THE ZEEMAN EFFECT OF THE SYMMETRICAL TOP ACCORDING TO WAVE MECHANICS

By Edward U. Condon†

Abstract

The alteration of the quantum-theoretical energy levels of a symmetrical top due to the action of a magnetic field on a charge which is fixed to the top, is investigated by means of the perturbation theory of the wave mechanics. The final formula for the change in the energy levels is given below in Eq. (10).

THE model of the rigid rotator with two different moments of inertia (symmetrical top) has proved useful in the theory of molecular spectra. Investigations of the unperturbed energy levels and radiation amplitudes (matrix components of the electric moment) according to wave mechanics have been given by Reiche, Reiche and Rademacher, Kronig and Rabi, and by Manneback.[1] Dennison[2] has also treated the problem by the matrix methods. Reiche has investigated the first-order Stark effect while Manneback has investigated the second-order Stark effect as well.

The Zeeman effect, i.e., the perturbation of the energy levels of the top by a magnetic field, has not been hitherto investigated. The results of the calculation of this perturbation are here communicated.

The notation here used is that of Kronig and Rabi. The top has two of its moments of inertia equal to A and the third, about the axis of symmetry, equal to C. The electrical properties of the top are summarized in the assumption that a charge, e, is fixed to the top at a point whose distance off the axis of symmetry is a, while the distance along the axis of symmetry from the center of gravity of the top to the foot of the perpendicular from this charge on to the axis is c.

The wave equation can be conveniently derived with the aid of a variation principle due to Fock.[3] The Lagrangian function for the particle in a magnetic field is

$$L=T-(e/c)\boldsymbol{A}\cdot\boldsymbol{v} \tag{1}$$

where T is the kinetic energy, $\boldsymbol{A}$ the vector potential, and $\boldsymbol{v}$ the velocity of the charged particle. Using the Eulerian angles θ, ϕ, ψ, one can write the magnetic term as

$$(e/c)\boldsymbol{A}\cdot\boldsymbol{v}=H(\alpha\dot{\theta}+\beta\dot{\phi}+\gamma\dot{\psi}) \tag{2}$$

† National Research Fellow.

[1] Reiche, Zeits. f. Physik **39**, 444, (1926); Reiche and Rademacher, Zeits. f. Physik **42**, 453 (1927); Kronig and Rabi, Phys. Rev. **29**, 262 (1927); Manneback, Phys. Zeits. **28**, 72 (1927).

[2] Dennison, Phys. Rev. **28**, 318 (1926).

[3] Fock, Zeits. f. Physik **38**, 242 (1926).

in which H is the field strength and

$$\begin{aligned}\alpha &= -2\pi\mu\nu \cdot a\cos\phi(c\cos\theta + a\sin\theta\sin\phi)\\ \beta &= 2\pi\mu\nu \cdot a(a\cos\theta - c\sin\phi\sin\theta)\\ \gamma &= 2\pi\mu\nu[a^2\cos^2\phi + (c\sin\theta - a\cos\theta\sin\phi)^2]\end{aligned} \tag{3}$$

where μ is the electronic mass and ν the electronic Larmor precession frequency for unit field strength.

The Hamiltonian function is obtained in the usual way by expressing $p_\theta\dot{\theta} + p_\phi\dot{\phi} + p_\psi\dot{\psi} - L$ as a function of the momenta, p_θ, p_ϕ, and p_ψ. The result is

$$\begin{aligned}H = &\frac{1}{2A}(p_\theta + H_\alpha)^2 + \frac{1}{2}\left(\frac{\cos^2\theta}{A\sin^2\theta} + \frac{1}{C}\right)(p_\phi + H_\beta)^2 + \frac{1}{2A\sin^2\theta}(p_\psi + H_\gamma)^2\\ &- \frac{\cos\theta}{A\sin^2\theta}(p_\phi + H_\beta)(p_\psi + H_\gamma)\end{aligned} \tag{4}$$

Applying Fock's variation process to this Hamiltonian function, one finds the following form for the wave-equation on neglecting terms in H^2:

$$DU + \frac{8\pi^2 E}{h^2}U = \frac{2\pi i H}{h}\Delta U \tag{5}$$

Here D is the differential operator occurring in the wave-equation for the unperturbed top while Δ is a linear differential operator of the first order representing the action of the magnetic field:

$$\begin{aligned}DU \equiv &\frac{1}{A\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial U}{\partial\theta}\right) + \left(\frac{\cos^2\theta}{A\sin^2\theta} + \frac{1}{C}\right)\frac{\partial^2 U}{\partial\phi^2} + \frac{1}{A\sin^2\theta}\frac{\delta^2 U}{\partial\psi^2}\\ &- \frac{2\cos\theta}{A\sin^2\theta}\frac{\partial^2 U}{\partial\phi\,\partial\psi}\end{aligned} \tag{6}$$

$$\begin{aligned}\Delta U \equiv &\frac{1}{A\sin\theta}\frac{\partial}{\partial\theta}(\alpha U\sin\theta) + \frac{\alpha}{A}\frac{\partial U}{\partial\theta} + \left(\frac{\cos^2\theta}{A\sin^2\theta} + \frac{1}{C}\right)\left(\frac{\partial}{\partial\phi}(\beta U) + \beta\frac{\partial U}{\partial\phi}\right)\\ &+ \frac{1}{A\sin^2\theta}\left(\frac{\partial}{\partial\psi}(\gamma U) + \gamma\frac{\partial U}{\partial\psi}\right) - \frac{\cos\theta}{A\sin^2\theta}\left(\frac{\partial}{\partial\phi}(\gamma U) + \frac{\partial}{\partial\psi}(\beta U)\right.\\ &\left. + \beta\frac{\partial U}{\partial\psi} + \gamma\frac{\partial U}{\partial\phi}\right).\end{aligned} \tag{7}$$

The unperturbed equation ($H = 0$) is degenerate in that the energy levels depend only on the quantum numbers, j and n, while the unperturbed characteristic functions are:

$$U_{jmn} = \Theta_{jmn}(\theta) \cdot e^{in\phi} \cdot e^{im\psi} \tag{8}$$

Since ψ does not occur explicitly in the perturbation term, ΔU, this coordinate remains separable and it is thus unnecessary to apply the special apparatus

of the perturbation theory for degenerate systems. According to the simple perturbation theory,[4] the amount of the perturbation becomes:

$$\Delta E_{jmn}=\frac{ihH}{4\pi}\int \bar{U}_{jmn}\Delta U_{jmn}\sin\theta\, d\theta\, d\phi\, d\psi \tag{9}$$

in which it is supposed that the characteristic functions have been normalized and where $\bar{U}_{jmn}$ means the conjugate complex function to U_{jmn}.

The computation of the perturbation energy is readily effected since besides integrals over exponential functions the only integral needed is

$$\int_0^\pi \Theta_{jmn}^2(\theta)\cdot\cos\theta\cdot\sin\theta\, d\theta=-nm/j(j+1)$$

The integral is a simple consequence of well-known properties of the hypergeometric function, to which $\Theta_{jmn}(\theta)$ is related.[5] The result, therefore, for ΔE_{jmn} is

$$\Delta E_{jmn}=-mh\nu_L\left[\frac{\mu(c^2+\frac{1}{2}a^2)}{A}+\frac{n^2}{j(j+1)}\left(\frac{\mu(c^2+\frac{1}{2}a^2)}{A}-\frac{\mu a^2}{C}\right)\right] \tag{10}$$

in which ν_L is the Larmor precession frequency for a particle of mass μ and charge e in a field of strength H, i.e.,

$$\nu_L=eH/2\mu c$$

The ratio $n^2/j(j+1)$ is to be given the value 1 when $j=n=0$.

One sees that the alteration of the energy levels for a molecule represented by this model will therefore be small compared with the Zeeman effect for atoms in the ratio of electron mass to nuclear mass.[6] (The distances a and c are of the same order of magnitude as the distances of the nuclei from the center of gravity of the top-molecule.) The formula deviates from that of the old quantum theory in the appearance of $j(j+1)$ in place of j^2, the same change as occurs in the formula for the unperturbed energy levels.

The model of a symmetrical top is often used for discussions of band spectra for diatomic molecules having states with a resultant electronic angular momentum about the line joining the two nuclei. In this case the moment of inertia, C, arises solely from the electronic structure of the molecule, hence the $\mu a^2/C$ is of the order of magnitude 1. The other terms may be neglected in comparison with it.

The minus sign which affects this term can then give rise to an inverted Zeeman effect, as already noted by Lenz as a consequence of the old theory. If $n=0$ in both initial and final states, there is no Zeeman effect of atomic order of magnitude. If $\Delta n=0$ there is a splitting into the normal Lorentz

[4] Schrödinger, Ann. d. Physik **80**, 437 (1926).

[5] See e.g. Reiche, Zeits. f. Physik **39**, 453, Eq. (44) (1926).

[6] For a review of the present status of theory and experiment concerning Zeeman effect of band spectra, see section on Zeeman effect by Kemble in the Report of the National Research Council on Molecular Spectar in Gases.

triplet (when one applies the selection rules for m as given quantum mechanically by Dennison, Kronig and Rabi, and Reiche) except that the spacing decreases with increasing j, i.e., as one moves away from the origin of a band. The spacing varies as $1/j(j+1)$ or almost inversely as the square of j. But if $n=0$ in one state and $n=1$ in the other then an inversion of one set of levels occurs. This has the consequence that a pattern of $2j+1$ equidistant lines appears, due to the non-splitting for $n=0$ and the splitting for $n=1$. The extreme width of the pattern is $2/(j+1)$. In other words for such bands the broadening due to the Zeeman effect will vary with the inverse first power of j instead of the inverse second.

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