Chapter 7 – atomic structure and spectra

Selection rules

$\vec{\mu} = -e\vec{r}$ electric dipole operator

$$\vec{\mu}_{if} = \langle i | \vec{\mu} | f \rangle$$

$\vec{\mu}_{if} = 0$ Unless integrand totally symmetric

$$\langle s | x | p_x \rangle \neq 0$$

$$\langle s | y | p_y \rangle \neq 0$$

$$\langle s | z | p_z \rangle \neq 0$$

$$\langle p_z | z | d_{z^2} \rangle \neq 0$$

Light photon has angular momentum = 1.
Since angular momenta, must be conserved $\Delta \ell = \pm 1$
upon photon abs. or emission

For *z*-pol. radiation $\Delta m_\ell = 0$

For *x*, *y*-pol. radiation $\Delta m_\ell = \pm 1$

Usually we focus on about electric dipole transitions but a transition that is dipole forbidden may still be allowed

Due to electric quadrupole (10^8 x weaker) $xy, \quad \Delta\ell = 0, \pm 2$

mag. dipole (10^5 x weaker) ℓ_z

Two-photon spectroscopy can see 1s $\rightarrow$ 2s.

Magnetic moments

Electron is charged particle

$\Rightarrow$ mag. moment associated with its ang. momentum from both spin and orb. ang. momentum

Classically, current of a charged particle moving in a circle.

$$I = -\frac{e\text{v}}{2\pi r}$$

v = speed

Magnetic dipole in the z direction

$$m_z = IA, \quad A = area \ \pi r^2$$

$$m_z = -\frac{1}{2} e\text{v}r$$

$$\ell_z = m_e \text{v}r \longleftarrow \ell = rxp = rx(m\text{v})$$

$$m_z = -\frac{e}{2m_e}\ell_z,$$

$$m_z = \gamma_e m_\ell \hbar, \quad m_\ell = -\ell, -\ell+1, \ldots, \ell$$

$$\vec{m} = \gamma_e \vec{\ell}$$

$$-\frac{e}{2m_e} = \gamma_e$$

magnetogyric ratio

$\mu_B = -\gamma_e \hbar =$ Bohr magneton (9.274 x 10^{-24} JT^{-1})

$$m_z = -\mu_B m_\ell$$

Z component of orbital magnetic moment

For spin $\vec{m} = g_e \gamma_e \vec{s}, \quad g_e = 2.002319$ (*g* factor)

Derived from relativistic Dirac Equation

$$m_z = -g_e \mu_B m_s, \quad m_s = \pm\frac{1}{2}$$

If both spin and the orbital angular momentum are non-zero, there are two magnetic moments that interact with one another

Spin-orbit coupling

Coupling of the spin and orbital angular momentum

$$H_{so} = \xi(r)\vec{\ell}\bullet\vec{s}, \quad \xi(r) = -\frac{e}{2m_e^2 rc^2}\frac{d\phi}{dr}$$

where ϕ is the electric potential $= \dfrac{Ze}{4\pi\varepsilon_0 r}$

$$\xi(r) = \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 r^3 c^2}$$

$$\left\langle n\ell m_\ell \left| \frac{1}{r^3} \right| n\ell m_\ell \right\rangle = \frac{Z^3}{n^3 a_0^3 \ell\left(\ell + \frac{1}{2}\right)(\ell + 1)}$$

$$hc\zeta_{n\ell} = \frac{Z^4 e^2}{8\pi\varepsilon_0 n^3 a_0^3 m_e^2 c^2 \ell\left(\ell + \frac{1}{2}\right)(\ell + 1)}$$

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_\ell e^2}, \qquad R = \frac{m_e e^4}{8\hbar^3 c\varepsilon_0^2}$$

$$\zeta_{n\ell} = \frac{\alpha^2 R Z^4}{n^3 \ell\left(\ell + \frac{1}{2}\right)(\ell + 1)}, \qquad \alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137}$$

fine structure constant

$$< \xi > \hbar^2 = hc\zeta$$ (Units of energy)

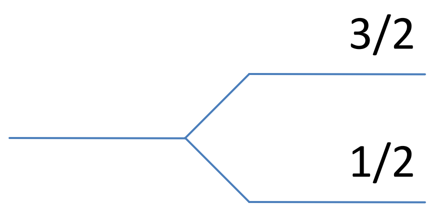
ζ Units of cm^{-1}

2p orbital H-atom – fine structure ~0.2 cm^{-1}
but note Z^4 dependence

As an example, consider an unpaired electron in a p orbital

$$\ell = 1, \quad s = \frac{1}{2}$$

$$j = \frac{3}{2}, \frac{1}{2}$$



$$E_{s0} = \left\langle \ell s;\, jm_j \middle| H_{s0} \middle| \ell s;\, jm_j \right\rangle$$

$$j^2 = \left| \vec{\ell} + \vec{s} \right| = \ell^2 + s^2 + 2\ell \bullet s$$

$$\ell \bullet s = \frac{j^2 - \ell^2 - s^2}{2}$$

$$E_{so} = Z^4 \alpha^2 hcR \left[\frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2n^3 \ell \left(\ell + \frac{1}{2} \right)(\ell + 1)} \right]$$

j = *3/2* all four states raised by

$$3/2\left(5/2\right)-1(2)-\frac{1}{2}\left(\frac{3}{2}\right)$$

$$=\frac{15}{4}-2-\frac{3}{4}=\frac{12}{4}-2=1$$

j = ½ both states are lowered by

$$1/2(3/2)-1(2)-\frac{1}{2}\left(\frac{3}{2}\right)$$

$$=3/4-2-3/4=-2$$

hence, the asymmetrical splitting

Term symbols $^{2S+1}\mathrm{L}_J$

$2S+1 \rightarrow$ multiplicity

So, in our previous example, we have $^2P_{3/2}$ and $^2P_{1/2}$ states