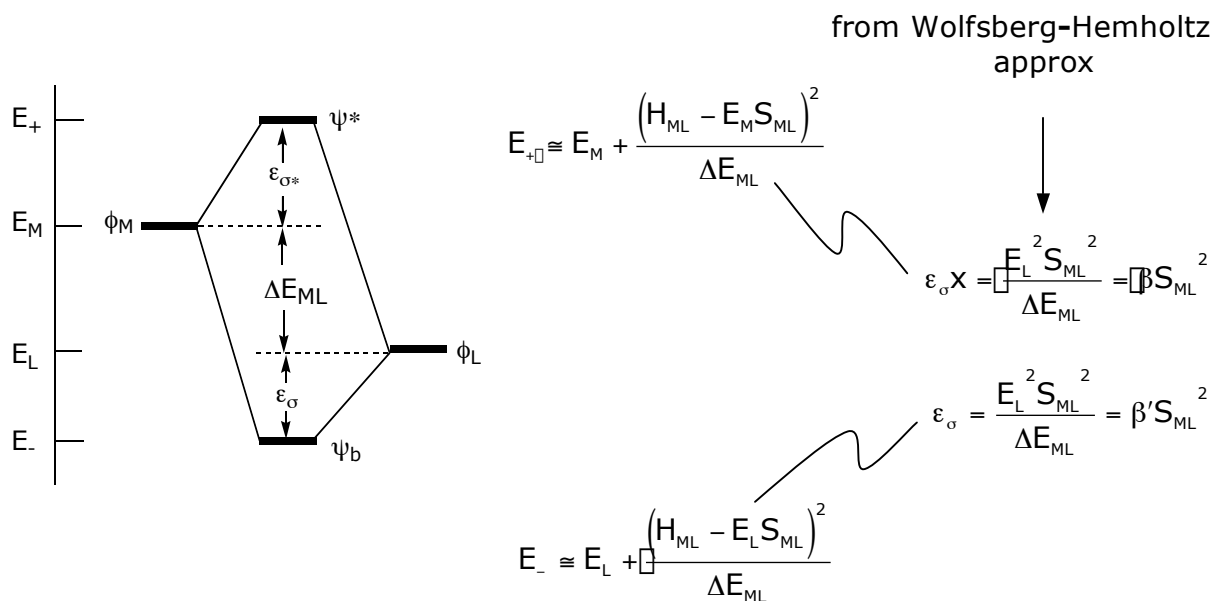


**Lecture 16: Angular Overlap Method (AOM) and M-L Diatomics**

We will begin by "solving" the Hamiltonian by a simple method, afforded by the Wolfsberg-Hemholtz approximation



$E_+$  and  $E_-$  are roots of secular determinant describing the LCAO wave function,

$$\psi = C_M \phi_M + C_L \phi_L$$

Thus by determining the overlap integral,  $S_{ML}$ , the relative energies of the metal and ligand based orbitals may be obtained... it is this energy difference that is measured by electronic spectroscopy.

Recall that the overall wave function is a product of radial and angular functions

$$\psi_{n,\ell,m_\ell} = \underbrace{R_{n,\ell}(r)}_{\text{radial}} \underbrace{Y_{\ell,m_\ell}(\theta, \phi)}_{\text{angular}}$$

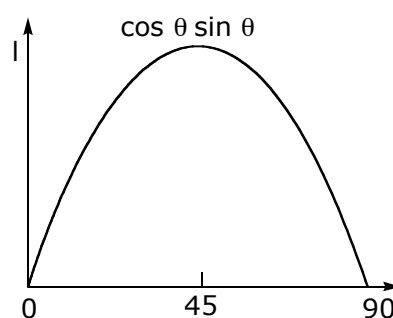
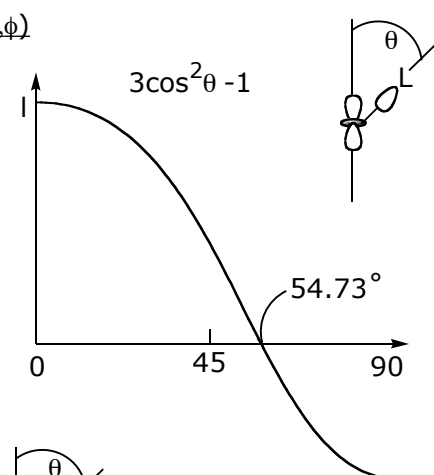
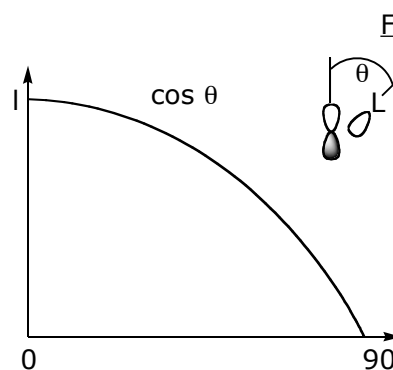
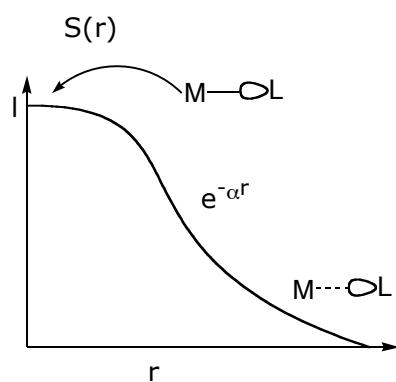
$$R_{n,\ell}(r) = \left[ \left( \frac{2z}{na_0} \right)^3 \frac{(n-\ell-1)!}{2n[(n-\ell)!]^3} \right]^{\frac{1}{2}} e^{-\rho/2} \cdot L_{n+\ell}^{2\ell+1}(\rho) \cdot \rho^\ell \quad \text{where } \rho = \frac{2z}{na_0} r$$

Laguerre polynomial

$$Y_{\ell,m_\ell}(\theta, \phi) = \underbrace{\left\{ (-1)^\ell \sqrt{\frac{2\ell+1}{2}} \cdot \frac{(\ell+m_\ell)!}{(\ell-m_\ell)!} \cdot \frac{1}{2^\ell \ell!} \cdot \frac{1}{\sin^{m_\ell} \theta} \cdot \frac{d^{\ell-m_\ell}}{(d \cos \theta)^{\ell-m_\ell}} \sin^{2\ell} \theta \right\}}_{\Theta_{\ell,m_\ell}(\theta)} \cdot \underbrace{\frac{1}{2\sqrt{\pi}} e^{im_\ell \phi}}_{\Phi_{m_\ell}(\phi)}$$

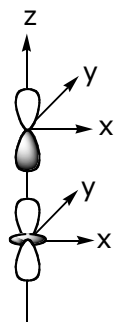
In the AOM Method, the overlap integral is also factored into a radial and angular product...

$$S_{ML} = S(r) F(\theta, \phi)$$

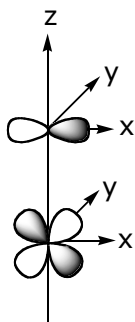


Under the condition of a fixed M-L distance, the overlap integral,  $S_{ML}$ , will depend only on  $F(\theta, \phi)$

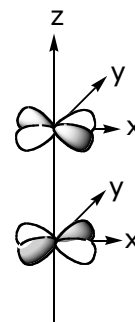
To begin, let's determine the energy of the d-orbitals for a M-L diatomic. There are three types of interactions



$E(d_{z^2}) = S_{ML}^2(\sigma) = \beta \cdot F_{\sigma}^2(\theta, \phi) = \beta \cdot 1 = e_{\sigma}$   
 the metal orbital bears the antibonding interaction... hence  $d_{z^2}$  is destabilized by  $e_{\sigma}$  (the corresponding L orbital is stabilized by  $\beta'^2 \cdot 1 = e_{\sigma}'$ )



$E(d_{yz}) = E(d_{xz}) = S_{ML}^2(\pi) = e_{\pi}$   
 the  $(M-L\pi)^*$  interaction above is for  $L\pi$  ligands...etc metal orbitals are destabilized by  $e_{\pi}$ . For  $\pi$  acceptors, the metal will be stabilized by  $e_{\pi}$ .



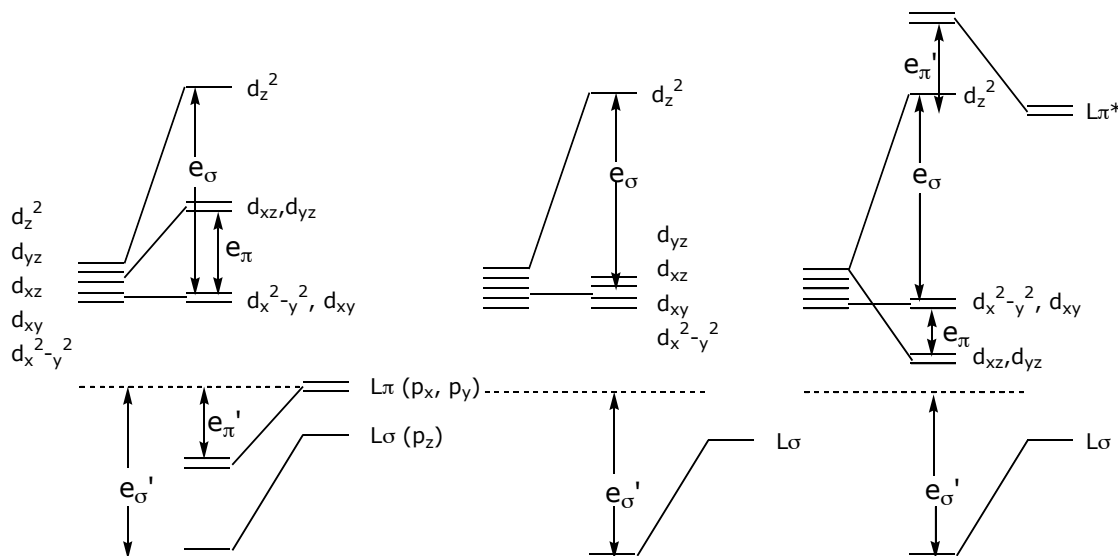
$E(d_{xy}) = E(d_{x^2-y^2}) = S_{ML}^2(\delta) = e_{\delta}$   
 $S_{ML}(\delta)$  is small compared to  $S_{ML}(\pi)$  or  $S_{ML}(\sigma)$ . Thus overlap integral and associated energy is ignored in most AOM treatments.

The overall energy level diagrams for the M-L diatomic are:

$\pi$  donor

$\sigma$ -only

$\pi$  acceptor



Of course, more than 1 ligand in a typical coordination compound. The power of AOM is that the  $e_{\sigma}$  and  $e_{\pi}$  energies are additive. Thus MO energy levels of the coordination compound are determined by simply summing  $e_{\sigma}$  and  $e_{\pi}$  for each M(d)-L interaction.