrical optics : Undulatory optics.

Typical quantum phenomena are analogous to typical wave phenomena like diffraction and interference.

For the conception of this analogy it is of considerable importance that the failure of ordinary mechanics does occur in dealing with very *tiny* systems. We can immediately control the order of magnitude at which a complete failure is to be expected, and we shall find that it is exactly the right one. The wave-length, say λ, of our waves is (see equations (5) and (8))

$$\lambda = \frac{u}{\nu} = \frac{h}{\sqrt{2m(E-V)}} = \frac{h}{mw}, \quad . \quad . \quad (9)$$

i.e. Planck's constant divided by the momentum of the mass-point. Now take, for the sake of simplicity, a circular orbit of the hydrogen-model, of radius a, but not necessarily a " quantized " one. Then we have by ordinary mechanics (without applying quantum rules):

$$mwa = n\frac{h}{2\pi},$$

where n is any real positive number (which for Bohr's quantized circles would be 1, 2, 3 . . .; the occurrence of h in the latter equation is for the moment only a convenient way of expressing the order of magnitude). Combining the last two equations, we get

$$\frac{\lambda}{a} = \frac{2\pi}{n}.$$

Now in order that we may be justified in the application of ordinary mechanics it is necessary that the dimensions of the path calculated in this way should turn out to be large compared with the wave-length. This is seen to be the case as long as the " quantum number " n is large compared with unity. As n becomes smaller and smaller, the ratio of λ to a becomes less and less favourable. A complete failure of ordinary mechanics is to be expected precisely in the region where we actually meet with it, viz. where n is of the order of unity, as it would be for orbits of the normal size of an atom (10^{-8} cm.).

3. Bohr's stationary energy-levels derived as the frequencies of proper vibrations of the waves.

Let us now consider the wave-mechanical treatment of a case which is inaccessible to ordinary mechanics; say, to fix our ideas, the wave-mechanical treatment of what in ordinary mechanics is called the motion of the electron in the hydrogen atom.

In what way are we to attack this problem?

Well, in very much the same way as we would attack the problem of finding the possible movements (vibrations) of an elastic body. Only, in the latter case the problem is complicated by the existence of *two* types of waves, longitudinal and transverse. To avoid this complication, let us consider an elastic fluid contained in a given enclosure. For the pressure, p, say, we should have a wave equation

$$\nabla^2 p - \frac{1}{u^2}\ddot{p} = 0, \quad \ldots \quad (10)$$

u being the *constant* velocity of propagation of longitudinal waves, the only waves possible in the case of a

fluid. We should have to try to find the most general solution of this partial differential equation that satisfies certain boundary conditions at the surface of the vessel. The standard way of solving is to try

$$p(x, y, z, t) = \psi(x, y, z) e^{2\pi i \nu t},$$

which gives for ψ the equation

$$\nabla^2 \psi + \frac{4\pi^2 \nu^2}{u^2} \psi = 0, \quad \cdot \quad \cdot \quad \cdot \quad (10')$$

ψ being subject to the same boundary conditions as p. We then meet with the well-known fact that a regular solution ψ satisfying the equation and the boundary conditions cannot be obtained for *all* values of the co-efficient of ψ, i.e. for *all* frequencies ν, but only for an infinite set of discrete frequencies $\nu_1, \nu_2, \nu_3, \ldots, \nu_k, \ldots$, which are called the characteristic or proper frequencies (*Eigenfrequenzen*) of the problem or of the body. Call ψ_k the solution (ordinarily unique apart from a multi-plying constant) that belongs to ν_k, then—since the equation and the boundary conditions are homogeneous—

$$p = \sum_k c_k \psi_k e^{2\pi i (\nu_k t + \theta_k)} \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

will, with arbitrary constants c_k, θ_k, be a more general solution and will indeed be *the* general solution, if the set of quantities (ψ_k, ν_k) is complete. (For physical applications we shall of course have to use the real part of the expression (11).)

In the case of the waves which are to replace in our thought the motion of the electron, there must also be some quantity p, subject to a wave equation like equation (10), though we cannot yet tell the physical meaning of p. Let us put this question aside for the moment.

In equation (10) we shall have to put (see above)

$$u = \frac{E}{\sqrt{2m(E - V)}} . \quad . \quad . \quad . \quad . \quad (8)$$

This is not a constant; it depends (1) on E, that is, essentially on the frequency ν ($= E/h$); (2) on the co-ordinates x, y, z, which are contained in the potential energy V. These are the two complications as compared with the simple case of a vibrating fluid body considered above. Neither of them is serious. By the first, the dependence on E, we are restricted in that we can apply the wave equation only to a function p whose dependence on the time is given by

$$p \sim e^{\frac{2\pi i E t}{h}},$$

whence
$$\ddot{p} = -\frac{4\pi^2 E^2}{h^2} p. \quad . \quad . \quad . \quad (12)$$

We need not mind that, since it is precisely the same assumption (*Ansatz*) as would be made in any case in the standard method of solution. Substituting from (12) and (8) in (10) and replacing the letter p by ψ (to remind us that now, just as before, we are investigating a function of the co-ordinates only), we obtain

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0. \quad . \quad . \quad (13)$$

We now see that the *second* complication (the dependence of u on V, i.e. on the co-ordinates) merely results in a somewhat more interesting form of equation (13) as compared with (10'), the quantity multiplying ψ being no longer a *constant*, but depending on the co-ordinates. This was really to be expected, since an equation that is to embody the mechanical problem cannot very well help

containing the potential energy of the problem. A simplification in the problem of the " mechanical " waves (as compared with the fluid problem) consists in the absence of boundary conditions.

I thought the latter simplification fatal when I first attacked these questions. Being insufficiently versed in mathematics, I could not imagine how proper vibration frequencies could appear *without* boundary conditions. Later on I recognized that the more complicated form of the coefficients (i.e. the appearance of $V(x, y, z)$) takes charge, so to speak, of what is ordinarily brought about by boundary conditions, namely, the selection of definite values of E.

I cannot enter into this rather lengthy mathematical discussion here, nor into the detailed process of finding the solutions, though the method is practically the same as in ordinary vibration problems, namely: introducing an appropriate set of co-ordinates (e.g. spherical or elliptical, according to the form of the function V) and putting ψ equal to a *product* of functions, each of which contains one co-ordinate only. I will state the result straightforwardly for the case of the hydrogen atom. Here we have to put

$$V = -\frac{e^2}{r} + \text{const.,} \qquad . \quad . \quad . \quad (14)$$

r being the distance from the nucleus. Then it is found that not for all, but only for the following values of E, is it possible to find regular, one-valued, and finite solutions ψ:

(A) $E_n = \text{const.} - \dfrac{2\pi^2 m e^4}{h^2 n^2}$; $n = 1, 2, 3, 4 \ldots$

(B) $E > \text{const.}$

$\left.\begin{array}{}\\ \\\end{array}\right\}$ (14′)

The constant is the same as in (14) and is (in non-relativistic wave mechanics) meaningless, except that we cannot very well give it the value which is usually adopted for the sake of simplicity, viz. zero. For then all the values (A) would become negative. And a negative frequency, if it means anything at all, means the same as the positive frequency of the same absolute value. Then it would be mysterious why all positive frequencies should be allowed, but only a discrete set of negative ones. But the question of this constant is of no importance here.

You see that our differential equation automatically selects as the allowed E-values (A) the energy-levels of the elliptic orbits quantized according to Bohr's theory; (B) all energy-levels belonging to hyperbolic orbits. This is very remarkable. It shows that, whatever the waves may mean physically, the theory furnishes a method of quantization which is absolutely free from arbitrary postulates that this or that quantity must be an integer. Just to give an idea *how* the integers occur here: if e.g. ϕ is an azimuthal angle and the wave amplitude turns out to contain a factor $\cos m\phi$, m being an arbitrary constant, then m must *necessarily* be chosen integral, since otherwise the wave function would not be *single-valued*.

You will be interested in the form of the wave functions ψ which belong to the E-values mentioned above, and will inquire whether any observable facts can be explained by them. This *is* the case, but the matter is rather intricate.

SECOND LECTURE

4. Rough description of the wave-systems in the hydrogen atom. Degeneracy. Perturbation.

The chief property of the amplitude functions is that those which belong to the discrete set of values E_n (" elliptic orbits ") fall off very rapidly with the distance from the nucleus, viz. like an exponential $e^{-\text{const.}\, r}$, which practically restricts them to a region of precisely the same order of magnitude as the corresponding Bohr orbit. The others, which belong to hyperbolic levels, fall off much less rapidly, viz. only like r^{-1}.

The detailed behaviour of the " elliptic " functions within the said region cannot very well be described in a unique way, for the following reason. To *one* value E_n there belongs in general not only one, but precisely n^2 independent solutions of the wave equation. From the mathematical point of view this is an exception due to the particular form of the potential energy V, especially to its spherical symmetry. This multiplicity of solutions belonging to one proper value corresponds to the well-known multiplicity of orbits belonging to the same energy-level in Bohr's theory. It is there called " degeneracy ", and we will keep this expression in wave mechanics also. Now, since the equation is linear and homogeneous, any linear aggregate with quite arbitrary coefficients will also be a solution belonging to *the same*

proper value. It is well known that in such a case no set of solutions is in any way distinguished from any other set, derived from the first by forming a set of independent linear aggregates, equal in number to the first set. By this process of forming linear aggregates we can reach solutions which exhibit a very different behaviour. To give an example: from a set of solutions whose node-surfaces are (1) concentric spheres, (2) co-axial cones, (3) planes passing through the cone-axis, you can form other solutions, in which the concentric spheres and the co-axial cones are replaced by two sets of confocal para-boloids. This is only one of the simplest cases. In general, taking arbitrary coefficients, the system of node-surfaces will be *much* more complicated.

This multiplicity of solutions, or, as is often said, of the proper values (which, by the way, is well known from ordinary vibration problems), is of the utmost importance in the case of the atom. If there is no multi-plicity (e.g. for the lowest frequency, $n = 1$), then a slight alteration of the potential energy V, corresponding e.g. to the application of a weak external electric field, will cause nothing but a slight displacement of the proper value and a slight alteration of the proper solution—just as a small piece of metal attached to a tuning fork would slightly alter its pitch and its form of vibration. But a multiple (say a-fold) proper value shows its actual multi-plicity in this case in that it splits up into a slightly different proper values; every one of them has now a quite definite proper function, which differs very little from a quite definite linear aggregate of the proper functions that belonged to the multiple value. This splitting up may, theoretically, be caused by the very slightest disturbance, yet may differ widely for two

disturbances that are different in character. For instance, a homogeneous electric field produces the parabolic node-surfaces mentioned before, whereas a magnetic field produces the spheres and cones.

It need hardly be said that this splitting up corresponds in the two cases just mentioned to the splitting up of the hydrogen lines in the Zeeman and Stark effects. The displacement of the lines is quantitatively described by the new theory just as it was by the older one. But something more is described, which was inaccessible to the older theory, namely, the state of *polarization* of the lines, their *intensities*, and, in particular, the *absence* of a lot of lines which we should expect to appear if we took into account *all* the possible differences of the split energy levels. We shall see this presently.

5. The physical meaning of the wave function. Explanation of the selection rules and of the rules for the polarization of spectral lines.

The high importance of the perturbation effects consists in the fact that as soon as the degeneracy is removed we have to deal with uniquely defined proper functions ψ_k and can now more easily test any hypothesis about the physical meaning of the quantity called ψ.

Let us call
$$E_k = h\nu_k \quad \text{and} \quad \psi_k(x, y, z)$$

the proper values, proper frequencies, and proper functions of a problem, whose potential energy V we suppose sufficiently unsymmetrical to do away with all degeneracy. Then

$$\psi = \sum_k c_k \psi_k e^{2\pi i(\nu_k t + \theta_k)}, \quad . \quad . \quad . \quad (15)$$

with arbitrary constants c_k, θ_k, will describe the most

general " vibration " of the system.* In order to avoid ambiguity, since every ψ_k in itself is only defined apart from an arbitrary multiplying constant, we shall subject the ψ_k's to the normalizing condition

$$\iiint \psi_k{}^2 \, dx \, dy \, dz = 1. \quad . \quad . \quad (16)$$

Perhaps this is the place to mention a very important property which the ψ_k's possess automatically, viz. they are " orthogonal " to each other:

$$\iiint \psi_k \psi_l \, dx \, dy \, dz = 0 \quad \text{for} \quad k \neq l, \quad . \quad (17)$$

and they form a *complete* orthogonal set; a function which is orthogonal to them *all* must necessarily vanish. (These properties are important for the development of an arbitrary function in a series in terms of the ψ_k's, but we shall not enter upon that here, as we do not need it for the moment.)

Now return to the general vibration function (15). We put the question: is it possible to ascribe a definite physical meaning to the quantity ψ in such a way that the emission of light with frequencies

$$\nu_{kk'} = \nu_k - \nu_{k'}$$

becomes intelligible? Yes, it is, but—strange to say— only if we make use of the *complex* ψ-function as it stands, instead of its real part, as we are accustomed to do in ordinary vibration problems.

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* Here we have not taken into account the " continuous spectrum ", corresponding to the hyperbolic orbits. We may either suppose these modes of vibration to be absent or we may take the $\sum\limits_{k}$ to include, as a limiting case, the integral, which would have to be added in order to take proper account of the continuous region of proper values. At all events I wished to avoid encumbering the formulæ more than necessary.

The hypothesis which we have to admit is very simple, namely that the square of the absolute value of ψ is proportional to an electric density, which causes emission of light according to the laws of ordinary electrodynamics. Since the square of the absolute value of ψ is formed by multiplying ψ by the conjugate complex quantity (which we will call $\overline{\psi}$), a glance at the expression (15) shows that the terms which compose $\psi\overline{\psi}$ contain the time in the form of cosine factors of the desired frequencies $\nu_k - \nu_{k'}$. More precisely, let us put, for the charge-density ρ,

$$\rho = -e\psi\overline{\psi} = -e\sum_k \sum_{k'} c_k c_{k'} \psi_k \psi_{k'} e^{2\pi i[(\nu_k - \nu_{k'})t + \theta_k - \theta_{k'}]}, \quad (18)$$

where e means the absolute electronic charge. Integrating this over the whole space and making use of equations (16) and (17), we find for the *total* charge

$$-e\sum_k c_k^2,$$

which shows that we shall have to postulate

$$\sum_k c_k^2 = 1$$

in order to make the total charge equal to the electronic charge (which we feel inclined to do).

It was said before that ψ, and hence ρ, is practically confined to a very small region of a few Ångstrom units. Since the wave-lengths of the light-radiations $\nu_k - \nu_{k'}$ are very large compared with this region, it is well known that the radiation of the fluctuating density ρ will be very nearly the same as that of an electric dipole whose electric moment has (e.g.) the z-component

$$\mathbf{M}_z = \iiint z\rho \, dx \, dy \, dz$$

(and similarly formed x- and y-components). Calcu-

lating $\mathbf{M}_z$ from (18), we find after an easy reduction

$$\mathbf{M}_z = - \sum_k c_k{}^2 a_{kk}$$
$$- 2 \sum_{(k,\,k')} c_k c_{k'} a_{kk'} \cos \left[2\pi (\nu_k - \nu_{k'}) t + \theta_k - \theta_{k'} \right]. \quad (19)$$

Here $a_{kk'}$ is an abbreviation for the following *constant*:

$$a_{kk'} = e \iiint z \psi_k \psi_{k'} \, dx \, dy \, dz, \quad . \quad . \quad (20)$$

and $\sum_{(k,\,k')}$ means a sum over all the *pairs* (k, k'). Hence the squares of these integrals (and the corresponding integrals relating to the x- and y-directions) determine the intensity of emitted light of frequency $| \nu_k - \nu_{k'} |$. The intensity is not determined by them alone; the amplitude-constants c_k also come into play, of course. But this is quite satisfactory. For the integrals $a_{kk'}$ are determined by the *nature* of the system, i.e. by its proper functions, regardless of its *state*. $a_{kk'}$ is the amplitude of the corresponding dipole, which would be produced by the proper vibrations ψ_k, $\psi_{k'}$, if only these two were excited, and with equal strength $\left(c_k = c_{k'} = \dfrac{1}{\sqrt{2}} \right)$.

The first sum in (19) is of no interest in our investigation of the emitted radiation, since it means a component of electric moment that is constant in time.

The correctness of our $\psi\bar{\psi}$-hypothesis has been checked by calculating the $a_{kk'}$'s in those cases where the ψ_k's are sufficiently well defined, namely in the case of the Zeeman and Stark effects. The so-called rules of selection and polarization and the intensity-distribution in these patterns are described by the $a_{kk'}$'s in the following obvious way, and the description is in complete agreement with experiment:

The *absence* of a line which might be expected to occur (" selection-rule ") is described by the *vanishing* of the corresponding $a_{kk'}$, *and* of the two other constants relating to the x- and y-directions.

The *linear polarization* of a line in a definite direction is described by the fact that *only* the constant $a_{kk'}$ relating to *this* direction differs from zero, whereas the two other constants vanish. In a similar way the circular polarization, say in the xy-plane, is indicated by (1) vanishing of the z-constant, (2) equality of the x- and y-constants, and (3) a phase-difference of $\pi/2$ between the corresponding cosine-functions in equation (19).

Finally, the *intensity relations* between the non-vanishing components in the Stark and Zeeman patterns of hydrogen are correctly indicated by the relations between the squares of the $a_{kk'}$'s in question; which is satisfactory, since the assumption that the c_k's will be equal for the fine-structure components of one *level* is very suggestive, notwithstanding our lack of knowledge of the c_k's in other respects.

Of course it is impossible to set forth in this lecture any of the calculations that led to the results just given; they would fill pages and pages, and are not at all difficult, but *very* tedious. In spite of their tediousness, it is rather fascinating to see all the well-known but not understood " rules " come out one after the other as the result of *very* familiar elementary and absolutely cogent analysis, like e.g. the fact that $\int_0^{2\pi} \cos m\phi \cos n\phi \, d\phi$ vanishes unless $n = m$. Once the hypothesis about $\psi\bar{\psi}$ has been made, no accessory hypothesis is needed or is possible; none could help us if the " rules " did not come out correctly. But fortunately they do.

I think I ought to draw attention to another fact which was only briefly mentioned at the beginning, namely, that the very fundamental " frequency-rule " of Bohr,

$$\nu_{kk'} = \nu_k - \nu_{k'} = \frac{1}{h}(E_k - E_{k'}),$$

may also be said to be explained by the $\psi\bar{\psi}$-hypothesis. Something exists in the atom which actually vibrates with the *observed* frequency, viz. a certain part of the electric density-distribution or, if you prefer, of $\psi\bar{\psi}$.

This might lead us to suspect that only the square of its absolute value, and not the ψ-function itself, has a real meaning. And this suspicion again might arouse the desire to replace the wave equation by an equation which describes the behaviour of $\psi\bar{\psi}$ directly. To remove this desire, I will remind you of a case in which a similar desire might occur for exactly similar reasons; yet all of you will confess that it would be fatal to pursue it.

Maxwell's equations describe the behaviour of the electromagnetic vectors. But these are not really accessible to observation. The only things that are observable are the ponderomotive forces, or, if you please, the energy, since the forces are caused by virtual energy-differences. But all these quantities (energy, Maxwellian-stresses) are *quadratic* functions of the field-vectors. Therefore we might desire to replace Maxwell's equations by others, that determine the observable *quadratic* functions of the field-vectors directly. But everyone will agree that this would at all events mean an immense complication and that it would not really be possible to do without Maxwell's equations.

6. Derivation of the wave equation (properly speaking) which contains the time.

The equation

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0, \qquad . \quad (13)$$

which we have used for the investigation of the hydrogen atom, only furnishes the distribution in space of the amplitude of the vibration, the dependence on time always being given by

$$\psi \sim e^{\frac{2\pi i E t}{h}}. \qquad . \quad . \quad . \quad (21)$$

The value of the frequency, E, is present in the equation, so that we are really dealing with a family of equations, each of the members being valid for one particular frequency only. The state of things is exactly the same as in ordinary vibration problems; our equation corresponds to the so-called " amplitude equation " (see section 3, equation (10′)),

$$\nabla^2 \psi + \frac{4\pi^2 \nu^2}{u^2}\psi = 0, \quad . \quad . \quad . \quad (10')$$

and not to

$$\nabla^2 p - \frac{1}{u^2}\ddot{p} = 0, \quad . \quad . \quad . \quad (10)$$

from which the former is derived in the manner described above (namely by supposing p to be a sine-function of the time). In our case the problem is to make the analogous step in the reverse direction, i.e. to remove the parameter E from the amplitude equation and introduce time-derivatives instead. This is easily done. Take *one* of the family (13) (with a particular value of E), then by (21) we have

$$\dot{\psi} = \frac{2\pi i E}{h}\psi \quad \text{or} \quad E\psi = \frac{h}{2\pi i}\dot{\psi}.$$

Using this, we get from (13)

$$\nabla^2 \psi - \frac{4\pi m i}{h} \dot\psi - \frac{8\pi^2 m V}{h^2} \psi = 0. \quad . \quad (22)$$

The *same* equation is reached whatever the value of E may have been (for E has been eliminated). Hence equation (22) will be valid for an arbitrary linear aggregate of proper vibrations, i.e. for the most general wave-motion that is a solution of the problem.

We may tentatively go a step farther and try to use it also in the case where the potential energy V contains the time-variable explicitly. It is by no means obvious that this is a correct generalization, for terms with $\dot V$, &c., might be missing—they could not possibly enter into equation (22), in view of the way we have reached this equation. But success will justify our procedure. Of course it would have been nonsense to introduce the assumption that V contained the time explicitly in equation (13), since the condition (21), by which this equation is restricted, would make it impossible to satisfy (13) in the case of an arbitrarily varying V-function.

7. An atom as perturbed by an alternating electric field.

This generalization enables us to solve the important problem: how does an atom behave under the influence of an external alternating electric field, i.e. under the influence of an incident wave of light? This is a very important question: for it contains not only the mechanism of secondary radiation and, in particular, of resonance-radiation, but also the theory of the changes of state of the atom under the influence of an incident radiation of appropriate frequency, and in addition the theory of

refraction and dispersion; for it is well known that dispersion—I mean the phenomenon of a refractive index—is caused by the superposition on the primary radiation of all the secondary wavelets, which every single atom of the body emits under the action of, and in phase with, the primary radiation. If an incident electric vector **E** causes every atom to emit a secondary wavelet *such* as would be emitted by a dipole of the electric moment

$$\mathbf{M} = a\mathbf{E} \quad . \quad . \quad . \quad . \quad (23)$$

(a being a constant), and if Z atoms are present in unit volume, then they produce an increase in the refractive index of

$$2\pi Z a. \quad . \quad . \quad . \quad . \quad (24)$$

Hence, studying the value of a (which usually depends on the frequency) means studying the phenomena of refraction and dispersion.

To investigate the behaviour of an atom in an external alternating electric field, let us take V in equation (22) to be composed of two parts, one describing the internal electrostatic field of the atom, V_0, and one describing the light-field, $Aez \cos 2\pi\nu t$; A, ν mean the amplitude and the frequency of the light-field, which we suppose polarized in the direction of z. (The negative sign of the electronic charge has been taken account of; our e is a positive number.) Hence equation (22) becomes

$$\nabla^2\psi - \frac{4\pi mi}{h}\dot{\psi} - \frac{8\pi^2 m}{h^2}(V_0 + Aez \cos 2\pi\nu t)\psi = 0. \quad (25)$$

We shall take A to be very small compared with the internal field (described by V_0) and solve the equation by approximation. If A were zero, by assuming (21) we

should get back to equation (13) (only with the notation V_0 instead of V). We shall assume the problem of the unperturbed atom to be completely solved, its normalized proper functions and proper values being

$$\psi_k \quad \text{and} \quad E_k (= h\nu_k).$$

Hence the most general solution of (25), when $A = 0$, is

$$\psi = \sum_k c_k \psi_k e^{2\pi i \nu_k t}, \quad \ldots \quad (26)$$

the c_k's being arbitrary complex constants.

We shall try to satisfy equation (25), with A also present, by (26), but with the c_k's varying slightly with time (method of variation of constants). Taking this into account, and also the facts that ψ_k, $h\nu_k$ are proper functions and proper values of the unperturbed equation, we easily obtain, by substituting (26) in (25):

$$\sum_k \dot{c}_k \psi_k e^{2\pi i \nu_k t} = \frac{2\pi i}{h} Aez \cos 2\pi\nu t \sum_k c_k \psi_k e^{2\pi i \nu_k t}. \quad (27)$$

This equation will be satisfied if (identically with respect to time) *all* the coefficients of the expansion of its left-hand side with respect to the *complete* system of orthogonal functions, ψ_k, are identical with the respective coefficients of the expansion of its right-hand side. Hence multiply by ψ_l and integrate over the whole space. Put for abbreviation (see section 5):

$$a_{kl} = e \iiint \psi_k \psi_l z \, dx \, dy \, dz. \qquad . \quad (20)$$

Then, owing to the normalization and orthogonality of the ψ_k's, we get

$$\dot{c}_l e^{2\pi i \nu_l t} = \frac{2\pi i}{h} A \cos 2\pi\nu t \sum_k a_{kl} c_k e^{2\pi i \nu_k t}$$

$$(l = 1, 2, 3, 4, \ldots). \quad \ldots \quad (28)$$

This infinite set of ordinary differential equations is *equivalent* to (27). Isolating $\dot{c}_l$ and splitting up the cosine into exponentials, we write it as follows:

$$\dot{c}_l = + \frac{\pi i A}{h} \sum_k a_{kl} c_k \left[e^{2\pi i (\nu_k - \nu_l + \nu)t} + e^{2\pi i (\nu_k - \nu_l - \nu)t} \right]. \quad (28')$$

Hitherto we have not made use of any approximation process. We will now do this in two different ways, one leading to the theory of secondary radiation (excluding the case of resonance) and of dispersion, the other furnishing the case of resonance and the changes of state of the atom.

THIRD LECTURE

8. Theory of secondary radiation and dispersion.

In equation (28′) we shall at first assume that all the aggregates

$$\nu_k - \nu_l \pm \nu,$$

which appear in the exponents are *large* as compared with the order of magnitude of

$$\frac{A a_{kl} c_k}{h}.$$

This means that the *difference* between the incident frequency and any one of the frequencies of spontaneous emission is large compared with the frequency that would correspond to the *potential energy* which the atom acquires in the external field. (Exclusion of exact or near *resonance*.) With this assumption the equations (28′) show that *all* the time-derivatives of the c_l's are small compared to the time-derivatives of the exponentials. After having stated this, let us take any one of the exponentials on the right-hand side of any one of the equations (28′). We may assume its coefficient c_k to be constant during a period of the exponential. Hence *this* term will only cause a *small* periodic oscillation of the c_l (on the left), which is restored (or nearly so) after

the exponential has gone through a period. But the same holds for *all* the exponentials. Hence *all* the c's execute a vast number of small oscillations around their mean values, oscillations which would of course vanish with vanishing A. We may therefore replace the c's on the *right*-hand side of equation (28') by constants, viz. by their mean values, since by neglecting the small oscillations here only terms in A^2 are dropped. We shall write $c_k{}^0$ for the said constants. The equations are now easily integrated. We get

$$c_l = c_l{}^0 + \frac{A}{2h} \sum_k a_{kl} c_k{}^0 \left[\frac{e^{2\pi i(\nu_k - \nu_l + \nu)t}}{\nu_k - \nu_l + \nu} + \frac{e^{2\pi i(\nu_k - \nu_l - \nu)t}}{\nu_k - \nu_l - \nu} \right].$$

Hence the lth term in our solution (26) will be:

$$c_l \psi_l e^{2\pi i \nu_l t} = c_l{}^0 \psi_l e^{2\pi i \nu_l t}$$
$$+ \frac{A \psi_l}{2h} \sum_k a_{kl} c_k{}^0 \left[\frac{e^{2\pi i(\nu_k + \nu)t}}{\nu_k - \nu_l + \nu} + \frac{e^{2\pi i(\nu_k - \nu)t}}{\nu_k - \nu_l - \nu} \right]. \quad (29)$$

Though we have not yet reached a point that can be compared with experiment, we will give in words the description of what happens, according to equation (29), under the influence of an incident light-wave. Every proper vibration ψ_l, whether it is itself excited from the beginning or not, is compelled to execute a multitude of small additional forced oscillations, namely two " in honour " of every proper vibration ψ_k that *is* excited appreciably ($c_k{}^0 \neq 0$). The frequencies of the two forced oscillations that ψ_l executes " in honour " of ψ_k, as we said, are $\nu_k \pm \nu$, i.e. the sum and difference of the incident frequency and the frequency of the " honoured " proper vibration. Their amplitudes are proportional to the amplitudes both of the external field and of the " honoured " vibration; they also contain as a factor a_{kl}, the constant

which governs the intensity of the spontaneous emission of frequency $|\nu_k - \nu_l|$. Further, in the two forced amplitudes two " resonance-denominators " appear, causing one of the two amplitudes to increase rapidly when the incident frequency approaches the frequency of spontaneous radiation $|\nu_k - \nu_l|$.

Before forming the complete solution from (26) and (29) we will restrict ourselves to the most important case, viz. that in which only *one* free vibration is excited, say ψ_k:

$$c_k{}^0 = 1 \qquad c_l{}^0 = 0 \quad \text{for} \quad l \neq k.$$

We may think of ψ_k as corresponding to the normal state. Then on the right-hand side of equation (29) the first term (except for $l = k$) and the summation sign are dropped, and we get for the complete solution (equation (26), in which k is to be replaced by l):

$$\psi = \psi_k e^{2\pi i \nu_k t} + \frac{A}{2h} \sum_l a_{kl} \psi_l \left[\frac{e^{2\pi i (\nu_k + \nu) t}}{\nu_k - \nu_l + \nu} + \frac{e^{2\pi i (\nu_k - \nu) t}}{\nu_k - \nu_l - \nu} \right]. \quad (30)$$

(Note that *now* the exponentials are independent of the index of summation, l; only *two* frequencies of forced vibration are present.)

To get information about the secondary radiation we form the component * M_z of the resultant electric moment from (30). Neglecting small terms of the second order (proportional to A^2), we find after reduction:

$$M_z = - e \iiint \psi \bar{\psi} z \, dx \, dy \, dz = - a_{kk}$$
$$+ \frac{2}{h} A \cos 2\pi \nu t \sum_l \frac{(\nu_l - \nu_k) a_{kl}{}^2}{(\nu_l - \nu_k)^2 - \nu^2}. \quad (31)$$

* In general, for an anisotropic atom, there will be an M_y and an M_x (orthogonal to the polarization of the incident radiation) as well. We will not deal with them here.

The first term $(-a_{kk})$ is independent of the time; it is the constant electric moment due to the excitation of the free vibration ψ_k. It is of no interest here. The second term determines the secondary wavelet. It is seen to coincide in frequency with the incident electric force $(A \cos 2\pi\nu t)$. Its phase is the same or opposite, depending on whether $\nu \lessgtr \nu_l - \nu_k$, just as in the classical theory. (This holds if ψ_k corresponds to the normal state, so that $\nu_l - \nu_k$ is always positive; if it is negative, the reverse is true; Kramers' terms of the dispersion formula.) The quantity α of equation (23), which by the expression (24) determines the contribution to the refractive index, is found from the second term on the right-hand side of (31) by dropping $A \cos 2\pi\nu t$. The denominators $(\nu_l - \nu_k)^2 - \nu^2$ furnish the phenomenon of anomalous dispersion in the neighbourhood of all *those emission* (or absorption) frequencies that involve the index k of ψ_k—remember that we supposed only this *one* free vibration to be excited. The quantity a_{kl}^2 in the numerator is the same as that which determines the intensity of spontaneous emission $|\nu_k - \nu_l|$. In all these respects the formula is a complete copy of the old Helmholtz formula (supplemented by Kramers' " negative " terms) and is thought to be in complete agreement with experiment.

Two additional points are worth mentioning. You know that Thomas and Kuhn formed a hypothesis concerning the *sum* of all the coefficients in the dispersion formula, in our case

$$\frac{2}{h} \sum_l (\nu_l - \nu_k) a_{kl}^2.$$

According to them it is to be equal to the value of the

coefficient for *one* elastically bound electron, i.e. it must be equal to

$$\frac{e^2}{4\pi^2 m}$$

(multiplied by *one*, in our case, for we are dealing with the *one*-electron atom; in general, multiplied by an integer). The equality of the two above-mentioned quantities can be *proved* for our dispersion formula—but the proof is a little lengthy, and I will therefore omit it.

The second remark is the following. Perhaps you remember the statement, first made by Smekal, that there should also exist secondary radiations, whose frequencies differ from the frequency ν of the incident radiation (*therefore* without phase relation, *therefore* without influence on the refraction phenomenon). The frequencies expected are

$$\nu \pm (\nu_k - \nu_{k'}).$$

Secondary radiations of precisely these frequencies are furnished by the present theory, if we give up our simplifying assumption that only *one free* vibration is excited, and suppose at least two of them, say ψ_k and $\psi_{k'}$, to be present.

9. Theory of resonance radiation, and of changes of the state of the atom produced by incident radiation whose frequency coincides, or nearly coincides, with a natural emission frequency.

At the beginning of the last section we had to make the assumption that all the aggregates like

$$\nu_k - \nu_l \pm \nu$$

are of appreciable size, which means that the frequency

of the incident light, ν, is excluded from the immediate neighbourhood of any natural frequency of the atom under consideration. We will now consider an incident frequency which is very close to one of the natural frequencies. To fix our ideas, let

$$\nu_k - \nu_l + \nu \text{ be very small and } \nu_l > \nu_k$$

("very small" means: of the order of magnitude of Aa_{kl}/h or smaller, possibly vanishing). Returning to equation (28'), you will now find on the right-hand side of this system of equations altogether *two* exponentials which vary slowly, viz.

$$e^{2\pi i(\nu_k - \nu_l + \nu)t} \quad \text{and} \quad e^{2\pi i(\nu_l - \nu_k - \nu)t},$$

the former appearing in the lth equation, the latter in the kth equation. These terms (as we shall see presently) now cause very appreciable "secular" changes in the two quantities c_k and c_l, however small the amplitude A of the incident wave may be. All the other exponentials will only cause small periodic disturbances, as before. It is therefore reasonable to drop them altogether, since we are now dealing with a much coarser phenomenon (viz. appreciable secular variations of c_k and c_l). We might even suppose all the other c's to be zero; this would have no effect, since they are certainly constant within the degree of accuracy we are aiming at. For determining c_k and c_l we get from (28') the two simple equations

$$\left. \begin{aligned} \dot{c}_l &= i\sigma c_k e^{i\epsilon t}, \\ \dot{c}_k &= i\sigma c_l e^{-i\epsilon t}, \end{aligned} \right\} \quad . \quad . \quad . \quad (32)$$

with the abbreviations

$$\sigma = \frac{\pi A a_{kl}}{h}, \quad \epsilon = \nu_k - \nu_l + \nu. \quad . \quad . \quad (33)$$

To solve them, we introduce new variables x, y by putting

$$c_l = xe^{\frac{i\epsilon t}{2}}, \qquad c_k = ye^{-\frac{i\epsilon t}{2}}. \quad . \quad . \quad (34)$$

The result can be written

$$\left(\frac{d}{dt} + \frac{i\epsilon}{2}\right)x = i\sigma y,$$

$$\left(\frac{d}{dt} - \frac{i\epsilon}{2}\right)y = i\sigma x.$$

These equations have *constant* coefficients and are readily solved by familiar methods. The solution can be written in the following form:

$$\left.\begin{array}{l} x = \rho c^{i(\gamma t+\phi)} + \mu\rho' e^{-i(\gamma t+\phi')}, \\ y = \mu\rho e^{i(\gamma t+\phi)} - \rho' e^{-i(\gamma t+\phi')}, \end{array}\right\} \quad . \quad . \quad (35)$$

with the abbreviations

$$\gamma = \sqrt{\frac{\epsilon^2}{4} + \sigma^2}, \quad \mu = \frac{\gamma + \frac{\epsilon}{2}}{\sigma}, \quad . \quad . \quad (36)$$

whereas ρ, ρ', ϕ, ϕ' are *arbitrary* real constants, non-negative if you like. We can put (35) in the form:

$$\left.\begin{array}{l} x = e^{\frac{i(\phi-\phi')}{2}}[(\rho + \mu\rho')\cos\theta + i(\rho - \mu\rho')\sin\theta], \\ y = e^{\frac{i(\phi-\phi')}{2}}[(\mu\rho - \rho')\cos\theta + i(\mu\rho + \rho')\sin\theta], \end{array}\right\} \quad (37)$$

with the abbreviation

$$\theta = \gamma t + \frac{\phi + \phi'}{2}. \quad . \quad . \quad (38)$$

From (37) we can easily form the squares of the absolute values of x and y, that is (by equation (34)) of c_l and c_k, and we can thus get information about the varying dis-

tribution of intensity between the two vibrations in question—which is the point of main interest. We obtain

$$\left.\begin{array}{l} |\,c_l\,|^2 = |\,x\,|^2 = (\rho - \mu\rho')^2 + 4\mu\rho\rho'\cos^2\theta, \\ |\,c_k\,|^2 = |\,y\,|^2 = (\mu\rho - \rho')^2 + 4\mu\rho\rho'\sin^2\theta. \end{array}\right\} \quad (39)$$

The sum of the intensities is constant, as might have been anticipated. It may be taken to consist of three parts, two " portions " fixed invariably to the two vibration-levels, the third (viz. $4\mu\rho\rho'$) oscillating slowly between them. To fix our ideas, let us take the case where at a certain time all the intensity was stored up in *one* vibration, say the lower one, c_k. Choosing the corresponding value of t so as to make $\cos\theta = 0$, this requires

$$\rho' = \frac{\rho}{\mu}.$$

We then find for the ratio between the oscillating portion of the intensity and its total amount

$$\frac{4\mu\rho\rho'}{(\mu\rho + \rho')^2} = \frac{4}{\left(\mu + \dfrac{1}{\mu}\right)^2} = \frac{\sigma^2}{\gamma^2} = \frac{\sigma^2}{\sigma^2 + \dfrac{\epsilon^2}{4}} \quad (40)$$

(by using the fact, obvious from (36), that

$$\mu = \frac{\gamma + \dfrac{\epsilon}{2}}{\sigma} = \frac{\sigma}{\gamma - \dfrac{\epsilon}{2}} \Bigg).$$

We see that when $\epsilon = 0$ the *total* intensity is oscillating. By (33), $\epsilon = 0$ means the case of *sharp* resonance. If the resonance is not complete, then (40) shows that only a certain fraction of the intensity oscillates, and that this fraction becomes inappreciable when the lack of resonance, ϵ, becomes large compared with the quantity

σ defined by (33). (The order of magnitude of σ is the *potential energy* (divided by h) which the atom acquires in the electric field of the light-wave, owing to the electric moment which is due to the co-operation of the kth and lth modes of vibration.) The quantity σ would, in a certain sense, give a measure of the natural sharpness of the resonance-line, if it were possible to form a universal idea of the amplitude A of the incident light. We shall not enter upon this question here.

The theory put forward here in its rough features describes both the change of state of the atom produced by radiation of appropriate frequency and the appearance of resonance-radiation. For of course the presence of the *two* vibrations ψ_k and ψ_l will give rise to their natural emission. It is worth while mentioning that on account of the exponentials appearing in equation (34) this emission should *not* have exactly the frequency $\nu_l - \nu_k$, but a frequency exactly equal to ν, the frequency of the incident light-wave.

10. Extension of wave mechanics to systems other than a single mass-point.

Hitherto we have applied the method of wave mechanics only to a very simple system, viz. a single mass-point moving in a field of force which was either constant or varying with the time. We will now proceed to a quite arbitrary mechanical system. We might have done this before; all that has been said about the influence of an alternating field would apply with very slight modification to an arbitrary system, e.g. to the many-electron atom. But I thought it better to have a clear and simple case before our mental eye.

The derivation of the fundamental wave equation

put forward in the first lecture is very easily generalized to a quite arbitrary system, the only difference being that the " space " in which the wave-propagation takes place is no longer ordinary three-dimensional space but the " configuration space ".

Let us recall the Hamilton-Maupertuis principle from which we started, namely,

$$\delta \int_A^B 2T \, dt = 0 \quad . \quad . \quad . \quad (1)$$

and which we transformed into

$$\delta \int_A^B \sqrt{2m(E - V)} \, ds = 0, \quad . \quad . \quad . \quad (2)$$

by putting

$$2T = mw^2 = m \left(\frac{ds}{dt}\right)^2 = 2(E - V) = \frac{ds}{dt} \sqrt{2m(E - V)}.$$

We then compared it with Fermat's principle for a wave-propagation:

$$\delta \int_A^B \frac{ds}{u} = 0, \quad . \quad . \quad . \quad . \quad (3)$$

which led us to

$$u = \frac{C}{\sqrt{2m(E - V)}}. \quad . \quad . \quad . \quad (4)$$

Now, *in general* T is *not* of the simple form $\frac{m}{2} \left(\frac{ds}{dt}\right)^2$ but

$$2T = \sum_l \sum_k b_{lk} \dot{q}_l \dot{q}_k, \quad . \quad . \quad . \quad (41)$$

where the b_{lk}'s are functions of the generalized co-ordinates q_l. We now *define* a line-element ds in the generalized q-space by

$$2T = \sum_l \sum_k b_{lk} \dot{q}_l \dot{q}_k = \left(\frac{ds}{dt}\right)^2,$$

or

$$ds^2 = \sum_l \sum_k b_{lk} \, dq_l \, dq_k. \quad . \quad . \quad (42)$$

The generalized non-Euclidean geometry, which is defined by the latter formula, is exactly the one which Heinrich Hertz used in his famous mechanics and which allowed him to treat the motion of an arbitrary system formally as the motion of a single mass-point (in a non-Euclidean, many-dimensional space). Introducing this geometry here, we easily see that all the considerations of the first lecture which led us to the fundamental wave equation may be transferred, even with a slight formal simplification, viz. that we have to put $m = 1$. In exactly the same way as before we obtain

$$u = \frac{E}{\sqrt{2(E - V)}},$$

and finally for the wave (or rather amplitude) equation:

$$\nabla^2 \psi + \frac{8\pi^2}{h^2}(E - V)\psi = 0. \quad . \quad . \quad (43)$$

For the wave equation properly speaking we get, just as before (section 6),

$$\nabla^2 \psi - \frac{4\pi i}{h}\dot{\psi} - \frac{8\pi^2 V}{h^2}\psi = 0. \quad . \quad . \quad (44)$$

But, of course, ∇^2 is now to be understood *not* as the simple Laplacian in three dimensions nor as the simple Laplacian in a many-dimensional Euclidean space (i.e. the sum of the second derivatives with respect to the single co-ordinates), but it is to be understood as the well-known generalization of the Laplacian in the case of a general line-element like (42). In the treatment of general problems we can usually avoid writing down the explicit expression for this operation; we need only know that it is a self-adjoint differential operator of the second order. (Never mind whether you know what " self-

adjoint " means, it is of no importance for the moment.)
Yet for the sake of completeness I will put down the
general expression for ∇^2. Let a_{lk} be the minor corres-
ponding to b_{lk}, divided by the determinant $\Sigma \pm b_{lk}$. Let
a be the determinant of the a_{lk}'s. Then

$$\nabla^2 \equiv a^{\frac{1}{2}} \sum_l \frac{\partial}{\partial q_l} \left(a^{-\frac{1}{2}} \sum_k a_{lk} \frac{\partial}{\partial q_k} \right). \quad . \quad . \quad (45)$$

In the case of a single mass-point of mass m, treated
in Cartesian co-ordinates, this reduces to $\dfrac{1}{m}$ times the
elementary ∇^2-operator (viz. $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$).
Or, if you chose to describe the motion of a single mass-
point by any other co-ordinates, e.g. polar or elliptic, you
would get $\dfrac{1}{m}$ times the expression for the elementary ∇^2
transformed to those co-ordinates. If the system consists
of n free mass-points, you get the sum of their elementary
∇^2-operators each divided by the appropriate mass.

The theory in its present form is applicable to systems
of any number of degrees of freedom more than, equal
to, or less than, three. I shall give a rapid account of a few
examples without going through the details of calculation
unless they present some physical interest.

11. Examples: the oscillator, the rotator.

Take the *one*-dimensional harmonic oscillator. The
expression for the energy in ordinary mechanics may be
taken to be

$$T + V = \frac{m}{2} \dot{q}^2 + 2\pi^2 \nu_0^2 m q^2$$

(we have expressed the coefficient of the potential energy
in terms of the classical proper frequency ν_0 which it

produces). This easily leads to the amplitude equation:

$$\frac{1}{m}\frac{d^2\psi}{dq^2} + \frac{8\pi^2}{h^2}(E - 2\pi^2\nu_0^2 q^2)\psi = 0.$$

It can be shown that this equation has solutions which are finite along the real q-axis, for the following values of E only:

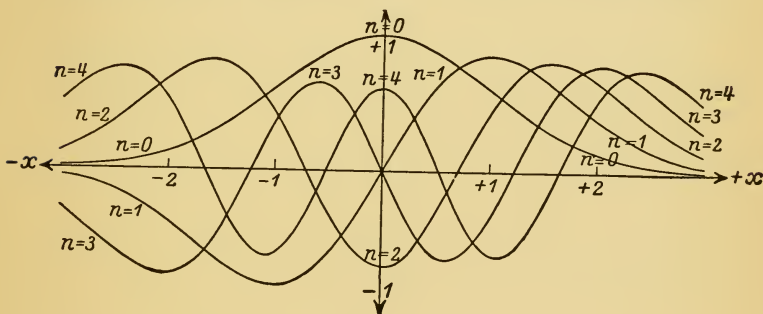$$E_n = (n + \tfrac{1}{2})h\nu_0; \quad n = 0, 1, 2, 3. \quad (46)$$

The proper functions are the so-called Hermite orthogonal functions

$$\psi_n = (2^n n!)^{-\frac{1}{2}} e^{-\frac{x^2}{2}} H_n(x) \quad . \quad . \quad (47)$$

with

$$x = q \cdot 2\pi\sqrt{\frac{m\nu_0}{h}}.$$

$H_n(x)$ is the so-called nth Hermite polynomial. A graph of the first five functions (47) is given in the figure.

The first five proper vibrations of the Planck oscillator according to undulatory mechanics. Outside of the region $-3 \leq x \leq +3$ represented here, all five functions approach the x-axis in monotonic fashion.

Though theoretically they extend to infinity, they are practically restricted by the exponential to a domain of the order of magnitude of the amplitude of the corresponding

classical mass-point. (This is very easy to prove.) We have not discussed the physical meaning of our generalized ψ-function. Yet the following statement is of interest. If the ψ_n's were the proper functions of a one-electron problem and q one of the rectangular co-ordinates, we would (following our $\psi\bar{\psi}$-hypothesis) estimate the intensity of emission of frequency $\frac{1}{h}|E_n - E_k|$, polarized in the direction of q, by the square of the integral

$$\int q\,\psi_k\,\psi_n\,dq.$$

If we try to do the same *here*, we get a most satisfactory result, viz. the integral *vanishes*, unless

$$|k - n| = 1.$$

This means that all the emission frequencies except $1 \,.\, \nu_0$ are excluded. We shall return later to the question of the physical meaning of ψ in the general case.

Take as a second example another one-dimensional problem: the simple rotator with its axis fixed in space. Here all the energy is kinetic, viz.:

$$\frac{A}{2}\left(\frac{d\phi}{dt}\right)^2,$$

where A = moment of inertia, ϕ = angle of rotation. The amplitude equation becomes

$$\frac{1}{A}\frac{d^2\psi}{d\phi^2} + \frac{8\pi^2 E}{h^2}\psi = 0,$$

which has the solutions:

$$\psi = \frac{\sin}{\cos}\left[\sqrt{\frac{8\pi^2 EA}{h^2}}\,\phi\right].$$

Obviously ψ must be restricted to be periodic in ϕ with

period 2π. Hence the coefficient of ϕ must be an integer; this condition furnishes the proper values

$$E_n = \frac{n^2 h^2}{8\pi^2 A}; \quad n = 0, 1, 2, 3, \ldots, \qquad (48)$$

in *complete* agreement with the older form of quantum theory. Let us try to get an estimate for the intensity of radiation in the same formal way as before. If, in ordinary mechanics, an electrified particle were fixed to the rotator at a distance a from the centre of gravity, its rectangular co-ordinates would be

$$\left. \begin{array}{c} x \\ y \end{array} \right\} = a \left\{ \begin{array}{c} \cos \\ \sin \end{array} \right\} \phi.$$

Now form

$$\int_0^{2\pi} \psi_n \psi_k \left\{ \begin{array}{c} x \\ y \end{array} \right\} d\phi = a \int_0^{2\pi} \left\{ \begin{array}{c} \sin \\ \cos \end{array} \right\} n\phi \left\{ \begin{array}{c} \sin \\ \cos \end{array} \right\} k\phi \left\{ \begin{array}{c} \sin \\ \cos \end{array} \right\} \phi \, d\phi.$$

Since the product of the first two $\left. \begin{array}{c} \sin \\ \cos \end{array} \right\}$ functions can always be expressed by the sum or difference of $\left. \begin{array}{c} \sin \\ \cos \end{array} \right\}$ $(n \pm k)\phi$, it is easily recognized that none of the eight quantities comprised in the above formula differs from zero, unless either $|n + k|$ or $|n - k|$ is unity; or, what amounts essentially to the same, unless

$$|n - k| = 1.$$

This is the well-known selection-rule for the rotator. It is interesting to treat the rotator again without the assumption that its axis is rigidly fixed in direction. We find for the amplitude equation

$$\nabla^2_{\theta, \phi} \psi + \frac{8\pi^2 A E}{h^2} \psi = 0.$$

Here $\nabla^2_{\theta, \phi}$ means *that* part of the elementary ∇^2-operator

(when expressed in polar co-ordinates) that contains the
differentiations with respect to the angles θ, ϕ only. It is
known that the above equation only has finite single-
valued solutions when the constant is the product of
two successive integers:

$$\frac{8\pi^2 AE}{h^2} = n(n+1); \quad n = 0, 1, 2, \ldots,$$

and that the solution is a spherical harmonic of order n.
(The proper value E_n is $(2n+1)$-fold degenerate, since
there are $2n+1$ independent spherical harmonics of
order n.) This furnishes the proper values

$$E_n = \frac{n(n+1)h^2}{8\pi^2 A}; \quad \ldots \quad (49)$$

this means essentially that " half-integers " are to be
inserted in place of n in the " classical " formula (48).
(For $n(n+1) = (n+\frac{1}{2})^2 - \frac{1}{4}$, and a common constant
in all the E_n's cancels out in forming their differences.)
It is known that the representation of band-spectra very
often *compelled* the use of " half-integers ", and it seems
that all of them are *compatible* with the new formula. (Of
course formula (49) is the correct one to use, and not (48),
because the axis of a molecule is never rigidly fixed.)
The selection rule comes out in exactly the same way as
in the former case, only by a more troublesome calcu-
lation.

FOURTH LECTURE

12. Correction for motion of the nucleus in the hydrogen atom.

In the first lecture we treated the hydrogen atom as a one-body problem, as if the nucleus were fixed in space. In ordinary mechanics it is well known that if we start with the problem of two bodies (of masses m and M), we can split it in two, viz.:

(1) Uniform rectilinear motion of the centre of gravity (inertial motion).

(2) Keplerian motion around a fixed centre of a body with the " combined mass " μ, such that

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}. \quad \cdots \quad (50)$$

According to Bohr's theory, this refined treatment of the hydrogen atom is quantitatively supported by the slight difference in frequency between the Helium$^+$-lines and *those* hydrogen-lines which would exactly coincide with them if the nucleus had infinite mass. (In other words, the slight difference between the Rydberg constant for He$^+$ and for H is quantitatively accounted for by taking into account the slight movement of the nucleus; Sommerfeld.)

We meet with exactly the same state of affairs in wave mechanics. The six-dimensional amplitude equation for the two-body problem is:

$$\frac{1}{m} \nabla_1^2 \psi + \frac{1}{M} \nabla_2^2 \psi + \frac{8\pi^2}{h^2}(E - V)\psi = 0. \quad (51)$$

By ∇_1^2 and ∇_2^2 we mean the elementary Laplacians with respect to the co-ordinates of the electron (x_1, y_1, z_1) and of the nucleus (x_2, y_2, z_2). About V we need only make the assumption that it depends on

$$r = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

only. Now, instead of $x_1, \ldots, z_2$, introduce the co-ordinates of the centre of gravity (ξ, η, ζ) and the relative co-ordinates of m with respect to M (say x, y, z). We can easily prove that

$$\frac{1}{m} \nabla_1^2 \psi + \frac{1}{M} \nabla_2^2 \psi = \frac{1}{m+M} \nabla^2_{\xi, \eta, \zeta} \psi + \frac{1}{\mu} \nabla^2_{x, y, z} \psi.$$

The meaning of the ∇^2's is obvious; μ is given by (50). By inserting this in (51) we get an equation which can be split up by supposing ψ to be the product of a function of ξ, η, ζ only (say ϕ) and one of x, y, z only (say χ). In the splitting up an arbitrary constant is introduced, which is represented by E_t in the following equations. For ϕ we get

$$\frac{1}{m+M} \nabla^2_{\xi, \eta, \zeta} \phi + \frac{8\pi^2 E_t}{h^2} \phi = 0, \quad . \quad (52)$$

and for χ

$$\frac{1}{\mu} \nabla^2_{x, y, z} \chi + \frac{8\pi^2}{h^2} (E - E_t - V) \chi = 0. \quad (53)$$

The former describes the motion of the centre of gravity under no forces, according to wave mechanics; the constant E_t corresponds to its translational energy and can have any non-negative value. $E - E_t$ corresponds to the internal energy. The second equation is exactly that of the one-body problem for a mass-point with mass μ moving in a fixed field V. Hence for the proper values corresponding to the internal energy there will be no

difference other than that m is replaced by μ (see (14')) in the formula for the Rydberg constant. Thus Sommerfeld's important result, mentioned above, is re-stated in wave mechanics. Owing to the analytical simplicity of this deduction, there has not been much ado about it in the literature. But it really is one of the most immediate proofs that there must be something true in the many-dimensional wave-treatment—however irritating the latter may be at first.

13. Perturbation of an arbitrary system.

The theory of the perturbation of an arbitrary system really presents no new features as compared with the perturbation theory of the one-electron atom, a special case of which has been discussed in sections 7–9; but we shall widen our outlook by stating it afresh in a concise form. The general wave equation (44) of section 10 can be written:

$$\dot{\psi} = \frac{2\pi i}{h}\left(-\frac{h^2}{8\pi^2}\nabla^2\psi + V\psi\right). \qquad . \quad (54)$$

We will write H for the *operator*

$$H = -\frac{h^2}{8\pi^2}\nabla^2 + V.$$

(V as an *operator* means: "to multiply by V".) Then by (43), section 10, the proper functions ψ_k are precisely *those* which are *reproduced* by the operator H, apart from a multiplying constant, which is the proper value:

$$H[\psi_k] = E_k\psi_k. \quad . \quad . \quad . \quad (55)$$

Equation (54) takes the simple form

$$\dot{\psi} = \frac{2\pi i}{h}H[\psi]. \quad . \quad . \quad . \quad (56)$$

Now, adding to V a small perturbing field, which may or may not contain the time explicitly, means altering the operator H slightly. (Of course an alteration of H might also be produced in another way, e.g. by altering one of the masses, &c. It will do no harm if this more general case is included in our treatment.) We shall call the altered operator $H + H'$, bearing in mind that H' is to be a " small " operator. We have to solve

$$\dot{\psi} = \frac{2\pi i}{h}(H[\psi] + H'[\psi]). \quad . \quad . \quad (57)$$

Tentatively substituting

$$\psi = \Sigma\, c_k \psi_k\, e^{\frac{2\pi i \nu_k}{h}}; \quad \nu_k = \frac{E_k}{h}, \quad . \quad . \quad (58)$$

with slowly varying time-functions c_k, we obtain in the first instance

$$\Sigma_k\, \dot{c}_k \psi_k\, e^{\frac{2\pi i \nu_k t}{h}} = \frac{2\pi i}{h} \Sigma_k\, c_k H'[\psi_k]\, e^{\frac{2\pi i \nu_k t}{h}}.$$

This equation will be satisfied if it is orthogonal to *all* the ψ_l's *. Multiply by ψ_l and integrate over the whole configuration-space:

$$\dot{c}_l = \frac{2\pi i}{h} \Sigma_k\, c_k a_{lk} e^{\frac{2\pi i t}{2}(\nu_k - \nu_l)}, \quad l = 1, 2, 3, 4, \ldots, (59)$$

where
$$a_{lk} = \int dq\, H'[\psi_k]\psi_l, \quad . \quad . \quad (60)$$

and $\int dq$ always means a multiple integral over the whole configuration-space. The a_{kl}'s are *small* quantities.

We will suppose the perturbation to be conservative.

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* We take it for granted that with respect to the completeness and orthogonality of the proper functions the general case behaves like the simple hydrogen case. That is quite safe. We also, as there, avoid encumbering our formulæ by explicitly taking account of a *continuous* spectrum of proper values.

Then the a_{kl}'s are constants; just as in the special cases treated before, only the exponentials with vanishing exponent will cause appreciable variations of the c_l's. First take the system to be non - degenerate. Then, dropping the other terms, which only furnish slight oscillations, you get, for every c_l,

$$\dot{c}_l = \frac{2\pi i a_{ll}}{h} c_l; \quad c_l = c_l^0 e^{\frac{2\pi i a_{ll}}{h}t}, \quad . \quad . \quad (61)$$

which, if you substitute it in (58), merely means that the frequency is slightly altered by the amount

$$\frac{a_{ll}}{h}.$$

Now take a case of degeneracy. Let the amplitudes $c_l, c_{l+1}, \ldots, c_{l+a-1}$ belong to a different proper functions, all belonging to the same proper value E_l, or proper frequency ν_l. Then in each of the equations relating to them you will have not only one, but a, vanishing exponents, which give rise to secular changes. Hence these a amplitudes will be determined by the following set of equations:

$$\dot{c}_{l+\rho} = \frac{2\pi i}{h} \sum_{\lambda=0}^{a-1} c_{l+\lambda} a_{l+\rho,\, l+\lambda}; \quad \rho = 0, 1, 2, \ldots, a-1. \quad (62)$$

These equations show that under the influence of a slight perturbation there will in general be an exchange of amplitudes between degenerate modes of vibration which belong to the same proper value. It is correct to talk of an *exchange*, since it is easily proved from equation (62) that
$$\sum_{\rho=0}^{a-1} |c_{l+\rho}|^2 = \text{const.}$$

Yet when thinking of this exchange we must remember

that the set of proper functions $\psi_{l+\rho}(\rho = 0, 1, \ldots, a-1)$ is arbitrary up to an orthogonal linear substitution of determinant 1. This induces a similar substitution of the amplitudes c_l. Given a definite perturbation, i.e. definite values of the quantities $a_{l+\lambda, l+\rho}$, it is always possible to find at least one orthogonal substitution of the $\psi_{l+\rho}$'s which brings the equations (62) into the simple form (61) of the non-degenerate case. Then these particular proper functions, selected in a way that suits this particular form of perturbation, will under its influence have *constant* amplitude-squares, but will in general belong to slightly different proper frequencies. The a-fold proper value has been split up into a slightly differing proper values; the degeneracy is removed by the disturbing field, and the particularly chosen proper functions of the degenerate problem are the non-degenerate proper functions " in zero approximation " to the single proper values of the perturbed problem. The a slight alterations in proper value can be shown to be the a roots of the " secular " equation

$$\begin{vmatrix} a_{ll} - x, & a_{l, l+1}, & \ldots, a_{l, l+a}, \\ a_{l+1, l}, & a_{l+1, l+1} - x, & \ldots, a_{l+1, l+a}, \\ \cdot \ \cdot \ \cdot & \cdot \ \cdot \ \cdot \ \cdot \ \cdot \ \cdot & \cdot \ \cdot \ \cdot \ \cdot \ \cdot \\ a_{l+a, l}, & a_{l+a, l+1}, & \ldots, a_{l+a, l+a} - x. \end{vmatrix} = 0$$

Of course it may happen that these roots are not all different; a certain degeneracy is then retained. We may either say that the members of an arbitrarily chosen set of the degenerate functions all vibrate with the unperturbed frequency, but exchange their amplitudes—or that the members of the appropriately chosen set have constant amplitudes, but that each function has a slightly different frequency: these two assertions are of course

identical. For—as we may put it—either: a vibration of varying amplitude has not really got the frequency which we ascribe to it; or: two or more slightly different frequencies, when superimposed, lead to a " beat phenomenon ", i.e. to a varying amplitude.

14. Interaction between two arbitrary systems.

Take now two arbitrary systems, at first without interaction, one of which is described according to wave mechanics (see equation (56)) by

$$\dot{\psi} = \frac{2\pi i}{h} H [\psi],$$

and the other by

$$\dot{\phi} = \frac{2\pi i}{h} L [\phi].$$

Multiply the first by ϕ, the second by ψ, and add the resulting equations; you get

$$\frac{d}{dt} (\phi\psi) = \frac{2\pi i}{h} (H + L) [\phi\psi],$$

since the operator H does not affect ϕ and L does not affect ψ. The latter equation is the wave equation of the " combined system ", i.e. of the system formed by *mentally* uniting the two systems to form one. (The process is exactly the reverse of what is so often done in " splitting up " an equation by supposing the solution to be the product of two functions, dependent on different individual variables.) The proper functions of the combined system are the *products* of any one of the proper functions of the first system and any one of the second system. The proper value that belongs to such a product is easily seen to be the *sum* of the respective proper values. (This corresponds to the additivity of energy in ordinary

mechanics.) By the addition of proper values a *new degeneracy* may be caused in the combined system, even though the single systems were non-degenerate. (Let us suppose the latter case, for the sake of simplicity.) Let E, E' be two proper values of the first system, F, F' two of the second system, and suppose that

$$E + F' = E' + F = G$$

or $$E - E' = F - F'.$$

Hence: if a common *difference of proper values* exists between the two systems, it will give rise to a two-fold degenerate proper value G of the combined system. For simplicity's sake, suppose that other relations of the same kind are absent, and *now* suppose that a slight *interaction* of the two systems takes place, changing the operator $H + L$ into $H + L + T$, where T will of course
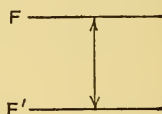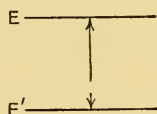
contain the variables both of the first and of the second system. Then the amplitudes belonging to $E + F'$ and to $E' + F$ will show a slow secular interchange, all the others remaining essentially constant. The sum of the squares of the two amplitudes in question is also constant. Interpreted in the single systems, this cannot very well have any other meaning but that e.g. the amplitude of F increases at the expense of that of F' and, so to speak, to compensate for the amplitude of E' increasing at the expense of that of E. This seems to be the appropriate wave-mechanical description of what in the older

form of the quantum theory was called the transfer of a quantum of energy $E - E'$ $(= F - F')$ from one system to the other.

15. The physical meaning of the generalized ψ-function.

Perhaps the latter conclusions are obscured by the fact that we have hitherto avoided putting forward any definite assumption as to the physical interpretation of the function $\psi(q_1, q_2, \ldots, q_n, t)$ relating to a system whose configuration in terms of ordinary mechanics is described by the generalized co-ordinates $q_1, q_2, \ldots, q_n$. This interpretation *is* a very delicate question. As an obvious generalization of the procedure of spreading out the electronic charge according to a relative density function $\psi\bar\psi$ (which furnished satisfactory results in the one-electron problem; see section 5), the following view would present itself in the case of a general mechanical system: the real natural system does not behave like the picture which ordinary mechanics forms of it (e.g. a system of point-charges in a definite configuration), but rather behaves like what would be the result of spreading out the system, described by $q_1, \ldots, q_n$, *throughout its configuration-space* in accordance with a relative density function $\psi\bar\psi$. This would mean that, if the ordinary mechanical picture is to be made use of at all, the actual system behaves like the ordinary mechanical picture, present in all its possible configurations at the same time, though " stronger " in some of them than in others.

I maintained this view for some time. The fact that it proves *very* useful can be seen from the one-electron problem (see section 5). *No* other interpretation of the ψ-function is capable of making us *understand* the large

amount of information which the constants a_{kl} furnish about the intensity and polarization of the radiation. Yet this way of putting the matter is surely not quite satisfactory. For what does the expression " to behave like " mean in the preceding sentences? The " behaviour " of the ψ-function, i.e. its development in time, is governed by nothing like the laws of classical mechanics; it is governed by the wave-equation.—

An obvious *statistical* interpretation of the ψ-function has been put forward, viz. that it does not relate to a single system at all but to an assemblage of systems, $\psi\bar{\psi}$ determining the fraction of the systems which happen to be in a definite configuration. This view is a little unsatisfactory, since it offers no explanation whatever why the quantities a_{kl} yield all the information which they do yield. In connexion with the statistical interpretation it has been said that to any physical quantity which would have a definite physical meaning and be in principle (*principiell*) measurable according to the classical picture of the atom, there belong definite proper values (just as e.g. the proper values E_k belong to the energy); and it has been said that the result of measuring such a quantity will always be one or the other of these proper values, but never anything intermediate. It seems to me that this statement contains a rather vague conception, namely that of *measuring* a quantity (e.g. energy or moment of momentum), which relates to the classical picture of the atom, i.e. to an obviously wrong one. Is it not rather bold to interpret measurements according to a picture which we know to be wrong? May they not have quite another meaning according to the picture which will finally be forced upon our mind? For example: let a beam of electronic rays pass through a layer of mercury vapour, and

measure the deflection of the beam in an electric and in a magnetic field before and after the beam has traversed the vapour. According to the older conceptions this is interpreted as a measurement of differences of energy-levels in the mercury atom. The wave-picture furnishes another interpretation, namely, that the frequency of part of the electronic waves has been diminished by an amount equal to the difference of two proper frequencies of the mercury. Is it quite certain that these two interpretations do not interfere with one another, and that the old one can be maintained together with the new one? Is it quite certain that the conception of energy, indispensable as it is in macroscopic phenomena, has *any* other meaning in micro-mechanical phenomena than the number of vibrations in h seconds?

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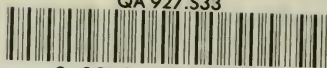1928.

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