334(4): The Anomalous Zeeman Effect Detected by Electron Spin Resonance.

In the usual theory the hamiltonian of the anomalous Zeeman effect is:

$$H = -\frac{e}{2m} g_J \underline{J} \cdot \underline{B} \quad -(1)$$

where

$$\underline{J} = \underline{L} + \underline{S} \quad -(2)$$

and

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad -(3)$$

is the Landé factor. The spin part of the hamiltonian (1) is:

$$H_{ESR} = -\frac{e}{2m} g_J \underline{S} \cdot \underline{B} \quad -(4)$$

If the magnetic field is aligned in the Z axis:

$$H_{ESR} = -\frac{e}{2m} g_J S_Z B_Z \quad -(5)$$

where

$$S_Z \phi = m_s \hbar \phi \quad -(6)$$

and

$$m_s = \pm 1/2 \quad -(7)$$

so the ESR resonance frequency is:

$$\omega = \frac{1}{2} g_J \frac{e B_Z}{m} \quad -(8)$$

where:

$$J = L + S,\ L + S - 1,\ \ldots,\ |L - S| \quad -(9)$$

by the Clebsch Gordan theorem.

So the ESR spectrum of one electron is split by the Landé factor g_J of the anomalous Zeeman effect. This is the most useful feature of ESR for chemical analysis.

For a free electron, as in note 334(3),

$$J = S,\ L = 0 \quad -(10)$$

so

$$g_J = 1 + \frac{2S(S+1)}{2S(S+1)} = 2. \quad -(11)$$

So for a free electron, the ESR resonance frequency is:

$$\omega_{ESR} = \frac{eB_Z}{m} \quad -(12)$$

These are results of the Dirac approximation. When the fully rigorous classical hamiltonian is used, eq. (12) for the free electron becomes:

$$\omega_{ESR} = 2\left(\frac{\gamma^2}{1+\gamma}\right)\frac{eB_Z}{m} \quad -(13)$$

and eq. (8) becomes:

$$\omega_{ESR} = \left(\frac{\gamma^2}{1+\gamma}\right) g_J \frac{eB_Z}{m} \quad -(14)$$

i.e.

$$\omega_{ESR} = \left(\frac{\gamma^2}{1+\gamma}\right)\left(1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right)\frac{eB_z}{m} \quad -(15)$$

where

$$J = L+S, \ldots, |L-S| \quad -(16)$$

If we use expectation values of the H atom:

$$\frac{\gamma^2}{1+\gamma} = \left(1-\left(\frac{\alpha}{n}\right)^2 + \left(1-\left(\frac{\alpha}{n}\right)^2\right)^{1/2}\right)^{-1} \quad -(17)$$

So the ESR splittings of this type are hamiltonian can be worked out from eqs. (15) and (17).