Molecular Orbital Theory

Lecture 3

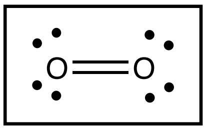
Outline

- **The Diatomic MO Diagram Part 1**
  - What is a MO diagram?
  - MO diagram checklist
  - Setting up a MO diagram
  - Forming the molecular orbitals
  - Determine the splitting energy of the MOs
  - Determine the symmetry of the MOs
  - Adding the electrons
  - How realistic are the MOs?
  - Photoelectron spectra

Why Study MO Theory?

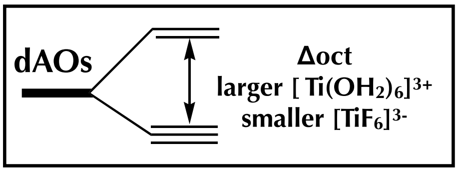
Supersedes VSEPR theory

- valence shell electron pair repulsion theory
- VSEPR predicts O_2 diamagnetic (paired electrons) the experimental evidence is that O_2 is paramagnetic (unpaired electrons)



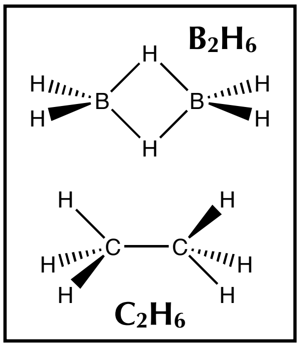
Supersedes Crystal Field Theory

- dAOs are split by the field of the ligands
- negative ligands should produce a larger Δ_{oct}
- but experimentally it is found that F^- ligands have a smaller Δ_{oct} than H_2O



Required for "odd" bonding situations

- structure of ethane is well known, diborane B_2H_6 was assumed to be similar!
- while a 2nd year undergraduate, H. Christopher Longuet-Higgins proposed the structure of diborane together with his tutor R. Bell, famous "banana bonds"

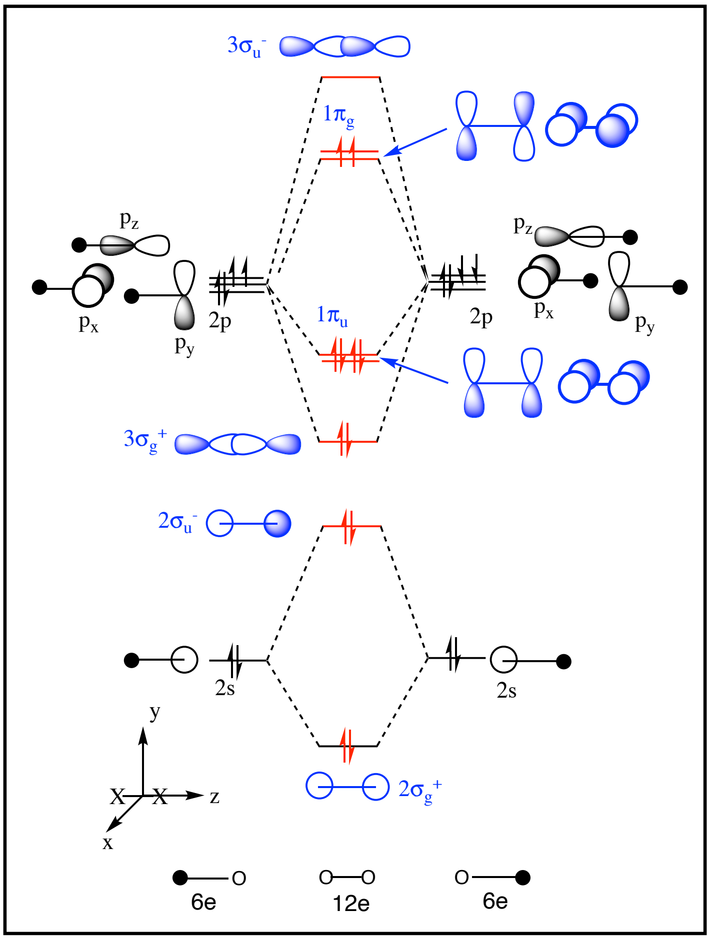


What is a MO Diagram?

shows how the atomic orbitals (AOs) interact to form bonding/ antibonding MOs

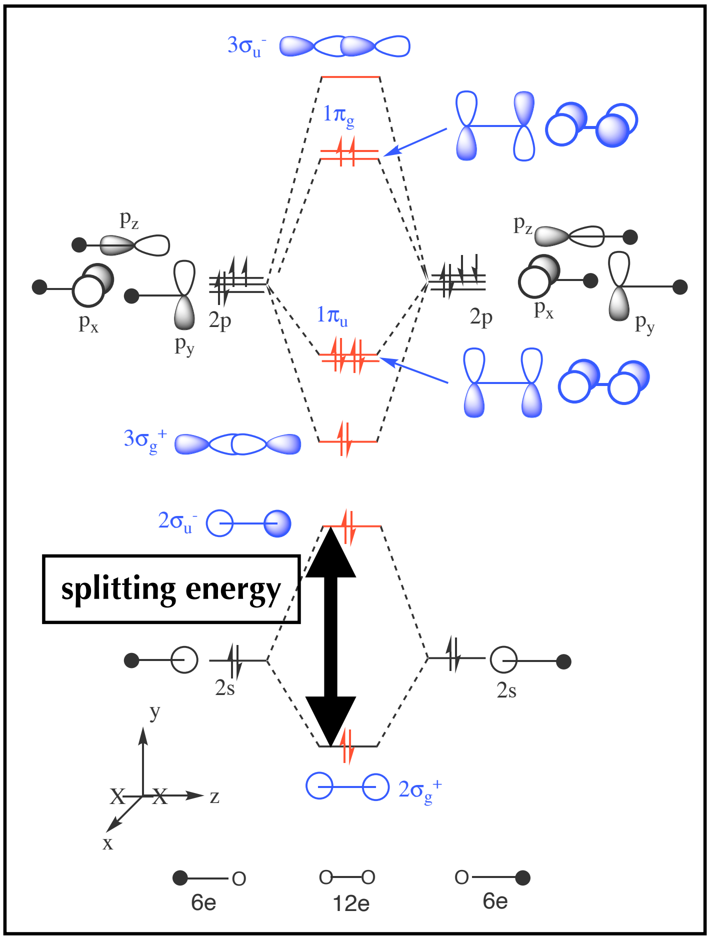
forms basis of the electronic structure of a moleculevertical axis: Energy

today we will build this MO diagram!



MO Diagram Components

- vertical axis: Energy
- horizontal axis: Fragments
- cartesian axis
- black=fragment orbitals (FOs) and energy levels
- red= MO energy levels, the arrows represent the paired electrons
- blue=molecular orbitals, with symmetry labels



MO checklist

Steps to construct a MO diagram

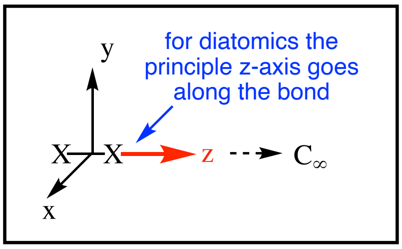
steps we will use today to form the MO diagram

VERY Important!

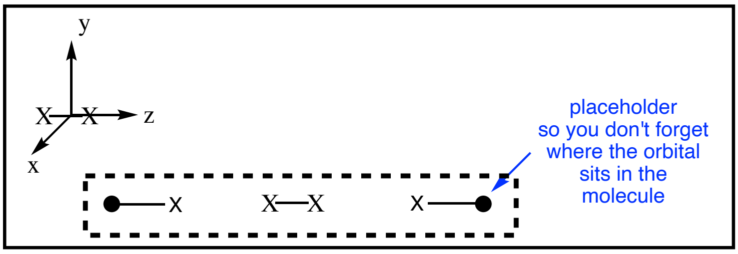
- determine the molecular shape and identify the point group
- define the axial system and identify the symmetry operations
- identify the chemical fragments, put them on the bottom of the diagram
- determine the energy levels and symmetry labels of the fragment orbitals (use H1s as a reference)
- combine fragment orbitals of the same symmetry, sketch out the MOs and analyse the bonding/antibonding character
- estimate the splitting energy for each pair of MOs, draw in the MO energy levels and MOs (in pencil!)
- determine the number of electrons in each fragment and hence the central MO region, add them to the diagram
- identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
- annotate the MO diagram
- use the MO diagram to understand the structure, bonding and chemistry of the molecule

Set-Up MO Diagram

- **determine the molecular shape and point group**
  - molecule is linear
  - point group is $D_{\infty h}$

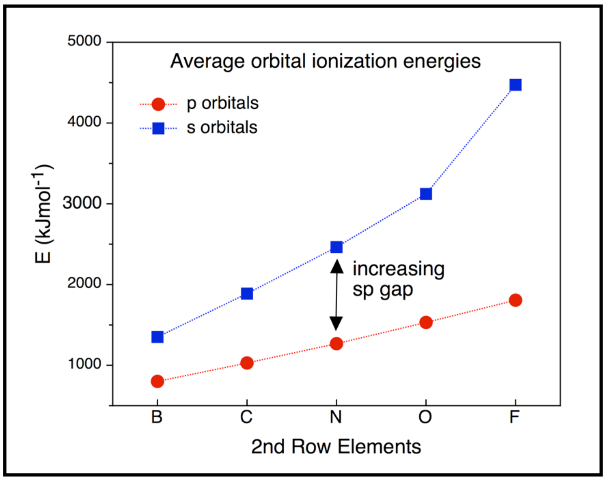


- **define the axial system**
  - z-axis is the principle axis (highest n-axis)
  - (C_∞ axis is explained in the notes online)
- **add the fragments along the bottom**
  - use place holder "dots" for the absent atoms
  - put the molecule in the middle



Position FO Energy Levels

- **MO diagrams are built by combining fragment orbitals**
  - FOs can be simple atomic orbitals
  - or they can be more complex fragments (covered later)

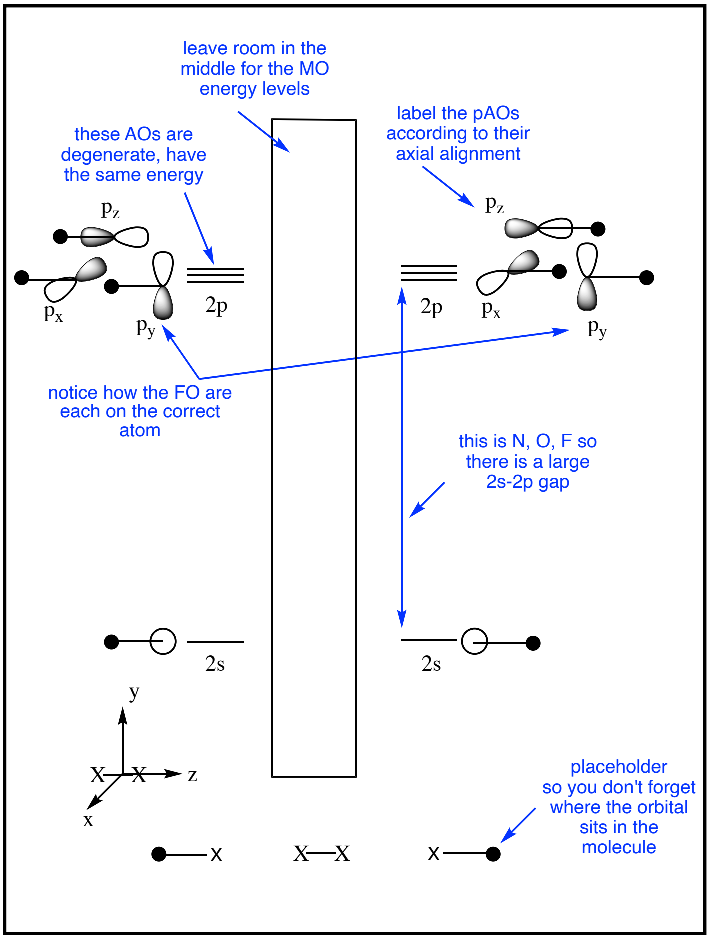


- **second row diatomic $(1s)^2(2s)^2(2p)^x$**
  - leave off the core 1s
  - do include 2s and 2p AOs
- **2s-2p gap increases across row**
  - gap is considered small for C
  - gap is large N, O, F
- **FOs are degenerate for X_2**

MO Diagram Components

- **put energy levels and fragment orbitals on the MO diagram**

take a moment to read the annotations on the diagram



Form the MOs

work out MOs first then the splitting

Important!

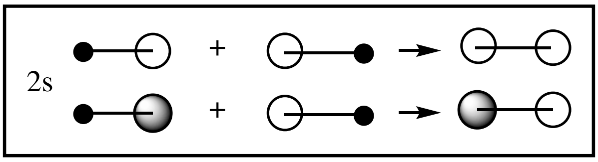
Form the MOs

- **"rules"**
  - FO of the same symmetry combine (more details on this in a later lecture)
  - FO can only combine ONCE

work out MOs first
then the splitting

Important!

- **Form MOs by**
  - “adding” FOs together “as is”
  - “adding” FOs with ONE FO phase inverted



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work out MOs first
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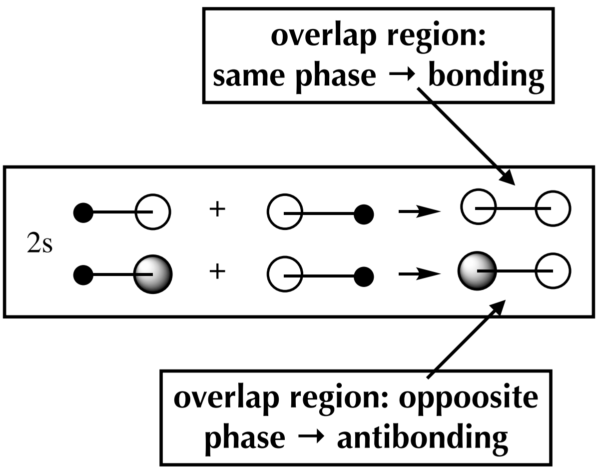
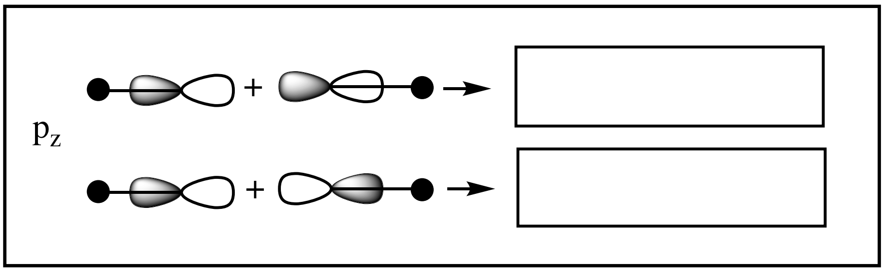
Important!

- **Form MOs by**
  - “adding” FOs together “as is”
  - “adding” FOs with ONE FO phase inverted
- **Bonding character**
  - bonding MOs are all the same phase (all the same sign) in the overlap region
  - antibonding MOs have opposite phase
- **NOTE**
  - we don't always draw the overlap explicitly, BUT it is assumed!



In-Class Acitivity P1

- **complete the diagrams for the pz-AO interaction**
- **label the bonding character of the internuclear region**



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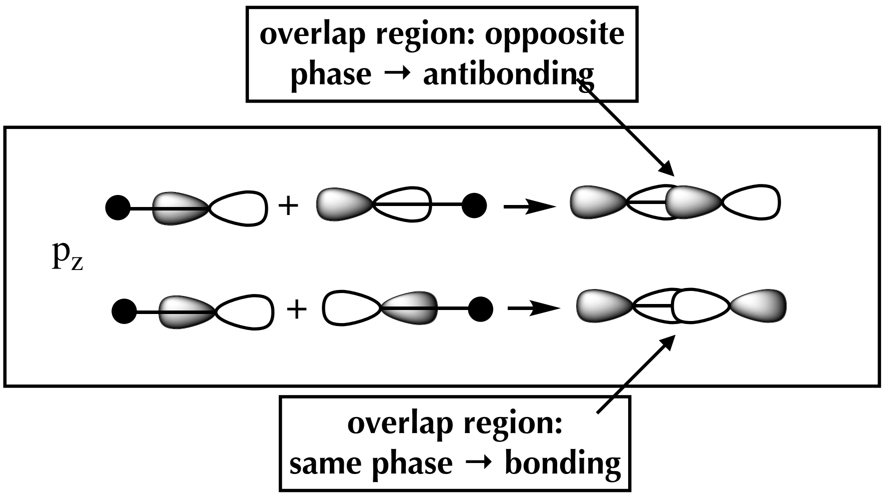
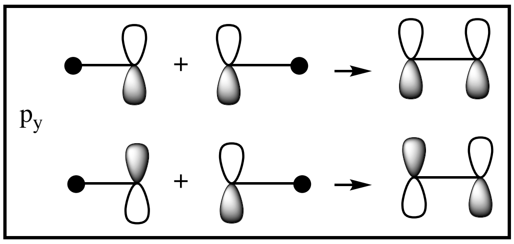


Forming the MOs

p_x and p_y are perpendicular to the bond

- overlap of side-by-side orbitals is weaker
- origin of the rule that π-bonds are weaker than σ-bonds
- the p_x and p_y based MOs remain degenerate



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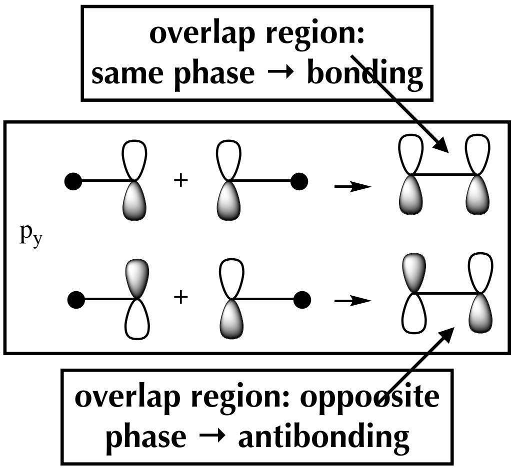

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  - overlap of side-by-side orbitals is weaker
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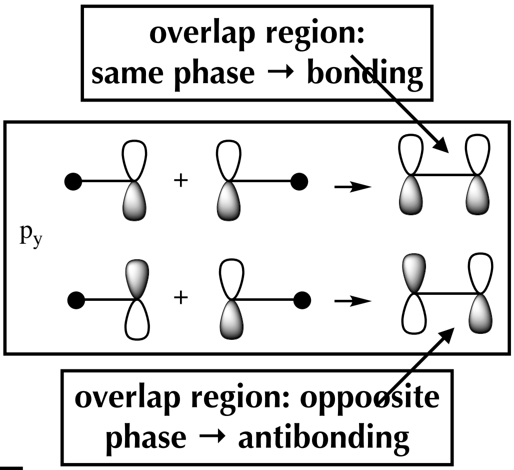
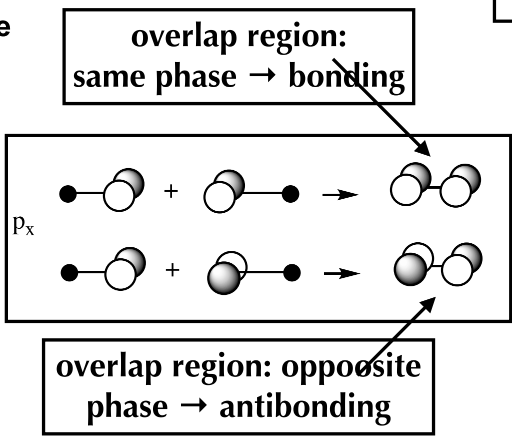
  - the p_x and p_y based MOs remain degenerate
  - the p_x MOs are drawn in "3D"



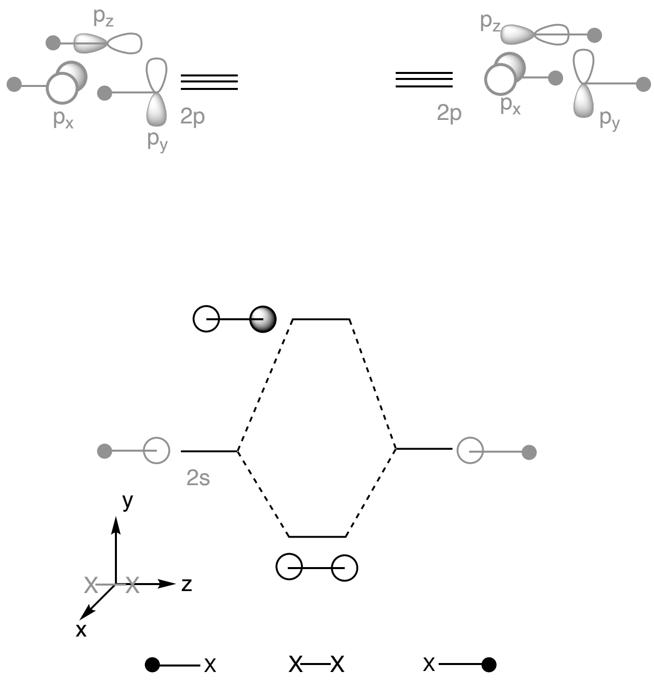


MO Splitting Energy

- **we will cover more fully in a later lecture**
- **general "rules" for energy splitting**
  - sAOs : moderate
  - directed end-to-end pAO strong overlap: large
  - side-to-side pAO weak overlap: small
- **antibonding MOs are destabilised more than bonding MOs are stabilised**
- **application on MO diagram**
  - decide on the spliting "distance" for the 2sAOs
  - reference other MO splitting to this reference "distance"
- **now add the MOs to the MO diagram!**

MO Diagram Components

- put MOs and MO energy levels on the MO diagram
  - 2sAO splitting is moderate
  - use the 2sAO based MO splitting as a "reference"



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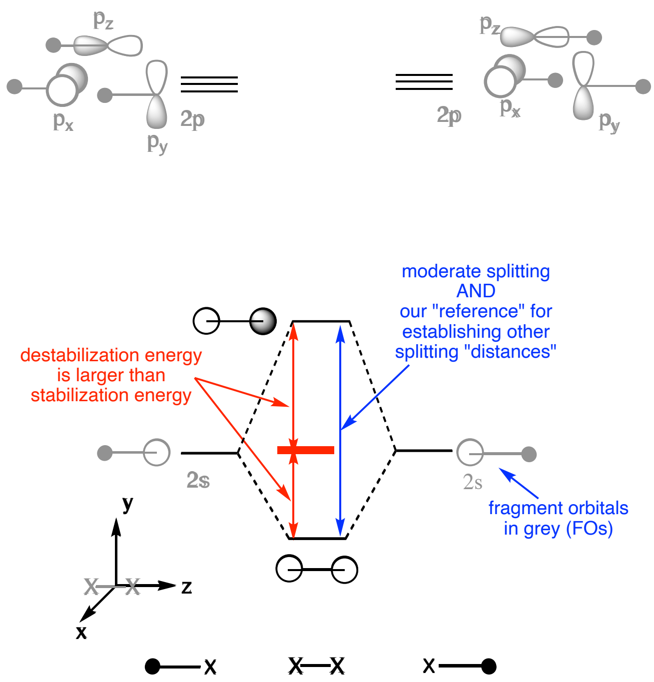

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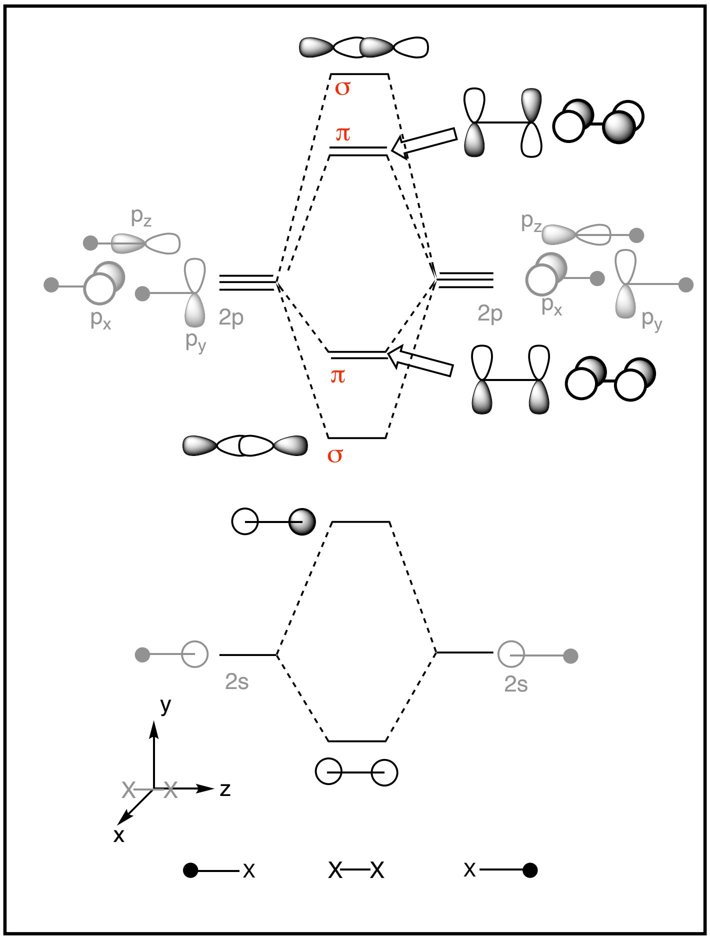
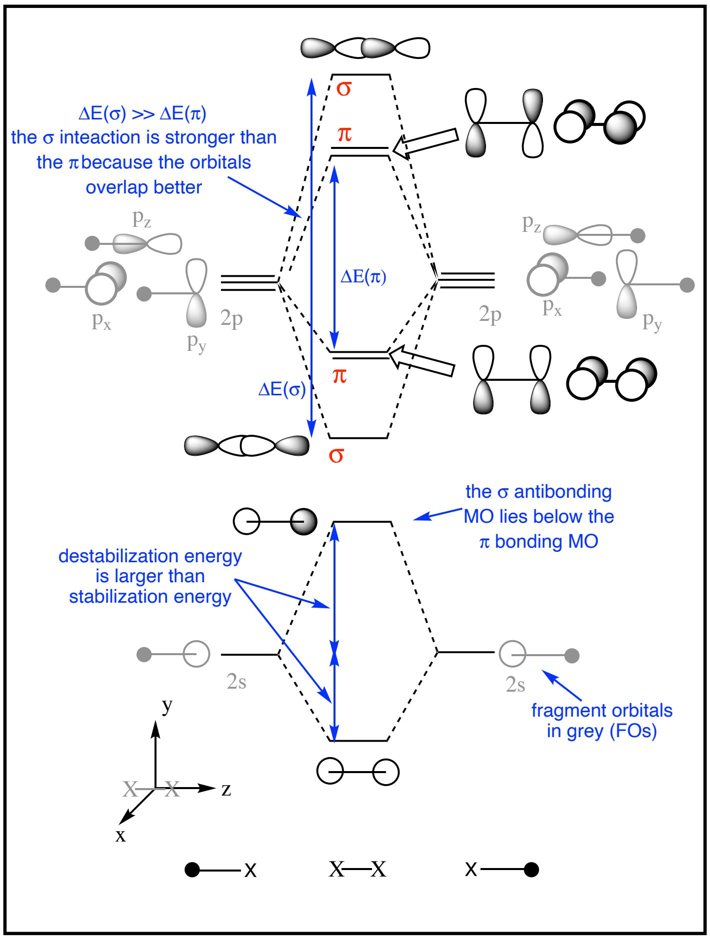


MO Diagram Components

- put MOs and MO energy levels on the MO diagram

take a moment to read the annotations on the diagram

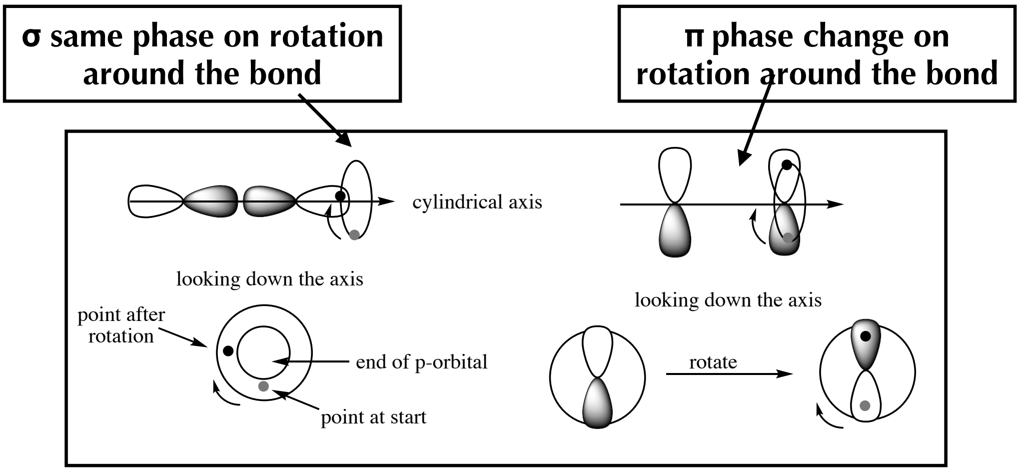


Determine MO Symmetry

use the character table

- no atoms on CoM, cannot use direct AOs
- representation table (long)
- use “pattern” method and general knowledge

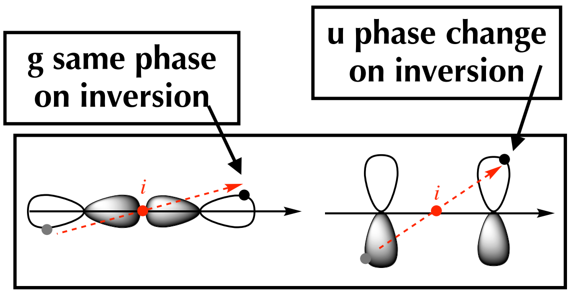
distinguish between σ and π



Determine MO Symmetry

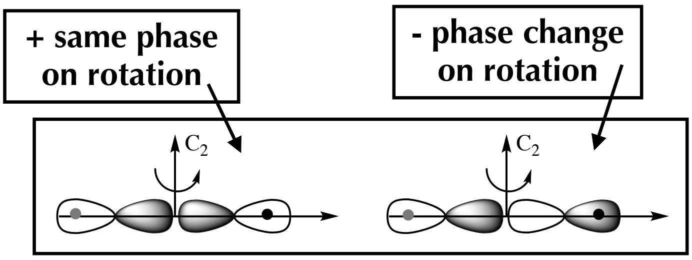
inversion: "u" and "g"

- g=gerade no phase change
- u=ungerade phase change



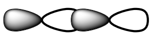
C_2 axis rotation

- "+" no phase change
- "-" phase change



In-Class Activity P2

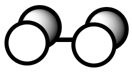
- **determin the symmetry labels for the following MOs (I've done one example for you)**



σ_u^-

symmetry
C_∞ rotation: σ
inversion: u
C_2 rotation: -

symmetry
C_∞ rotation:
inversion:
C_2 rotation:



symmetry
C_∞ rotation:
inversion:
C_2 rotation:

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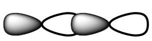
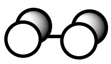


σ_u^-

symmetry
C_∞ rotation: σ
inversion: u
C_2 rotation: -

σ_g^+

symmetry
C_∞ rotation : σ
inversion: g
C_2 rotation: +

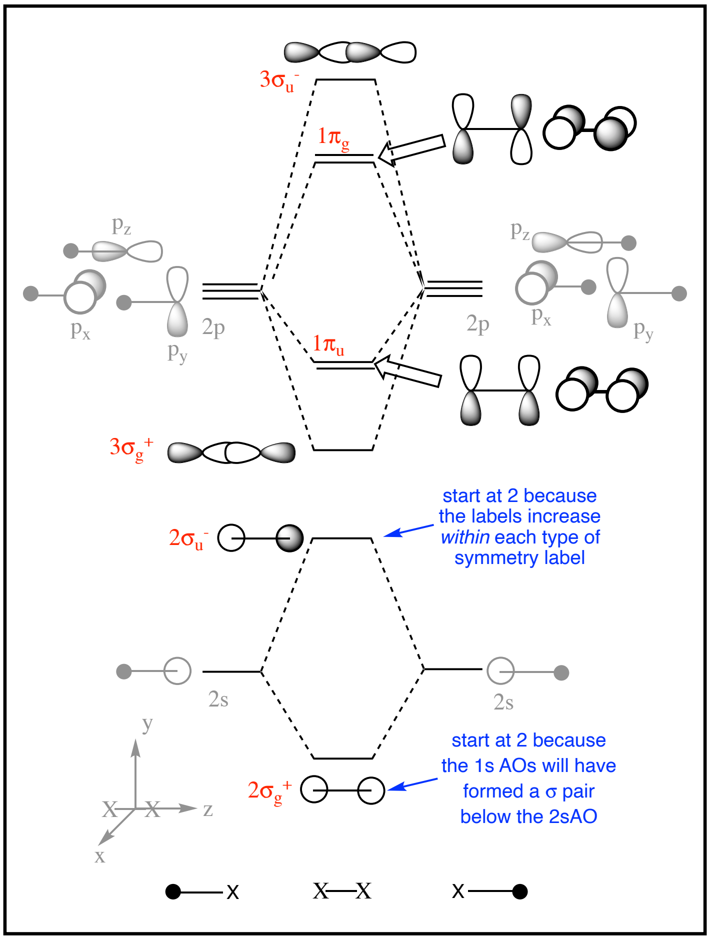


π_u

symmetry
C_∞ rotation : π
inversion: u
C_2 rotation: (-) not-labeled for π MOs

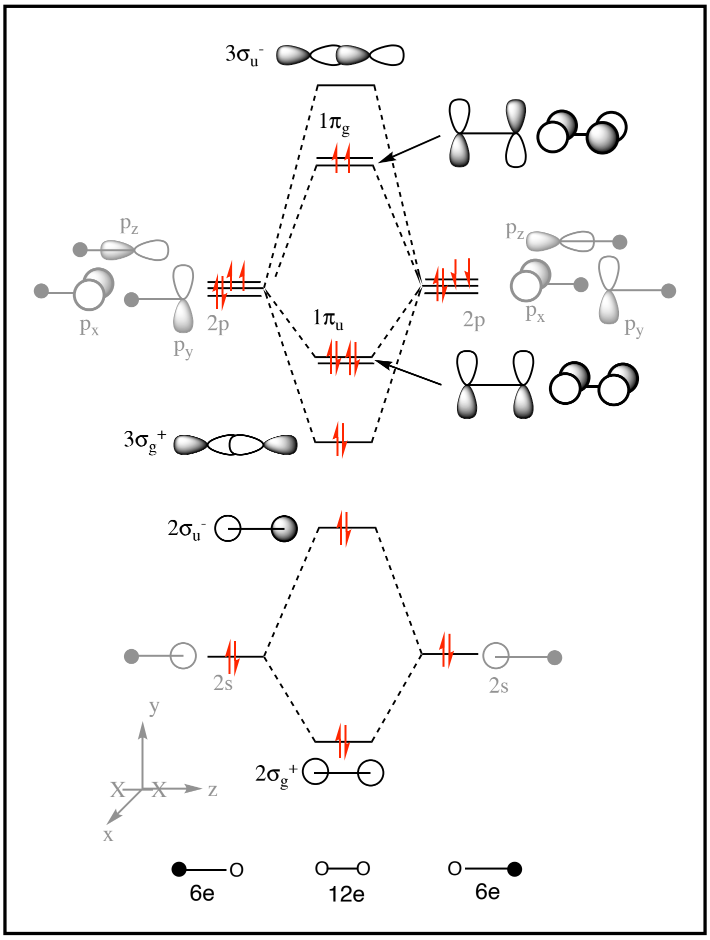
MO Symmetry

- **determine the symmetry of the MOs**
  - label sequentially within each symmetry label group
  - $1\sigma_g^+$, $2\sigma_g^+$, $3\sigma_g^+$ and so on
  - we can include the core MOs in the numbering ($1\sigma_g^+$ and $1\sigma_u^-$)



Add Electrons

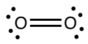
- **use X=O to form O_2**
  - O has 6 valence electrons $(2s)^2(2p)^4$
  - thus O_2 has 12 electrons in MO diagram
- **follow Pauli exclusion and Hund's rule**
  - Hund's rule: fill sequentially from lowest energy to highest energy
  - Pauli exclusion: fill orbitals with parallel spin until required to pair electrons



Use MO Diagram

problem:

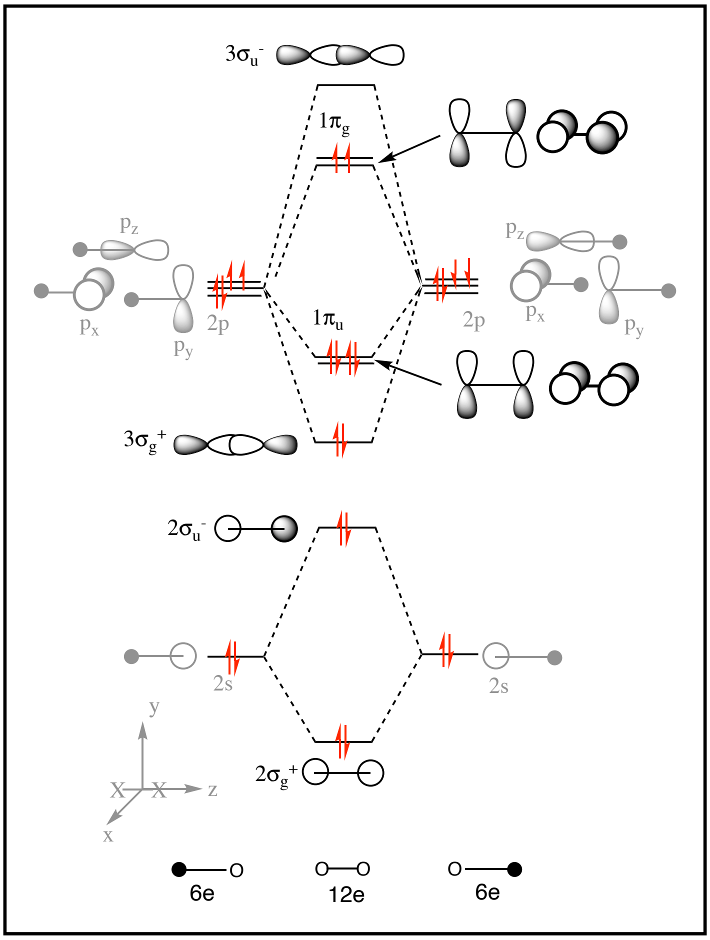
- VSEPR theory O_2 has no unpaired spins, is diamagnetic
- Experiments O_2 is paramagnetic meaning it does have unpaired spin



6 valence electrons each
2 into the double bond
2 lone pairs

MO theory

- O_2 does have un-paired electrons
- due to degenerate π_g higest occupied MOs (HOMOs)
- 6 electrons in 2pAO based bonding MOs, 2e in antibonding, overall bond order of 2



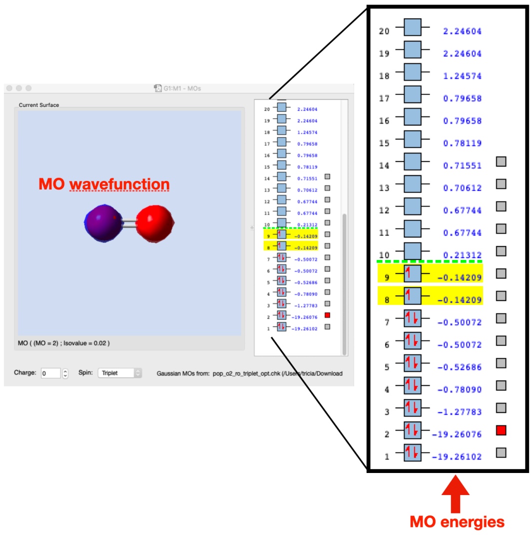
How Realistic are the MOs?

full representation requires calculation solving the molecular Schrödinger Equation

- pen-and-paper MO diagrams are qualitative
- BUT they provide a very good approximation!

our qualitative MO diagram is

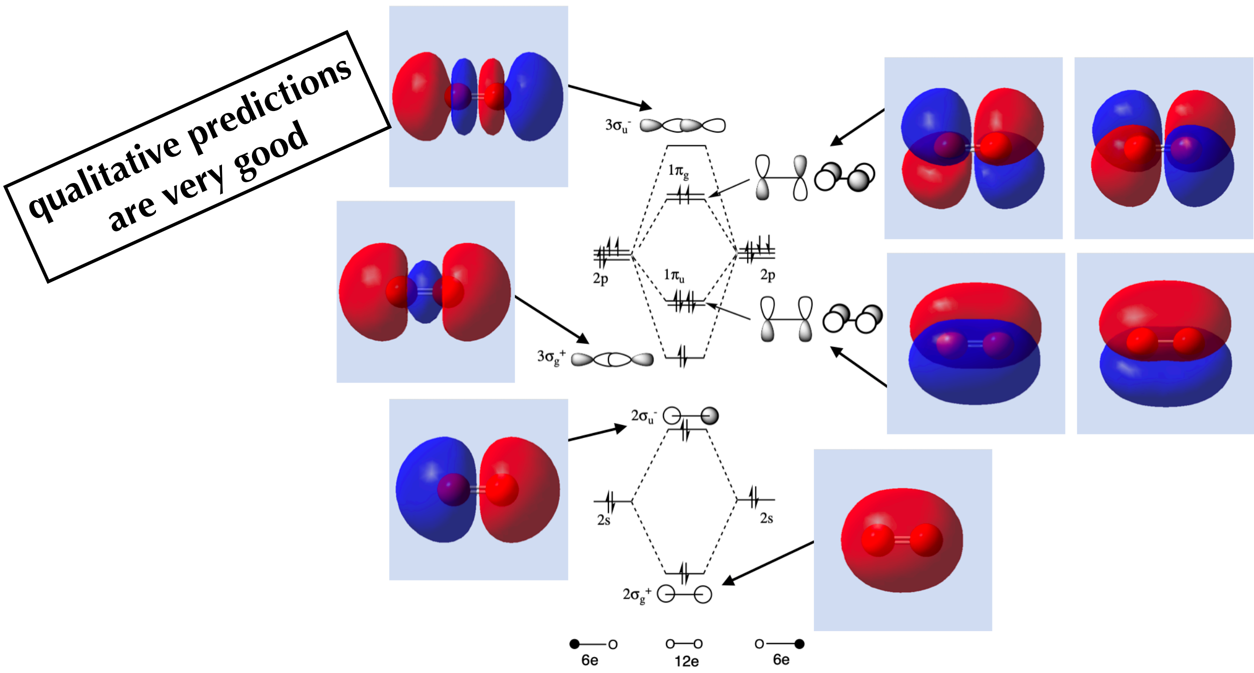
solving the Schrödinger equation without any maths!!



example output information for a calculation on O_2

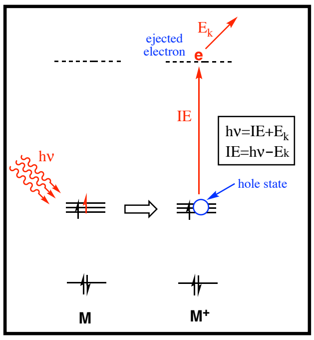
How Realistic are the MOs?

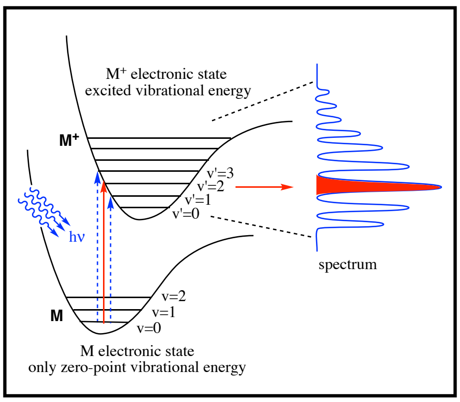
- **compare qualitative MOs to computed MOs**



Experimental Evidence?

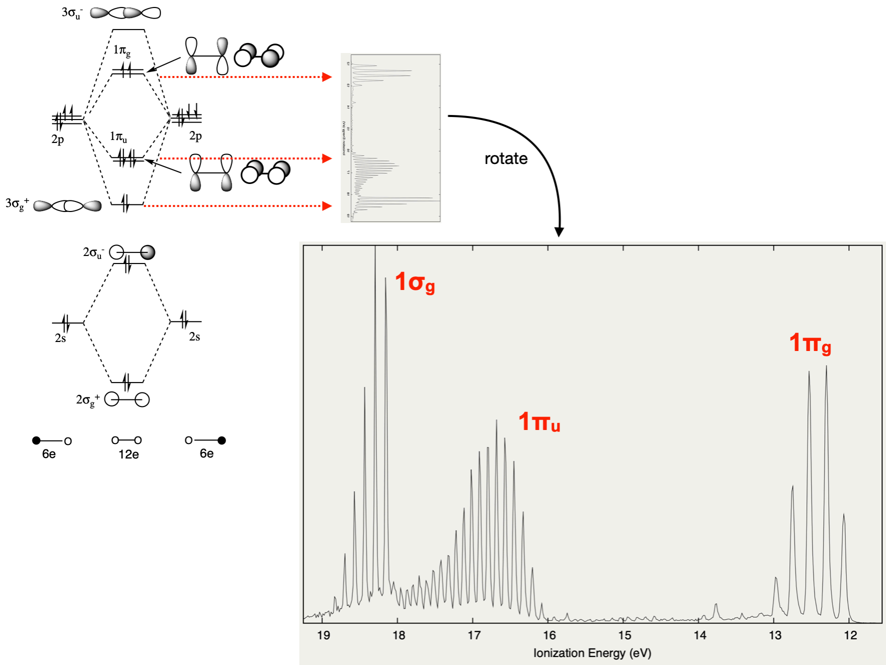
- **compare to experiments**
- **photoelectron spectroscopy (PES)**
  - high energy light (hν) is used to eject an electron
  - measure the kinetic energy of ejected electrons (E_k)
  - can obtain the ionization energy (IE) of electrons from each MO
- **gives us the "energy level" of each MO**
- **often get vibrational fine structure**
  - M+ is formed in a vibrationally excited state
  - adds/subtracts a small amount of energy
  - removing an electron from a strong bonding or antibonding MO changes the bond length
  - shifts the excited state PES, resulting in extensive vibrational fine structure





Experimental Evidence?

- **PES of O_2 matches with MO diagram**



Key Points

- **be able to write down the MO checklist**
- **be able to draw a MO diagram for a homonuclear diatomic X_2**
- **be able to discuss how the 2s-2p energy gap changes across the first row and be able to use this knowledge in constructing MO diagrams**
- **be able to evaluate, discuss and illustrate the bonding/antibonding**
- **be able to evaluate, discuss and illustrate the splitting energy**
- **be able to determine and explain the symmetry of MOs**
- **be able to recognise the accuracy of qualitative MO diagrams relative to full MO theory**
- **be able to describe how a PES is generated and to discuss the origin of vibrational fine structure**
- **be able to interpret a PES in terms of a MO diagram, and alternatively be able to predict the PES of a molecule from knowledge of the MO diagram**