# Lecture #5 of 15

(3: TThF, 5: MTWThF, 4: MTWTh, 2: TW)

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# Chemical Properties

Quiz Time!

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## 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

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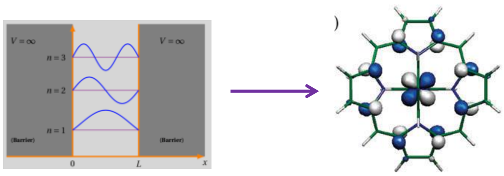
## From a Simple Box to a Complex Box




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

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## Schrödinger Equation

Elegant master equation that allows one to determine internal energies, $\mathrm{E}_n$, of a system

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

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

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

$\mathrm{E} = h\nu = \hbar\omega$ (Planck)
$\mathrm{E} = mc^2 = pc$ (Einstein)
$p = \frac{h\nu}{c} = \frac{h}{\lambda} = h\bar{\nu} = \hbar k$ (de Broglie)

… 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 ($\hat{\boldsymbol{p}}$)momentum = ($m$)ass x ($\hat{v}$)elocity = $-i\hbar\frac{\partial}{\partial x}$…

$\hat{V}(x) = \mathrm{PE} = 0$… 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), $\omega$ (angular freq)…

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

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

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## Solving the Schrödinger Equation

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

$$\hat{H} = \hat{E}_{\mathrm{K,electron}} + \hat{E}_{\mathrm{K,nucleus}} + \hat{V} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_\mathrm{N}}\nabla_\mathrm{N}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

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

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

… 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 … $\Lambda^2 Y = -l(l+1)Y$

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

… solving the bottom radial equation gives **energy eigenvalues**, **$\mathrm{E}_n$, with $n \geq 1$**…
… and solving the top spherical harmonics equation gives **angular momentum eigenvalues**, **$l$ = [0, …, $n$–2, $n$–1]**, with discrete **projections on the z-axis**, **$m_l$ = [–$l$, –$l$+1, …, 0, …, $l$–1, $l$]**

## Atomic Orbitals

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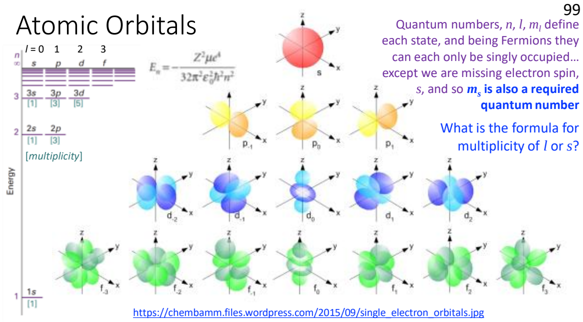


Quantum numbers, $n$, $l$, $m_l$ define each state, and being Fermions they can each only be singly occupied… except we are missing electron spin, $s$, and so $m_s$ **is also a required quantum number**

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

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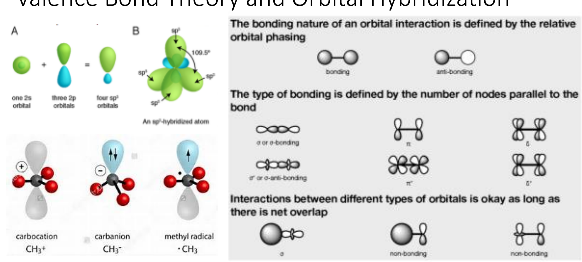


https://quizlet.com/190582013/1-6-sp3-hybrid-orbitals-and-the-structure-of-methane-flash-cards/
https://socratic.org/questions/598bfedd7c01494e88568d61

## Molecular Orbital Theory

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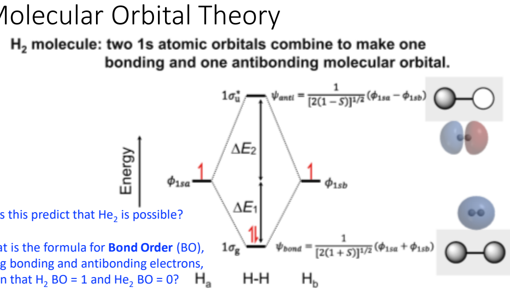


$\psi_{anti} = \frac{1}{[2(1-S)]^{1/2}}(\phi_{1sa} - \phi_{1sb})$

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

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, $\psi$, of Atomic Orbitals, $\phi$, (LCAO)

# Molecular Orbital Theory

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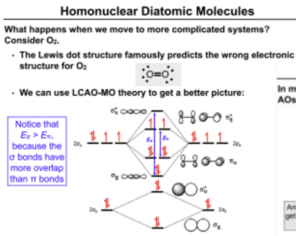
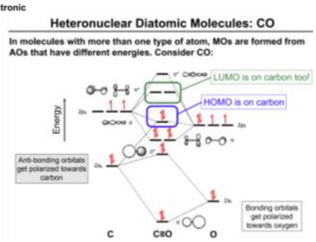



What is the Bond Order for $O_2$?
What do the bonds look like?

What is the Bond Order for CO?




# Band Diagrams

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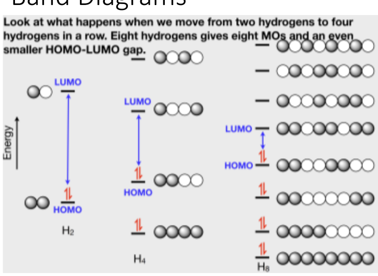


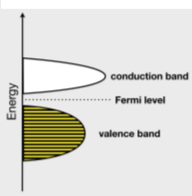


Bonds are delocalized over the entire "molecule" in this ideal representation

# Crystal Field Theory

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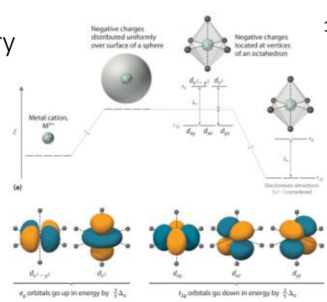
Crystal field stabilization energy (CFSE) = $\Delta_o$...

... 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

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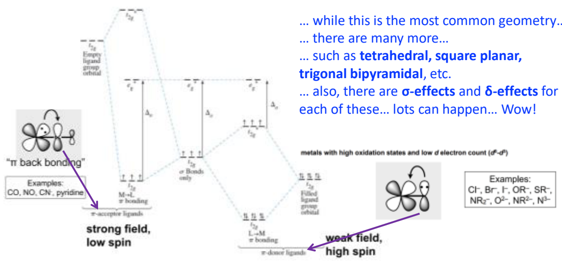
**π-Effects in Octahedral Complexes**




… 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!

## Chemical Properties *(summary for today)*

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Paper Time!