

SCHRÖDINGER EQUATION REVIEW

THE 3-D SCHRÖDINGER EQUATION

In 3-D, the Schrodinger equation is written for Cartesian & spherical coordinats as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}$$

To solve this using separation of variables, assume that $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$, giving

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} (rR\Theta\Phi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial R\Theta\Phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 R\Theta\Phi}{\partial \phi^2} = -\frac{2M}{\hbar^2} [E - V(r)]R\Theta\Phi.$$

This is solved for a function, $\Phi(\phi)$ equal to functions of r and θ that must be a constant, $-m^2$,

$$\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \quad \Rightarrow \quad \frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Phi \quad \text{or} \quad \Phi'' = -m^2 \Phi \quad \text{The } \Phi \text{ equation}$$

which has a solution

$$\Phi_m(\phi) = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots$$

Rearrangnig the $R(r)$ and $\Theta(\theta)$ equations and setting each side equal to $-k$ gives an equation in θ solved by Legendre who found solutions for $k = \ell(\ell + 1)$, $\ell = 0, 1, 2, \dots, n$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta_{\ell, m}}{\partial \theta} \right) + \left(\ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right) \Theta_{\ell, m} = 0 \quad \text{The } \Theta \text{ equation}$$

Whose solutions are Associated Legendre Functions where $\Theta_{\ell, -m} = (-1)^m \Theta_{\ell, m}$

| | $\ell = 0$ | $\ell = 1$ | $\ell = 2$ |
|-------------|--|--|---|
| $m = 0$ | $\Theta_{0,0} = \sqrt{\frac{1}{4\pi}}$ | $\Theta_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$ | $\Theta_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$ |
| $m = \pm 1$ | | $\Theta_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta$ | $\Theta_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta$ |
| $m = \pm 2$ | | | $\Theta_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta$ |

Spherical Harmonics are the normalized products of the theta and psi solutions (T. p. 183)

$$Y_{\ell, m}(\theta, \phi) = \Theta_{\ell, m}(\theta)\Phi_m(\phi) \quad \int_0^{2\pi} \int_0^\pi Y_{\ell', m'}^*(\theta, \phi) Y_{\ell, m}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{\ell' \ell} \delta_{m' m}$$

For the single electron in the hydrogen atom,

$$U(r) = -\frac{ke^2}{r} \quad \text{and} \quad E = -\frac{m_e (ke^2)^2}{2\hbar^2} \frac{1}{n^2} = -\frac{E_R}{n^2} = -\frac{13.6}{n^2} \text{ eV}$$

the R equation becomes

$$\frac{\partial^2}{\partial r^2}(rR) = \frac{2m_e}{\hbar^2} \left[-\frac{ke^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} - \frac{E_R}{n^2} \right] (rR) \quad \text{The R equation for hydrogen}$$

Solutions to this for $n = 1, 2, 3$ and $\ell = 0, 1, 2$ are given on Townsend p. 191.

| | $n = 1$ | $n = 2$ | $n = 3$ |
|------------|--|---|--|
| $\ell = 0$ | $R_{1,0} = \frac{2}{\sqrt{a_B^3}} e^{-r/2a_B}$ | $R_{2,0} = \frac{1}{\sqrt{2a_B^3}} \left(1 - \frac{r}{2a_B}\right) e^{-r/2a_B}$ | $R_{3,0} = \frac{2}{\sqrt{27a_B^3}} \left(1 - \frac{2r}{3a_B} + \frac{2r^2}{27a_B^2}\right) e^{-r/3a_B}$ |
| $\ell = 1$ | | $R_{2,1} = \frac{1}{\sqrt{24a_B^5}} r e^{-r/2a_B}$ | $R_{3,1} = \frac{8}{27\sqrt{6a_B^5}} \left(1 - \frac{r}{6a_B}\right) r e^{-r/3a_B}$ |
| $\ell = 2$ | | | $R_{3,2} = \frac{4}{81\sqrt{30a_B^7}} r^2 e^{-r/3a_B}$ |

These use the normalization constant from $dP(r) = r^2|R(r)|^2$

HYDROGENIC WAVE FUNCTIONS

The stationary states of the electron in the hydrogen atom are thus described by

$$\Psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r) \Theta_{\ell,m}(\theta) \Phi(\phi)$$

for $n = 1, 2, 3, \dots$

$\ell = 0, 1, 2, \dots, (n - 1)$

$m = -\ell, -(\ell - 1), \dots, 0, \dots, (\ell - 1), \ell$

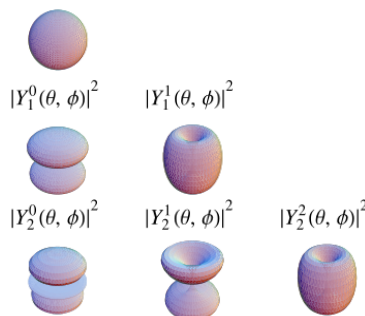
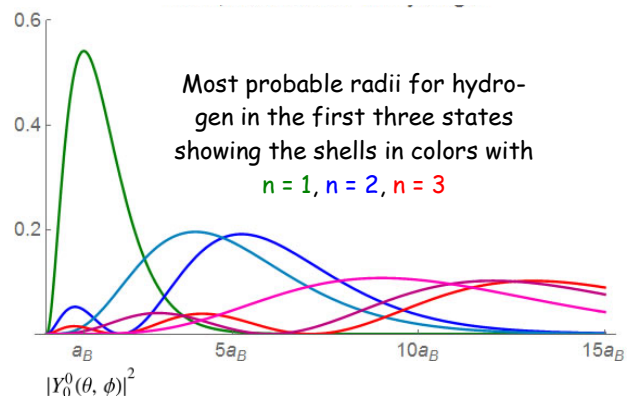
Energy Shells (n values)

These are determined by energy and the most probable radii of the electrons.

The angular momentum determines the orbital and, though spherically symmetric, not all values of θ are as likely to be occupied.

Orbitals (ℓ and m values)

The most probable angular positions of the electrons are determined by the Spherical Harmonics. These create symmetric, but not uniform regions of electron positions that ultimately influence chemical bonding in molecules.



THE ZEEMAN EFFECT

QUANTUM NUMBERS GIVE PHYSICAL QUANTITIES

(THAT WE CAN MEASURE IN THE LAB!)

Principle Q.N. n gives the energy of a state:

$$n = 1, 2, 3, \dots$$

$$E_n = -\frac{1}{2} \frac{m_e (ke^2)^2}{n^2 \hbar^2} = \frac{-13.6 \text{ eV}}{n^2}$$

Ang. Mom. Q.N. ℓ gives the magnitude of the angular momentum:

The orbitals are named for the ℓ values,

s: $\ell = 0$ = sharp

p: $\ell = 1$ = principle

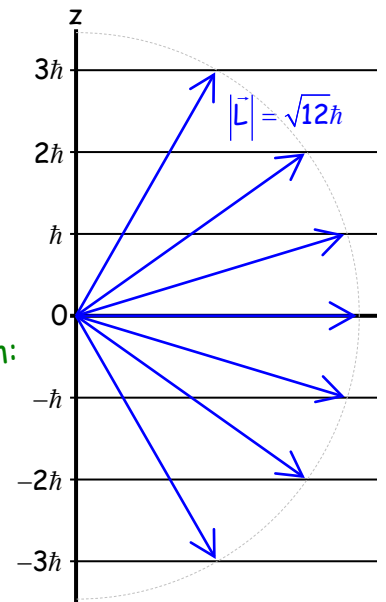
d: $\ell = 2$ = diffuse

f: $\ell = 3$ = fundamental

$$\ell = 0, 1, 2, 3, \dots, (n - 1)$$

$$|\vec{L}| = \hbar \sqrt{\ell(\ell + 1)}$$

} Named for spectral line classifications



Magnetic Q.N. m gives the z-component of the angular momentum:

$$m = -\ell, \dots, 0, \dots, \ell \quad L_z = m\hbar$$

ELECTRON SPIN

The Spin Angular Momentum of the electron is similar to its orbital angular momentum with a magnitude given by:

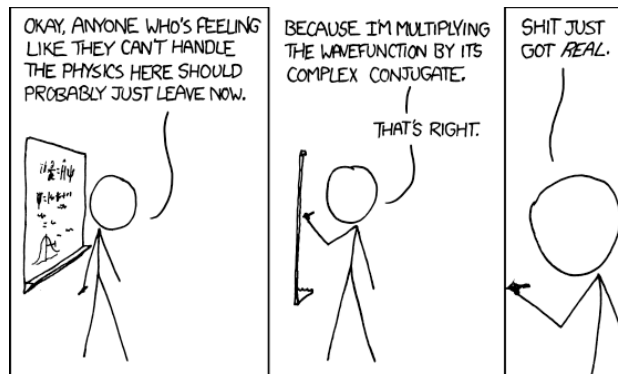
$$|\vec{S}| = \hbar \sqrt{s(s + 1)} = \frac{\sqrt{3}}{2} \hbar$$

Where s can only be one value, $s = \frac{1}{2}$.

The orientation of the spin vector is given by the Spin Quantum Number, $m_s = \pm \frac{1}{2}$.

$$S_z = m_s \hbar$$

Only electrons with opposite spins can occupy the same quantum level (where n , ℓ , and m_ℓ are equal). Thus the Pauli Exclusion Principle states that electrons must differ in at least one quantum number.



ATOMS IN MAGNETIC FIELDS

An applied magnetic field changes the energy of the electron orbits due to the orbital and spin angular momenta. This is similar to the torque on a current loop in a magnetic field $\vec{\Gamma} = i\vec{A} \times \vec{B}$ with the magnetic moment defined as $i\vec{A}$ (current times the area of the loop). For electrons in atoms these are

Orbital Magnetic Moment:
$$\vec{\mu}_{\text{orbital}} = -\frac{e}{2m_e} \vec{L} \tag{TZDII 9.22}$$

Spin Magnetic Moment:
$$\vec{\mu}_{\text{spin}} = -\frac{e}{m_e} \vec{S} \tag{TZDII 9.22}$$

Zeeman Effects

The changes in the energy of an electron in a magnetic field is due to the work done by the field, $W = \vec{F} \cdot \vec{r} = \vec{\Gamma} \cdot \vec{\theta}$

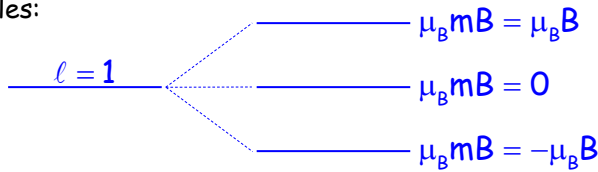
$$\Delta E_{\text{orbital}} = \left(\frac{e\hbar}{2m_e} \right) mB = \mu_B mB \quad \left(\frac{e\hbar}{2m_e} \right) = \text{Bohr Magneton}$$

$$\Delta E_{\text{spin}} = \left(\frac{e\hbar}{m_e} \right) m_s B = \pm 2\mu_B B \quad \left(\frac{e\hbar}{m_e} \right) = 5.79 \times 10^{-5} \frac{\text{eV}}{\text{T}}$$

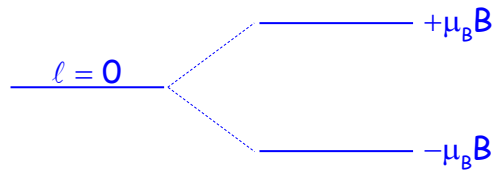
Where $\mu_B = 5.79 \times 10^{-5} \text{ eV/T}$. Thus the energy of a given level is

$$E_{\text{total}} = E_{n\ell m_s} + (\Delta E_{\text{orbital}} + \Delta E_{\text{spin}})$$

Examples:



Zeeman splitting for an $l = 1$ state.



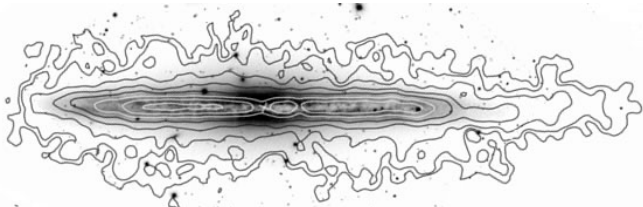
Anomalous Zeeman splitting for an $l = 0$ state.

FINE STRUCTURE:

Since the electron "sees" the proton orbiting itself, it responds to the current loop created by the orbiting proton. This creates "spin-orbit" splitting for all states.

HYPERFINE STRUCTURE:

The spin of both the proton and the electron in the hydrogen atom also create magnetic fields so that the lowest energy level has antiparallel spins. The "spin-flip" from parallel to antiparallel results in a 1420 MHz photon ... the 21 cm line of hydrogen.



NGC 891 Radio Halo from Swaters, Sancisi, & vander Hulst, 1997, [ApJ. 763, 148](#)

Radio spectrum of UGC 11707 from Haynes, et al., 1998, [AJ, 115, 62](#)

