331(3): Relativistic Splitting of the Zeeman Effect

Consider the 2p to 3d transition in atomic hydrogen. This occurs at 656.3 nm in the Balmer series. Zeeman was awarded the Nobel Prize for his observation that a magnetic field splits it into three lines: the Zeeman effect.

In fact these three lines are made up of three groups of three lines each at the same energy. This is the result of the Laporte selection rule:

$$\Delta l = \pm 1 \quad -(1)$$

and the selection rule:

$$\Delta m = 0, \pm 1 \quad -(2)$$

In left circularly polarized radiation, linearly polarized and right circularly polarized, $\Delta m = 1, 0, -1$ respectively.

With reference to UFT306 and its background notes the transitions are as follows.

1) <u>LCP ($\Delta m = 1$)</u>

$$2p(n=2, l=1, m=0) \rightarrow 3d(n=3, l=2, m=1)$$

$$2p(n=2, l=1, m=1) \rightarrow 3d(n=3, l=2, m=2)$$

$$2p(n=2, l=1, m=-1) \rightarrow 3d(n=3, l=2, m=0)$$

2) <u>Linear ($\Delta m = 0$)</u>

$$2p(n=2, l=1, m=0) \rightarrow 3d(n=3, l=2, m=0)$$

2) $2p(n=2, l=1, m=1) \to 3d(n=3, l=2, m=1)$

$2p(n=2, l=1, m=-1) \to 3d(n=3, l=2, m=-1)$

3) Right CP ($\Delta m = -1$)

$2p(n=2, l=1, m=0) \to 3d(n=3, l=2, m=-1)$

$2p(n=2, l=1, m=1) \to 3d(n=3, l=2, m=0)$

$2p(n=2, l=1, m=-1) \to 3d(n=3, l=2, m=-2)$

For example the effect in linear polarization is:

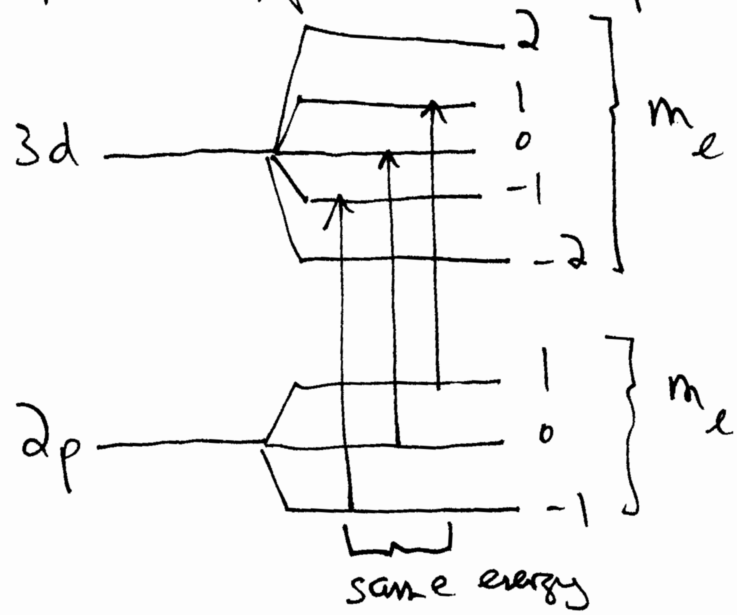


Fig (1)

Non Relativistic Theory

The total energy is:

$$E = \frac{-me^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} - \frac{e\hbar}{2m} m_l B_z \quad -(3)$$

in atomic H. For all three lines in Fig (1):

$$\Delta m_l = 0 \quad -(4)$$

So the energy change for all three lines is the

3) same:

$$\Delta E = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{9}-\frac{1}{4}\right) = \frac{5}{36}\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \quad -(5)$$

This is observed at 656.3 nm, and is the central line of the three Zeeman lines in the presence of a magnetic field. The other two Zeeman lines of the non relativistic theory are at:

$$\Delta E = \frac{5}{36}\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} - \frac{e\hbar}{2m}B_Z \quad -(6)$$

for $\Delta m = 1$ and

$$\Delta E = \frac{5}{36}\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} + \frac{e\hbar}{2m}B_Z \quad -(7)$$

for $\Delta m = -1$.

<u>Relativistic Theory</u>

The total energy is:

$$E = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} - \frac{e\hbar}{2m}m_e B_Z\left(1-\frac{2.66567\times10^{-5}}{n^2}\right) \quad -(8)$$

Consider the three transitions in linear polarization. The first is:

$$(n=2, m=0, l=1) \rightarrow (n=3, m=0, l=2) \quad -(9)$$

4) From eq. (8), the energy difference is

$$\Delta E = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{5}{36}\right) \quad -(10)$$

The second is:

$$(n=2, \ell=1, m=1) \rightarrow (n=3, \ell=2, m=1) \quad -(11)$$

The lower energy level is:

$$E_1 = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{4}\right) - \frac{e\hbar B_z}{2m}\left(1 - \frac{2.66567\times10^{-5}}{4}\right) \quad -(12)$$

The higher energy level is:

$$E_2 = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{9}\right) - \frac{e\hbar B_z}{2m}\left(1 - \frac{2.66567\times10^{-5}}{9}\right) \quad -(13)$$

The difference is

$$\Delta E = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{5}{36}\right) - 3.7023\times10^{-6}\,\frac{e\hbar B_z}{2m} \quad -(14)$$

The third is

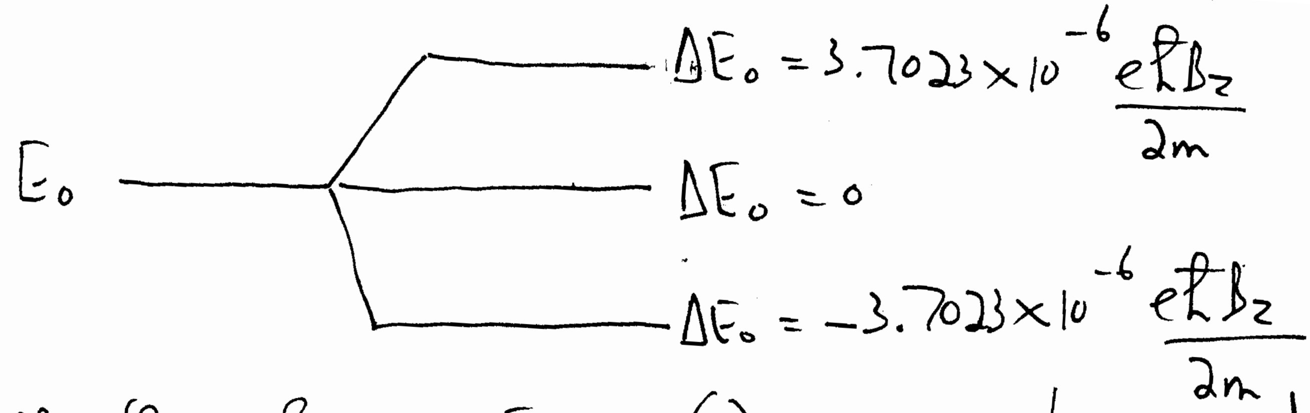
$$(n=2, \ell=1, m=-1) \rightarrow (n=3, \ell=2, m=-1) \quad -(15)$$

so

$$\Delta E = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{5}{36}\right) + 3.7023\times10^{-6}\,\frac{e\hbar B_z}{2m} \quad -(16)$$

So the line is split into three:

5)



So the three lines in Figure (1) are no longer at the same frequency, and appear as three lines. These are separated by a frequency:

$$\boxed{\Delta\omega = \pm 3.7023\times10^{-6}\frac{e}{2m}B_Z \quad -(17)}$$

Therefore:

$$\Delta\omega = 3.255\times10^{5}\, B_Z \text{ radians } s^{-1} \quad -(18)$$

which is in the megahertz range of frequencies. This absorption frequency can be measured by radio frequency spectroscopy, by an arrangement similar to visible / radio frequency double resonance.

The pattern of relativistic shifts is different for each atom and molecule.