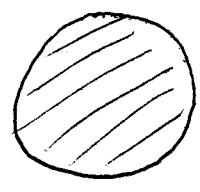


$Y_{l,m}(\theta, \phi)$: spherical harmonics

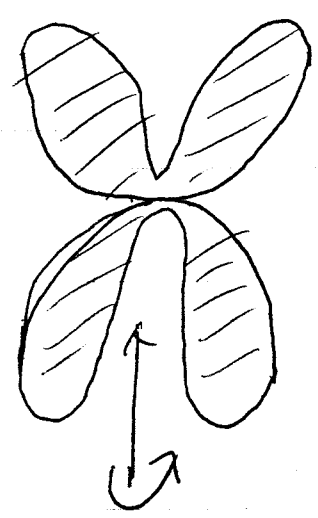
$l=0, m_l=0:$ $Y_{0,0} = \sqrt{\frac{1}{4\pi}}$



$l=1, m_l = \pm 1:$ $Y_{1,m} = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$



$l=2, m_l = \pm 1:$



radial solution $R_{n,l}(r)$:

$$R_{n,l}(r) = N_{n,l} \left(\frac{r}{a_0}\right)^l L_{n,l}(\rho) e^{-\rho/2n}$$

|
associated Laguerre polynomial

with $\rho = \frac{2Zr}{a_0}$ $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 52.9177 \text{ pm}$
Bohr radius

Orbital

1s ($n=1$ $l=0$) $R_{n,l} = 2 \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$

2s ($n=2$ $l=0$) $R_{n,l} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \frac{1}{2}\rho) e^{-\rho/4}$

2p ($n=2$ $l=1$) $R_{n,l} = \frac{1}{4\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/4}$

quantum number $n \Rightarrow$ energy E_n $n = 1, 2, 3$

quantum number $l \Rightarrow$ angular momentum
 $= \sqrt{l(l+1)} \hbar$ $l = 0, 1, 2, \dots, n-1$

quantum number $m_l \Rightarrow$ z-component of angular momentum
 $= m_l \hbar$
 $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

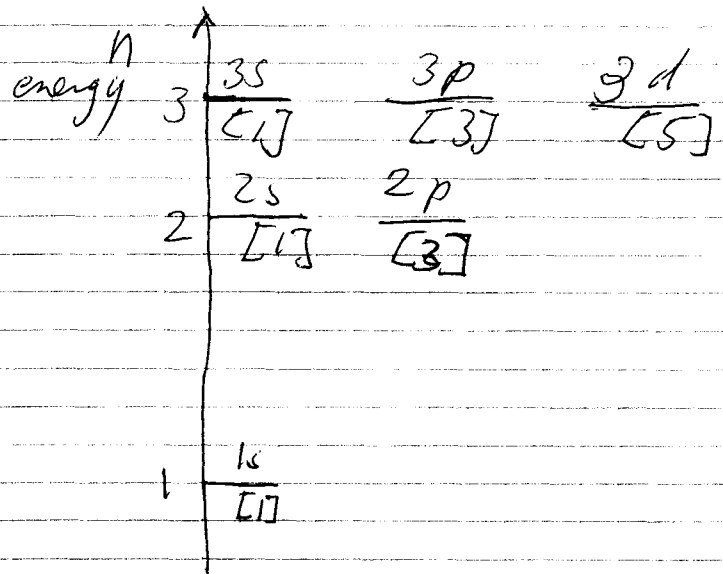
shells ~~part~~ subshells and orbitals

n = 1 2 3 4 shells
K L M N

l = 0 1 2 3 4 subshells

s p d f g

m_l = -1, 0, +1 orbitals



s-orbitals:

All s orbitals are spherically symmetric, but differ in the number of radial nodes

1s: $\psi = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$ decays from the nucleus

2s: radial node for $r = \frac{2a_0}{Z}$

3s: two radial nodes for $\frac{1.9 a_0}{Z}$ and $\frac{7.1 a_0}{Z}$

⋮
⋮
⋮

mean radius of an orbital

$$\begin{aligned}
\langle r \rangle &= \int \psi^* r \psi d\tau = \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} r R_{nl}^2 \frac{1}{4\pi} r^2 dr \sin\theta d\theta d\phi \\
&= \int_0^\infty r^3 R_{nl}^2 dr
\end{aligned}$$

$$\langle r_{nl} \rangle = n^2 \left\{ 1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right\} \frac{a_0}{Z}$$

p-orbitals

$$\begin{aligned}
m_l = 0 \quad \psi_{p_0} &= \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a_0} \right)^{5/2} r \cos\theta e^{-Zr/a_0} = r \cos\theta f(r) \\
&= 2 f(r) = \psi_{p_z}
\end{aligned}$$

$$m_l = \pm 1$$

$$\psi_{p_{\pm 1}} = \mp \frac{1}{\sqrt{2}} r \sin\theta e^{\pm i\phi} f(r)$$

$$\Rightarrow \psi_{p_x} = -\frac{1}{\sqrt{2}} (p_+ - p_-) = x f(r)$$

$$\psi_{p_y} = \frac{i}{\sqrt{2}} (p_+ + p_-) = y f(r)$$

d-orbitals

$$d_{xy} = xy f(r) \quad d_{yz} = yz f(r) \quad d_{zx} = zx f(r)$$

$$d_{x^2-y^2} = \frac{1}{2} (x^2 - y^2) f(r) \quad d_{z^2} = \frac{1}{2\sqrt{3}} (3z^2 - r^2) f(r)$$

Spectroscopic selection rules

allowed \leftrightarrow forbidden

$$\Delta L = \pm 1$$

$$\Delta m_l = 0, \pm 1$$

justification

$$\vec{p}_i = \langle i | p | i \rangle \quad p_x = -e_x, \quad p_y = -e_y, \quad p_z = -e_z$$

$$\begin{aligned}
 p_{z, i \rightarrow i} &= -e \int \psi_f^* z \psi_i d\tau = -2 = \sqrt{\frac{4\pi}{3}} r Y_{1,0} \\
 &= \sqrt{\frac{4\pi}{3}} \int_0^\infty R_{n_f, l_f} R_{n_i, l_i} r^2 dr \int_0^\pi \int_0^{2\pi} Y_{l_f, m_f}^* Y_{1,0} Y_{l_i, m_i} \sin\theta d\theta d\phi \\
 &= \int_0^\pi \int_0^{2\pi} Y_{l_f, m_f}^* Y_{1,0} Y_{l_i, m_i} \sin\theta d\theta d\phi
 \end{aligned}$$

$$\neq 0 \text{ for } l_f = l_i \pm 1 \quad m_{l_f} = m_{l_i} + m$$

$$\Rightarrow \Delta L = \pm 1 \quad \Delta m_l = 0$$

Many-electron atoms

orbital approximation each e^- is occupying its own orbital

$$\Psi(r_1, r_2, \dots) = \psi(r_1) \psi(r_2) \dots$$

+ Pauli principle :

When the labels of any 2 identical fermions are exchanged, the total wavefunction changes sign.

When the labels of any 2 identical bosons are exchanged, the total wavefunction retains the same sign

energies of subshells in
a many-electron atom: $s < p < d < f$

⇒ building-up principle:
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s

the most probable distance of a 3d e⁻ from the nucleus is less than that for a 4s e⁻, so two 3d e⁻ repel each other more strongly than 2 4s e⁻.