

251(5): Calculation of Transition Frequencies and Spectra

Recall that the basic Hamiltonian is:

$$H\psi = -\frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}_1 \left(\psi + r \frac{\partial \psi}{\partial r} \right) + \frac{e}{2m} \underline{\sigma} \cdot \underline{B}_1 \underline{\sigma} \cdot \underline{L} \psi \quad - (1)$$

$$= (H_1 + H_2 + H_3) \psi$$

where

$$H_1 \psi = -\frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}_1 \psi \quad - (2)$$

$$H_2 \psi = -\frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}_1 r \frac{\partial \psi}{\partial r} \quad - (3)$$

$$H_3 \psi = \frac{e}{2m} \underline{\sigma} \cdot \underline{B}_1 \underline{\sigma} \cdot \underline{L} \psi \quad - (4)$$

Eq (1) is derived from the well known classical Hamiltonian: - (5)

$$H\psi = -\frac{e}{2m} (\underline{\sigma} \cdot \underline{p} \underline{\sigma} \cdot \underline{A} + \underline{\sigma} \cdot \underline{A} \underline{\sigma} \cdot \underline{p}) \psi$$

with

$$\underline{p}\psi = -i\hbar \nabla \psi \quad - (6)$$

The spin angular momentum operator is defined as:

$$\underline{S} = \frac{1}{2} \hbar \underline{\sigma} \quad - (7)$$

In general:

$$\underline{\sigma} \cdot \underline{B}_1 = \underline{\sigma} \cdot \underline{B} - \frac{1}{r^2} \underline{\sigma} \cdot \underline{r} \underline{r} \cdot \underline{B} \quad - (8)$$

2) If the magnetic field is aligned in Z :

$$\underline{\sigma} \cdot \underline{B}_1 = \sigma_z B_z - \frac{Z B_z}{r^2} \underline{\sigma} \cdot \underline{r} \quad (9)$$

$$= \left(\frac{Z}{r}\right)^2 \sigma_z + \frac{YZ}{r^2} \sigma_y + \frac{XZ}{r^2} \sigma_x$$

However, the only well defined component of spin angular momentum in quantum mechanics is:

$$S_z \psi = \pm \frac{1}{2} \hbar \psi \quad (10)$$

So the only term of relevance in eq. (9) is:

$$\underline{\sigma} \cdot \underline{B}_1 = \left(1 - \left(\frac{Z}{r}\right)^2\right) \sigma_z B_z \quad (11)$$

In spherical polar coordinates:

$$1 - \left(\frac{Z}{r}\right)^2 = 1 - \cos^2 \theta = \sin^2 \theta \quad (12)$$

So

$$\underline{\sigma} \cdot \underline{B}_1 = \sin^2 \theta \sigma_z B_z \quad (13)$$

and:

$$H_1 \psi = - \frac{e \hbar}{2m} \sin^2 \theta \sigma_z B_z \psi \quad (14)$$

$$H_2 \psi = - \frac{e \hbar}{2m} \sin^2 \theta \sigma_z B_z r \frac{\partial \psi}{\partial r} \quad (15)$$

$$H_3 \psi = \frac{e}{2m} \sin^2 \theta \sigma_z B_z \underline{\sigma} \cdot \underline{L} \psi \quad (16)$$

3) These give three different types of spectra based on the energy eigenvalues:

$$E_1 = -\frac{e\hbar}{2m} \sigma_z B_z \int \psi^* \sin^2 \theta \psi d\tau \quad (17)$$

$$E_2 = -\frac{e\hbar}{2m} \sigma_z B_z \int \psi^* \sin^2 \theta r \frac{\partial \psi}{\partial r} d\tau \quad (18)$$

$$\text{and } E_3 = \frac{e}{2m} \sigma_z B_z \int \psi^* \sin^2 \theta \underline{\hat{S}} \cdot \underline{\hat{L}} \psi d\tau \quad (19)$$

In order to evaluate eq. (19) we:

$$\underline{\hat{S}} \cdot \underline{\hat{L}} \psi = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)) \psi \quad (20)$$

$$\text{where } j = l + s, \dots, |l - s| \quad (21)$$

$$\text{so } E_3 = \frac{e\hbar}{2m} (j(j+1) - l(l+1) - s(s+1)) \sigma_z B_z \int \psi^* \sin^2 \theta \psi d\tau \quad (22)$$

$$\text{In these expressions: } \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (23)$$

and resonance is induced between the states of σ_z .
Therefore there are three new types of spin resonance.

4) The three resonance frequencies are:

$$\omega_1 = \frac{eB_z}{m} \int \psi^* \sin^2 \theta \psi d\tau \quad - (24)$$

$$\omega_2 = \frac{eB_z}{m} \int \psi^* r \sin^2 \theta \frac{\partial \psi}{\partial r} d\tau \quad - (25)$$

$$\omega_3 = \frac{eB_z}{m} (j(j+1) - l(l+1) - s(s+1)) \int \psi^* \sin^2 \theta \psi d\tau \quad - (26)$$

In each case the resonance frequencies depend on the wave function being considered. In spherical polar coordinates:

$$d\tau = r^2 dr \sin \theta d\theta d\phi \quad - (27)$$

so:

$$\int \psi^* \sin^2 \theta \psi d\tau = \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \psi^* r^2 \sin^4 \theta \psi dr d\theta d\phi \quad - (28)$$

and

$$\int \psi^* r \sin^2 \theta \frac{\partial \psi}{\partial r} d\tau = \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \psi^* r^3 \sin^4 \theta \frac{\partial \psi}{\partial r} dr d\theta d\phi \quad - (29)$$

In general: $\psi = \psi(r, \theta, \phi) \quad - (30)$

5) Note carefully that all the results originate from the standard Hamiltonian (5) of ESR and NMR theory, but with an original use of Pauli algebra.

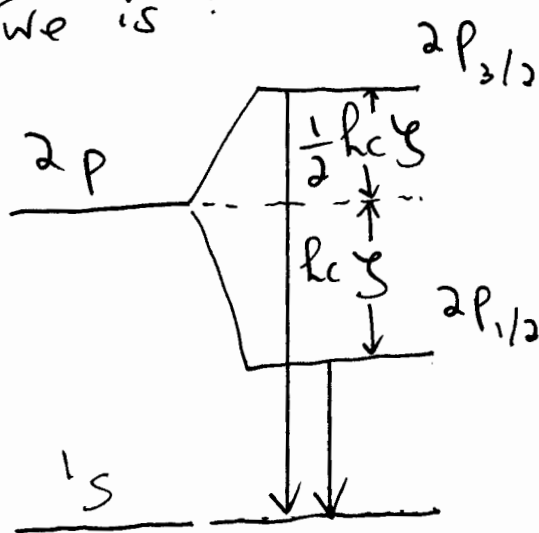
These results must be carefully distinguished from the Zeeman effect, which is:

$$H\psi = -\frac{e\hbar}{2m} g_L J_z B_z \psi \quad (31)$$

where g_L is the Landé factor and:

$$J_z \psi = m_J \hbar \psi \quad (32)$$

The Lyman α transition of atomic hydrogen the fine structure is:



$$j = 3/2, l = 1, s = 1/2$$

$$m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$$

$$j = 1/2, l = 1, s = -1/2$$

$$m_j = -\frac{1}{2}, \frac{1}{2}$$

This is a fine structure emission spectrum. For the

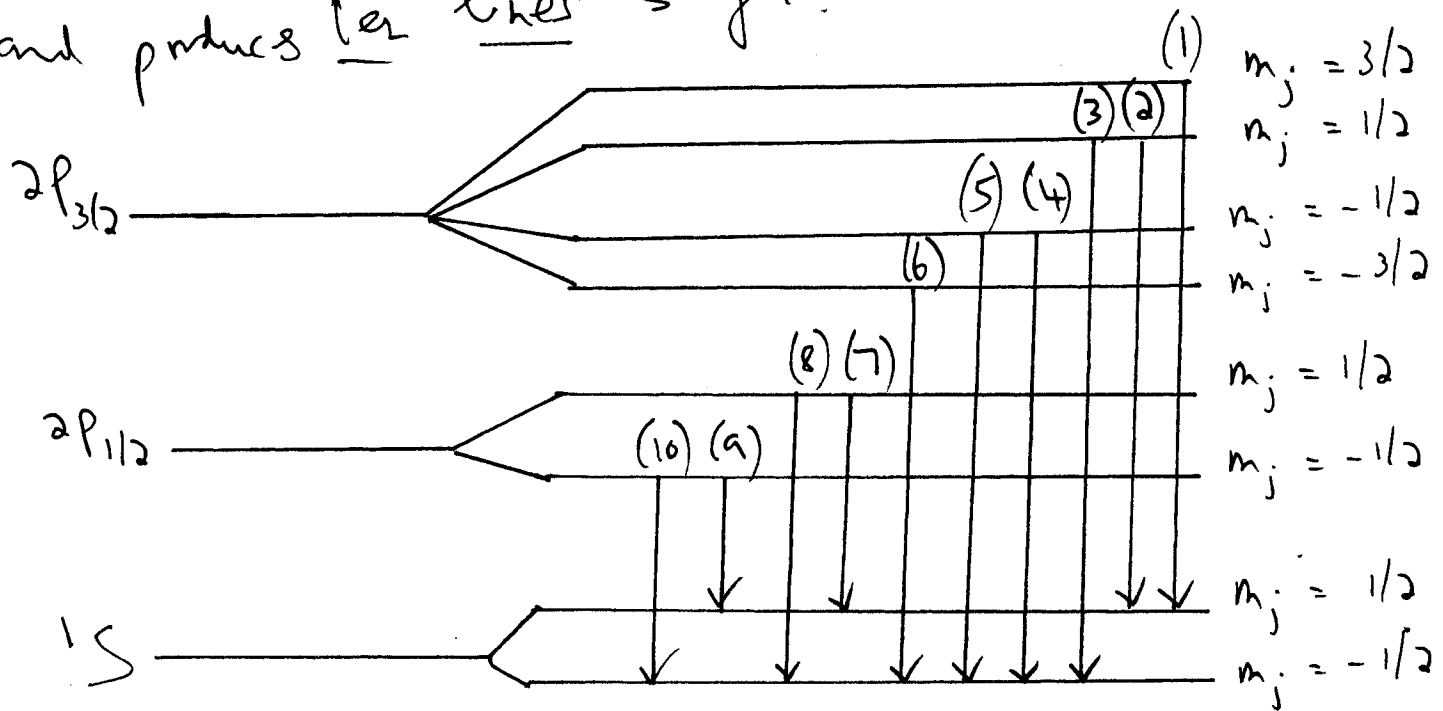
$$2p_{3/2} \text{ level: } j(j+1) - l(l+1) - s(s+1) = 1 \quad (33)$$

$$\text{For the } 2p_{1/2} \text{ level: } j(j+1) - l(l+1) - s(s+1) = -2 \quad (34)$$

b) The Zeeman effect is described by the selection rule

$$\Delta m_j = 0, \pm 1 \quad - (35)$$

and produces ten lines as follows



The selection rules are:

$$\Delta n = 1, \quad - (35)$$

wit:

- 1) $\Delta m_j = 1 = 3/2 - 1/2$
- 2) $\Delta m_j = 0 = 1/2 - 1/2$
- 3) $\Delta m_j = 1 = 1/2 - (-1/2)$
- 4) $\Delta m_j = -1 = -1/2 - 1/2$
- 5) $\Delta m_j = 0 = -1/2 + 1/2$
- 6) $\Delta m_j = -1 = -3/2 + 1/2$
- 7) $\Delta m_j = 0 = 1/2 - 1/2$
- 8) $\Delta m_j = 1 = 1/2 - (-1/2)$
- 9) $\Delta m_j = -1 = -1/2 - 1/2$
- 10) $\Delta m_j = 0 = -1/2 - (-1/2)$