10.7. The Paschen-Back Effect.—In deriving the interaction energy between an atom containing one single valence electron and an external magnetic field, it was assumed that the field was weak as compared with the internal fields due to the spin and orbital motion of the electron. When the external field becomes greater than these internal

fields the internal motions are greatly perturbed and the atom gives rise to the so-called *Paschen-Back effect*.

Just as the doublet fine-structure separations are a measure of the classical frequency with which l^* and s^* precess around their resultant j^* (see Sec. 10.4), so the Zeeman separations of the same energy states in a weak magnetic field are a measure of the frequency with which j^* precesses around H. In calculating the Zeeman separations in Sec. 10.4, it was tacitly assumed that the precession of l^* and s^* around j^* was much faster than that of j^* around H. This was necessary in order that the components of l^* and s^* normal to j^* average to zero and do not appreciably perturb the other precession. If now the field H is increased until the two precessions are of the same order of magnitude, then the Zeeman levels of the doublet will begin to overlap, there will be no averaging to zero, and Eqs. (10.17) and (10.19) will not hold. Under these conditions the coupling between l^* and s^* will be partially broken down, the classical motions of l^* and s^* will become complicated, and j^* will no longer be fixed in magnitude. As the field H is still further increased, l^* and s^* will soon become

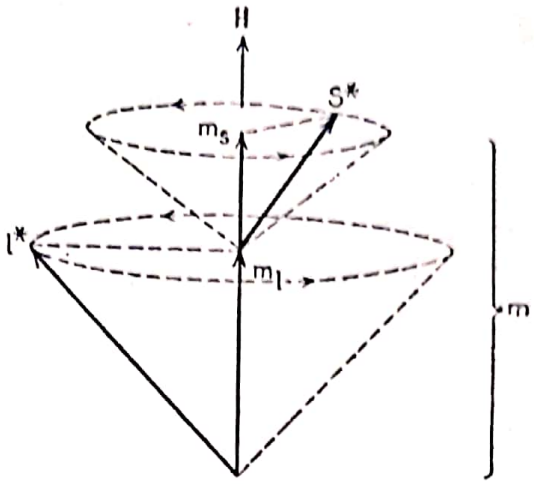

FIG. 10.10.—Vector model for the Paschen-Back effect where the field is so strong that l^* and s^* precess independently around the field direction H.

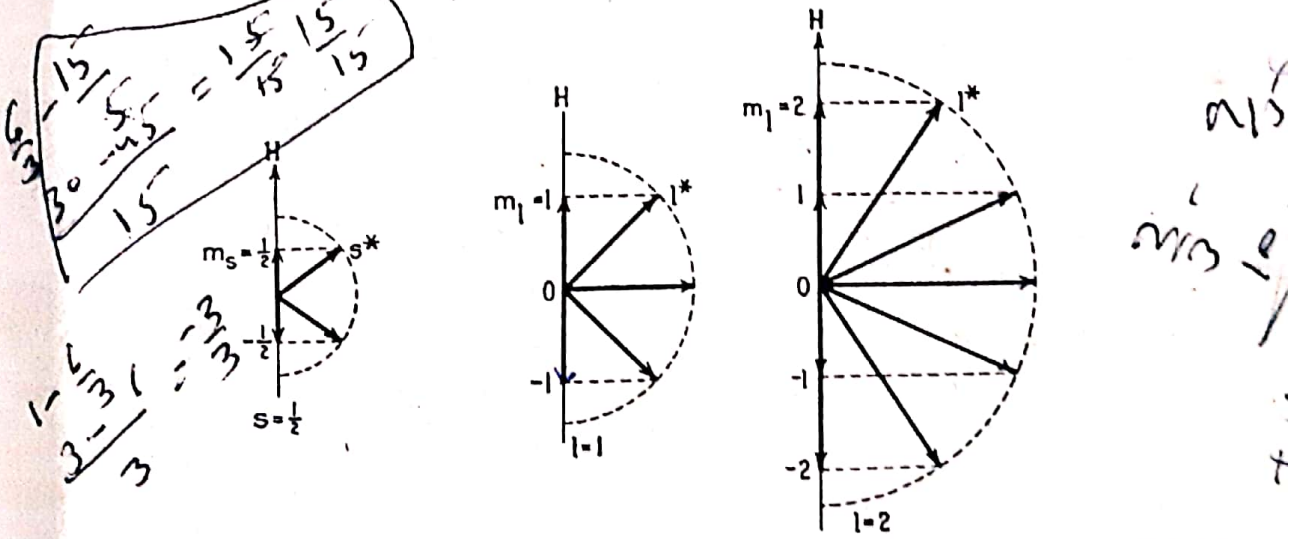

FIG. 10.11.—Space-quantization diagrams for p and d electrons in a strong magnetic field, Paschen-Back effect.

quantized separately and precess more or less independently around H (see Fig. 10.10). This is the Paschen-Back effect.[1]

The quantum conditions in a strong Paschen-Back field are: (1) The projection of l^* on H takes integral values from $m_l = +l$ to $m_l = -l$. (2) The projection of s^* on H takes one of the two values $m_s = +\frac{1}{2}$, or

[1] PASCHEN, F., and E. BACK, *Ann. d. Phys.*, **39**, 897, 1912; **40**, 960, 1913.

$-\frac{1}{2}$. For a p electron with $l = 1$, $s = \frac{1}{2}$, there are six possible states of these cases are given in Fig. 10.11. Since for every electron there are two values of m_s and $2l + 1$ values of m_l, there are $2(2l + 1)$ combinations of the quantum numbers corresponding to $2(2l + 1)$ different states of the atom. As might be expected, this is exactly the number of weak-field levels.

$m_l = 1$, 0, and -1, when $m_s = \frac{1}{2}$ or $-\frac{1}{2}$. Space-quantization diagrams

The total energy of the atom in a field strong enough to give the Paschen-Back effect is made up of the three parts: (1) *the energy due to the precession of l^* around H;* (2) *the energy due to the precession of s^* around H:* (3) *the interaction energy between l^* and s^*.* By Larmor's theorem [Eq. (3.58)], the precessional angular velocities are given by H times the ratio between the magnetic and mechanical moments:

$$\omega_{l^*} = H\frac{e}{2mc} \text{ and } \omega_{s^*} = 2H\frac{e}{2mc}. \tag{10.23}$$

Since the ratio between the magnetic and mechanical moment for the spin of the electron is twice the orbital ratio, s^* should, on the classical picture, precess twice as fast as l^*. Multiplying each of these angular velocities by the projection of the angular momentum on H [see Eq. (10.15)], one gets the first two terms of the energy:

$$\Delta W_{l,H} = H\frac{e}{2mc}l^*\frac{h}{2\pi}\cos(l^*H) = H\frac{e}{2mc}m_l\frac{h}{2\pi}, \tag{10.24}$$

$$\Delta W_{s,H} = 2H\frac{e}{2mc}s^*\frac{h}{2\pi}\cos(s^*H) = 2H\frac{e}{2mc}m_s\frac{h}{2\pi}. \tag{10.25}$$

The sum of these two energies accounts for the main energy shift from the unperturbed energy level and is

$$\Delta W_H = (m_l + 2m_s)H\frac{eh}{4\pi mc}. \tag{10.26}$$

Dividing by hc, the term shift in wave numbers becomes

$$-\Delta T_H = (m_l + 2m_s)\frac{He}{4\pi mc^2}\text{ cm}^{-1}, \tag{10.27}$$

or in Lorentz units of $He/4\pi mc^2$,

$$-\Delta T_H = (m_l + 2m_s)\text{L cm}^{-1}. \tag{10.28}$$

To this magnetic energy the small correction term due to the interaction between l^* and s^* must be added. Although these two vectors precess independently around H, each motion still produces a magnetic field at the electron which perturbs the motion of the other. This interaction energy, though small as compared with that due to the external field, is of the same order of magnitude as the fine-structure

doublet separations in field-free space, which by Eqs. (8.14), (8.18), and (8.19) are given by the Γ factor,

$$\Gamma = -\Delta T_{l,s} = al^*s^* \cos(l^*s^*), \tag{10.29}$$

where

$$a = \frac{R\alpha^2 Z^4}{n^3 l(l+\frac{1}{2})(l+1)} \text{ cm}^{-1}. \tag{10.30}$$

In field-free space, the angle between l^* and s^* is constant and the cosine term $\cos(l^*s^*)$ is easily evaluated. In the present case, however, the angle is continually changing, so that an average value of the cosine must be calculated. From a well-known theorem in trigonometry it may be shown that with s^* and l^* precessing independently with fixed angles around a third direction H,

$$\overline{\cos(l^*s^*)} = \cos(l^*H) \cdot \cos(s^*H). \tag{10.31}$$

Making this substitution in (10.29),

$$\Gamma = -\Delta T_{l,s} = al^* \cos(l^*H) s^* \cos(s^*H). \tag{10.32}$$

These are just the projections of l^* and s^* on H, so that

$$-\Delta T_{l,s} = am_l m_s = \Gamma. \tag{10.33}$$

Adding this term to Eq. (10.28), the total energy shift becomes

$$-\Delta T_{cm^{-1}} = (m_l + 2m_s)\mathrm{L} + am_l m_s. \tag{10.34}$$

We may now write down a general relation for the term value of any strong field level,

$$T_{cm^{-1}} = T_0 - (m_l + 2m_s)\mathrm{L} - am_l m_s, \tag{10.35}$$

where T_0 is the term value of the hypothetical center of gravity of the fine-structure doublet.

10.8. Paschen-Back Effect of a Principal-series Doublet.—As an example of the Paschen-Back effect, consider first the calculation of terms and term separations involved in a principal-series doublet $^2S_{\frac{1}{2}}$–$^2P_{1,\frac{1}{2}}$. The fine-structure separations due to the interaction of l^* and s^* in field-free space are given in Col. 2, Table 10.2 (see Fig. 8.9). In the next three columns the weak-field energies are calculated (see Fig. 10.8). In the last five columns the strong-field energies are calculated, using Eq. (10.34).

The values tabulated are shown schematically in Fig. 10.12. At the left the undisturbed fine-structure levels and the observed transitions are shown. The weak-field Zeeman levels are next shown with the observed Zeeman patterns below. In the strong field the Paschen-Back levels are shown with, and without, the small l^*s^* coupling correction