THE ZEEMAN EFFECT AND STARK EFFECT OF HYDROGEN IN WAVE MECHANICS; THE FORCE EQUATION AND THE VIRIAL THEOREM IN WAVE MECHANICS

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Abstract

The Zeeman levels of hydrogenic atoms are determined by a new and simple method, neglecting terms in H^2. The frequency of the Larmor precession is $L=L_0\,(1+E/mc^2)$. L_0 is the frequency of precession obtained by Newtonian mechanics and E the energy of the atom. This agrees with a formula of Pauli obtained by ordinary relativity mechanics. The formulae for the first order Stark effect and for the Paschen-Back effect can be obtained by similar methods.

An extension of Ehrenfest's law of motion for a particle is proved. It is applicable to any conservative system. From it, a theorem of wave mechanics analogous to the virial theorem is obtained.

1. The Zeeman Effect and Stark Effect of Hydrogen in Wave Mechanics

THE Zeeman effect of hydrogen has been treated in terms of the new mechanics by several authors, neglecting the modifications due to the relativistic change of mass of the electron. Heisenberg and Jordan[1] studied the Zeeman effect by means of matrices. Epstein[2] treated the problem by obtaining the energy of a system composed of the atom and the apparatus which produces the field. This procedure is advantageous, for it is capable of showing the nature of the interaction between the atom and the magnetic field. For example, it is well known that when a quantum jump occurs there may be an exchange of angular momentum between the atom and the field producing mechanisms, as well as a contribution of angular momentum to the radiation field. This indicates that we might expect a difference between the energy of a quantum and the decrease of energy of the emitting atom, because of a possible interchange of energy between the atom and the magnet. The calculation of Epstein shows that the correct result is the same as that obtained by neglecting the reaction of the atom on the field,—that is, by treating the field strength H as quite independent of the behavior of the emitting atom. Brillouin[3] has treated the problem in wave mechanics, without the modifications due to relativity.

The method is to set up the wave equation, and transform it to coordinates rotating about the lines of magnetic force with the frequency $L_0=eH/4\pi mc$ of the Larmor precession. (The charge of the electron is taken to be $-e$, where $e=4.77\ 10^{-10}$ electrostatic units.) In these coordinates the

[1] Heisenberg and Jordan, Zeits. f. Physik **37,** 263 (1926).
[2] Epstein, Proc. Nat. Acad. Sci. **12,** 634, (1926).
[3] Brillouin, J. de Physique **8,** 74, (1927).

wave distribution is identical with that of the field free atom and the solution contains the factor

$$\exp\left[i(m\zeta-2\pi\nu_0 t)\right], \tag{1}$$

m being the equatorial quantum number, $h\nu_0$ the energy of the atom, and ζ the equatorial angle, as measured in the rotating coordinates. The equatorial angle ϕ in the resting coordinates is given by

$$\phi=\zeta+2\pi L_0 t.$$

Substituting this in (1) we obtain

$$\exp\left[im\phi-2\pi i(\nu_0+mL_0)t\right] \tag{2}$$

Thus the energy in the resting coordinates is

$$E_0+mL_0h=E_0+\frac{meHh}{4\pi mc} \tag{3}$$

It is possible to solve the problem in relativistic wave mechanics in a somewhat similar fashion, but there is a complication which would make it necessary to resort to perturbation methods. In ordinary relativity mechanics, the variation of mass of the electron causes small but rapid variations of the speed of the Larmor precession. In relativistic wave mechanics, a corresponding effect appears. It is found that there is no privileged coordinate system in which the wave system appears like that of the field free atom. The velocity of precession which will make the layer of the ψ distribution between radii r and $r+dr$ appear like the corresponding layer of the undisturbed atom is found to be a function of r. We are confronted with a problem analogous to that of motions within a nebula, instead of that of a rigid rotating body. To avoid these complications, we adopt a much shorter method, based on the virial theorem for a system of particles.

In either relativistic or Newtonian mechanics, the theorem may be stated as follows:

For a system of particles in periodic motion or in a steady state,

$$\overline{\sum mv^2}=\overline{-\sum(xX+yY+zZ)}.$$

m is the actual mass, (not the rest mass) of a typical particle of the system, x, y, z, its coordinates, and X, Y, Z, the components of force acting on it. $\sum$ indicates a summation over all the particles and the bars denote time averages. It is shown in many texts[4] that if the potential energy V_0 of an

[4] See appendix of any edition of Sommerfeld's "Atombau." The following is a useful extension of this theorem:

If the potential energy is the sum of several functions, $V_1+V_2+\cdots$, homogeneous in the coordinates, and of degrees n_1, n_2, $\cdots$, respectively, then

$$\overline{\sum mv^2}=n_1\bar{V}_1+n_2\bar{V}_2+\cdots$$ (next page)

atom or molecule is a homogeneous function of the coordinates, of the nth degree, then the virial theorem reduces to

$$\overline{\sum mv^2} = \overline{nV_0} \tag{5}$$

For the particles of an atom, subjected to Coulomb forces, $n=-1$, and in non-relativistic mechanics, (5) yields the relations,

$$-\overline{T_0} = \overline{V_0}/2 = E_0, \tag{6}$$

where E_0 is the total energy. If a uniform constant magnetic field H is applied, then each electron experiences an additional force $-(e/c)[v\mathbf{H}]$. The average value of the potential energy is unchanged, and if $\overline{T}$ is the time average of the kinetic energy, then (4) yields the result

$$T = -\frac{\overline{V_0}}{2} + \frac{e}{2mc}\overline{Hp_H} \tag{7}$$

where p_H is the component of angular momentum parallel to the field. It must be noted that p_H is not the same as the variable conjugate to ϕ, which we call p_ϕ. In the presence of an electromagnetic field having the vector potential A_x, A_y, A_z, the variables conjugate to x, y, and z, are given by the relations

$$p_x = mv_x - eA_x/C.$$

For a magnetic field parallel to the Z-axis

$$A_x = -\tfrac{1}{2}yH, \quad A_y = \tfrac{1}{2}xH, \quad A_z = 0.$$

A brief computation shows that

$$p_\phi = p_H - eH(x^2+y^2)/2c = p_H - 2\pi L_0 m(x^2+y^2), \tag{8}$$

which tells us that p_ϕ is the angular momentum in the *rotating* coordinates.

In equation (7) p_H can be replaced by p_ϕ if we are interested only in terms containing the first power of H. Since ϕ is an ignorable coordinate, p_ϕ is constant. Adding to (7) the equation

$$\overline{V} = 2E_0,$$

and neglecting the term in H^2, we get

$$T+V = E = E_0 + (eH/2mc)p_\phi \tag{9}$$

In ordinary mechanics, we write for p_ϕ its quantized value $mh/2\pi$, and obtain the change of energy $\Delta E \equiv E - E_0$:

$$\Delta E = L_0 mh, \quad m = 0, \pm 1, \pm 2, \cdots. \tag{10}$$

This follows at once from Euler's theorem for homogeneous functions if we substitute

$$-(\partial V_1/\partial x) - (\partial V_2/\partial x) - \cdots$$

for X in (4), and similar expressions for Y and Z.

To solve the same problem in wave mechanics, we start with (9) in the form

$$p_\phi - \Delta E/2\pi L_0 = 0. \tag{9a}$$

This is really a Hamilton-Jacobi equation to determine p_ϕ. By going through the usual variation principle procedure, using the complete wave equation, we can show that it is legitimate to substitute the operator $h\partial/2\pi i\partial\phi$ for p_ϕ, to obtain a simplified wave equation from (9a). Applying the operator thus formed to the wave amplitude function, ψ, we have

$$\frac{h}{2\pi i}\frac{\partial\psi}{\partial\phi} - \frac{\psi\Delta E}{2\pi L_0} = 0. \tag{11}$$

The solution is $\psi = Fe^{im\phi}$, where F represents the part of ψ depending on coordinates other than ϕ, and $mh = \Delta E/L_0$. In order to make this solution have the same period as the corresponding classical motion of the electron, it is necessary that m be an integer, so we arrive at the formula (10) for the change of energy in the presence of the field.

In relativistic wave mechanics the value of ΔE is obtained by a similar device. Pauli[5] solved the corresponding problem in ordinary mechanics, including the effect of the variation of mass with velocity. His result is this:

$$\Delta E = L_0\left(1+\frac{E_0}{mc^2}\right)2\pi p_\phi \tag{12}$$

The evaluation of E proceeds just as before, in both ordinary and wave mechanics, the final formula being

$$\Delta E = L_0\left(1+\frac{E_0}{mc^2}\right)mh, m = 0, \pm 1, \pm 2, \tag{13}$$

The methods used in this section are extensions of those introduced by the author in a previous paper[6] and are capable of other applications. For example, the first order Stark effect and the Zeeman levels of atoms exposed to a very strong magnetic field are easily obtained. Each case must first be examined by the aid of the general wave equation, however, to be sure that the simplified procedure is legitimate.

2. The Force Equation and the Virial Theorem in Wave Mechanics

Ehrenfest[7] has derived an equation which can be considered as a generalization of Newton's law of motion, by considering the motion of the center of gravity of the wave group accompanying a particle. His proof is given for a particle with only one degree of freedom, but can easily be extended to a conservative system containing any number of particles, as follows:

[5] Pauli, Zeits. f. Physik **31**, 373 (1925). Handbuch der Physik, volume 23, page 154.
[6] Ruark, J.O.S.A. and R.S.I. **16**, 40, (1928).
[7] Ehrenfest, Zeits. f. Physik, **45**, 455 (1927).

Let the ith particle in the system have mass m_i, and Cartesian coordinates x_i, y_i, z_i. Define new coordinates by the relations

$$X_i = m_i^{1/2} \cdot x_i, \quad Y_i = m_i^{1/2} \cdot y_i, \quad Z_i = m_i^{1/2} \cdot z_i.$$

Then the element of volume in the coordinate space used by Schrödinger is

$$d\tau = dX_1 dY_1 dZ_1 dX_2 \cdots$$

The wave equation is

$$\Delta\Psi - \frac{8\pi^2}{h^2} V\Psi - \frac{4\pi i}{h} \frac{\partial \Psi}{\partial t} = 0. \tag{14}$$

Also

$$\Delta\Psi^* - \frac{8\pi^2}{h^2} V\Psi^* + \frac{4\pi i}{h} \frac{\partial \Psi^*}{\partial t} = 0. \tag{15}$$

if Ψ^* is the complex conjugate of Ψ.

We shall need the auxiliary relation

$$\Psi\Delta\Psi^* - \Psi^*\Delta\Psi + \frac{4\pi i}{h}\left(\frac{\partial \Psi^*}{\partial t}\Psi + \frac{\partial \Psi}{\partial t}\Psi^*\right) = 0. \tag{16}$$

Let us *define* the X-coordinate of the nth particle by the equation

$$\xi_n = \frac{\int X_n \Psi\Psi^* d\tau}{\int \Psi\Psi^* d\tau} = \int X_n \Psi\Psi^* d\tau \tag{17}$$

(The denominator is unity because Ψ is normalized.)

Differentiating ξ_n with respect to t, we obtain

$$\dot{\xi}_n = \frac{h}{2\pi i} \int \Psi \frac{\partial \Psi^*}{\partial X_n} d\tau, \tag{18}$$

after using (16) and integrating by parts.

In evaluating the integral, we use the fact that Ψ and its derivatives vanish at the boundaries of the coordinate space in problems of the type dealt with here. Equation (18) defines the momentum of the center of gravity of the wave group, in the coordinate space. Differentiating (18),

$$\ddot{\xi}_n = \frac{h}{2\pi i} \int \left(\frac{\partial \Psi}{\partial t} \frac{\partial \Psi^*}{\partial X_n} + \Psi \frac{\partial^2 \Psi^*}{\partial X_n \partial t}\right) d\tau \tag{19}$$

We replace $\partial\Psi/\partial t$ and $\partial^2\Psi^*/\partial X_n \partial t$ by their values obtained from the wave equation and $\ddot{\xi}_n$ reduces to

$$\int \Psi\Psi^* \left(-\frac{\partial V}{\partial X_n}\right) d\tau - \frac{h^2}{8\pi^2 m} \int \left(\Delta\Psi \cdot \frac{\partial \Psi^*}{\partial X_n} - \Psi \frac{\partial \Delta\Psi^*}{\partial X_n}\right) d\tau$$

Integrating the last term by parts, and applying Green's theorem to the second integral, we find that it vanishes. Then, if we write $\xi_n = m_n^{1/2}\,\bar{x}_n$, we have

$$m_n^{1/2}\ddot{\bar{x}}_n = \int \Psi\Psi^*(-\partial V/\partial(m_n^{1/2}\cdot x_n))\,d\tau$$

or

$$m_n\ddot{\bar{x}}_n = \int \Psi\Psi^*(-\partial V/\partial x_n)\,d\tau \tag{20}$$

This is the generalized law of motion, which reduces to Newton's if appreciable values of Ψ are confined to a narrow range in the immediate neighborhood of $\bar{x}_n$; for then the right-hand member reduces to $-(\partial V/\partial \bar{x}_n)\int \Psi\Psi^* d\tau$, or $(-\partial V/\partial \bar{x}_n)$ since Ψ is so normalized that the last integral is unity.

Schrödinger showed that the group velocity of a nearly-monochromatic "Wellenpaket" is such that the point of coinciding phase obeys the laws of classical mechanics. The content of his theorem is different from that of equation (20), although the two are related. Equation (20) holds true whenever (14) is valid, provided Ψ is properly normalized. In many ways it is to be considered more fundamental than Schrödinger's theorem.

Let us apply (20) to obtain a theorem analogous to the virial theorem of ordinary mechanics. Dropping the use of bars to denote centroids and noting that $d(mx\dot{x})/dt = m\dot{x}^2 + mx\ddot{x}$, we have for each particle

$$\overline{m\dot{x}^2} = -\overline{mx\ddot{x}} + \overline{d(mx\dot{x})/dt} \tag{21}$$

where now the bars denote time averages. Summing equations of this type over all the coordinates and applying the usual restriction that the system is either periodic or in a condition of kinetic equilibrium, we obtain the generalized virial theorem, on substituting the values of x, $\dot{x}$, and $\ddot{x}$.

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