A Rigorous Introduction to Molecular Orbital Theory and its Applications in Chemistry

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Quantum Mechanics

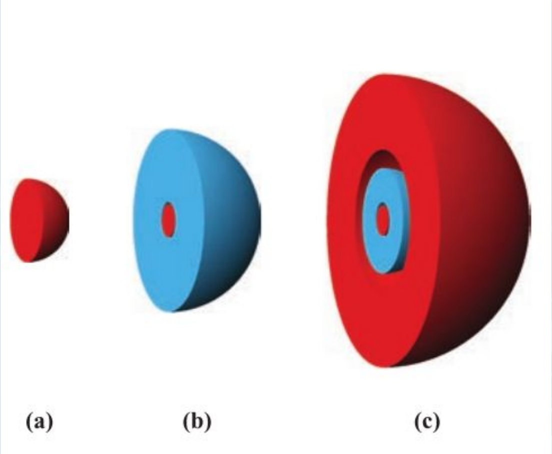
Atomic Orbitals and Early Bonding Theory

Quantum Numbers

- n: principal quantum number
    - Describes the size of the orbital
- l: angular quantum number
    - Describes the shape of the orbital
- m_l: magnetic quantum number
    - Describes orientation of orbital in space
- m_s: electron spin quantum number
    - Describes the spin of the electron

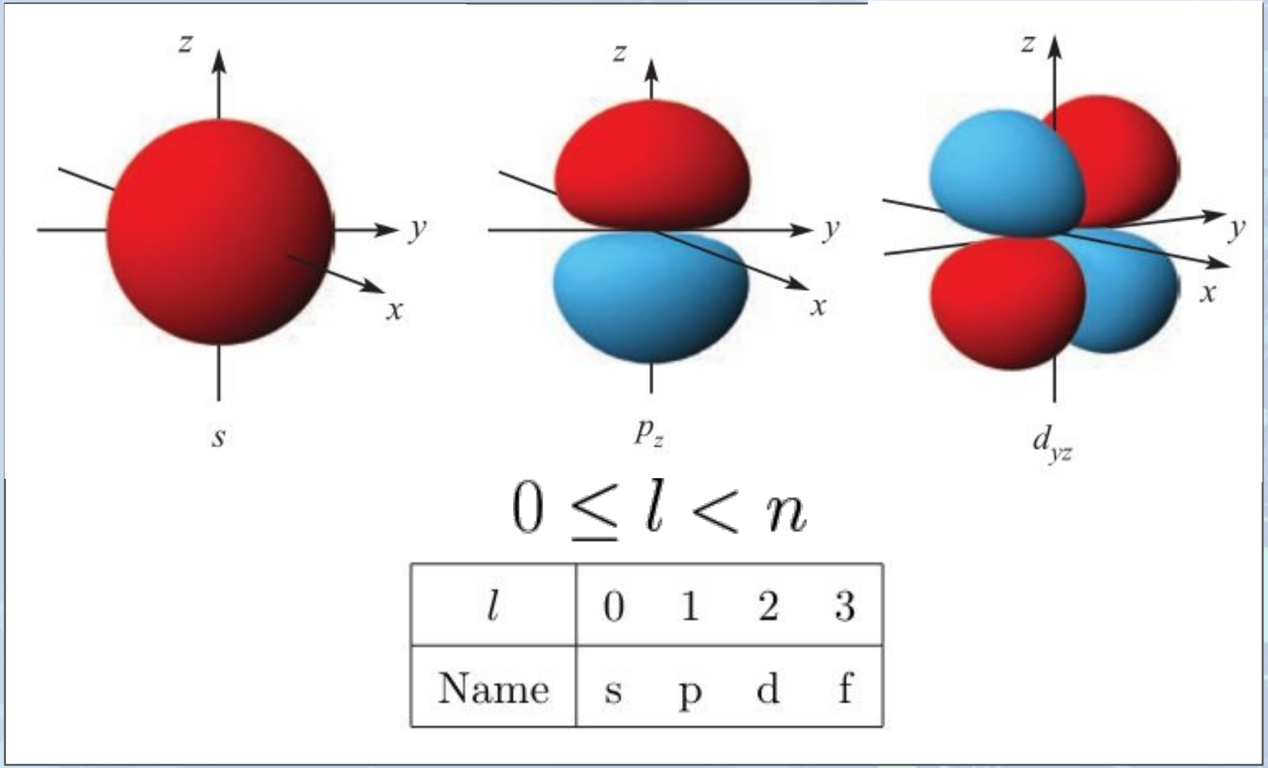
Principal Quantum Number

For any particular element, n is upper bounded by its period in the Periodic Table



$$1 \leq n \leq p$$

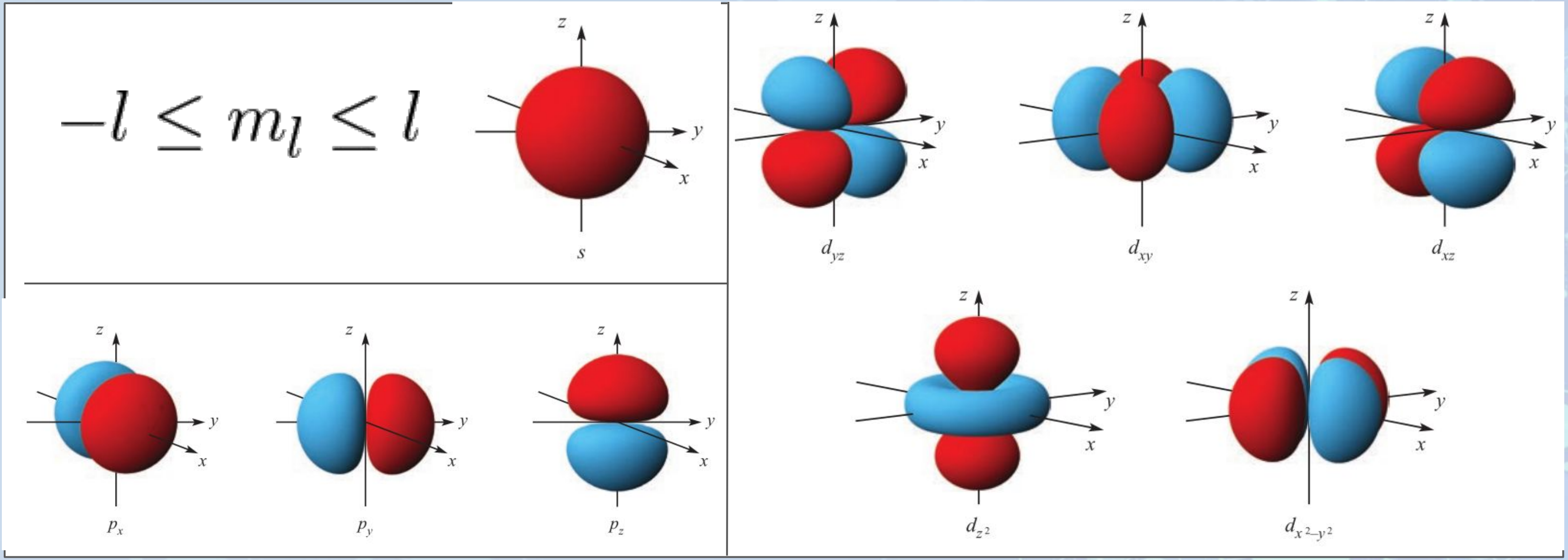
Angular Quantum Number



$$0 \leq l < n$$

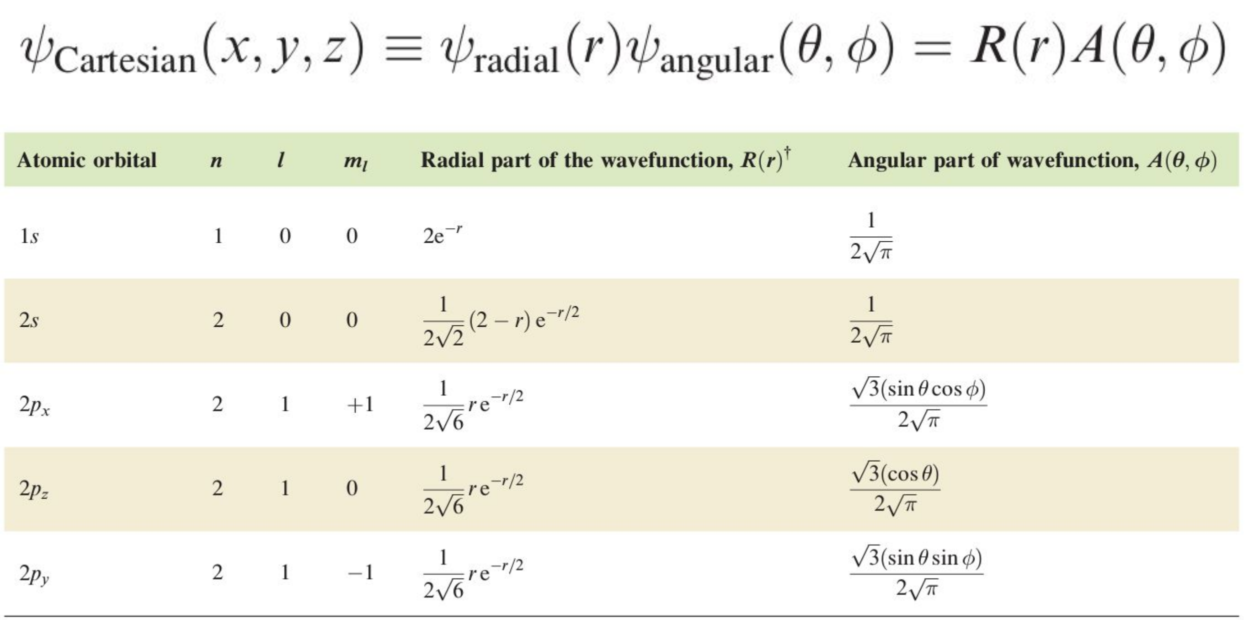
l	0	1	2	3
Name	s	p	d	f

Magnetic Quantum Number



$$-l \leq m_l \leq l$$

Hydrogenic Wavefunctions

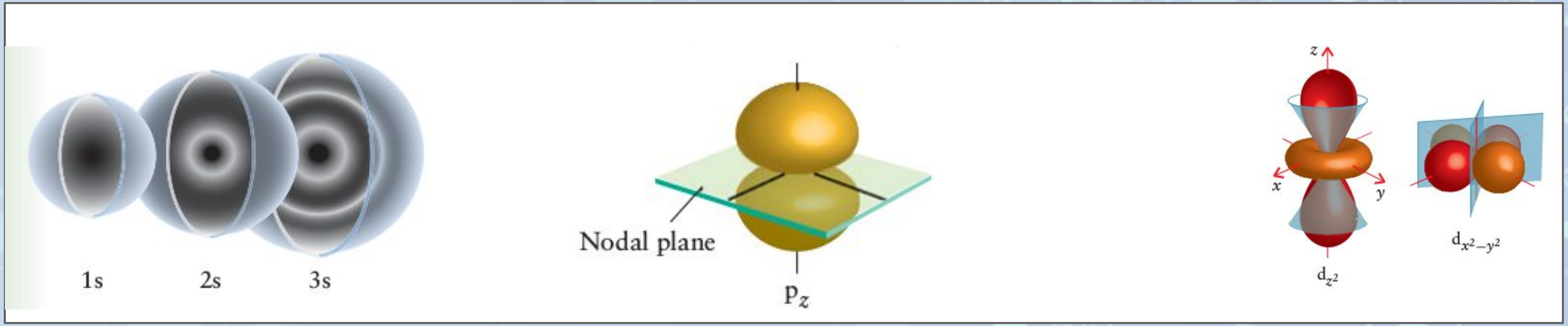


$$\psi_{\text{Cartesian}}(x, y, z) \equiv \psi_{\text{radial}}(r)\psi_{\text{angular}}(\theta, \phi) = R(r)A(\theta, \phi)$$

Atomic orbital	n	l	m_l	**Radial part of the wavefunction, $R(r)^{\dagger}$**	**Angular part of wavefunction, $A(\theta, \phi)$**
$1s$	1	0	0	$2e^{-r}$	$\frac{1}{2\sqrt{\pi}}$
$2s$	2	0	0	$\frac{1}{2\sqrt{2}}(2-r)\,e^{-r/2}$	$\frac{1}{2\sqrt{\pi}}$
$2p_x$	2	1	+1	$\frac{1}{2\sqrt{6}}r\,e^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\cos\phi)}{2\sqrt{\pi}}$
$2p_z$	2	1	0	$\frac{1}{2\sqrt{6}}r\,e^{-r/2}$	$\frac{\sqrt{3}(\cos\theta)}{2\sqrt{\pi}}$
$2p_y$	2	1	−1	$\frac{1}{2\sqrt{6}}r\,e^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\sin\phi)}{2\sqrt{\pi}}$

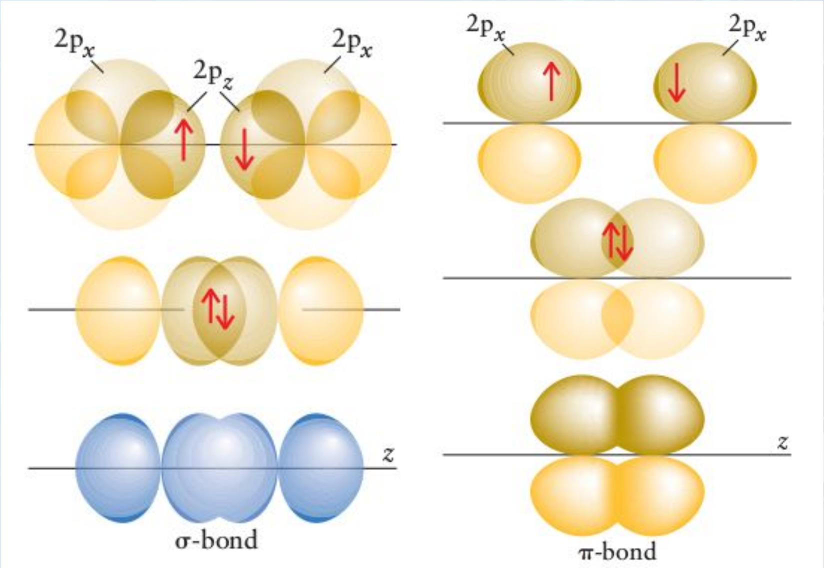
Nodes

- Area where wavefunction is 0 | no electrons are present at nodes
- An AO with quantum number n has $n-1$ nodes
  - Angular node: nodes that are described in the angular part of the wavefunction
    - An AO with angular quantum number l has l angular nodes
  - Radial node: nodes that are described in the radial part of the wavefunction
    - An AO with quantum number n and angular quantum number l has $n-l-1$ radial nodes



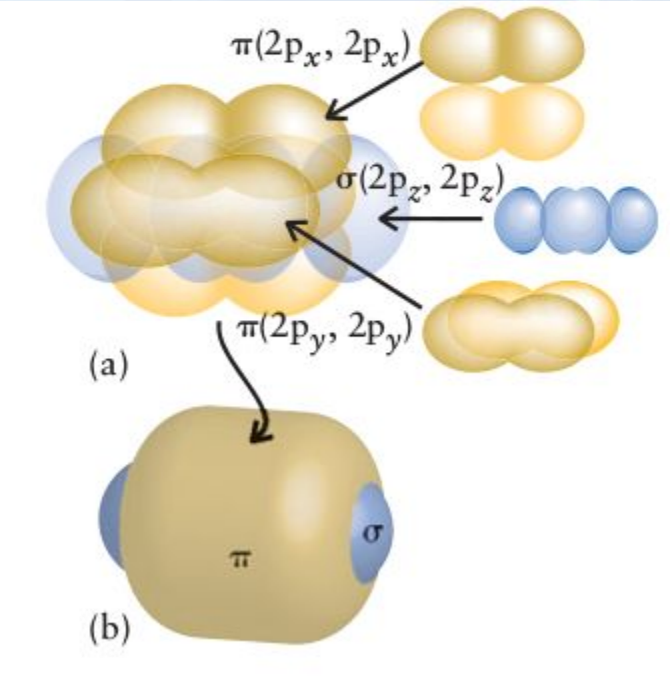
VB Theory

- Two electrons are shared between two atoms in a bonding orbital
- Sigma bonds: direct overlap of two AOs
- Pi bonds: sideways overlap of two AOs
    - Due to the symmetry of the s orbital, pi bonds are never made with s orbitals

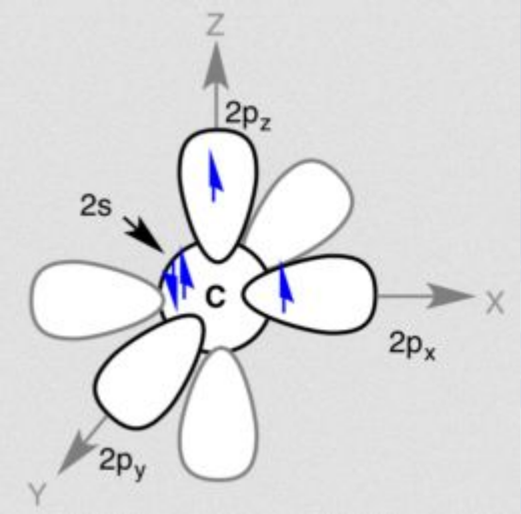


Bond Order

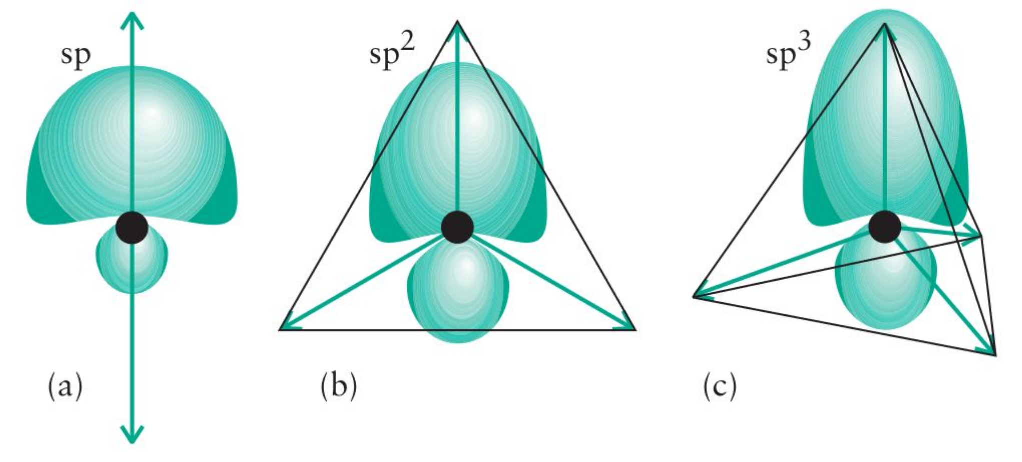
- A single bond consists of one sigma bond
- A double bond consists of one sigma bond and one pi bond
- A triple bond consists of one sigma bond and two pi bonds



So… methane?



Hybridization



* not entirely accurate either, s and p orbitals are orthogonal

Orbital Mixing

Linear Combination of Atomic Orbitals (LCAO)

- Atomic orbitals (AOs) combine to form molecular orbitals (MOs)
- We approximate MOs as a linear combination of AOs

$$\psi_i = c_{1\mathrm{i}}\chi_1 + c_{2\mathrm{i}}\chi_2 + \cdots + c_{mi}\chi_m = \sum_{\mu} c_{\mu i}\,\chi_{\mu}$$

- All the c_{ab} are coefficients (real numbers) that represent the amount of atomic orbital χ_a in molecular orbital ψ_b

Linear Combination of Atomic Orbitals (LCAO)

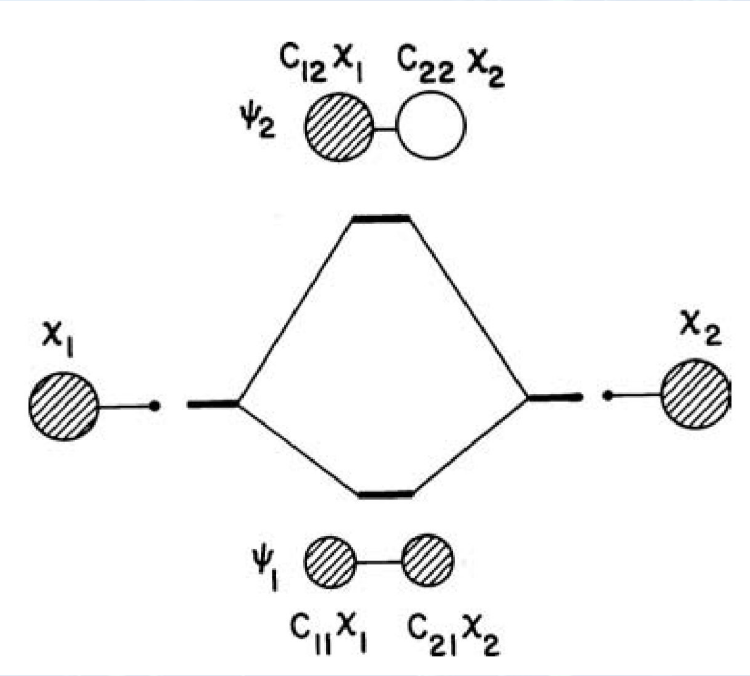
- Orbital overlap: as discussed previously, S_{12} is a measure of spatial overlap and H_{12} is a measure of the interaction between two orbitals, with the values being directly proportional to each other
- If two orbitals have $S_{12} = 0$, they are **orthogonal**
- Orthogonal orbitals do not mix/interact

Linear Combination of Atomic Orbitals (LCAO)

- The final MOs of the molecule **must** be orthogonal to each other (otherwise they will “mix again” until they are orthogonal)
- When we interact two orbitals, we always form one bonding (lower in energy) and one antibonding (higher in energy) orbital
- Orbital conservation: # of orbitals in = # of orbitals out

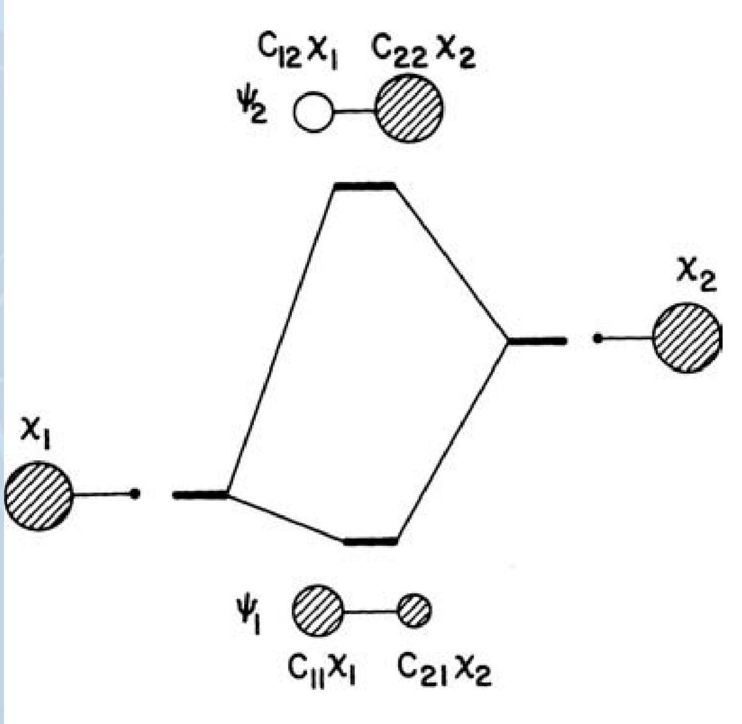
2 orbital problem (degenerate): H2 molecule

- As discussed previously, bonding orbitals represent the constructive overlap of wavefunctions, while antibonding orbitals represent destructive overlap
- Constructive overlap is represented by *in-phase mixing* while destructive overlap is represented with *out-of-phase mixing*, as shown in the left diagram



2 orbital problem (nondegenerate): H-He molecule

- The same principles apply:
  bonding = constructive overlap
  antibonding = destructive overlap
- The bonding orbital will always have more character of the lower-energy AO (He), while the antibonding orbital will always have more character of the higher-energy AO (H)



2 orbital problem (general)

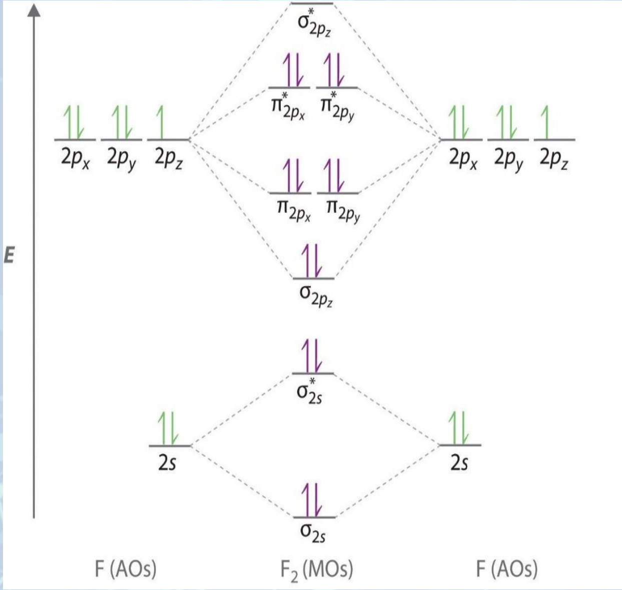
- Antibonding orbital always increases by more energy than bonding orbital decreases by
- If orbitals are fully occupied, mixing is **unfavorable**, so the molecules will not interact with each other
- Important: both the bonding and antibonding orbitals contain **both** of the AOs. The bonding orbital has a greater fraction of the lower-energy orbital while the antibonding orbital has a greater fraction of the higher-energy orbital

2 orbital problem (general)

- Amount of mixing correlated to both spatial overlap (S_{ab}) and energetic difference of the AOs - the closer the AOs are in energy or the greater the spatial overlap, the greater extent of mixing
- Orbitals greater than 1 Rydberg (13.6 eV) can be assumed to not mix to any significant extent. For example, the F 2s (-46.4 eV) does not mix significantly with almost any other orbital
- Many problems can be reduced to the 2 orbital problem!

Diatomic fluorine MO diagram

- The two 2s can mix with each other, because they are both so low in energy!
- The $2p_z$ orbitals will interact in a sigma (head-on) fashion
- The $2p_x$ and $2p_y$ orbitals will interact in a pi fashion; these orbitals are degenerate
- Head-on interaction has greater overlap, so extent of mixing is larger. In general, sigma > pi > delta bonds



3 (or more) orbital problem

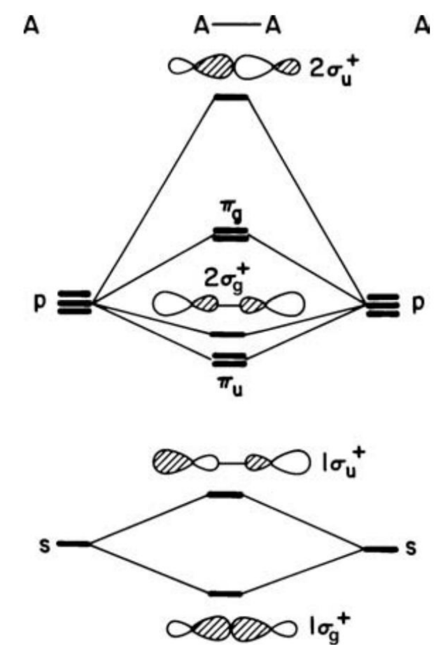
- AOs on the same molecule must be orthogonal (just like MOs must be orthogonal)
- How can we have more than 2 orbitals interacting then?
- Suppose there are 2 AOs on one atom that can both mix with one AO on another atom
- Consider hydroxide: the H 1s can mix with the O 2s and the O 2p. In increasing energy: O 2s, O 2p, H 1s. Data attainable from Valence Orbital Ionization Energy (VOIE) chart

More complex diatomics

- Consider diatomic nitrogen, for example
- p_x and p_y orbitals will still interact as before
- Now both 2s and $2p_z$ orbitals can interact with each other, but mixing them directly can be quite hard
- Easy method: first mix the 2s orbitals and $2p_z$ orbitals separately, then mix the resulting MOs with each other

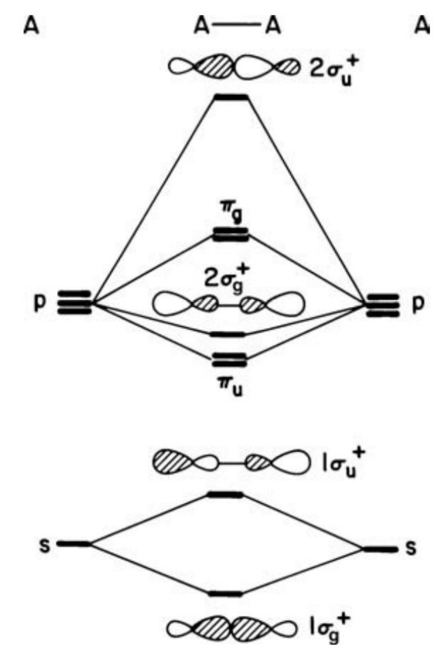
More diatomic molecular orbitals

- We first mix to form the sigma/sigma* pairs for both 2s and $2p_z$
- Note that the two bonding orbitals can mix, and the two antibonding orbitals can also mix
- As a result, the two orbitals originally derived from 2s mixing both go down in energy, while the other two go up



More diatomic molecular orbitals

- This is called s-p mixing
- The more s-p mixing, the more the sigma($2p_z$) orbital increases in energy.
- Li-N have 2s and 2p closer in energy, so they will have enough s-p mixing to push sigma($2p_z$) higher in energy than pi_x and pi_y
- O and F have 2s and 2p orbitals separated by a large enough energy gap, so there is not enough s-p mixing and sigma($2p_z$) is lower in energy than pi_x and pi_y



Diatomic oxygen

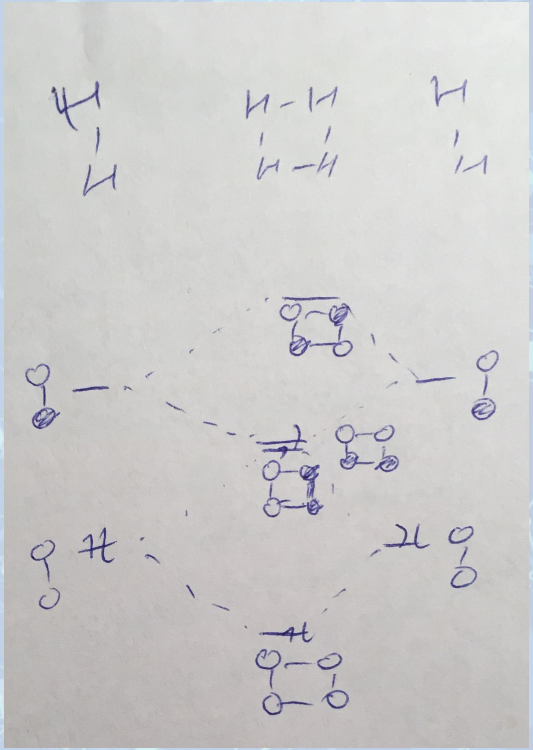
- With diatomic oxygen, there are 2 total electrons residing in the pi_x* and pi_y* degenerate set; by Hund's rule, they will preferably have one electron in each (with parallel spins)
- Diatomic oxygen is thus a diradical! Having a total nonzero spin means that O_2 is *paramagnetic*, meaning that it is attracted to a magnetic field. In fact, this can be shown in real life - O_2 moves into a magnetic field, while N_2 or F_2 do not!

Constructing MOs from fragments

- Now consider H_4 - how do we start in determining its molecular orbitals?
- One way to do this would be to take the MOs of 2 H_2 fragments and mix them together!
- Formation of these MOs follow the same principles as those of combining AOs to form MOs
- Note that the in-phase MO of one H_2 fragment is orthogonal to the out-of-phase MO of the other H_2 fragment and vice versa, but the two in-phase and two out-of-phase MOs can mix with each other

H_4 MO diagram

- Each pair of interacting MOs creates a bonding/antibonding pair, though note that the "antibonding" orbital from the in-phase MOs is roughly nonbonding because it has both bonding and antibonding interactions
- Why are the two middle orbitals degenerate?
- Can either tell because they are equivalent when rotated, or through symmetry - which we will discuss soon!

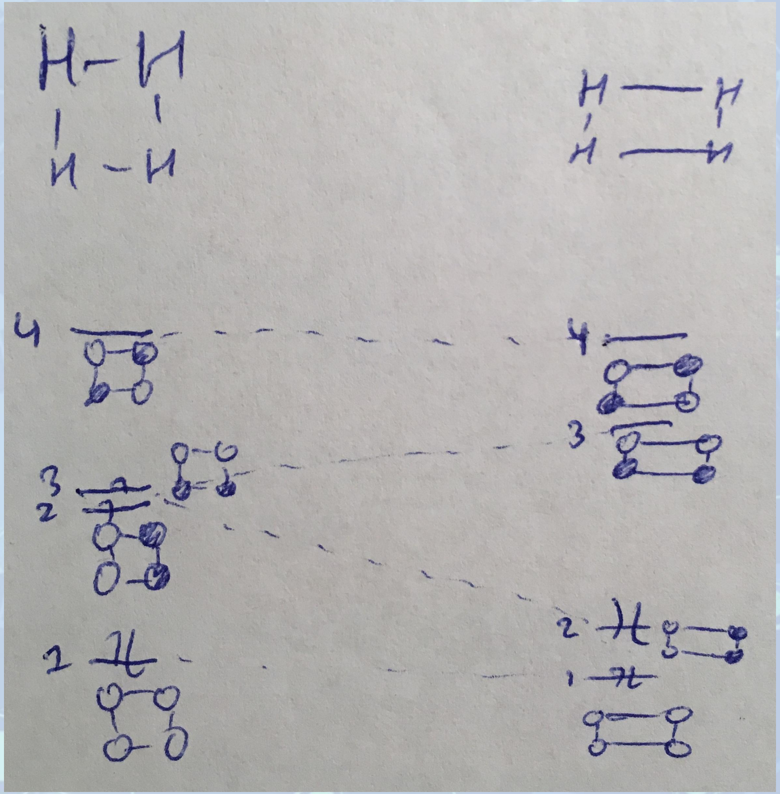


Perturbation Theory

- Suppose we distort the square to a rectangle. What happens?
- Interaction between “vertical” pairs increases, while interaction between horizontal pairs “decreases”
- How do the MOs change?
- Top and bottom MOs stay roughly constant in energy (bottom gains bonding interactions through “vertical” pairs, but loses bonding interactions through “horizontal pairs”; top behaves similarly except with antibonding interactions)
- Degenerate set splits into two distinct orbitals, one much lower and one much higher in energy

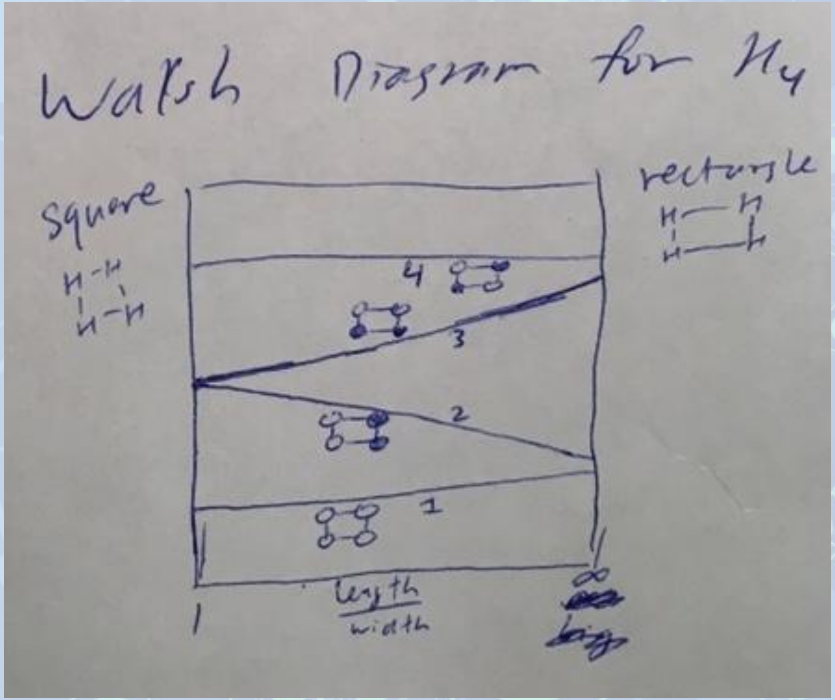
Perturbation Theory

- What geometry will be preferred if the H_4 molecule is neutral?
- It prefers rectangular because the highest-occupied molecular orbital (HOMO) drops in energy substantially, while the lowest bonding orbital stays similar
- What about if H_4 has a -2 charge?
- It prefers square, because the HOMO decreases in energy compared to rectangular - this is known as Walsh's Rule



Walsh diagrams

- Walsh's rule states that the molecule prefers to lower the energy of the HOMO
- Walsh diagram above demonstrates how the various orbitals change in energy as the molecule geometry changes (in this case, square -> rectangular)

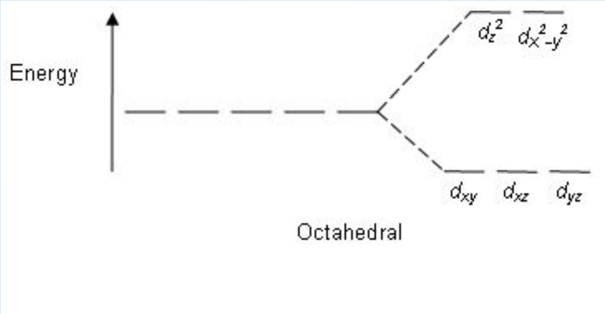


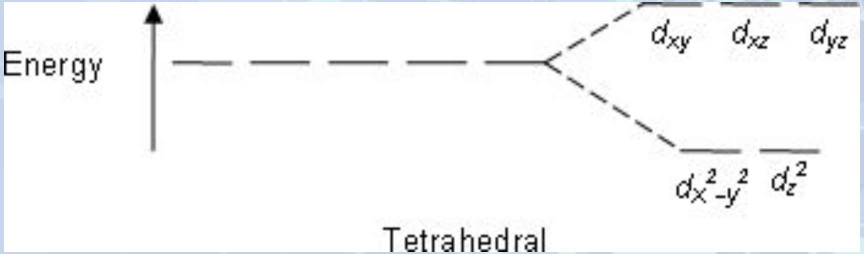
Symmetry

Applications of MO in Inorganic Chemistry

Crystal Field Theory

- Assumes that all ligands are (negative) point charges
- Point charges repel the electrons in the d orbitals, which will raise their energies
- Can be used to determine splitting diagrams for different ML_x diagrams; shown below are those for octahedral and tetrahedral





Crystal Field Theory (CFT)

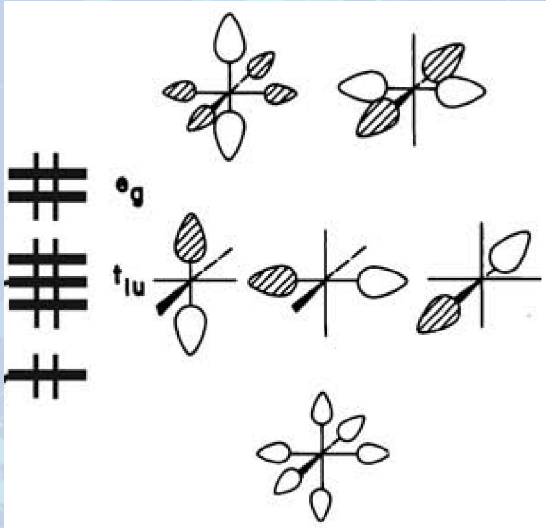
- Tetrahedral field splitting is smaller than octahedral field splitting (around 4/9)
- Why is this the case?
- Interactions are not head on and fewer point charges surrounding metal

Ligand Field Theory (LFT)

- Let’s consider the molecular orbitals of an ML_6 octahedral compound
- We first derive the SALCs of the L_6 fragment, then mix them with the metal orbitals

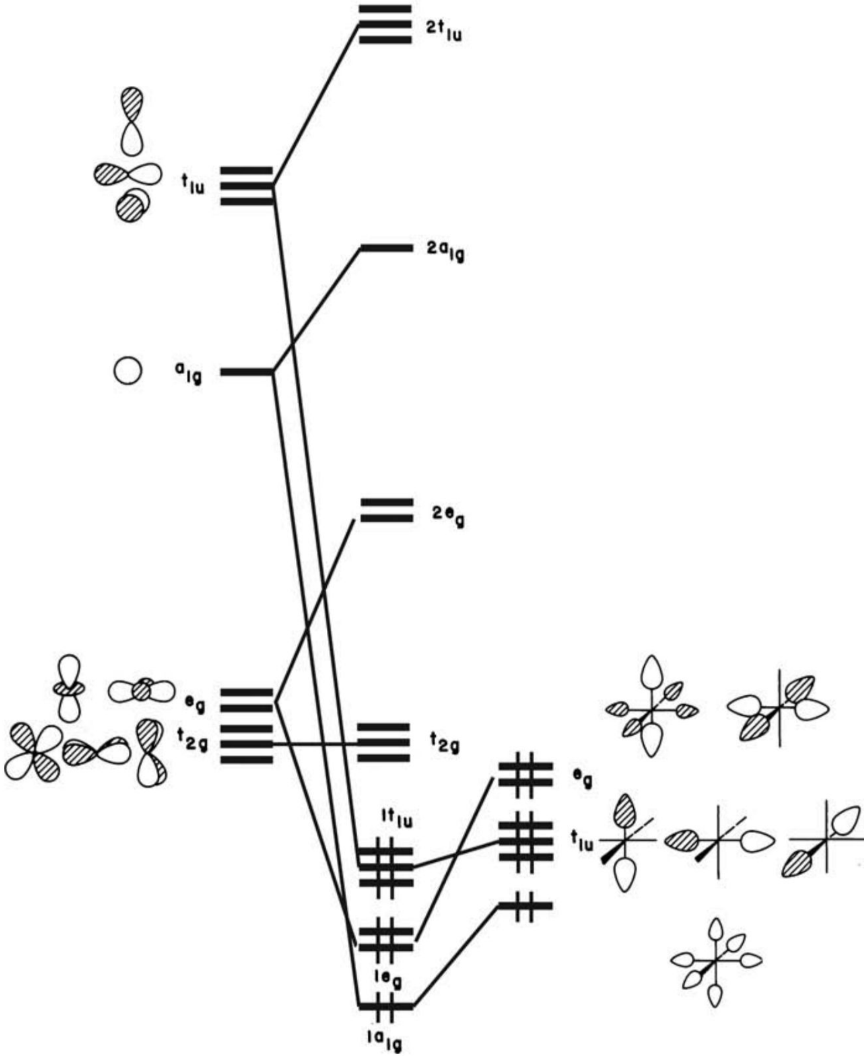
Ligand Field Theory (LFT)

- First, assume that all ligands are identical sigma donors (only interact head-on)
- Note that the A_{1g} orbital (the lowest-energy one) mixes with the metal 4s orbital, the T_{1u} set mixes with the metal 4p orbitals, and the E_g set mixes with the metal d_{z2} and d_{x2-y2} orbitals
- Ligand orbitals tend to be much lower in energy than metal orbitals (with 3d < 4s < 4p)
- When we mix the orbitals together, we get...



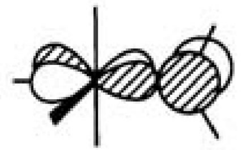
ML_6 MO diagram

- Note that the T_{2g} orbitals are completely nonbonding, which contrasts with CFT
- The metal d orbitals refer to the T_{2g} and $2E_g$ orbitals, though of course the $2E_g$ orbitals will have some ligand character as well
- This confirms the 18 electron rule for octahedral complexes: occupying $2E_g$ is quite unfavorable as they are antibonding orbitals!



Pi donating effects

- Most ligands are not pure sigma donors. Consider halides or amide, for example, which can also interact with the metal in a pi-fashion using one of their lone pairs:



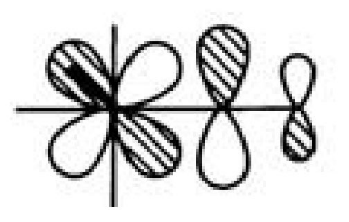
- The entire T_{2g} set of orbitals has pi-symmetry with respect to the ligands, so they will interact with the ligand lone pairs. Note that because the ligand lone pairs will be lower in energy (more electronegative atom), the ligand orbitals will go down in energy while the T_{2g} set will go up in energy (again, the T_{2g} set does not purely consist of d orbitals, but it is primarily d orbital in character)

Pi donating effects

- Since T_{2g} goes up in energy, the gap between E_g and T_{2g} (the octahedral field splitting energy) decreases; thus, ligands such as halides, amide, and hydroxide are considered **weak-field ligands**
- What would we predict for the ordering of the halides (from weakest field to strongest field)?
- I < Br < Cl < F (due to higher energy and better overlap of the larger halides, which causes greater mixing)

Pi accepting effects

- Some ligands can also experience pi accepting effects (meaning a higher-lying orbital of pi symmetry interacts with the lower-lying metal d orbital, “accepting” electron density by forming a bonding interaction)
- Examples include CN^- and CO



- The pi* orbital is unfilled and lies **above** the metal T_{2g} orbitals (since it is highly antibonding in character), so it will cause the T_{2g} orbitals to decrease in energy!

Pi accepting effects

- Would an alkene be better or worse at pi accepting than CN^-/CO?
- Worse!
- Note that in CN^-/CO, the amount of mixing between the N (O in CO) $2p_x/2p_y$ and the C $2p_x/2p_y$ is not nearly as large as the amount of mixing between that of the 2 Cs in an alkene, due to a large energetic gap
- This causes pi* to increase in energy (from the C 2p energy) by a smaller amount, so it is lower in energy
- As a result, pi* mixes better with with T_{2g} orbitals in CN^-/CO, so CN^-/CO would be better pi acceptors!

Spectrochemical series

- Determines the relative field strengths of various different common ligands
- Ultimately determined empirically, though we can use MO to explain why we observe such trends
- O_2^{2-} < I^- < Br^- < S^{2-} < SCN^- (S–bonded) < Cl^- < N_3^- < F^- < NCO^- < OH^- < $C_2O_4^{2-}$ < H_2O < NCS^- (N–bonded) < CH_3CN < gly (glycine) < py (pyridine) < NH_3 < en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) < NO_2^- < PPh_3 < CN^- < CO
-

Other effects

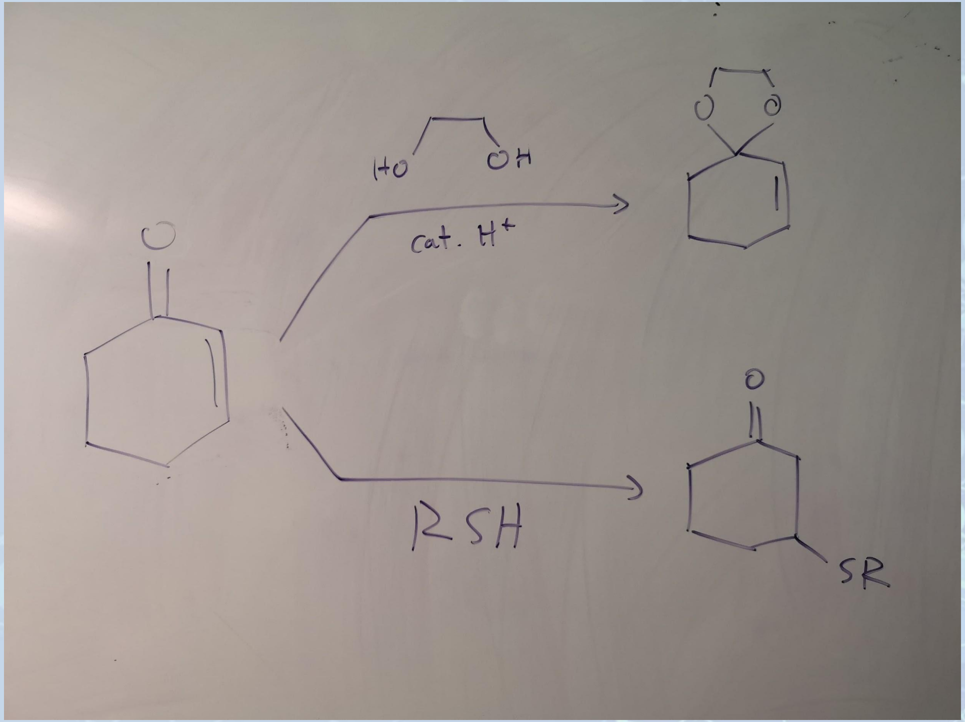
- Metal oxidation state also plays an important role in determining field strength
- Does field strength increase or decrease as the metal becomes more oxidized?
- Increases: a more positively charged metal will electrostatically attract the ligands, bringing them closer to the metal center. This increases overlap of orbitals, which widens the field splitting
- How about the period of the metal?
- Second and third row transition metals have much higher splitting energies than the first row. This is because the much larger and more diffuse orbitals allow the larger metal orbitals to overlap much better with ligand orbitals

Meaning of the splitting energy

- Ultimately, what does the splitting energy tell us?
- It allows us to fill in the d electrons!
- Strong field means the splitting energy is larger than the energy required for spin pairing, so electrons prefer to fully occupy the T_{2g} set before occupying the E_g set
- Weak field means that the electrons prefer to be spin-parallel, so they will singly occupy each d orbital before pairing electron spin in the T_{2g} orbitals

Applications of MO in Organic Chemistry

Cyclohexenone Reactivity



Why?

Hard vs Soft reactive sites

- Hard: reactive sites characterized by small dense orbitals
  - Charge interactions are most important
- Soft: reactive sites characterized by large fluffy orbitals
  - Orbital interactions are most important

Hard and Soft Reagent Examples

Hard nucleophiles
F^-, **OH^-**, **RO^-**, SO_4^{2-}, Cl^-,

H_2O, ROH, ROR′, RCOR′,

NH_3, RMgBr, RLi

Borderline
N_3^-, **CN^-**

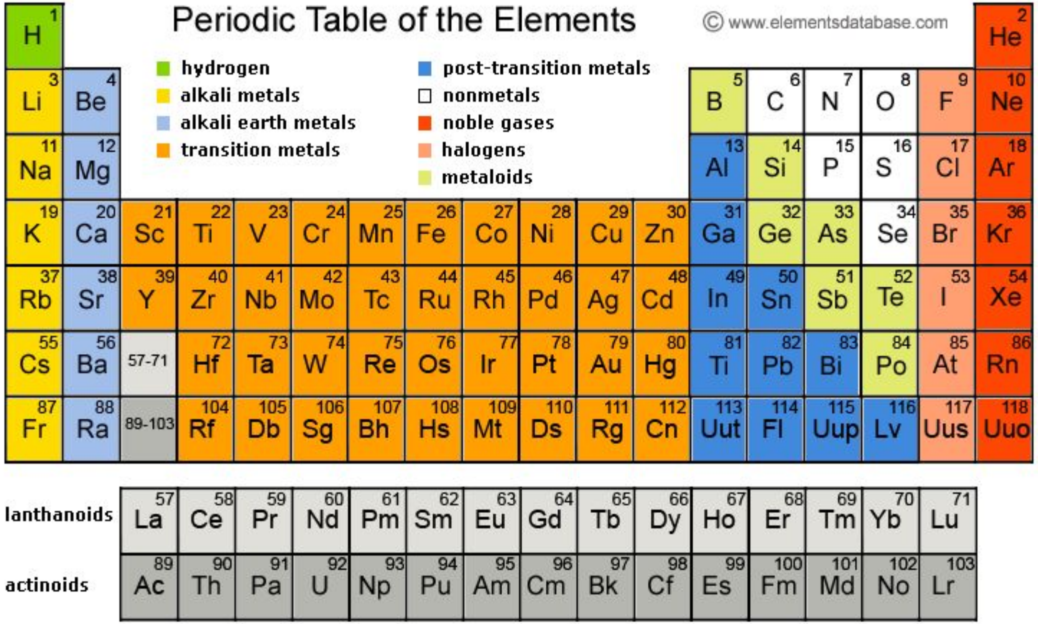
RNH_2, RR′NH,

Br^-

Soft nucleophiles
I^-, RS^-, RSe^-, S^{2-}

RSH, RSR′, R_3P

alkenes, aromatic rings



Periodic Table of the Elements

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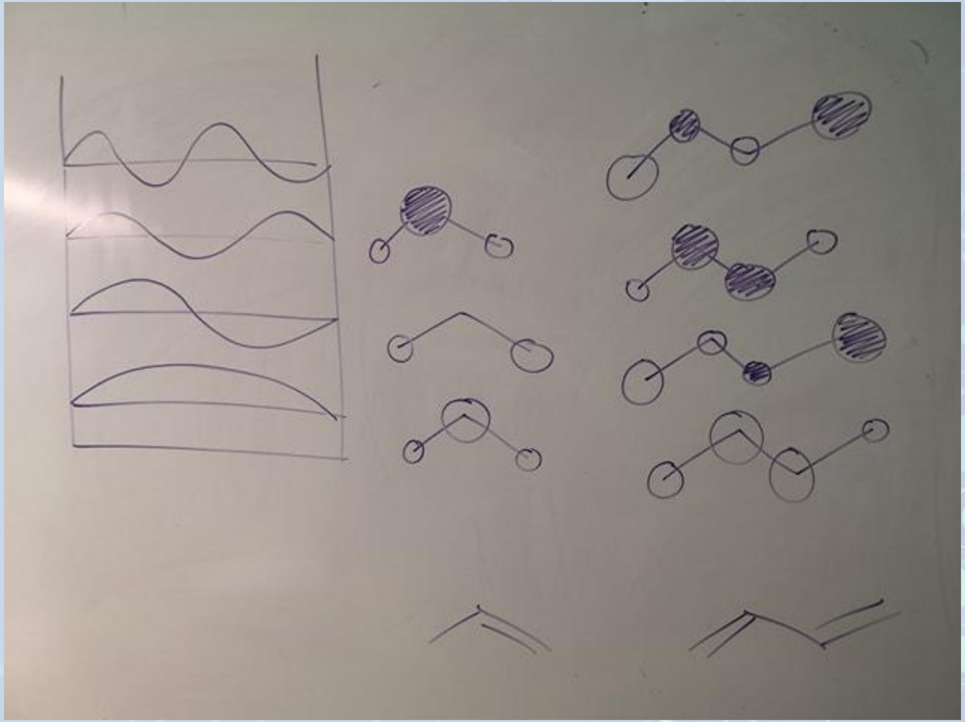
- ■ hydrogen
- ■ alkali metals
- ■ alkali earth metals
- ■ transition metals
- ■ post-transition metals
- ☐ nonmetals
- ■ noble gases
- ■ halogens
- ■ metaloids

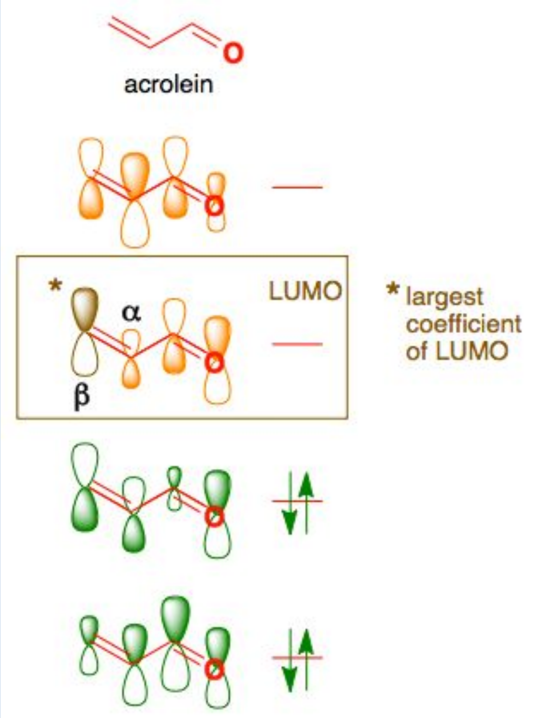
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

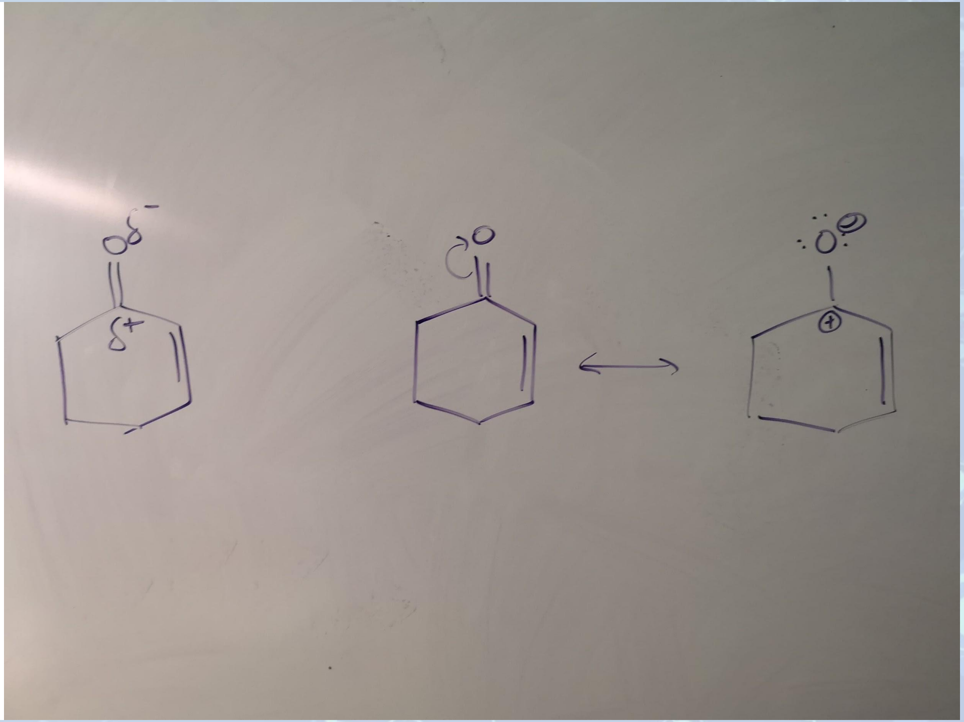
lanthanoids	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoids	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

“Particle In A Box” Heuristic

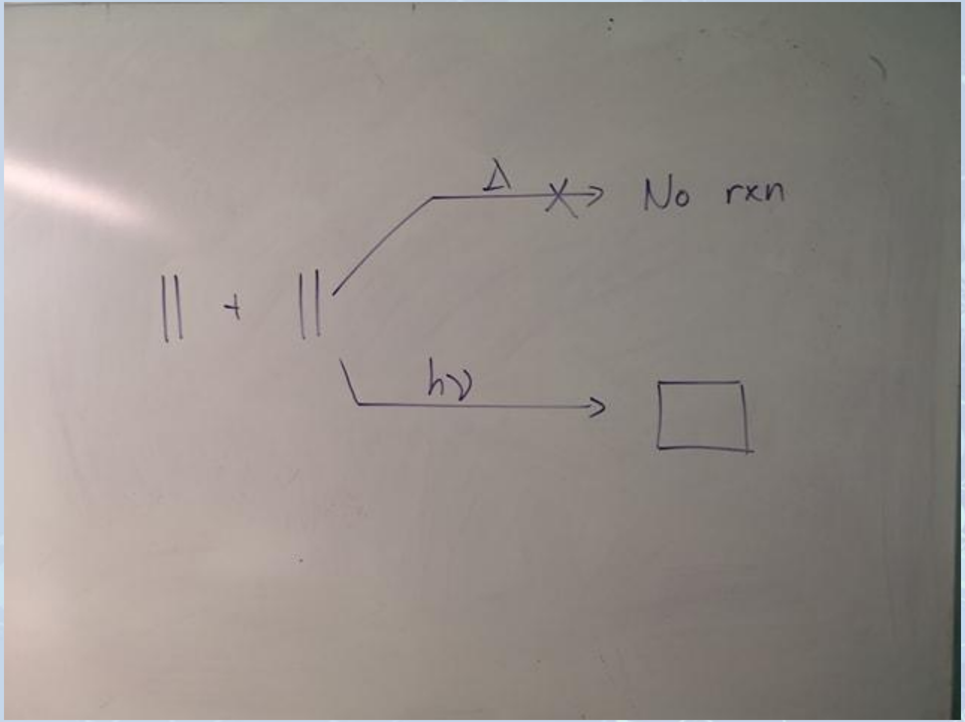


Electrophile: “acrolein”

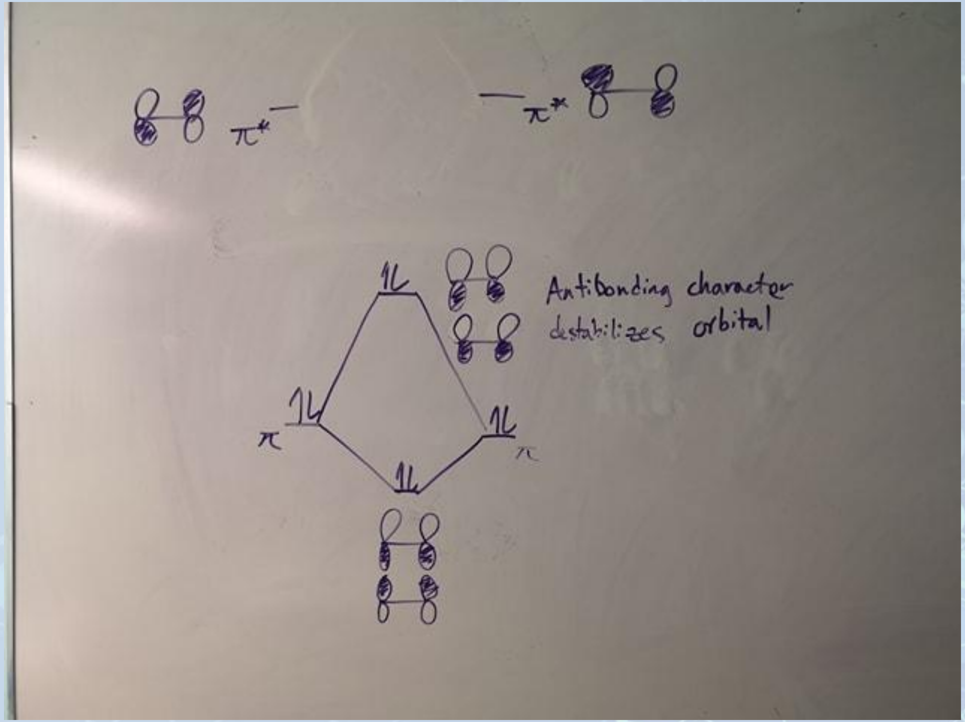




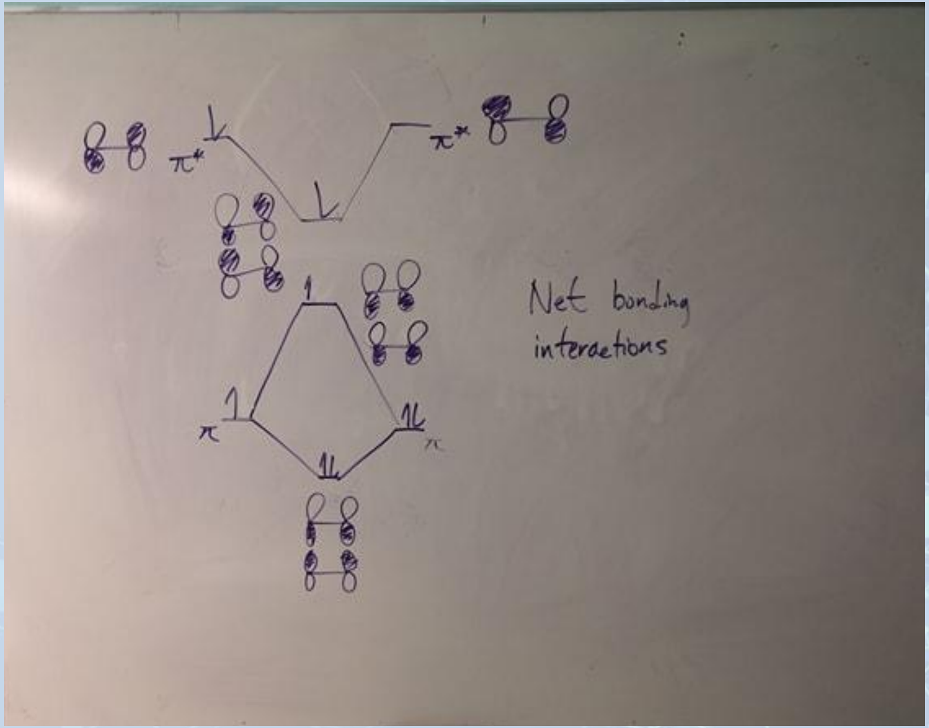
Electrocyclic Reactions: [2+2] Addition



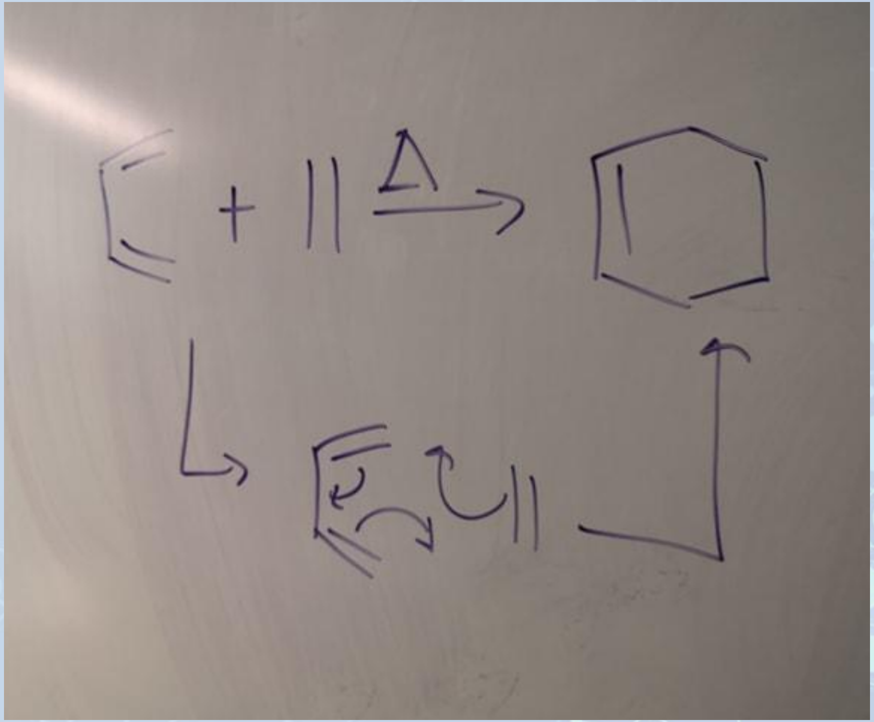
Thermal [2+2] is Forbidden



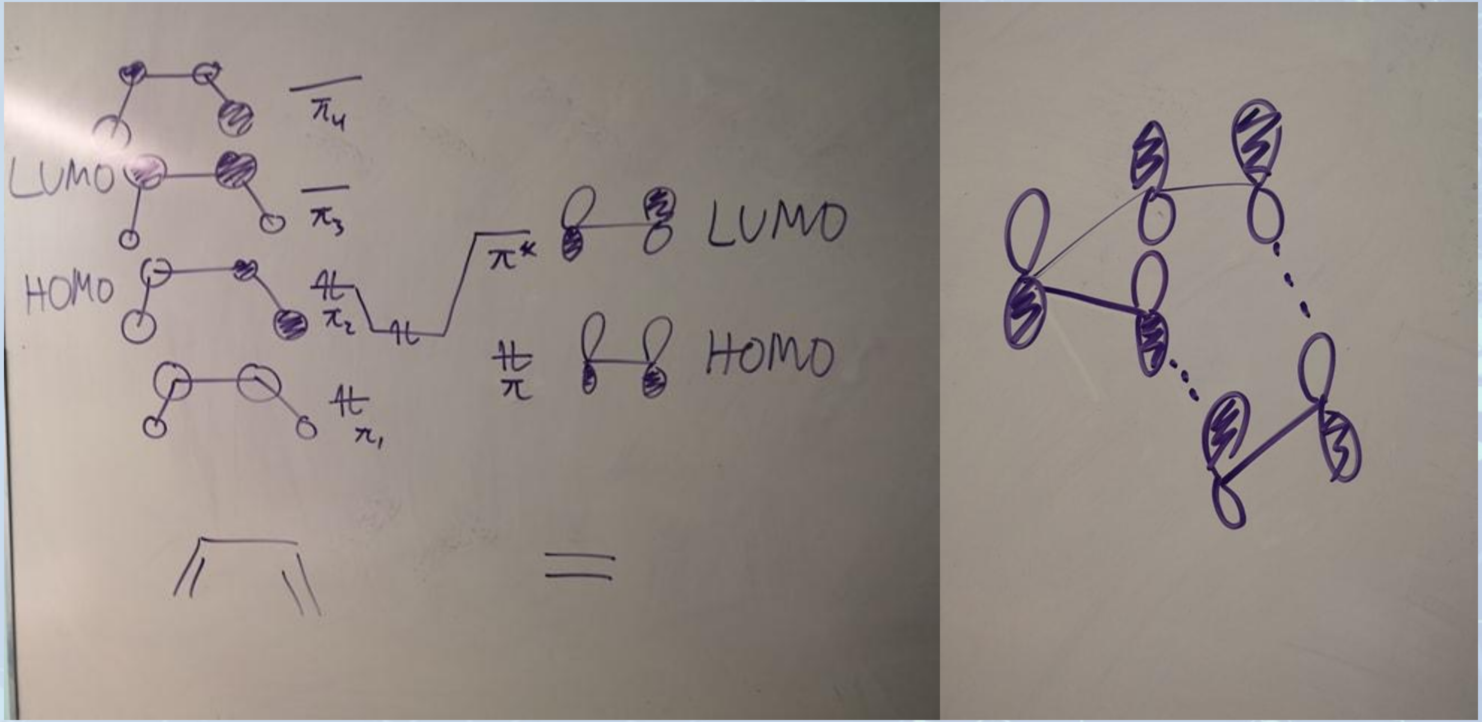
Photochemical [2+2] is Allowed



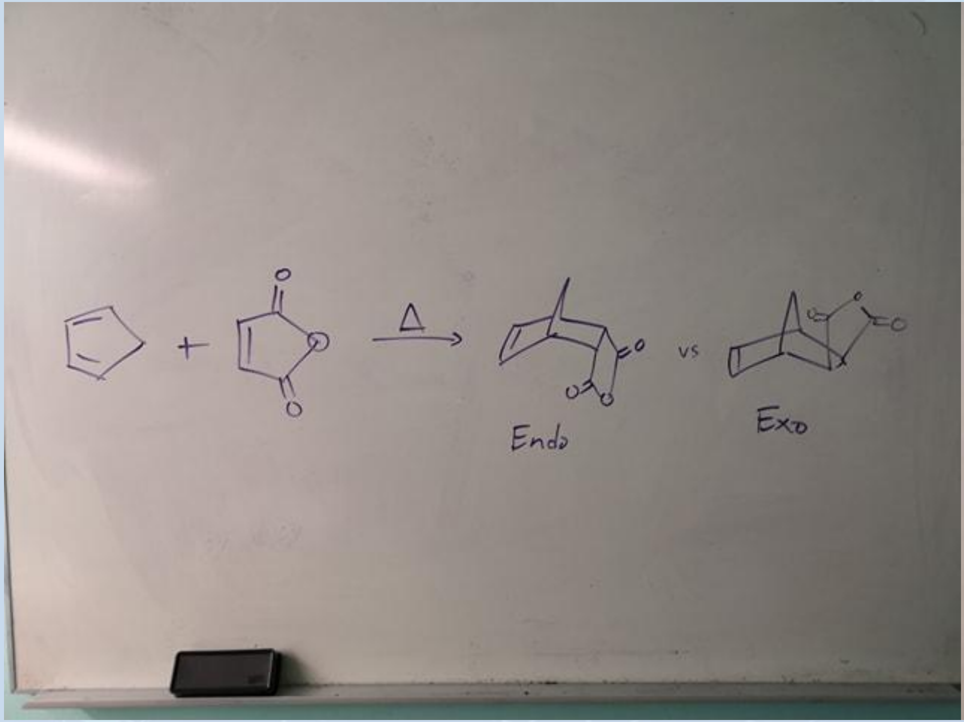
Cycloaddition Reactions: Diels Alder

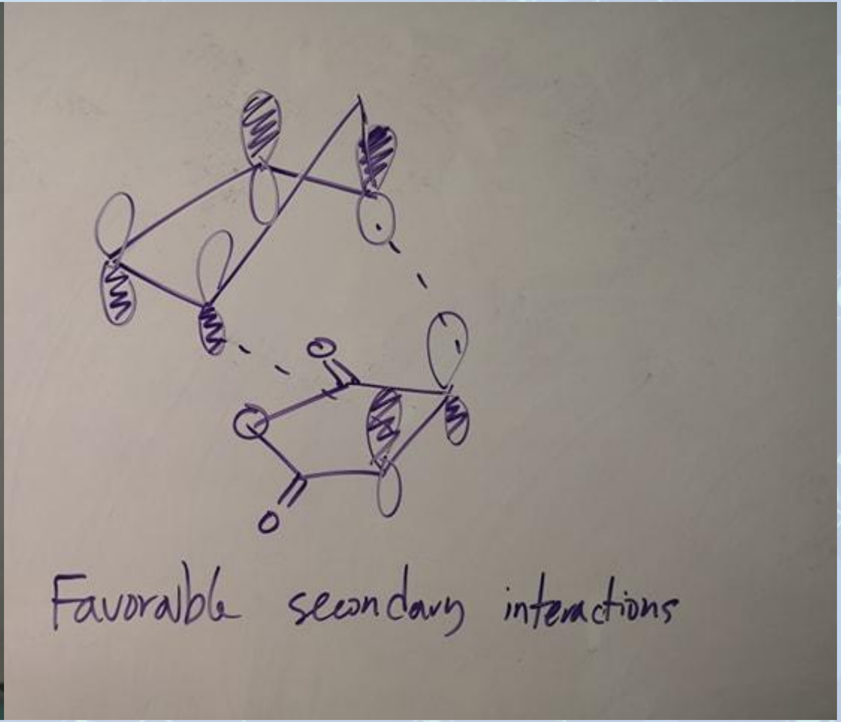


MOs of Diels Alder

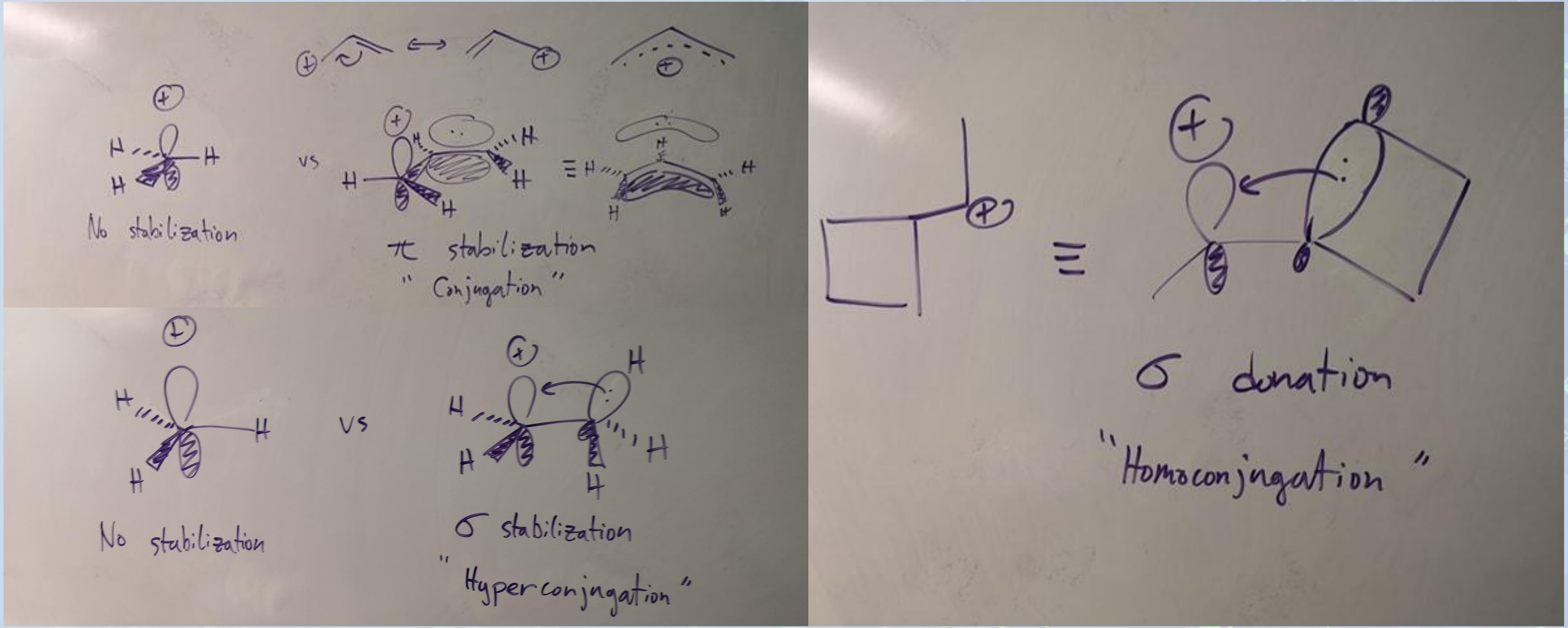


Diels Alder Stereoselectivity: Endo Rule

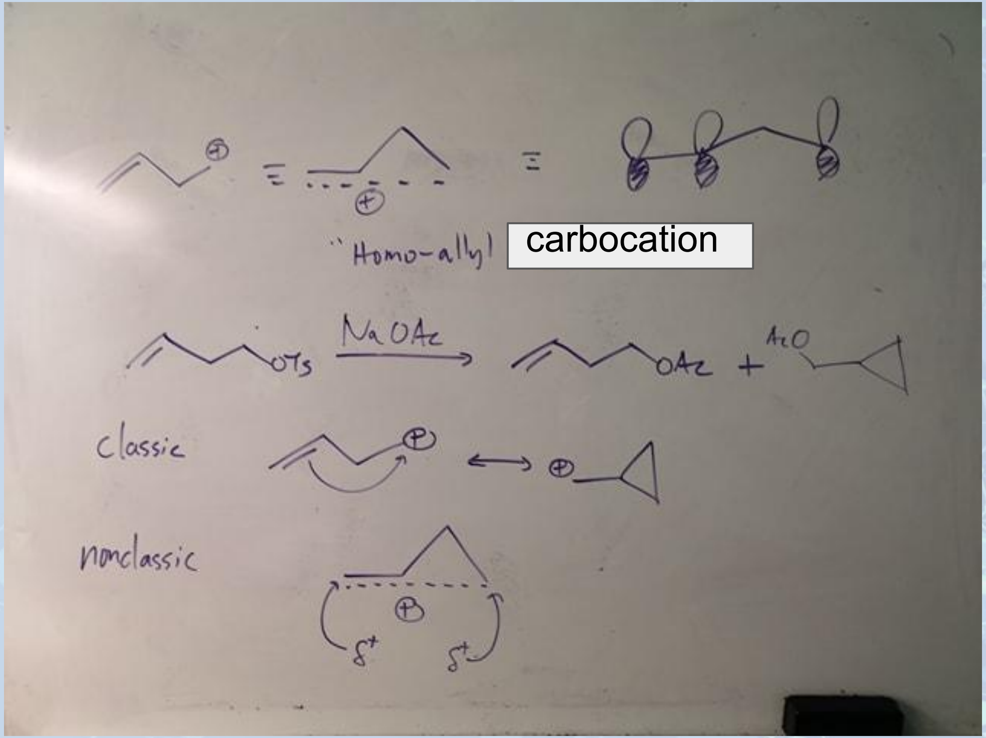



Favorable secondary interactions

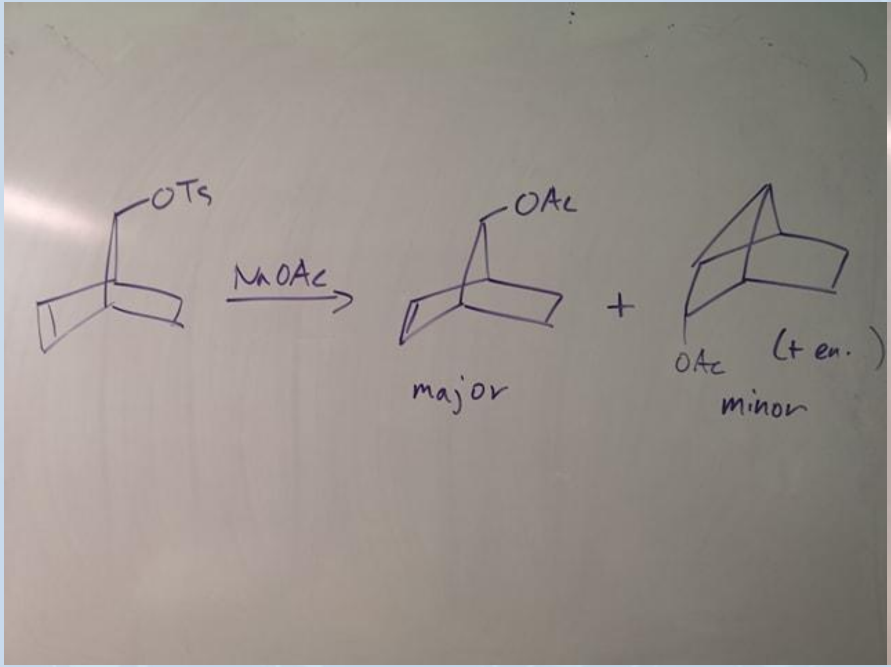
Carbocations: Different Forms of Stabilization

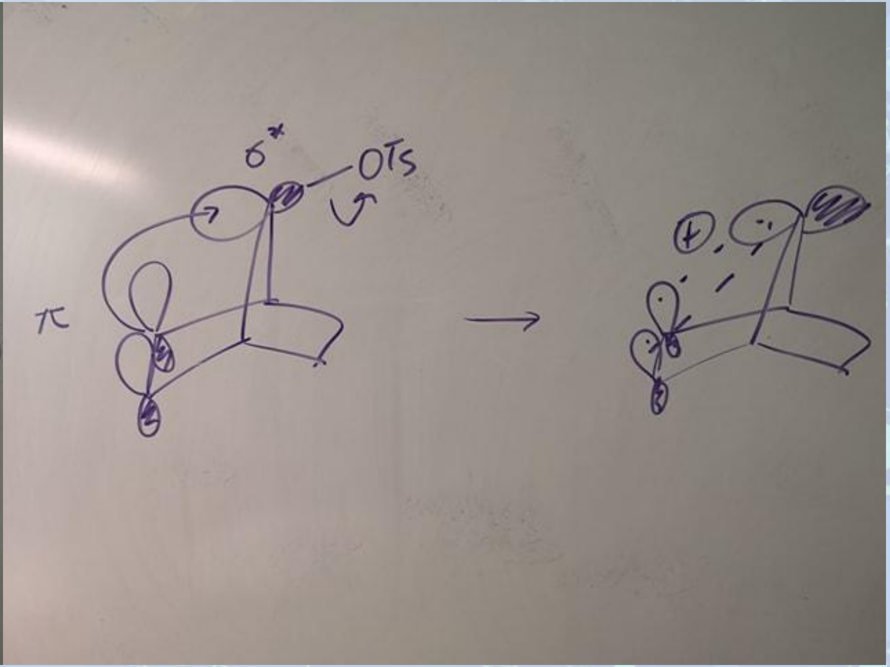


Nonclassical Carbocations: Homo-allyl

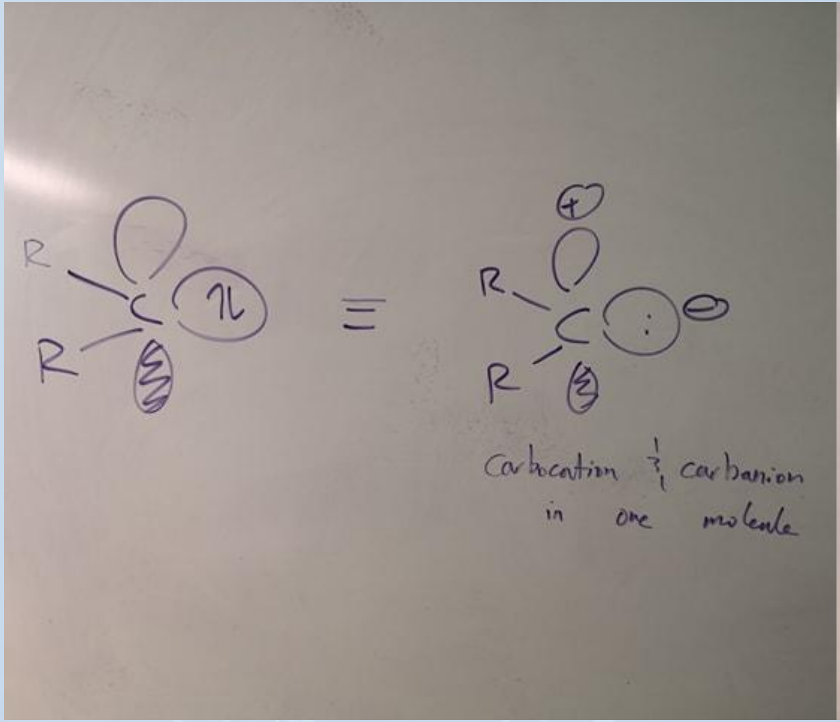


Nonclassical Carbocations: Norbornene

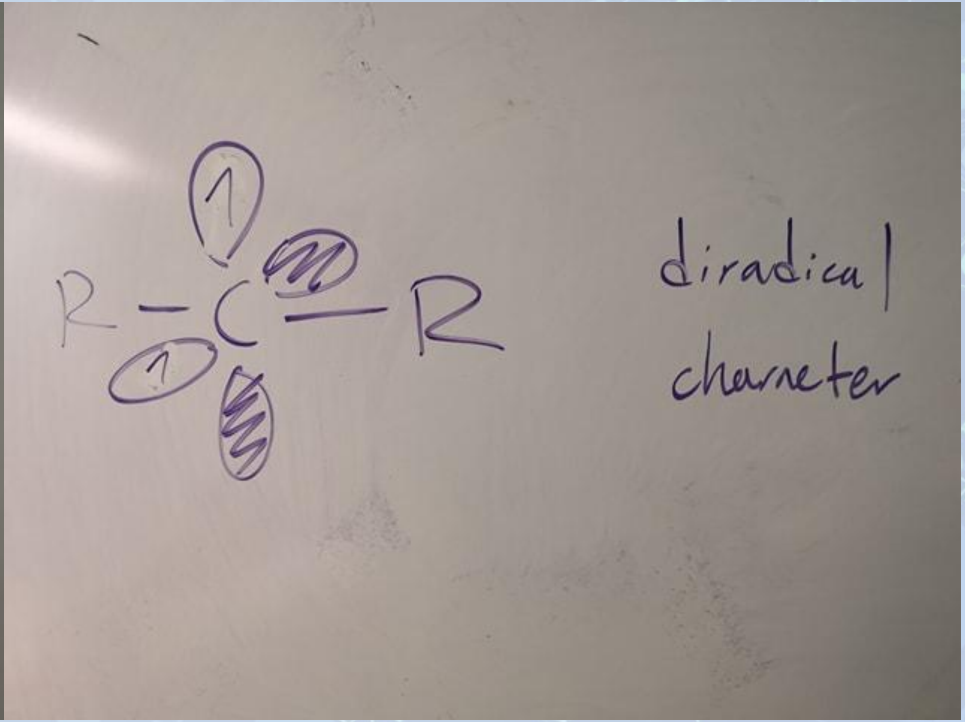




Carbenes: Singlet and Triplets



carbocation & carbanion in one molecule



diradical character

Singlet vs Triplet Reactivity