Stark Effect: Zeeman effect 1897

1913 → Stark demonstrated that every line of the Balmer series of hydrogen, when excited in a strong electric field of at least 100000 volts per cm., is split into a number of components.

Viewed perpendicular to the field;
Some of the components of each line pattern are observed to be plane-polarized with the electric vector parallel to the field → p components.
Others polarized with the electric ~~field~~ vector normal to the field (s components).
Viewed parallel to the field only the s component appear → unpolarized.

The Stark Effect of Hydrogen

We write the general energy relations for a hydrogen atom in an electric field and then interpret them in terms of atomic models and the observed spectrum lines.

The interaction energy of a hydrogen-like atom in an electric field is given by

$$\Delta T = AF + BF^2 + CF^3 + \text{—} \quad (1)$$

ΔT → change in the term value of the atom in wave numbers i.e. the shift in the energy levels from the field-free states to the states in the ~~DATE~~ electric field.

F → strength of the field in electrostatic units.

Coefficients A, B and C → Calculated by classical and quantum mechanical considerations

$$A = \frac{3h}{8\pi^2 mec} n(n_2 - n_1),$$

$$B = \frac{h^5}{2^{10}\pi^6 m^3 e^6 c} n^4 \left\{17n^2 - 3(n_2 - n_1) - 9m_l^2 + 29\right\}$$

$$C = \frac{3h^9}{2^{15}\pi^{10} m^5 e^{11} c} n^7 \left\{23n^2 - (n_2 - n_1)^2 + 11m_e^2 + 35\right\} \quad \text{——(2)}$$

n → usual quantum number

n_1, n_2, m_l are electric quantum numbers subject to the condition

$$m_l = n - n_2 - n_1 - 1 \quad \text{——(3)}$$

The allowed values are

$n = 1, 2, 3, \text{----} \infty$, $n_1 = 0, 1, 2, 3 \text{----} n-1$

$m_l = 0, \pm1, \pm2, \text{---} \pm(n-1)$, $n_2 = 0, 1, 2, 3 \text{---} n-1$ ——(4)

If the field is expressed in volts per centimeters the independent constants in these expressions are 6.42×10^{-5}, 5.22×10^{-16} and 1.53×10^{-25} for A, B, C respectively.

first term in eqn 1 → F in first power
→ first-order stark effect

The second term involving F to the second power → second order stark effect etc.

If the field is not too large (F < 100000 volts per cm), the lower states of the hydrogen atom (n small) → show only a first-order Stark effect.

Such fields result in a symmetrical splitting of the energy levels about their field-free positions.

Second-order effect → Always present and becomes large for higher states and higher fields → results in a unidirectional displacement of each line.

Weak-field Stark Effect in Hydrogen

Kramers → Treatment of the hydrogen atom in a weak electric field → neglecting electron spin

Schlapp → Treatment including spin
↓
Employs the Dirac electron theory

Weak electric field in hydrogen → one in which the interaction energy between the electron resultant j^* and the field F is considerably less

[redacted]

↳ in comparison to the magnetic interaction energy between l^* and s^*.

Weak field → Stark splitting is small in comparison to the fine-structure splitting.

In a weak field → electron with spin → classically as a small magnet, does not interact with the field so that the coupling of j^* with F is due only to interaction of l^* with F.

In the classical picture of a precessing atom the electron mechanical resultant $j^* h/2\pi$ precesses around the field F. The projection of j^* on the field direction F is given by m_j, m_j → taking values differing from each other by unity from $+j$ to $-j$.

Important difference between the Zeeman Effect and the Stark effect → each pair of levels $+m_j$ and $-m_j$ arising from a given level have the same energy when in electric field but different energies when in a magnetic field.

The state $m_j = 3/2$, for example has the same energy as that the state $m_j = -3/2$. Similarly the states $m_j = +\frac{1}{2}$ and $m_j = -\frac{1}{2}$ have the same energy.

Instead of a level $j = 3/2$ being split up into four components is the Zeeman effect, there are two levels.

Reason → classical orbital model or the quantum mechanical model of electron clouds. The nature of the forces acting on the electron are purely electrostatic → energy of the electron in an orbit of given n and l depends only on the inclination of the orbit plane w.r.t. the electric field, or to the distribution of charge on the quantum-mechanical model, → not on the direction of rotation or motion of the electron in its orbit.

States with $+m_j$ and $-m_j$ → correspond to the same inclination of the orbital plane, or the same charge distributions → same ~~S~~ distortion or energy change → due to the applied field. In magnetic field the energy depends on the direction of rotation and the energies change sign when m_j changes sign.