Atomic orbitals

One electron wavefunction in atoms are known as atomic orbitals.

p-orbitals

$\cancel{Y_{210}(r,\theta,\phi)} = R_{21}(r)\, Y_{10}(\theta,\phi)$

$\psi_{210}(r,\theta,\phi)$

$$R_{21}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{2\sqrt{6}} \rho_n$$

$$Y_{10}(\theta,\phi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$\psi_{210}(r,\theta,\phi) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{2\sqrt{6}} \rho_n \sqrt{\frac{3}{4\pi}} \cos\theta$$

$n=2$
$Z=1$

$$\psi_{210}(r,\theta,\phi) = \frac{1}{2\sqrt{6}} \sqrt{\frac{3}{4\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{2Zr}{na_0}\cdot\frac{1}{2}} \frac{2Zr}{na_0}$$

$$= \frac{1}{2\sqrt{6}} \sqrt{\frac{3}{4\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{2Zr}{2a_0}\cdot\frac{1}{2}} \cdot \frac{2Zr}{2a_0} \cos\theta$$

$$= \frac{1}{2\sqrt{6}} \sqrt{\frac{3}{4\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{2a_0}} \frac{r}{a_0} \cos\theta$$

$$= (\text{constant})\ \underbrace{r\cos\theta}\, f(r) \quad z\ (\text{constant})\ z f(r)$$

$$\Psi_{210}(r,\theta,\phi) = (\text{constant})\ z\, f(r) \leftarrow z\text{-axis}$$

$\downarrow$

p_z orbital

$$\Psi_{211}(r,\theta,\phi) = R_{21}(r)\ Y_{11}(\theta,\phi)$$

$$\left\{\begin{aligned} \Psi_{211}(r,\theta,\phi) &= \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2} \frac{1}{2\sqrt{6}} \rho_n \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi} \\ &= (\text{Constant})\ r \sin\theta\, e^{i\phi} f(r) \\ \Psi_{21-1}(r,\theta,\phi) &= R_{21}(r)\ Y_{1-1}(\theta,\phi) \\ &= (\text{constant})\ r \sin\theta\, e^{-i\phi} f(r) \end{aligned}\right.$$

$$\Psi_{211} + \Psi_{21-1} \simeq r \sin\theta \cos\phi\ f(r)$$

$$= \underline{\underline{x}}\, f(r) \rightarrow p_x \text{ orbital}$$

<u>Degenerate orbitals</u>

$\Psi_1, \Psi_2 \Rightarrow$ degenerate

$$\left.\begin{aligned} \hat{H}\Psi_1 &= E_1 \Psi_1 \\ \hat{H}\Psi_2 &= E_2 \Psi_2 \end{aligned}\right\} \underline{\underline{E_1 = E_2}}$$

(degeneracy)

$$\Psi = \Psi_1 + \Psi_2$$

$$\begin{aligned}
\hat{H}\Psi &= \hat{H}(\Psi_1 + \Psi_2) \\
&= \hat{H}\Psi_1 + \hat{H}\Psi_2 \\
&= E_1\Psi_1 + E_2\Psi_2 \\
&= E(\Psi_1 + \Psi_2)
\end{aligned}$$

Selection rules for atomic transitions

$\Delta l = \pm 1$

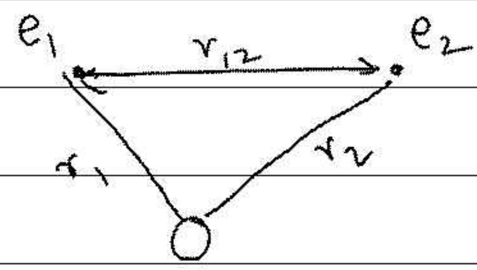
$\Delta m_l = 0, \pm 1$

$\Delta n \Rightarrow$ no specific rule; it can be any value

$l = 2$ (d-orbital)

$$l = 2 \left\{ \begin{array}{l} \xrightarrow{+1} l = 3 \ \ (nf) \\ \xrightarrow{-1} l = 1 \ \ (np) \end{array} \right\} \begin{array}{l} \Delta m_l = 0 \\ \text{or } = \pm 1 \end{array}$$

Helium atom:



$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\text{e-e repulsion}}$$

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}}_{\hat{H}_1} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{\hat{H}_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$