Lecture #5 of 15

(3: TThF, 5: MT*W*ThF, 4: MT*W*Th, 2: TW)

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Chemical Properties

Quiz Time!

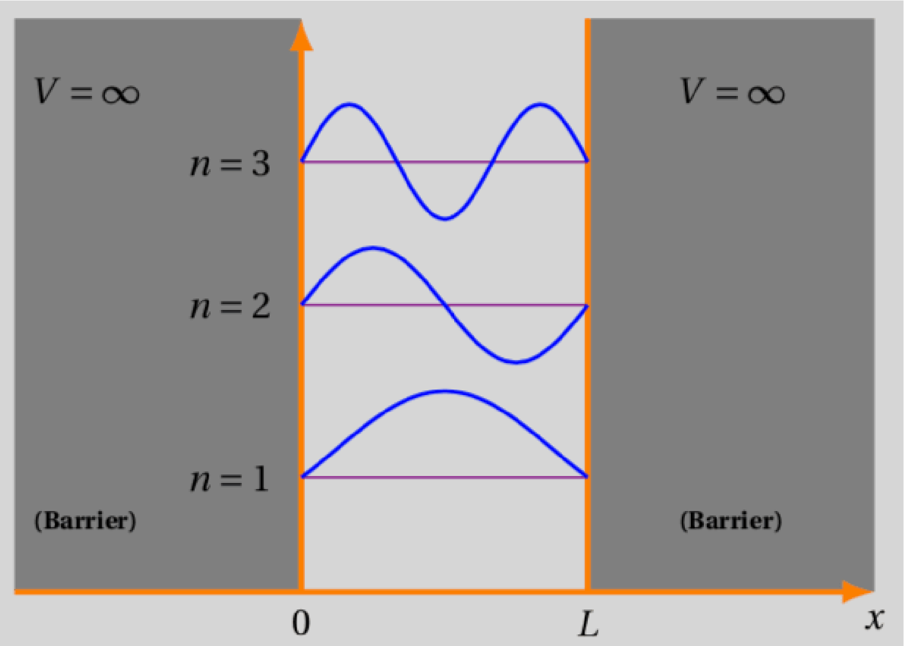
Prof. Shane Ardo
Department of Chemistry
University of California Irvine

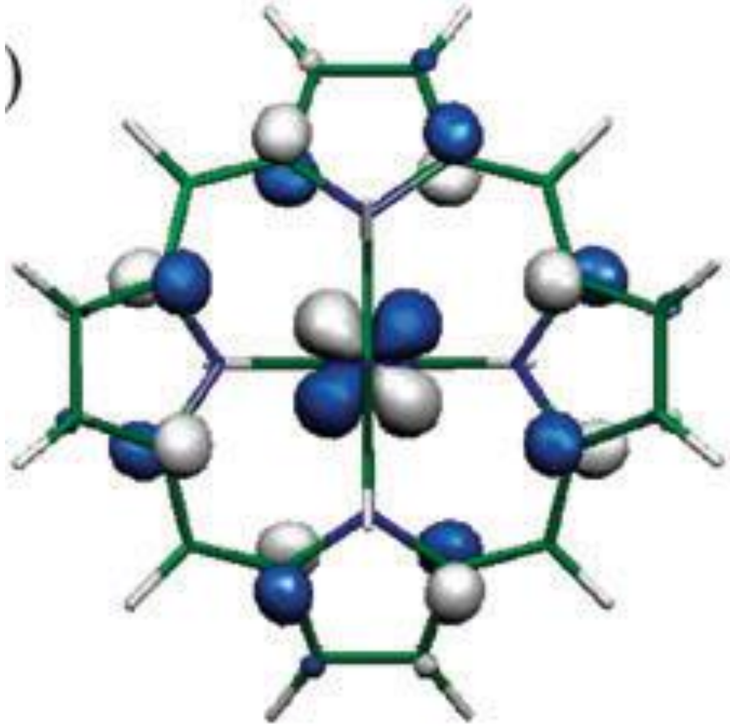
Chemical Properties

- Molecular nomenclature, Solutions, Balanced chemical reactions
- State functions, Standard states, Thermochemistry
- Non-ideal gases, Intermolecular forces, Physical properties, Phase changes, Colligative properties, Water activity
- Free energy, (X)Chemical potential, Chemical equilibrium, van’t Hoff equation, Activity coefficients, Le Chatelier’s principle
- **Schrödinger equation, Internal energy, Atomic orbitals, Hybridization**
- **Valence bond theory, Molecular orbital theory, Band diagrams**
- **Crystal field theory, Ligand field theory**

Great online resource: http://www.rnlkwc.ac.in/pdf/study-material/chemistry/Peter_Atkins__Julio_de_Paula__Physical_Chemistry__1_.pdf

From a Simple Box to a Complex Box





https://daniloroccatano.blog/2020/02/17/the-one-dimensional-time-independent-schrodinger-equation/
https://www.semanticscholar.org/paper/Saddle-shaped-six-coordinate-iron(iii)-porphyrin-Cheng-Chao/f057b748f8ddb4217eda70ea67725299910d77fc

Schrödinger Equation

Elegant master equation that allows one to determine internal energies, E_n, of a system

$$\boldsymbol{\hat{H}\psi_n(x) = \mathrm{E}_n\psi_n(x)}$$

… but this is not good enough for photochemists, or physicists, where time-varying oscillating electromagnetic fields often interact with matter…

$\mathrm{E} = h\nu = \hbar\omega$ (Planck)

$\mathrm{E} = mc^2 = pc$ (Einstein)

$p = \frac{h\nu}{c} = \frac{h}{\lambda} = h\bar{\nu} = \hbar k$ (de Broglie)

$$\boldsymbol{\hat{H}\Psi_n(x,t) = i\hbar\frac{\partial}{\partial t}\Psi_n(x,t)}$$

… so, how does one solve either of these Schrödinger equations?… We need to know $\hat{H}$!

$$\hat{H} = \hat{T} + \hat{V}$$

… um… well that didn't really help us at all… anyway, so instead, we need to know $\hat{T}$ and $\hat{V}$?

$\hat{T}(x) = \mathrm{KE} = \frac{1}{2}m\hat{v}^2 = \frac{\hat{p}^2}{2m}$… with ($\boldsymbol{\hat{p}}$)momentum = ($m$)ass x ($\hat{v}$)elocity = $\boldsymbol{-i\hbar\frac{\partial}{\partial x}}$…

$\hat{V}(x) = \mathrm{PE} = 0$… for particle-in-a-box…

$\hat{V}(x) = \frac{1}{2}k_f x^2 = \frac{1}{2}m\omega^2x^2$… for harmonic oscillator, with k_f (force const), ω (angular freq)…

$\hat{V}(r) = -\frac{q^2}{4\pi\varepsilon_o r}$… for Hydrogen atom, with $F = qN_\mathrm{A}$ (Faraday const), ε_o (vacuum permittivity)

… let's examine the hydrogen atom in more detail… because it seems like it may be fairly important to chemists ☺

Solving the Schrödinger Equation

So, let’s solve the Schrödinger equation using the Hamiltonian for the hydrogen(ic) atom…

$$\hat{H} = \hat{E}_{\mathrm{K,electron}} + \hat{E}_{\mathrm{K,nucleus}} + \hat{V}$$

$$= -\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla_{\mathrm{e}}^2 - \frac{\hbar^2}{2m_{\mathrm{N}}}\nabla_{\mathrm{N}}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

… which can be written for the motion of the electron with respect to the nucleus using the reduced mass, μ, as…

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi \qquad \frac{1}{\mu} = \frac{1}{m_{\mathrm{e}}} + \frac{1}{m_{\mathrm{N}}}$$

… the solutions to this equation are separable into radial (R) and angular (Y) components…

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

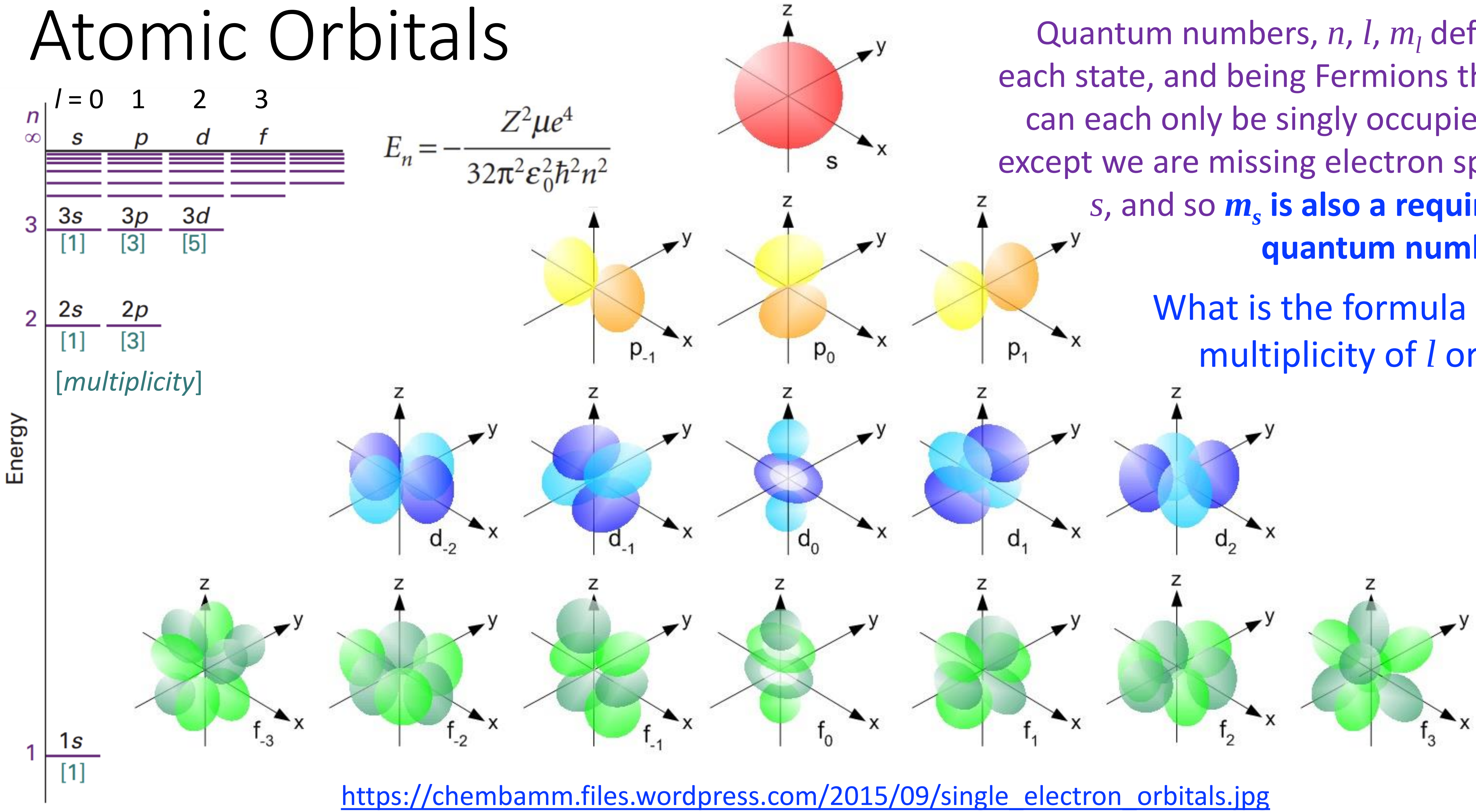
… and thus two equations … $\Lambda^2 Y = -l(l+1)Y$

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + V_{\mathrm{eff}}u = Eu \qquad u = rR \qquad V_{\mathrm{eff}} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

… solving the bottom radial equation gives **energy eigenvalues**, **E_n, with $n \geq 1$**…

… and solving the top spherical harmonics equation gives **angular momentum eigenvalues**, **$l = [0, \ldots, n-2, n-1]$**, with discrete **projections on the z-axis**, **$m_l = [-l, -l+1, \ldots, 0, \ldots, l-1, l]$**

Atomic Orbitals



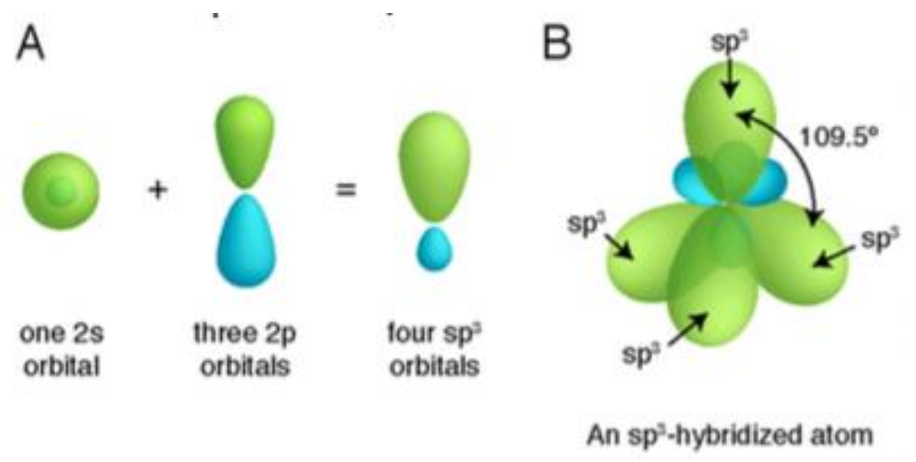
$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n^2}$$

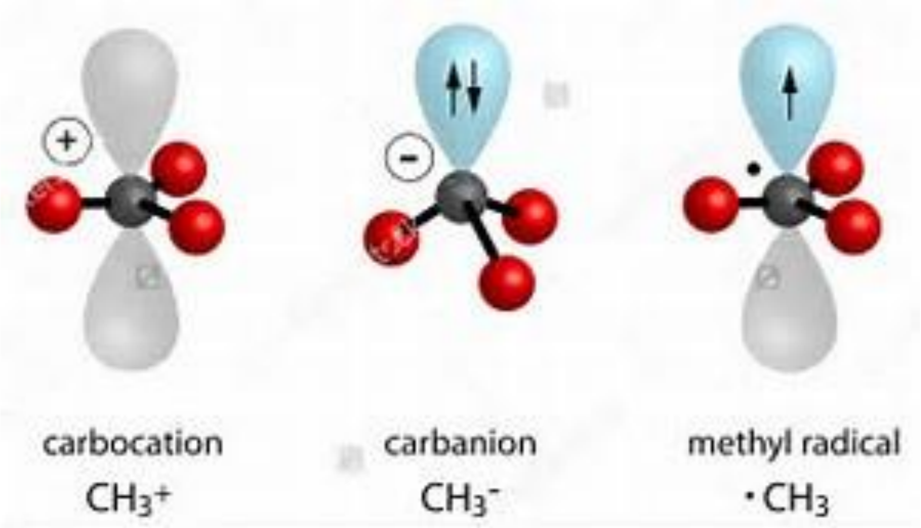
Quantum numbers, n, l, m_l define each state, and being Fermions they can each only be singly occupied… except we are missing electron spin, s, and so m_s **is also a required quantum number**

What is the formula for multiplicity of l or s?

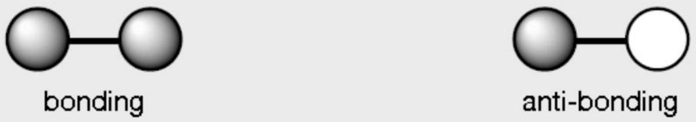
https://chembamm.files.wordpress.com/2015/09/single_electron_orbitals.jpg

Valence Bond Theory and Orbital Hybridization

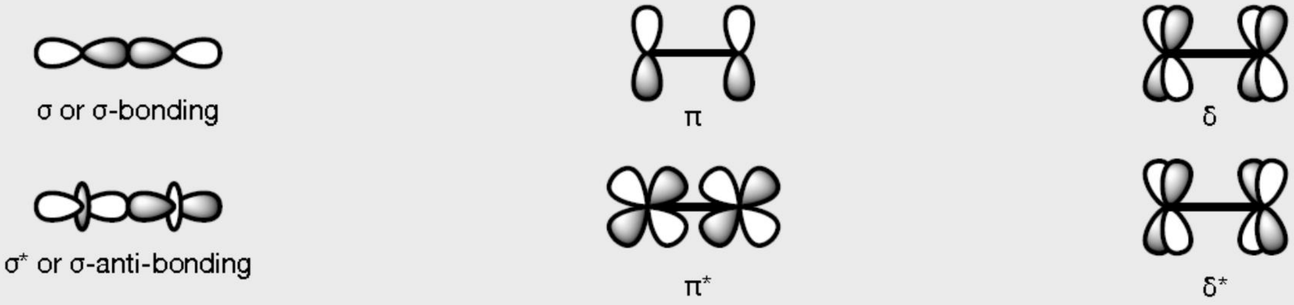




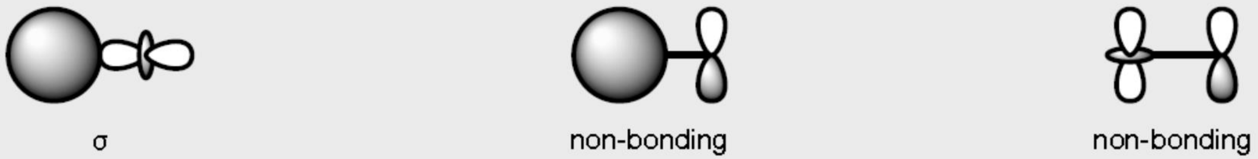
The bonding nature of an orbital interaction is defined by the relative orbital phasing



The type of bonding is defined by the number of nodes parallel to the bond



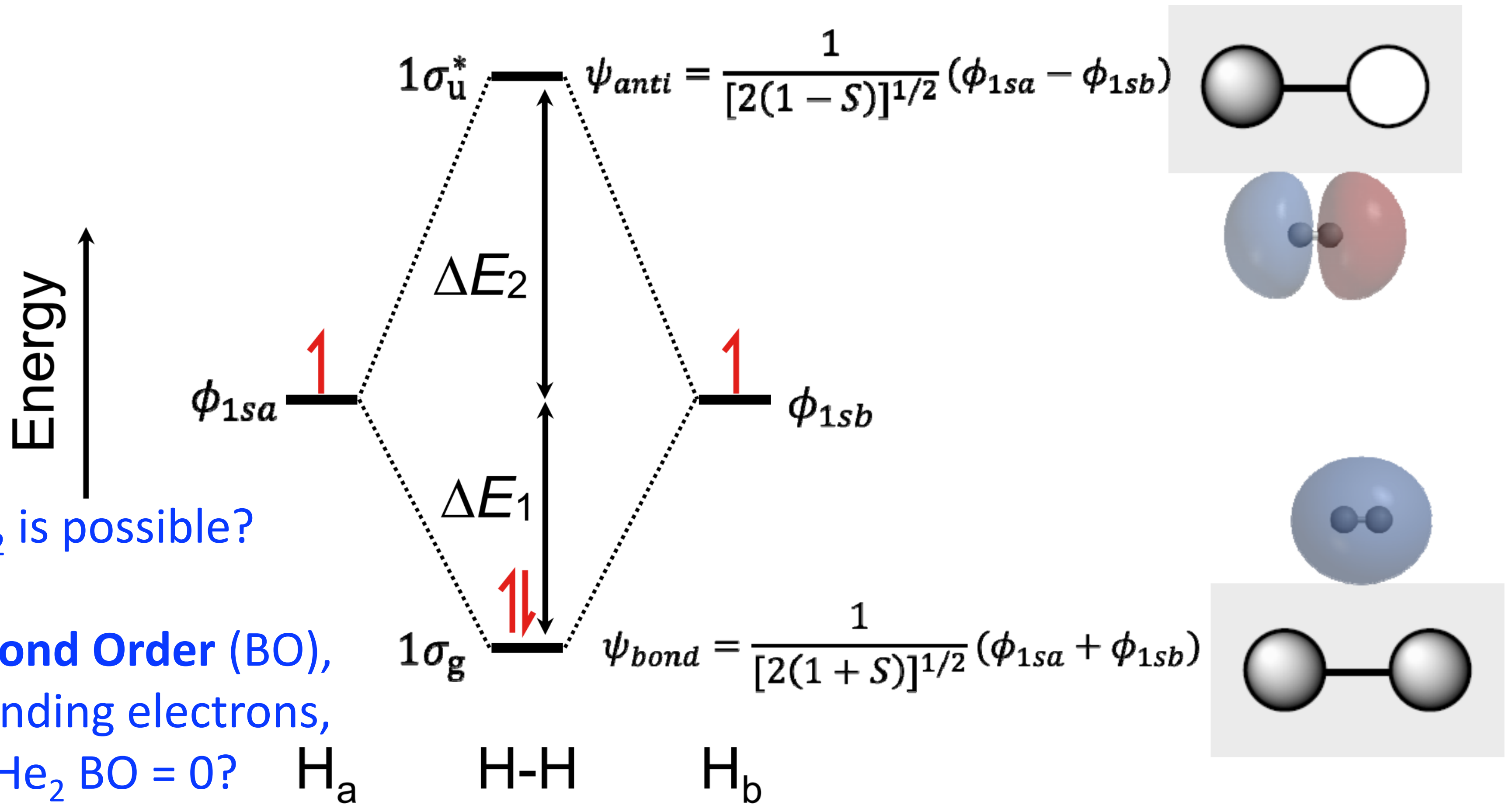
Interactions between different types of orbitals is okay as long as there is net overlap



https://quizlet.com/190582013/1-6-sp3-hybrid-orbitals-and-the-structure-of-methane-flash-cards/
https://socratic.org/questions/598bfedd7c01494e88568d61

Molecular Orbital Theory

H_2 molecule: two 1s atomic orbitals combine to make one bonding and one antibonding molecular orbital.



$$\psi_{anti} = \frac{1}{[2(1-S)]^{1/2}}(\phi_{1sa} - \phi_{1sb})$$

$$\psi_{bond} = \frac{1}{[2(1+S)]^{1/2}}(\phi_{1sa} + \phi_{1sb})$$

Does this predict that He_2 is possible?

What is the formula for **Bond Order** (BO), using bonding and antibonding electrons, given that H_2 BO = 1 and He_2 BO = 0?

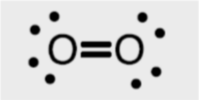
… just take Linear Combinations, ψ, of Atomic Orbitals, ϕ, (LCAO)

Molecular Orbital Theory

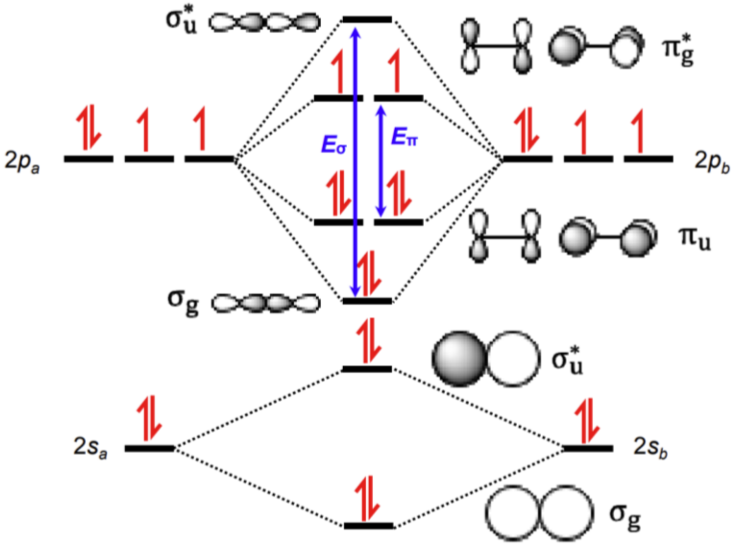
Homonuclear Diatomic Molecules

What happens when we move to more complicated systems?
Consider O_2.

- **The Lewis dot structure famously predicts the wrong electronic structure for O_2**



- **We can use LCAO-MO theory to get a better picture:**



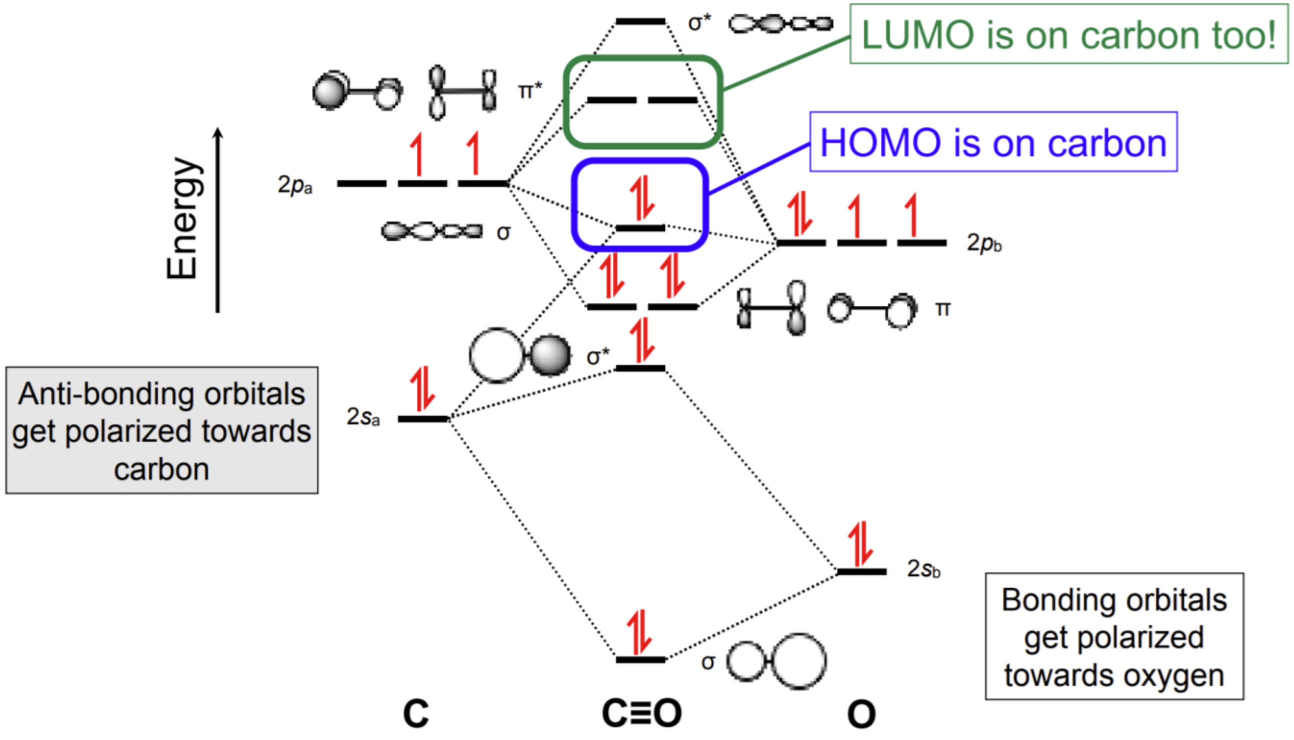
Notice that $E_\sigma > E_\pi$, because the σ bonds have more overlap than π bonds

What is the Bond Order for O_2?
What do the bonds look like?

What is the Bond Order for CO?

Heteronuclear Diatomic Molecules: CO

In molecules with more than one type of atom, MOs are formed from AOs that have different energies. Consider CO:



LUMO is on carbon too!

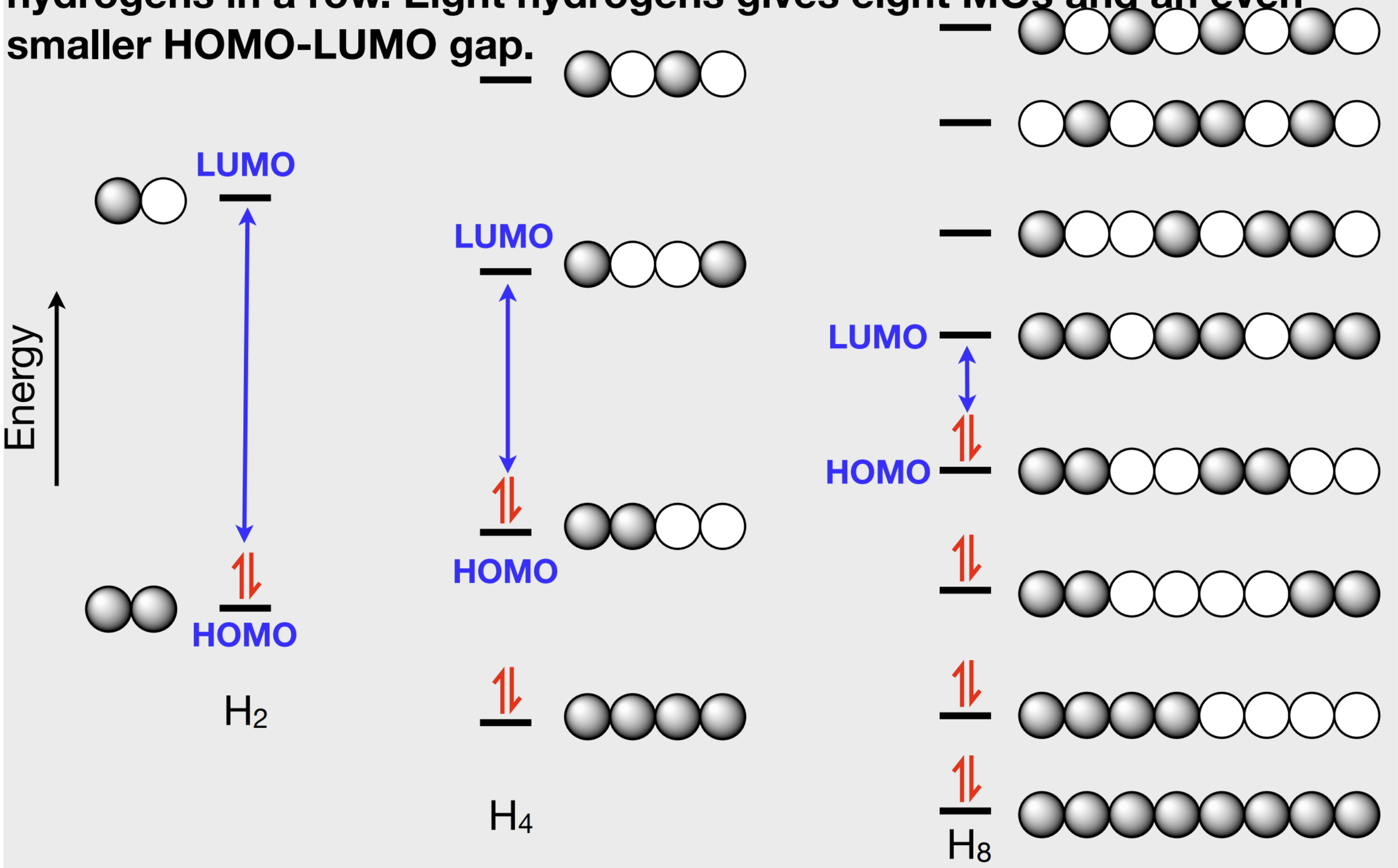
HOMO is on carbon

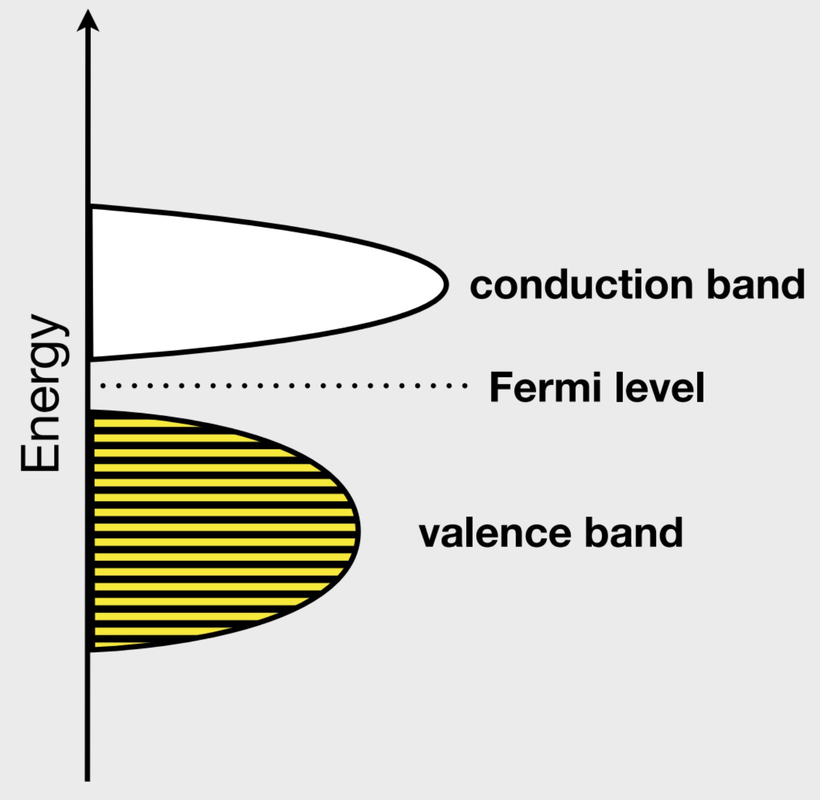
Anti-bonding orbitals get polarized towards carbon

Bonding orbitals get polarized towards oxygen

Band Diagrams

Look at what happens when we move from two hydrogens to four hydrogens in a row. Eight hydrogens gives eight MOs and an even smaller HOMO-LUMO gap.





Bonds are delocalized over the entire "molecule" in this ideal representation

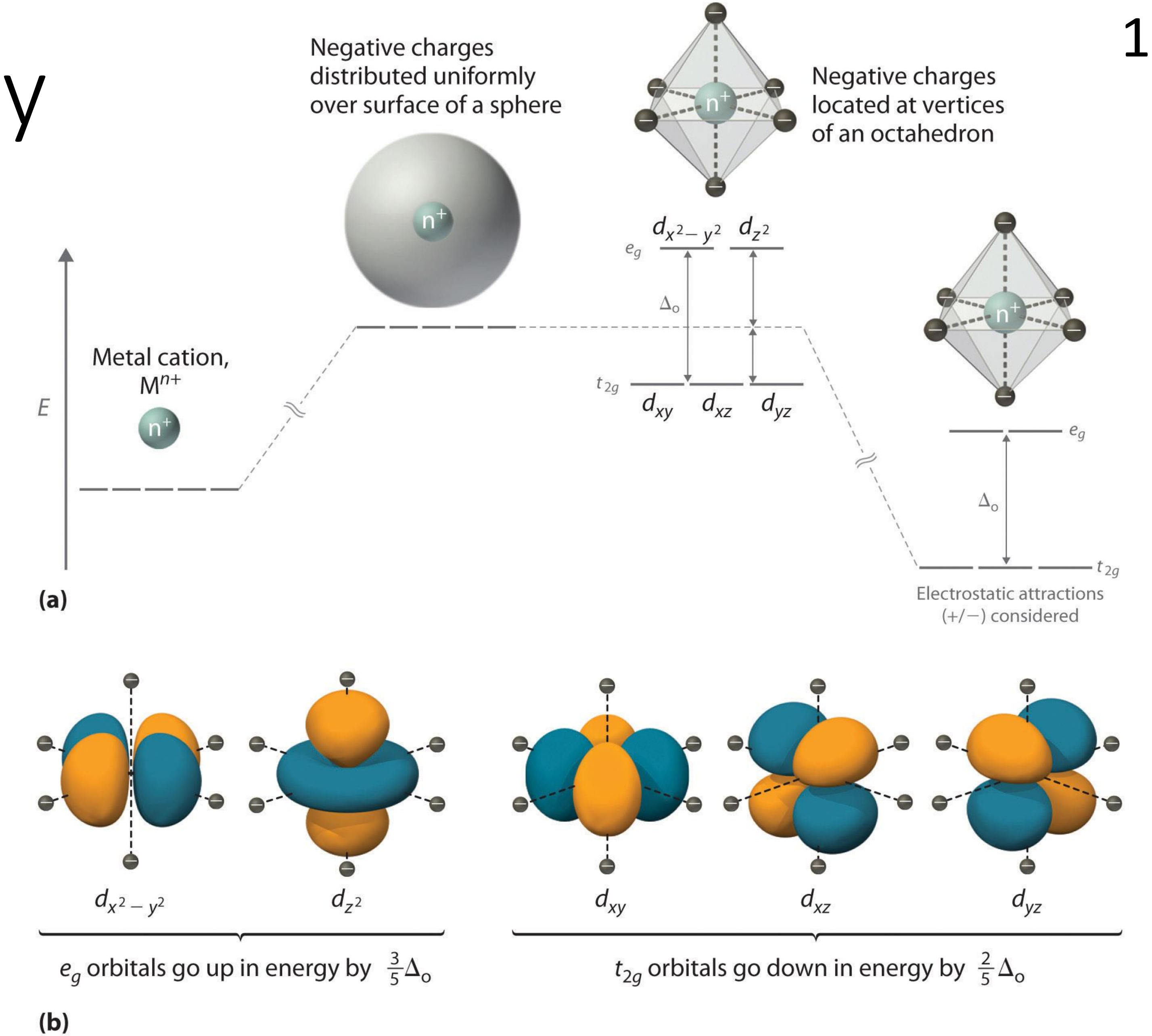
Crystal Field Theory

Crystal field stabilization energy (CFSE) = Δ_o…

… electron occupancy can either be **low spin** or **high spin** depending on the size of CFSE *vs.* the electron pairing energy…

… why do some orbitals go up in energy, and others down?

… moderately accurately predicts colors and magnetism of many molecules and materials



https://chem.libretexts.org/Courses/Douglas_College/DC%3A_Chem_2330_(O'Connor)/4%3A_Crystal_Field_Theory/4.3%3A_High_Spin_and_Low_Spin_Complexes

Ligand Field Theory

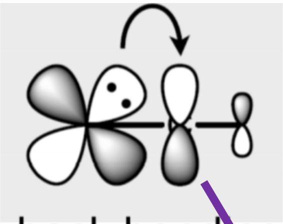
π-Effects in Octahedral Complexes

... while this is the most common geometry...

... there are many more...

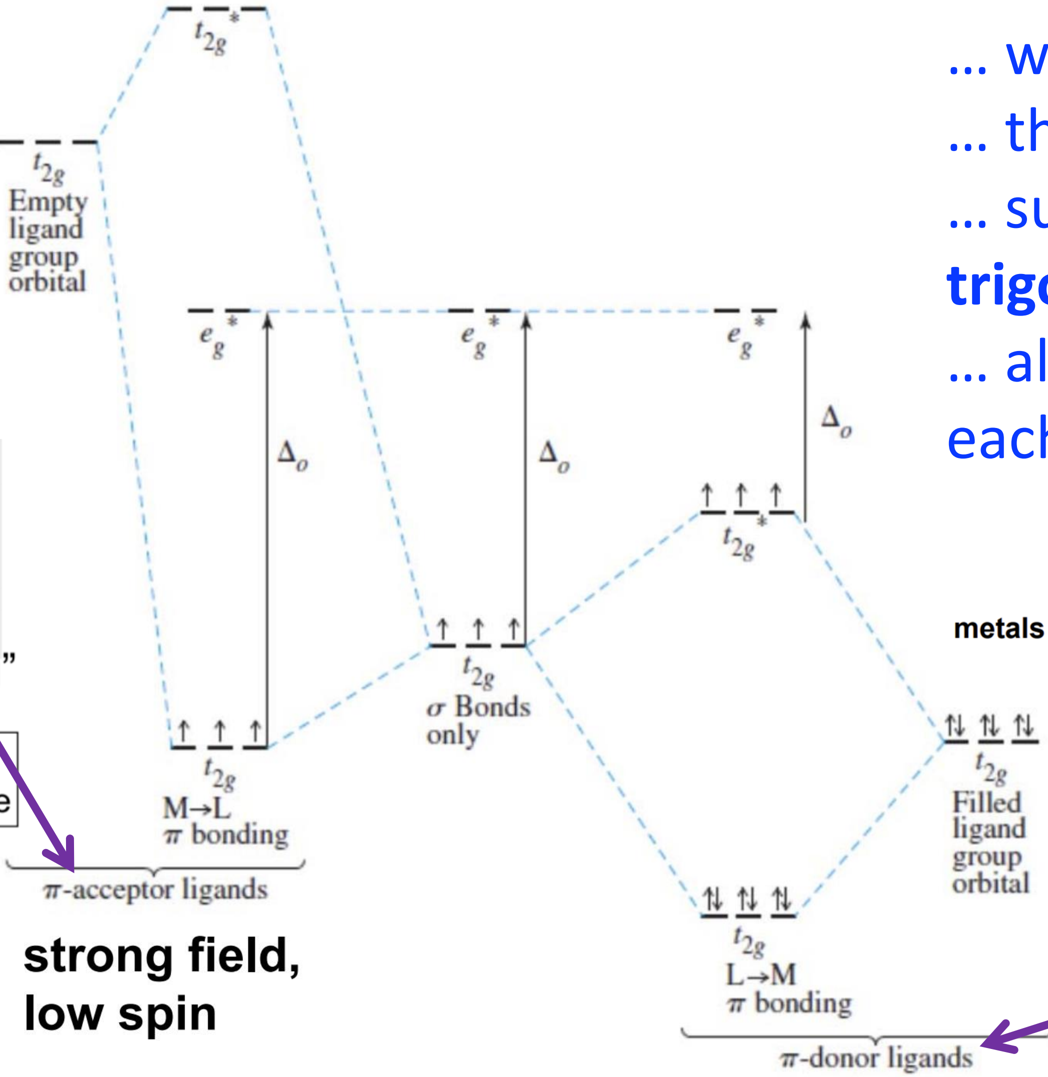
... such as **tetrahedral, square planar, trigonal bipyramidal**, etc.

... also, there are **σ-effects** and **δ-effects** for each of these... lots can happen... Wow!



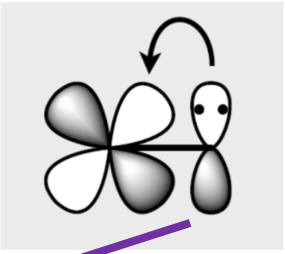
"π back bonding"

Examples:
CO, NO, CN^-, pyridine



strong field, low spin

metals with high oxidation states and low *d* electron count (d^0-d^3)



Examples:
Cl^-, Br^-, I^-, OR^-, SR^-,
NR_2^-, O^{2-}, NR^{2-}, N^{3-}

weak field, high spin

Chemical Properties *(summary for today)*

- **Molecular nomenclature, Solutions, Balanced chemical reactions**
- **State functions, Standard states, Thermochemistry**
- **Non-ideal gases, Intermolecular forces, Physical properties, Phase changes, Colligative properties, Water activity**
- **Free energy, (X)Chemical potential, Chemical equilibrium, van’t Hoff equation, Activity coefficients, Le Chatelier’s principle**
- **Schrödinger equation, Internal energy, Atomic orbitals, Hybridization**
- **Valence bond theory, Molecular orbital theory, Band diagrams**
- **Crystal field theory, Ligand field theory**

Paper Time!