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AN UNDULATORY THEORY OF THE MECHANICS OF ATOMS AND MOLECULES

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ABSTRACT

The paper gives an account of the author's work on a new form of quantum theory. §1. The Hamiltonian analogy between mechanics and optics. §2. The analogy is to be extended to include real "physical" or "undulatory" mechanics instead of mere geometrical mechanics. §3. The significance of wave-length; macro-mechanical and micro-mechanical problems. §4. The wave-equation and its application to the hydrogen atom. §5. The intrinsic reason for the appearance of discrete characteristic frequencies. §6. Other problems; intensity of emitted light. §7. The wave-equation derived from a Hamiltonian variation-principle; generalization to an arbitrary conservative system. §8. The wave-function physically means and determines a continuous distribution of electricity in space, the fluctuations of which determine the radiation by the laws of ordinary electrodynamics. §9. Non-conservative systems. Theory of dispersion and scattering and of the "transitions" between the "stationary states." §10. The question of relativity and the action of a magnetic field. Incompleteness of that part of the theory.

1. The theory which is reported in the following pages is based on the very interesting and fundamental researches of L. de Broglie[1] on what he called "phase-waves" ("ondes de phase") and thought to be associated with the motion of material points, especially with the motion of an electron or proton. The point of view taken here, which was first published in a series of German papers,[2] is rather that material points consist of, or are nothing but, wave-systems. This extreme conception may be wrong, indeed it does not offer as yet the slightest explanation of why only such wave-systems seem to be realized in nature as correspond to mass-points of definite mass and charge. On the other hand the opposite point of view, which neglects altogether the waves discovered by L. de Broglie and treats only the motion of material points, has led to such grave difficulties in the theory of atomic mechanics

[1] L. de Broglie, Ann. de Physique 3, 22 (1925).

[2] E. Schrödinger, Ann. d. Physik 79, 361, 489, 734; 80, 437 81, 109 (1926); Die Naturwissenschaften 14, 664 (1926).

—and this after century-long development and refinement—that it seems not only not dangerous but even desirable, for a time at least, to lay an exaggerated stress on its counterpart. In doing this we must of course realize that a thorough correlation of all features of physical phenomena can probably be afforded only by a harmonic union of these two extremes.

The chief advantages of the present wave-theory are the following.

a. The laws of motion and the quantum conditions are deduced simultaneously from one simple Hamiltonian principle.

b. The discrepancy hitherto existing in quantum theory between the frequency of motion and the frequency of emission disappears in so far as the latter frequencies coincide with the differences of the former. A definite localization of the electric charge in space and time can be associated with the wave-system and this with the aid of ordinary electrodynamics accounts for the frequencies, intensities and polarizations of the emitted light and makes superfluous all sorts of correspondence and selection principles.

c. It seems possible by the new theory to pursue in all detail the so-called "transitions," which up to date have been wholly mysterious.

d. There are several instances of disagreement between the new theory and the older one as to the particular values of the energy or frequency levels. In these cases it is the new theory that is better supported by experiment.

To explain the main lines of thought, I will take as an example of a mechanical system a material point, mass m, moving in a conservative field of force $V(x, y, z)$. All the following treatment may very easily be extended to the motion of the "image-point," picturing the motion of a wholly arbitrary conservative system in its "configuration-space" (q-space, not pq-space). We shall effect this generalization in a somewhat different manner in Section 7. Using the usual notations the kinetic energy T is

$$T = \tfrac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = (1/2m)(p_x^2 + p_y^2 + p_z^2). \tag{1}$$

The well-known Hamiltonian function of action W,

$$W = \int_{t_0}^{t} (T - V)dt, \tag{2}$$

taken as a function of the upper limit t and of the final values of the coordinates x, y, z satisfies the Hamiltonian partial differential equation,

$$\partial W/\partial t + (1/2m)\left[(\partial W/\partial x)^2 + (\partial W/\partial y)^2 + (\partial W/\partial z)^2\right] + V(x, y, z,) = 0. \tag{3}$$

To solve this equation, we put as usual

$$W = -Et + S(x, y, z),\qquad(4)$$

E being an integration constant, viz., the total energy, and S a function of x, y, z only. Eq. (3) may then be written

$$|\,\mathrm{grad}\,W\,| = [2m(E-V)]^{\frac{1}{2}}.\qquad(5)$$

In this form it lends itself to a very simple geometrical interpretation. Assume t constant for the moment. Any function W of space alone can be described by giving geometrically the system of surfaces on which W is constant and by writing down on each one of these surfaces the constant value, say W_0, which the function W takes on it. On the other hand, we can easily construct a solution of Eq. (5) starting from an arbitrary surface and an arbitrarily chosen value W_0, which we ascribe to it. For after having chosen starting surface and starting value and after—still arbitrarily—having designated one of its two sides or "shores" as the positive one, we simply have to extend the normal at every point of the chosen surface to the length, say

$$dn = dW_0 / [2m(E-V)]^{\frac{1}{2}}.$$

The totality of points arrived at in this way will fill a surface to which we obviously have to ascribe the value $W_0 + dW_0$. The continuation of this procedure will supply us the whole system of surfaces and values of constants belonging to them, i.e. the whole distribution in space of the function W, at first for t constant.

Now let the time vary, Eq. (4) shows that the system of surfaces will not vary, but that the values of the constants will travel along the normals from surface to surface with a certain speed u, given by

$$u = E / [2m(E-V)]^{\frac{1}{2}}.\qquad(6)$$

The velocity u is a function of the energy-constant E and besides, since it contains $V(x,y,z)$ is a function of the coordinates.

Instead of thinking of the surfaces as fixed in space and letting the values of the constant wander from surface to surface, we may equally well think of a certain numerical value of W as attached to a certain individual surface and let the surfaces wander in such a way that each of them continually takes the place and exact form of the following one. Then the quantity u, given by Eq. (6) will denote the normal-velocity of any surface at any one of its points. Adopting this view we arrive at a picture which exactly coincides with the propagation of a stationary wave-system in an optically non-homogeneous (but isotropic)

medium, W being proportional to the phase and u being the phase-velocity. (The index of refraction would have to be taken proportional to u^{-1}.) The above-mentioned construction of normals dn is obviously equivalent to Huygens' principle. The orthogonal curves of our system of W-surfaces form a system of rays in our optical picture; they are possible orbits of the material point in the mechanical problem. Indeed it is well known that

$$p_x = m\dot{x} = \partial W/\partial x \tag{7}$$

(with two analogous equations for y and z). It may be useful, to remark, that the phase-velocity u is not the velocity of the material point. The latter is, by (7) and (5)

$$v = (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)^{\frac{1}{2}} = [2(E-V)/m]^{\frac{1}{2}}. \tag{8}$$

Comparing (6) and (8) we see, that u and v vary even inversely to each other. The well-known mechanical principle due to and named after Hamilton can very easily be shown to correspond to the equally well-known optical principle of Fermat.

2. Nothing of what has hitherto been said is in any way new. All this was very much better known to Hamilton himself than it is in our day to a good many physicists. Indeed, the theory of the propagation of light in a non-homogeneous medium, which Hamilton had developed about ten years earlier, became, by the striking analogy which occurred to him, the starting-point for his famous theories in pure mechanics. Notwithstanding the great popularity reached by the latter, the way which had led to them was nearly forgotten.[3] Stress must now be laid on the fact, that though in our above-stated reasoning such conceptions as "wave-surfaces," "Huygens' principle," "Fermat's principle" come into play, nevertheless the whole established analogy deals rather with geometrical optics than with real physical or undulatory optics. Indeed the chief and fundamental mechanical conception is that of the path or orbit of the material particle, and it corresponds to the conception of rays in the optical analogy. Now the conception of rays is thoroughly well-defined only in pure abstract geometrical optics. It loses nearly all significance in real physical optics as soon as the dimensions of the beam or of material obstacles in its path become comparable with the wave-length. And even when this is not the case, the notion of rays is, in

[3] See F. Klein, Jahresber. d. Deutsch. Math. Ver. 1 (1891); Zeits. f. Math. u. Phys. 46 (1901); (Ges. Abh. II, 601, 603); E. T. Whittaker, Analytical Dynamics, Chap. 11. A. Sommerfeld, Atombau, German ed., p. 803. The analogy has been rediscovered in relativistic mechanics in the paper of L. de Broglie, quoted above.

physical optics, merely an approximate one. It is wholly incapable of being applied to the fine structure of real optical phenomena, i.e. to the phenomena of diffraction. Even in extending geometrical optics somewhat by adding the notion of Huygens' principle (in the simple form, used above) one is not able to account for the most simple phenomena of diffraction without adding some further very strange rules concerning the circumstances under which Huygens' envelope-surface is or is not physically significant. (I mean the construction of "Fresnel's zones.") These rules would be wholly incomprehensible to one versed in geometrical optics alone. Furthermore it may be observed that the notions which are fundamental to real physical optics, i.e. the wave-function itself (W is merely the phase), the equation of wave-propagation, the wavelength and frequency of the waves, do not enter at all into the above stated analogy. The phase-velocity u does enter but we have seen that it is not very intimately connected with the mechanical velocity v.

At first sight it does not seem at all tempting, to work out in detail the Hamiltonian analogy as in real undulatory optics. By giving the wave-length a proper well-defined meaning, the well-defined meaning of rays is lost at least in some cases, and by this the analogy would seem to be weakened or even to be wholly destroyed for those cases in which the dimensions of the mechanical orbits or their radii of curvature become comparable with the wave-length. To save the analogy it would seem necessary to attribute an exceedingly small value to the wavelength, small in comparison with all dimensions that may ever become of any interest in the mechanical problem. But then again the working out of an undulatory picture would seem superfluous, for geometrical optics is the real limiting case of undulatory optics for vanishing wavelength.[4]

Now compare with these considerations the very striking fact, of which we have today irrefutable knowledge, that ordinary mechanics is really not applicable to mechanical systems of very small, viz. of atomic dimensions. Taking into account this fact, which impresses its stamp upon all modern physical reasoning, is one not greatly tempted to investigate whether the non-applicability of ordinary mechanics to micro-mechanical problems is perhaps of exactly the same kind as the non-applicability of geometrical optics to the phenomena of diffraction or interference and may, perhaps, be overcome in an exactly similar way? The conception is: the Hamiltonian analogy has really to be worked out towards undulatory optics and a definite size is to be at-

[4] A. Sommerfeld and I. Runge, Ann. d. Physik **35**, 290 (1911).

tributed to the wave-length in every special case. This quantity has a real meaning for the mechanical problem, viz. that ordinary mechanics with its conception of a moving point and its linear path (or more generally of an "image-point" moving in the coordinate space) is only approximately applicable so long as they supply a path, which is (and whose radii of curvature are) large in comparison with the wave-length. If this is not the case, it is a phenomenon of wave-propagation that has to be studied. In the simple case of one material point moving in an external field of force the wave-phenomenon may be thought of as taking place in the ordinary three-dimensional space; in the case of a more general mechanical system it will primarily be located in the coordinate space (q-space, not pq-space) and will have to be projected somehow into ordinary space. At any rate the equations of ordinary mechanics will be of no more use for the study of these micro-mechanical wave-phenomena than the rules of geometrical optics are for the study of diffraction phenomena. Well known methods of wave-theory, somewhat generalized, lend themselves readily. The conceptions, roughly sketched in the preceding are fully justified by the success which has attended their development.

3. Let us return to the system of W-surfaces, dealt with in Section 1 and let us associate with them the idea of stationary sinusoidal waves whose phase is given by the quantity W, Eq. (4). The wave-function, say ψ, will be of the form

$$\psi = A(x,y,z)\sin(W/K)$$
$$= A(x,y,z)\sin[-Et/K + S(x,y,z)/K], \tag{9}$$

A being an "amplitude" function. The constant K must be introduced and must have the physical dimension of *action* (energy$\times$time), since the argument of a sine must always be a pure number. Now, since the frequency of the wave (9) is obviously

$$\nu = E/2\pi K \tag{10}$$

one cannot resist the temptation of supposing K to be a *universal constant*, independent of E and independent of the nature of the mechanical system, because if this be done and K be given the value $h/2\pi$, then the frequency ν will be given by

$$\nu = E/h, \tag{11}$$

h being Planck's constant. Thus the well known universal relation between energy and frequency is arrived at in a rather simple and unforced way.

In ordinary mechanics the absolute value of the energy has no definite meaning, only energy-differences have. This difficulty can be met and a zero-level of energy can be defined in an entirely satisfactory way by using relativistic mechanics and·the conception of equivalence of mass and energy.[1] But it is unnecessary to dwell on this subject here. While the frequency ν of our waves by Eq. (10) or (11) is indeed dependent on the zero-level of energy, their wave-length is not. And after what has been said above, it is the wave-length that is of greatest interest. The comparison of this quantity with the dimensions of the path or orbit of the material particle, calculated according to ordinary mechanics, will tell us whether the latter calculation is or is not of physical significance, whether the methods of ordinary mechanics are approximately applicable to the special problem or not. The wave-length λ by (11) and (6) is

$$\lambda = u/\nu = h/[2m(E-V)]^{\frac{1}{2}} \tag{12}$$

Here $E - V$ is the kinetic energy $\frac{1}{2}mv^2$ which indeed is independent of the zero-level of the total energy. Inserting its value we have

$$\lambda = h/mv. \tag{13}$$

To test the question whether an electron, moving in a Keplerian orbit of atomic dimensions may, following our hypotheses, still be dealt with by ordinary mechanics, let a be a length of atomic dimensions and compare λ with a.

$$\lambda/a = h/mva \tag{14}$$

The denominator on the right is certainly of the order of magnitude of the moment of momentum of the electron, and the latter is well known to be of the order of magnitude of Planck's constant for a Keplerian orbit of atomic dimensions. So λ/a becomes of the order of unity and, following our conceptions, ordinary mechanics will be no more applicable to such an orbit than geometrical optics is to the diffraction of light by a disk of diameter equal to the wave-length. Were a physicist to try to understand the latter phenomenon by the conception of rays, with which he is acquainted from macroscopic geometrical optics, he would meet with most serious difficulties and apparent contradictions. The "rays" (stream lines of the flow of energy) would no longer be rectilinear and would influence one another in a most curious way, in full contradiction with the most fundamental laws of geometrical optics. In the same way the conception of orbits of material points seems to be inapplicable to orbits of atomic dimensions. It is very satisfactory, that the limit of applicability of ordinary mechanics is, by equating K (essentially)

to Planck's constant (Eq. 11), determined to an order of magnitude, which is exactly the one to be postulated, if the new conception is to help us in our quantum difficulties. We may add, that by Eq. (13) for a Keplerian electronic orbit of the order of magnitude of a high quantum orbit, the relation of wave-length to orbital dimensions becomes of the order of magnitude of the reciprocal of the quantum number. Hence ordinary mechanics will offer a better and better approximation in the limit of increasing quantum number (or orbital dimensions), and this is just what is to be expected from any reasonable theory.

By the fundamental equation $\nu = E/h$ (Eq. 11) the phase velocity u, given by Eq. (6) proves to be dependent on the frequency ν. Therefore Eq. (6) is an equation of dispersion. By this a very interesting light is thrown on the relation of the two velocities (1) velocity v of the moving particle, Eq. (8); (2) phase-velocity u, Eq. (6). v is easily proved to be exactly the so-called group velocity belonging to the dispersion formula (6).[5] By using this interesting result it is possible to form an idea how ordinary mechanics is capable of giving an approximate description of our wave motion. By superposing waves of frequencies in a small interval ν; $\nu + d\nu$ it is possible to construct a "parcel of waves," the dimensions of which are in all directions rather small, though they must be rather large in comparison to the wave-length. Now it can be proved, that the motion of—let us say—the "center of gravity" of such a parcel will, by the laws of wave propagation, follow exactly the same orbit as the material point would by the laws of ordinary mechanics. This equivalence is always maintained, even if the dimensions of the orbit are not large in comparison with the wave-length. But in the latter case it will have no significance, the wave parcel being spread out in all directions far over the range of the orbit. On the contrary, if the dimensions of the orbit are comparatively large, the motion of the wave parcel as a whole may afford a sufficient idea of what really happens, if we are not interested in its intrinsic constitution. As stated above this "motion as a whole" is governed by the laws of ordinary mechanics.

4. We shall not dwell on this question further, but proceed to the far more interesting applications of the theory to micro-mechanical problems. As stated above, the wave-phenomena must in this case be studied in detail. This can only be done by using an "equation of wave propagation." Which one is this to be? In the case of a single material point, moving in an external field of force, the simplest way is to try to use the ordinary wave-equation

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[5] This important theorem is due to L. de Broglie, l.c. The relation is: $v = d\nu/d(\nu/u)$

$$\Delta\psi - \ddot{\psi}/u^2 = 0 \tag{15}$$

and to insert for u the quantity given by Eq. (6), which depends on the space coordinates (through the potential energy V) and on the frequency E/h. The latter dependence restricts the use of (15) to such functions ψ as depend on the time only through the factor $e^{\pm 2\pi i t E/h}$. (A similar restriction is always imposed on the wave equation, as soon as we have dispersion.) So we shall have

$$\ddot{\psi} = -4\pi^2 E^2 \psi / h^2$$

Inserting this and Eq. (6) in Eq. (15) we get

$$\Delta\psi + 8\pi^2 m(E - V)\psi / h^2 = 0, \tag{16}$$

where ψ may be assumed to depend on x, y, z only. (We omit changing the notation of the dependent variable, which we really ought to do.)

Now what are we to do with Eq. (16)? At first sight this equation seems to offer ill means of solving atomic problems, e.g. of defining discrete energy-levels in the hydrogen atom. Being a partial differential equation, it offers a vast multitude of solutions, a multitude of even a higher transcendent order of magnitude than the system of solutions of the ordinary differential equations of ordinary mechanics. But the deficiency of the latter in atomic problems consisted, as is well known, by no means in that they supplied too small a number of possible orbits, but quite on the contrary, much too many. To select a discrete number of them as the "real" or "stationary" ones is, according to the view hitherto adopted, the task of the "quantum-conditions." Our wave equation (16), by augmenting the possibilities indefinitely, instead of restricting them, seems to lead us from bad to worse.

Happily because of the very interesting character which Eq. (16) takes in actual atomic problems, this fear proves to be erroneous. Putting for instance

$$V = -e^2/r, \tag{17}$$

(e = electronic charge, $r = (x^2 + y^2 + z^2)^{\frac{1}{2}}$, we get for the simplified hydrogen atom or one body problem:

$$\Delta\psi + 8\pi^2 m(E + e^2/r)\psi / h^2 = 0. \tag{18}$$

Now this equation for a great part of the possible values of the energy or frequency constant E, proves to offer no solution at all which is continuous, finite and single-valued throughout the whole space; for the E-values in question, every solution ψ, that satisfies the two other conditions (viz. continuity and single-valuedness) grows beyond all

limits either in approaching infinity or in approaching the origin of co-
ordinates. The only E-values, for which this is not the case i.e. for which
solutions exist, that are continuous, finite and single-valued throughout
the whole space are the following ones

(1) $E > 0$

(2) $E = -2\pi^2 m e^4 / h^2 n^2$ $(n = 1, 2, 3, 4 \cdots)$ (19)

The first set corresponds to the hyperbolic orbits in ordinary mechanics.
It is the general view, that according to ordinary quantum theory the
hyperbolic orbits are not submitted to quantization. In our treatment
this turns out quite spontaneously from the fact that every positive
value of E leads to finite solutions. The second set corresponds exactly
to Bohr's stationary energy levels of the elliptic orbits.

Though I cannot enter here upon the exact and rather tiresome proof
of the foregoing statements, it may be interesting to describe in rough
feature the solutions belonging to the second series of E-levels. The
solution may be performed in three-dimensional[6] polar coordinates, by
assuming ψ to be a product of a function of the polar angles and a function
of the radius r only. The former is a spherical surface harmonic whose
order, increased by unity, corresponds to the azimuthal quantum num-
ber. The functions of r, which come into play, somewhat resemble (in
rough feature) the Bessel functions, though with the difference that they
have but a finite number of positive roots, and this number exactly
corresponds to the radial quantum number. These roots lie within a
region from the origin of about the same order of magnitude as the
corresponding Bohr orbit. After having passed the last root with in-
creasing r and a maximum or minimum not far away from it, the function
tends to diminish exponentially as r approaches infinity. So the whole
of the wave-phenomenon, though mathematically spreading throughout
all space, is essentially restricted to a small sphere of a few Angstroms
diameter which may be called "the atom" according to undulatory
mechanics. Any one of the above mentioned solutions (consisting of a
product of a spherical surface-harmonic and a function of r only) greatly
resembles a fundamental vibration of an elastic sphere, with a finite
number of (1) spheres, (2) cones, (3) planes as "node surfaces." But
it is surely not permissible to think that the wave-motion constituting
the atom is, in general, restricted to one of these solutions, the special
selection and separation of which is very much influenced by the choice

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[6] It is of course not allowed to restrict the problem to two dimensions as in ordinary
mechanics since the wave-phenomenon is essentially three-dimensional.

of coordinates. To every one of the discrete values of E belongs a finite number of special solutions. In forming a linear aggregate of them with arbitrary constant multipliers we get the most general solution of Eq. (18) for the particular value of E. The number of arbitrary constants entering into this aggregate is exactly equal to what is called the "statistical weight" of this energy-level, or in other words, to the number of separate levels into which it is split up according to Bohr's theory (and, by the way, also according to the present theory) by the addition of perturbing forces, that do away with the so-called "degeneration" of the problem. It will perhaps be remembered, that in ordinary quantum theory the number of states that is supplied by the method alluded to, is not exactly correct. Definite experimental evidence compels us to exclude by additional reasoning, more or less convincing from the theoretical point of view, a definite number of states, viz. those which have the equatorial quantum number zéro. It is gratifying to be able to state, that according to the present theory the above mentioned number of arbitrary constants or, in other words, the number of separate levels or frequencies into which a degenerated E-level is split up by a perturbing potential is quite correct from the beginning. The theory needs no supplementation since it precludes a vibrational state corresponding to a Bohr-orbit with equatorial quantum number zero.

To complete this description we may add, that to the lowest E-level, or from the wave-motion point of view its "fundamental tone" which corresponds to the normal state of the atom, there belongs but one mode of vibration, and this is a very simple one; the function ψ shows complete spherical symmetry and there are no node surfaces at all. Both the radial quantum number as well as the order of the spherical surface harmonic vanish.

5. I should like to discuss in a few words the question, why Eq. (18) possesses finite solutions only for certain selected values of the constant E. The whole behavior described on the foregoing pages would be quite familiar to every physicist, if the problem were a so-called "boundary-condition problem," i.e. if the function ψ were required only in the interior of a given surface, let us say a sphere of given radius and had to fulfill certain conditions on the boundary of this sphere, e.g. to vanish. Now though this is not the case, the problem is indeed equivalent to a boundary-condition problem, the boundary being the infinite sphere. Thus the selected values (19) are quite properly to be named "characteristic values" and the solutions, that belong to them, "characteristic functions" of the problem connected with Eq. (18). The mathematical

reason,[7] why no boundary conditions in the proper sense of the word are neither needed nor allowed at the infinite boundary, is that a singular point of Eq. (18) is approached when we recede in any direction in space toward infinity. This can easily be seen by splitting up the equation in the way described above, using polar coordinates. The resulting ordinary differential equation with the variable r has two singularities, at $r = 0$ and at $r = \infty$. It offers (for negative values of E) but one solution that remains finite at $r = 0$, and but one that remains finite at $r = \infty$. These two solutions are in general not identical, but they are for the selected values of E given by (19).

But instead of dwelling on this purely mathematical side of the subject, I should like to present an idea why Eq. (18) shows such a queer behavior so as to make the matter clear to anyone who is acquainted only with the most general principles of wave theory. If E is negative the bracket in Eq. (18) will be negative outside a certain sphere. Now remembering the way in which Eq. (18) was derived from Eq. (15), we see that a negative value of the bracket in (18) clearly means a negative value of the square of wave-velocity, or an imaginary value of wave-velocity. What does this imply? The Laplacian operator is well known to be intimately connected with the average excess of the neighboring values over the value of the function at the point considered. Thus the ordinary wave-equation (15) with a positive value of u^2 provides an accelerated increase (or a retarded decrease) of the function at all those points, where its value is lower than the average of the neighboring values; and, vice versa, a retarded increase (or an accelerated decrease) at those points where the function exceeds the average of its neighborhood. Thus the ordinary wave-equation represents a certain tendency to smooth out again all differences between the values of the function at different points, though not at the very moment they appear and not indefinitely—as in the case of the equation for heat conduction. It will however certainly prevent the function from increasing or decreasing beyond all limit.

If the quantity u^2, instead of being positive, is negative which we have seen to be sometimes the case with Eq. (18), then all the foregoing reasoning is just reversed. There is in the course of time a tendency to exaggerate infinitely all "humps" of the function and even spontaneously to form humps out of quite insignificant traces. Evidently a function which is subject to such a revolutionary sort of equation, is continually

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[7] See e.g. R. Courant and D. Hilbert, Methoden der mathematischen Physik I (Berlin, Springer 1924), Chap. 5, §9, p. 1.

exposed to the very highest danger of increasing or decreasing beyond all limit. At any rate it is no longer astonishing, that special conditions must be fulfilled to prevent such an occurrence. The mathematical treatment shows that these conditions consist exactly in E having one of the second set of characteristic values given by (19), whereas the first set obviously prevents all accidents by making the square of the phase-velocity positive throughout the space.

6. I will now give an account of some of the results that have hitherto been obtained with this new mechanics. Rather simple problems are offered by the harmonic oscillator and the rotator. The E-levels of the former prove to be

$$(n+\tfrac{1}{2})h\nu_0 \; ; \qquad\qquad n = 0,1,2,3 \; \cdots$$

instead of $nh\nu_0$ according to the ordinary quantum theory. The E-levels of the rotator are

$$n(n+1)h^2/8\pi^2 I$$

(I = moment of inertia), the well known n^2 being replaced by $n(n+1)$. If we are interested only in the differences of levels—as is actually the case—this amounts to the same as replacing n^2 by $(n+\tfrac{1}{2})^2$, for

$$(n+\tfrac{1}{2})^2 - n(n+1) = \tfrac{1}{4},$$

independent of n. It is well known that so-called half-quantum numbers are actually supported by the experimental evidence on most of the simple band spectra, and are probably contradicted by none of them. Mr. Fues, whose valuable help I owe to the Rockefeller Institution (International Education Board), has worked out[s] the band theory of diatomic molecules in detail, taking into account the mutual influence of rotation and oscillation and the fact, that the latter is not of the simple harmonic type. The result is in exact agreement with the ordinary treatment except that the quantum-numbers become half-integer also in all correction-terms. It would hardly have been possible to attack the problem just mentioned, as well as many similar ones, by direct methods, since the differential equation (16) is in general of a very difficult type. In many cases, however, this difficulty is overcome by the theory of perturbations which the writer has developed together with Mr. Fues. This theory, though much simpler, yet shows an interesting parallelism to the well known theory of perturbations in ordinary mechanics. It allows the calculation by mere quadratures of the small modification of characteristic values and characteristic functions, that are caused by

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[s] E. Fues, Ann. d. Physik **80**, 367 (1926); another paper in press.

introducing an additional small term (function of the independent vari-. ables) in the coefficients of an equation whose characteristic values and characteristic functions are known.

An interesting example of the application of this mathematical theory is afforded by the perturbation of the hydrogen-atom caused by an external homogeneous electric field (Stark-effect). The discrete Balmer levels, shown in Eq.(19-2) are, as characteristic values, not simple but many fold. Each of them corresponds to n^2 characteristic values that coincide by chance or, more properly speaking, because of the high symmetry or simplicity of the coefficients of Eq. (18). The addition of an external electric field, small in comparison with the atomic field, does away with this symmetry and splits up every one of the Balmer-levels into a set of near neighboring levels, though not into as many as n^2, because the splitting up in this case is not thorough. The writer has been able to show that these levels exactly coincide with those given by the well known formula of Epstein, a rather severe test of our undulatory mechanics, since experimentally no deviation whatever, at least in the limit of a weak field, would have been allowed from this famous formula.

But not only the levels, i.e. the frequencies, but also the intensities and polarizations of the emitted lines in the Stark effect can be calculated from undulatory mechanics in very fair agreement with experiment. Hitherto we have not attached a definite physical meaning to the wave-function ψ. It is possible, however, to give it a certain electrodynamical meaning, which will be discussed in detail in Section 8 and which converts our atom into a system of fluctuating charges, spread out continuously in space and generating a resultant electric moment, that changes with time with a superposition of frequencies, which exactly coincide with the differences of the vibration-frequencies E/h, i.e. coincide with the frequencies of the emitted light. This in itself is highly satisfactory. But in addition it is possible to calculate the amplitudes of the harmonic components of the electric moment for any direction in space, e.g., in the case of the Stark effect, parallel to the electric field or perpendicular to the field. If the theory is correct, the squares of these amplitudes ought to be proportional to the intensities of the several line components, polarized in either direction. The rather laborious calculations have been performed and the result is shown in Fig. 1.[9] In comparing theory with experiment it must be born in mind that the calculations have been performed only in the limit of a very weak external

[9] The experimental data were taken from I. Stark, Ann. d. Physik **48**, 193 (1915). In these figures theoretical intensities that are too small to be indicated by a line of the proper length are marked by a dot.

field and that in the region of field-strength used in experiments (about 100,000 volts/cm) a very marked influence on the intensities is found both by experiment and by theory. In particular the very weak or vanishing components are enhanced with increasing field. The sum of the intensities of all the perpendicular components of one Balmer line turns out exactly equal to the sum of the parallel components of the same line. This is in full agreement with Stark's statement that no polarization of the emitted light as a whole is produced by the field.

I ought to emphasize here, that I was led to the foregoing nearly classical calculation of intensities by noticing *a posteriori*, i.e. after the main features of undulatory mechanics had been developed, its complete mathematical agreement with the theory of matrices put forward by Heisenberg, Born and Jordan.[10] The results shown in Fig. 1 may as well be called the results of the latter theory though they have not yet been calculated by its direct application. The connection of the two theories is a rather intricate one and is by no means to be observed at first sight.

7. It was stated in the beginning of this paper that in the present theory both the laws of motion and the quantum conditions can be deduced from one Hamiltonian principle. To prove this it must be shown that the wave-equation (16) can be derived from an integral-variation principle; for this equation is indeed the only fundamental equation of the theory (in the case of a single material point, moving in a conservative field of force, the only one considered in detail on the foregoing pages).

The connection of Eq. (16) with a Hamiltonian principle is very simple and almost exactly the same as in ordinary vibration problems. Furthermore this connection affords the simplest means of almost cogently extending the theory to a wholly arbitrary conservative system.

Suppose, the extreme values of the following integral extending over all space were required.

$$I_1 = \int \int \int \left\{ h^2 [(\partial\psi/\partial x)^2 + (\partial\psi/\partial y)^2 + (\partial\psi/\partial z)^2]/8\pi^2 m + V\psi^2 \right\} dx\, dy\, dz,$$

$$(20)$$

all single-valued, finite and continuously differentiable functions ψ being "admitted to concurrence" that give the following "normalizing" integral a constant value, say 1:

[10] W. Heisenberg, Zeits. f. Physik **33**, 879 (1925); M. Born and P. Jordan, ibid. **34**, 858 (1925); M. Born, P. Jordan and W. Heisenberg, ibid. **35**, 557 (1926); M. Born and N. Wiener, ibid. **36**, 174 (1926); W. Heisenberg and P. Jordan, ibid. **37**, 263 (1926); W. Pauli, Jr., ibid. **36**, 336 (1926); P. A. M. Dirac, Proc. Roy. Soc. **109**, 642 (1925); **110**, 561 (1925); **111**, 281, 405 (1926).

$$I_2 = \int \int \int \psi^2 \, dx \, dy \, dz = 1 \tag{21}$$

In carrying out the variation under this "accessory condition" in the well known manner, Eq. (16) is found as the well known necessary condition for an extreme value of (20) the constant $-E$ being the Lagrangian multiplier with which the variation of the second integral has to be multiplied and added to the first, so as to take care of the accessory condition. Thus the normalized characteristic functions of Eq. (16) are exactly the so-called extremals of the integral (20) under the normalizing condition (21), whereas the characteristic values i.e. the values, that are admissible for the constant E are nothing else than the extreme values of integral (20). (This property of the Langrangian multiplier is well known and is easily recognized by observing, that the non-conditioned, extreme value of $I_1 - EI_2$ can be but zero, any other value being capable as well of augmentation as of diminution by simply multiplying ψ by a constant.)

Now the integrand of (20) proves on closer inspection to have a very simple relation to the ordinary Hamiltonian function of our mechanical problem—in the sense of ordinary mechanics. The said function is, (cf. Section 1):

$$(1/2m)(p_x^2 + p_y^2 + p_z^2) + V(x, y, z). \tag{22}$$

Take this function to be a homogeneous quadratic function of the momenta p_x etc. and of unity and replace therein p_x, p_y, p_z, 1 by $(h/2\pi)$ $(\partial\psi/\partial x)$, $(h/2\pi)$ $(\partial\psi/\partial y)$, $(h/2\pi)$ $(\partial\psi/\partial z)$, ψ, respectively. There results the integrand of (20). This immediately suggests extending our variation problem and hereby our wave-equation (16) to a wholly arbitrary conservative mechanical system. The Hamiltonian function of such will be of the form

$$\frac{1}{2} \sum_{l=1}^{N} \sum_{k=1}^{N} a_{lk} p_l p_k + V \tag{23}$$

with $a_{lk} = a_{kl}$, the a_{lk} and V being some functions of the N generalized coordinates $q_1 \cdots q_N$. Take (23) to be a homogeneous quadratic function of $p_1 \cdots p_N$, 1 and replace these quantities by $(h/2\pi)$ $(\partial\psi/\partial q_1)$, $\cdots$ $(h/2\pi)$ $(\partial\psi/\partial q_N)$, ψ respectively. Writing Δ_p for the determinant

$$\Delta_p = \left| \sum \pm a_{lk} \right|$$

we form the integral

$$I_1 = \int \cdots \int [(h^2/8\pi^2) \sum_l \sum_k a_{lk} (\partial\psi/\partial q_l)(\partial\psi/\partial q_k) + V\psi^2] \Delta_p^{-\frac{1}{2}} dq_1 \cdots dq_N \tag{24}$$

taken over the whole space of coordinates and seek its extreme values under the accessory condition

$$I_2 = \int \cdots \int \psi^2 \Delta_p^{-\frac{1}{2}} dq_1 \cdots dq_N = 1 \tag{25}$$

This leads to the generalization of Eq. (16), viz.

$$\Delta_p^{\frac{1}{2}} \sum_l \frac{\partial}{\partial q_l}\left(\Delta_p^{-\frac{1}{2}} \sum_k a_{lk}\partial\psi/\partial q_k\right) + (8\pi^2/h^2)(E-V)\psi = 0, \tag{26}$$

$-E$ being, as before, the Lagrangian multiplier of (25). The double sum appearing in (26) is a sort of generalized Laplacian in the N-dimensional, non-euclidean space of coordinates. The necessary appearance of $\Delta_p^{-\frac{1}{2}}$ in an integral like (24) or (25) is well known from Gibbs' statistical mechanics; $\Delta_p^{-\frac{1}{2}} dq_1 \cdots dq_N$ is simply the non-euclidean element of volume, e.g. $r^2 \sin \theta d\theta d\phi dr$ in the case of one material point of unit mass, whose position is fixed by three polar coordinates r, θ, ϕ. (In omitting the determinant the integrals would not be invariant relative to point transformations; they would depend on the choice of generalized coordinates.) It is Eq. (26) that has been used in all problems mentioned in Section 6.

8. The question of the real physical meaning of the wave-function ψ has been delayed (see Section 6) until now for the sake of discussing it but once in full generality for a wholly arbitrary system. Eq. (16) or in the more general case, Eq. (26) gives the dependence of the wave-function ψ on the coordinates only, the dependence on time being given for every one particular solution, corresponding to a particular characteristic value $E = E_l$, by the real part of

$$\exp[(2\pi E_l t/h + \theta_l)i], \qquad\qquad i = \sqrt{-1}$$

the θ_l being phase constants. So if u_l ($l=1, 2, 3 \cdots$) be the characteristic functions the most general solution of the wave-problem will be (the real part of)

$$\psi = \sum_{l=1}^{\infty} c_l u_l \exp[(2\pi E_l t/h + \theta_l)i]. \tag{27}$$

(For simplicity's sake we suppose the characteristic values to be all single and discrete.) The c_l are real constants. Now form the square of the absolute value of the complex function ψ. Denoting a conjugate complex value by a bar, this is

$$\psi\bar{\psi} = 2 \sum_{l,l'} c_l c_{l'} u_l u_{l'} \cos[2\pi(E_l - E_{l'})t/h + \theta_l - \theta_{l'}]. \tag{28}$$

This of course, like ψ itself, is in the general case a function of the generalized coordinates $q_1 \cdots q_N$ and the time,—not a function of ordinary space and time as in ordinary wave-problems. This raises some difficulty in attaching a physical meaning to the wave-function. In the case of the hydrogen atom (taken as a one-body problem) the difficulty disappears. In this case it has been possible to compute fairly correct values for the intensities e.g. of the Stark effect components (see Section 6, Fig. 1) by the following hypothesis: the charge of the electron is not concentrated in a point, but is spread out through the whole space, proportional to the quantity $\psi\,\bar\psi$.
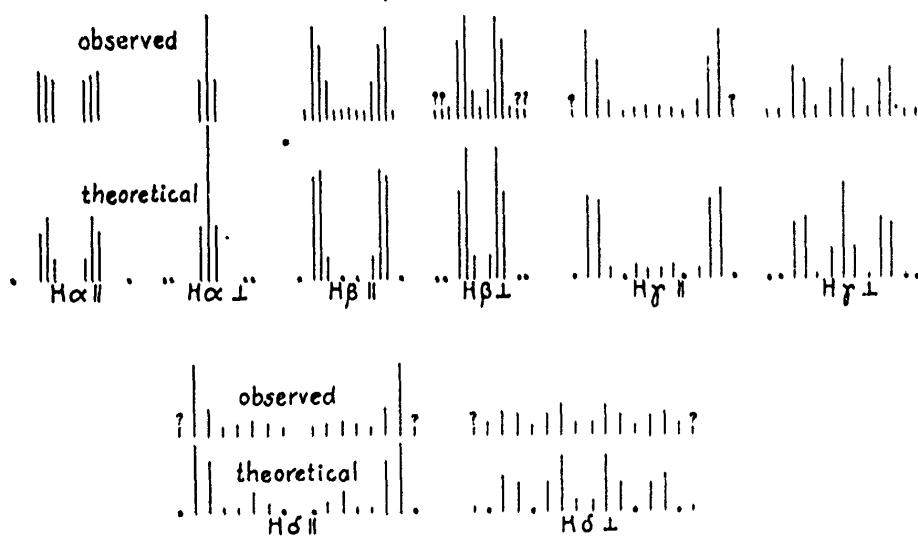

FIG. 1

It has to be born in mind, that by this hypothesis the charge is nevertheless restricted to a domain of, say, a few Angstroms, the wave-function ψ practically vanishing at greater distance from the nucleus (see Section 4). The fluctuation of the charge will be governed by Eq. (28), applied to the special case of the hydrogen atom. To find the radiation, that by ordinary electrodynamics will originate from these fluctuating charges, we have simply to calculate the rectangular components of the total electrical moment[11] by multiplying (28) by x, y, z respectively, and integrating over the space, e.g.[12]

$$\int \int \int z\psi\bar\psi\,dx\,dy\,dz = 2 \sum_{l,l'} c_l c_{l'} \cos\left[2\pi(E_l - E_{l'})t/h + \theta_l - \theta_{l'}\right]$$

[11] This procedure is legitimate only because and as long as the domain to which the charge is practically restricted remains small in comparison with the optical wave-length that corresponds to the frequencies $(E_l - E_{l'})/yh$.

[12] In the sum $\sum_{l,l'}$ each pair of values of l,l' is to be taken but once and the terms with $l' = l$ are to be halved.

$$\int \int \int z u_l u_{l'} dx dy dz \tag{29}$$

Thus the total electric moment is seen to be a superposition of dipoles, which are associated with the pairs of characteristic functions which vibrate harmonically with the frequencies $(E_l - E_{l'})/h$, well known from N. Bohr's famous frequency-condition. The intensity of emitted radiation of a particular frequency is to be expected proportional to the square of

$$c_l c_{l'} \int \int \int z u_l u_{l'} dx dy dz.$$

The supposition made on the c_l, in calculating the intensities of the Stark effect components, Fig. 1, is, that the c_l be equal for every set of characteristic values derived from one Balmer level (Eq. 19-2) by the action of the electrical field. The relative intensities of the fine structure components will then be proportional to the square of the triple integral. This is found to be in fair agreement with experiment.

The triple integral may be shown to be equal to what in Heisenberg's theory would be called the "element of matrix $z(l, l')$". This constitutes the intimate connection between the two theories. But the important achievement of the present theory—imperfect as it may in many respects be —seems to me to be that by a definite localization of the charge in space and time we are able from ordinary electrodynamics really to derive both the frequencies and the intensities and polarizations of the emitted light. All so-called selection principles automatically result from the vanishing of the triple integral in the particular case.

Now how are these conceptions to be generalized to the case of more than one, say of N, electrons? Here Heisenberg's formal theory has proved most valuable. It tells us though less by physical reasoning than by its compact formal structure that Eq. (29) giving a rectangular component of total electric moment has to be maintained with the only differences that (1) the integrals are $3N$-fold instead of three fold, extending over the whole coordinate space; (2) z has to be replaced by the sum $\sum e_i z_i$ i.e. by the z-component of the total electrical moment which the point-charge model would have in the configuration $(x_1, y_1, z_1; x_2, y_2, z_2; \cdots x_N, y_N, z_N)$ that relates to the element $dx_1 \cdots dz_N$ of the integration.

But this amounts to making the following hypothesis as to the physical meaning of ψ which of course reduces to our former hypothesis in the case of one electron only: the real continuous partition of the charge is a sort of mean of the continuous multitude of all possible configurations

of the corresponding point-charge model, the mean being taken with the quantity $\psi\,\bar\psi$ as a sort of weight-function in the configuration space.

No very definite experimental results can be brought forward at present in favor of this generalized hypothesis. But some very general theoretical results on the quantity $\psi\,\bar\psi$ persuade me that the hypothesis is right. For example the value of the integral of $\psi\,\bar\psi$, taken over the whole co-ordinate space proves absolutely constant (as it should, if $\psi\,\bar\psi$ is a reasonable weight function) not only with a conservative, but also with a non-conservative system. The treatment of the latter will be roughly sketched in the following section.

9. Eq. (16) or more generally (26) which is fundamental to all our reasoning has been arrived at under the supposition that ψ depends on the time only through the factor

$$e^{\pm 2\pi i E t / h} \tag{30}$$

But this amounts to saying, that

$$\dot\psi = \pm 2\pi i E\psi/h. \tag{31}$$

From this equation and from Eq. (26) the quantity E may be eliminated and so an equation be formed that must hold in any case, whatever be the dependence of the wave-function ψ on time:

$$\Delta_p{}^{\frac12} \sum_l \frac{\partial}{\partial q_l}\left(\Delta_p{}^{-\frac12}\sum_k a_{lk}\partial\psi/\partial q_k\right) - 8\pi^2 V\psi/h^2 \mp (4\pi i/h)\partial\psi/\partial t = 0 \tag{32}$$

The ambiguous sign of the last term presents no grave difficulty. Since physical meaning is attached to the product $\psi\,\bar\psi$ only, we may postulate for ψ either of the two equations (32); then $\bar\psi$ will satisfy the other and their product will remain unaltered.

Eq. (32) lends itself to generalization to an arbitrary non-conservative system by simply supposing the potential function V to contain the time explicitly. A case of greatest interest is obtained by adding to the potential energy of a conservative system a small term; viz., the non-conservative potential energy, produced in the system by an incident light wave. We cannot enter here into the details, but shall only present the main features of the solution. The effect of the incident light wave is, that with each free vibration of the undisturbed system, frequency E_l/h, there are associated two forced vibrations with, in general, very small amplitudes and with the two frequencies $E_l/h \pm \nu$, ν being the frequency of the incident beam of light. Following the same principles as in the foregoing section we find every free vibration, cooperating with

its associated forced vibrations to give rise to a forced light emission with the difference frequency

$$E_l/h - (E_l/h \pm \nu) = \mp \nu$$

i.e. with exactly the frequency of the incident beam of light. This forced emission is of course to be identified with the secondary wavelets that are necessary to account for absorption, dispersion and scattering. In calculating their amplitudes one finds them, indeed, to increase very markedly as soon as the incident frequency ν approaches any one of the emission frequencies $(E_l - E_{l'})/h$. The final formula is almost identical with the well known Helmholtz dispersion formula in the form presented by Kramers.[13]

The case of resonance cannot yet be treated quite satisfactorily, since a damping-term seems to be missing in our fundamental equation, even in the case of a free conservative system. (The radiation, which according to the assumptions of Section 8 is emitted by the cooperation of every pair of free vibrations, must of course in some way alter their amplitudes. This it does not do according to the assumptions hitherto made.) But it is quite interesting to observe that also with that damping term still missing, we do not encounter the accident of infinite amplitudes in the case of resonance, well known from the classical treatment of the subject. The only thing that happens is that an incident light wave of ever so small an amplitude will raise the forced vibration of the system to a finite amplitude. And furthermore if, for example, from the beginning only one free vibration was set up, say that belonging to $E_{l'}$ and if

$$h\nu = E_{l'} - E_l,$$

then the forced vibration, raised to finite amplitude, is in shape and frequency identical with the free vibration belonging to $E_{l'}$. At the same time the amplitude of the vibration E_l is markedly diminished. The sum of squares of all amplitudes remains constant under all circumstances. This behavior seems to afford an insight (though incomplete) into the so-called transition from one stationary state to another which hitherto has been wholly inaccessible to computation.

10. In the foregoing report the undulatory theory of mechanics has been developed without reference to two very important things, viz. (1) the relativity modifications of classical mechanics, (2) the action of a magnetic field on the atom. This may be thought rather peculiar since L. de Broglie, whose fundamental researches gave origin to the present

[13] H. A. Kramers, Nature, May 10 (1924), Aug. 30 (1924); H. A. Kramers and W. Heisenberg, Zeits. f. Physik 31, 681 (1925).

theory, even started from the relativistic theory of electronic motion and from the beginning took into account a magnetic field as well as an electric one.

It is of course possible to take the same starting point also for the present theory and to carry it on fairly far in using relativistic mechanics instead of classical and including the action of a magnetic field. Some very interesting results are obtained in this way on the wave-length displacement, intensity and polarization of the fine structure components and of the Zeeman components of the hydrogen atom.[14] There are two reasons why I did not think it very important to enter here into this form of the theory. First, it has until now not been possible to extend the relativistic theory to a system of more than one electron. But there is the region in which the solution of new problems is to be hoped from the new theory, problems that were inaccessible to the older theory.

Second, the relativistic theory of the hydrogen atom is apparently incomplete; the results are in grave contradiction with experiment, since in Sommerfeld's well known formula for the displacement of the natural fine structure components the so-called azimuthal quantum number (as well as the radial quantum number) turns out as "half-integer," i.e. half of an odd number, instead of integer. So the fine structure turns out entirely wrong.

The deficiency must be intimately connected with Uhlenbeck-Goudsmit's[15] theory of the spinning electron. But in what way the electron spin has to be taken into account in the present theory is yet unknown.

ZÜRICH, SWITZERLAND,
    September 3, 1926.

[14] V. Fock, Zeits. f. Physik **38**, 242 (1926).
[15] G. E. Uhlenbeck and S. Goudsmit, Physica (1925); Nature, Feb. 20 (1926).