H-atom-supplement

Chem 2430

The orbitals for $\ell \geq 1$ and $|m| \geq 1$ are complex due to the $e^{\pm im\phi}$ factors.

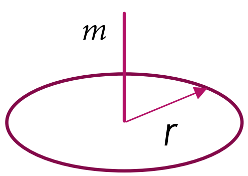
One can make real linear combinations giving, e.g., p_x, p_y in addition to p_z

$$p_x \sim re^{-Zr/a} \sin\theta \cos\phi$$
$$p_y \sim re^{-Zr/a} \sin\theta \sin\phi$$

p_x and p_y are not eigenfunctions of $\hat{L}_Z$

Because the p_+ and p_- orbitals are degenerate, the energy is unchanged by taking the linear combinations that give p_x and p_y.

Zeeman effect



current I in loop of area A gives a magnetic moment $|m| = IA$

A charge (Q) moving with velocity (v) generates a magnetic field

$$\boldsymbol{B} = \frac{\mu_o}{4\pi}\frac{Q\mathrm{v}\mathrm{x}r}{r^3}\left(\mu_o = 4\pi \times 10^{-7}\, NC^{-2}s^2\right) \quad (1 \text{ Tesla} = 1\, NC^{-1}m^{-1})$$

$$I = \frac{Q\mathrm{v}}{2\pi r} \qquad |m| = \text{current x area} = \frac{Q\mathrm{v}}{2\pi r}\pi r^2 = \frac{Q\mathrm{v}r}{2} = \frac{Qrp}{2m}$$

$$\boldsymbol{m}_L = \frac{Q\boldsymbol{r}x\boldsymbol{p}}{2m} = \frac{Q}{2m}\boldsymbol{L}$$

if $Q = -e$, the magnetic moment is

$$\boldsymbol{m}_L = \frac{-e\boldsymbol{L}}{2m_e}$$

$$|m_L| = \frac{e\hbar}{2m_e}\sqrt{\ell(\ell+1)} = \beta_e\sqrt{\ell(\ell+1)}$$

$$\beta_e = \frac{e\hbar}{2m_e} = \text{Bohr magneton} = 9.274 \times 10^{-24}\ \mathrm{J/T}$$

Now what happens if the H atom is in an external magnetic field?

$$E_B = -\boldsymbol{m}\cdot\boldsymbol{B}$$ where B is the external field

$$= \frac{e}{2m_e}\boldsymbol{L}\cdot\boldsymbol{B}$$

assume the field is along the z direction

$$\boldsymbol{B} = B\boldsymbol{k}$$

$$E_B = \frac{e}{2m_e}BL_z = \frac{\beta_e}{\hbar}BL_z$$

In a QM treatment

$$\hat{H}_\beta = \frac{\beta_e}{\hbar}B\hat{L}_z$$

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{free}} + \hat{H}_B,$$ $\hat{H}_{free}$ is the Hamiltonian without the field.

$$\left(\hat{H}_{free} + \hat{H}_B\right)RY_\ell^m = \hat{H}RY_\ell^m + \hat{H}_BRY_\ell^m$$

$$= \frac{-Z^2}{n^2}\frac{e'^2}{2a} + \beta_eBmRY_\ell^m$$

So for a p orbital, m = -1, 0, 1
different energies

Results don't agree with experiment because we have neglected the electron spin