

Molecules Module – Lecture 7: Molecular Orbital Theory continued

Learning Objective	Openstax 2e Chapter
Molecular Orbital Theory	<u>8.4</u>

Suggested Practice Problems

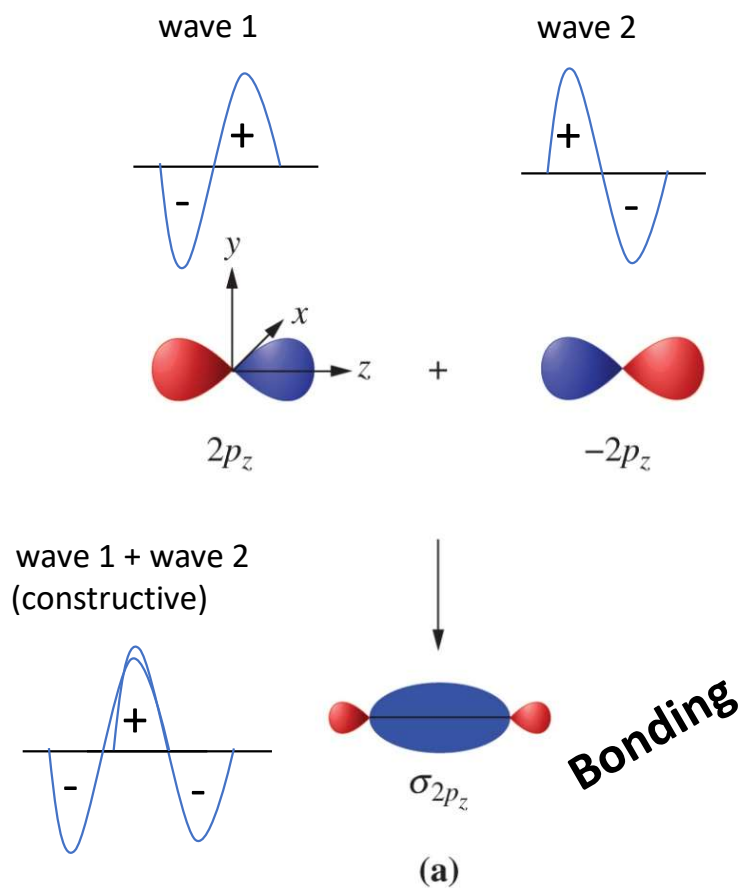
[Chapter 8 Exercises](#) – Questions: 29, 41, 47, 49

Answers can be found in the [Chapter 8 Answer Key](#)

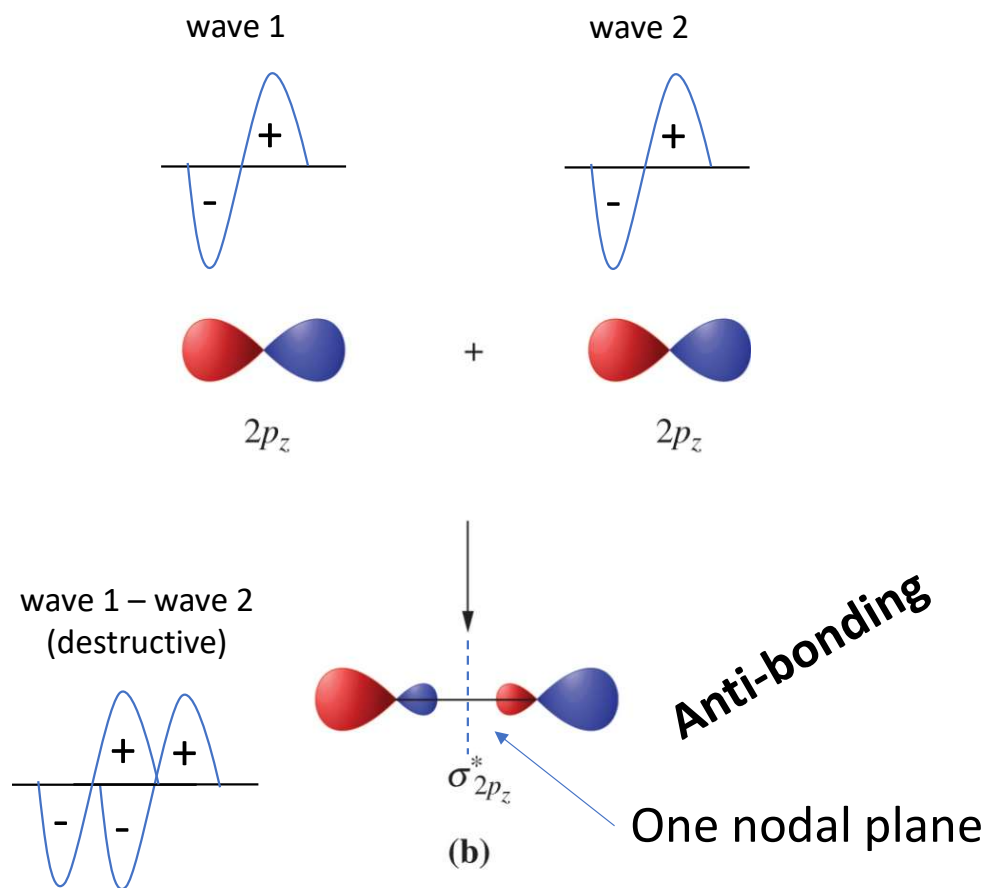
Molecular Orbitals – 2nd Period Elements

- First period (row) elements use only 1s AOs.
- Second period (row) elements have 2s and 2p AOs available.
- Overlap of two AOs of the s type produces a sigma bond (σ).
- Two types of overlap from AOs of the p type:
 - End-to-end overlap – **sigma bond (σ)**
 - Side-to-side overlap – **pi bond (π)**

MOs from p Orbitals – σ Overlap

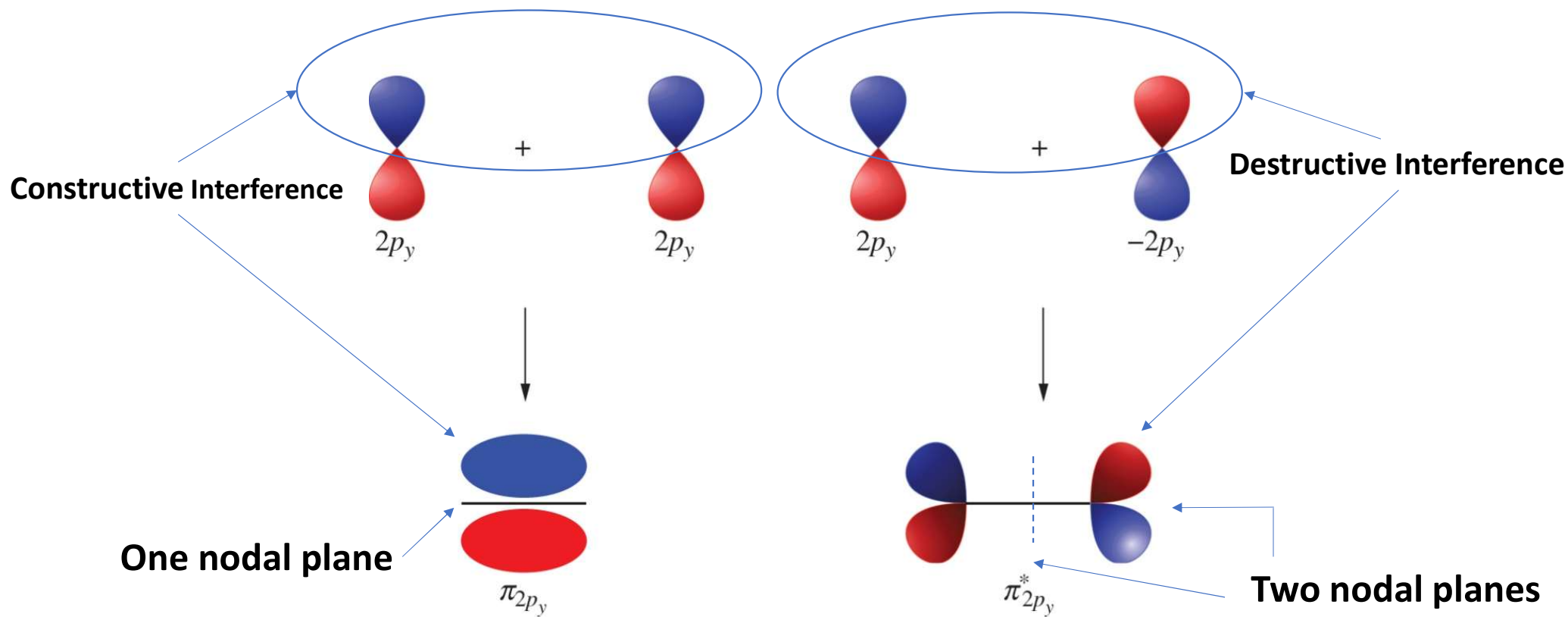


$$\psi_{Mol} = \psi_1 + \psi_2$$



$$\psi_{Mol} = \psi_1 - \psi_2$$

MOs from p Orbitals – π Overlap



How do we fill electrons?

- **Example: O₂**
 - Recall that none of the previous chemical bonding theories (Lewis and VB) can explain why O₂ is paramagnetic.
 - We have a total of 16 electrons for O₂ (core+valence electrons). We use the same rules as adding electrons to the AOs.

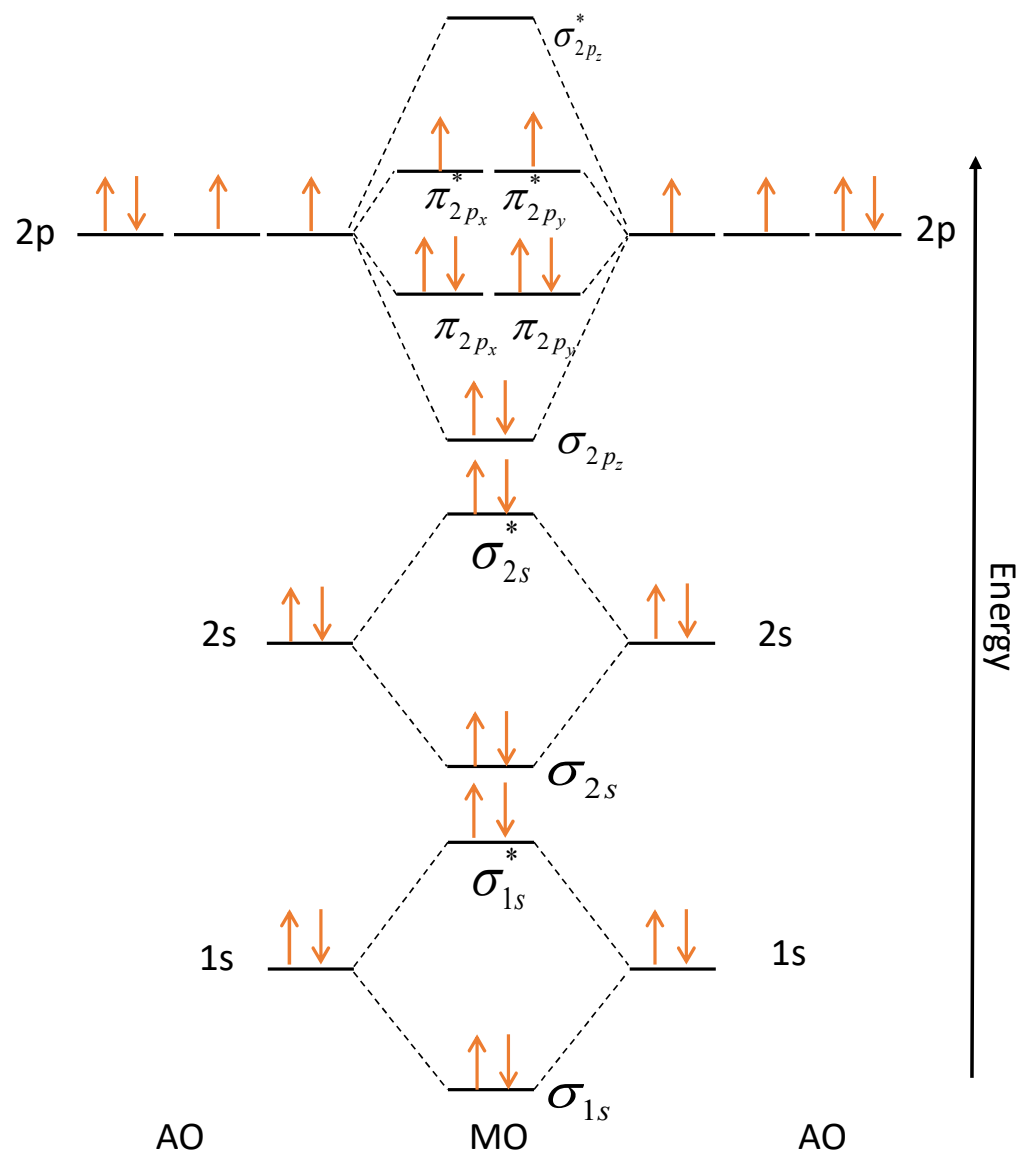
So O₂ has unpaired electrons!

Electron configuration for O₂ molecule,
 $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2pz})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

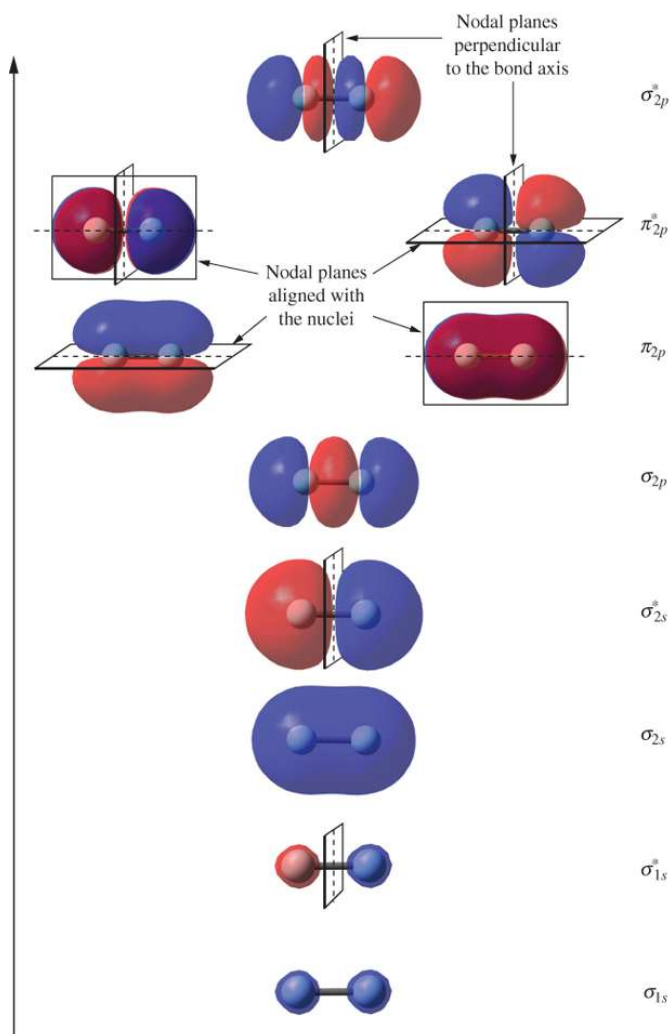
B. O. = $(10 - 6)/2 = 2$ (O₂ has a double bond!)

Total # of e⁻ in
bonding MOs

Total # of e⁻ in
antibonding MOs

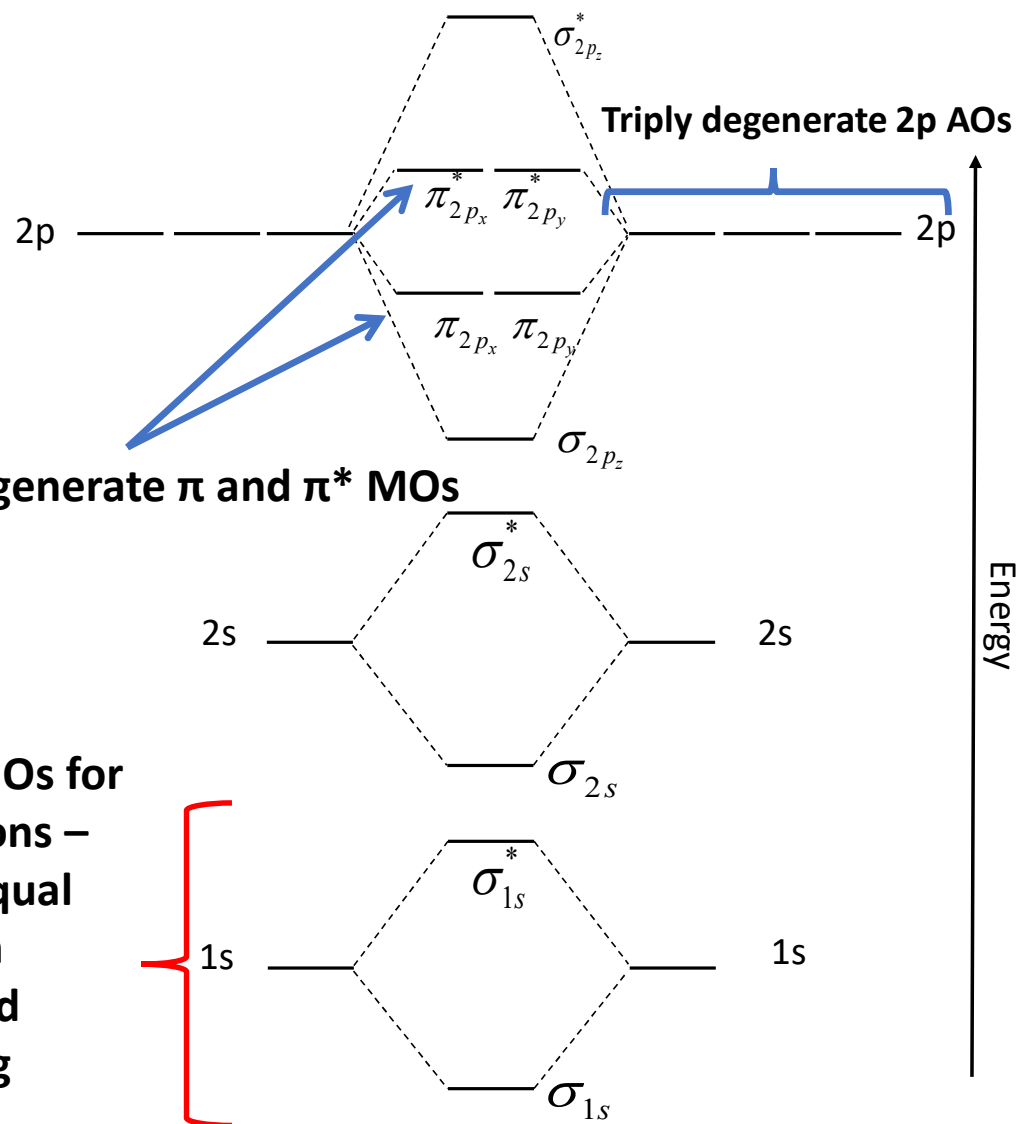


Let's Take a Closer Look:



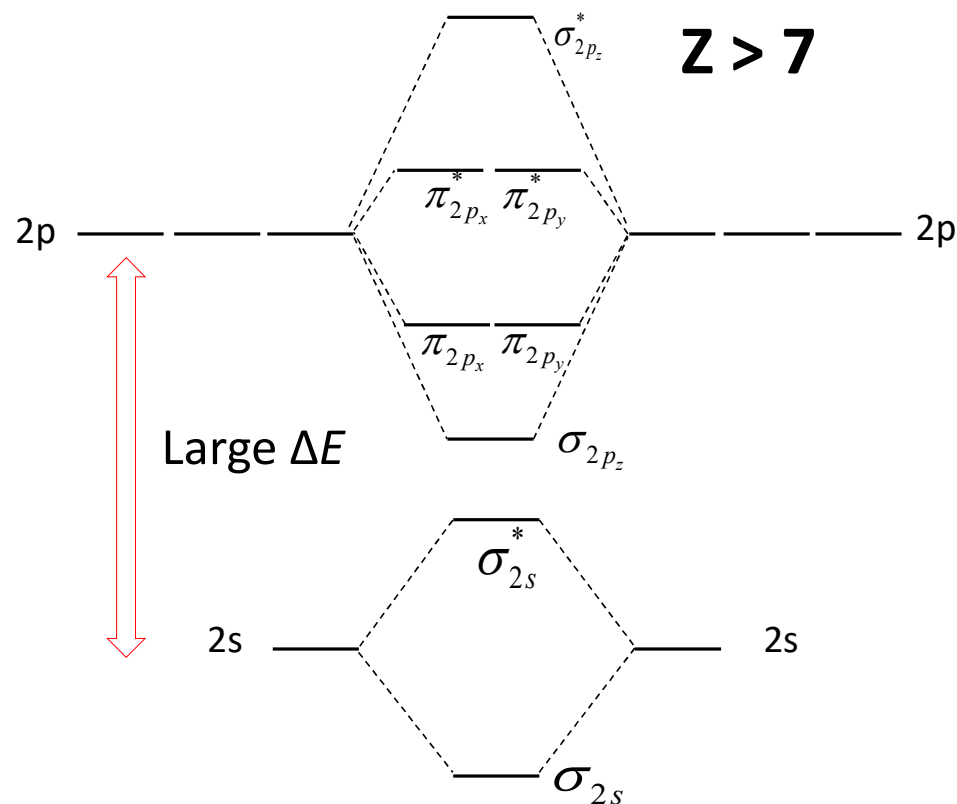
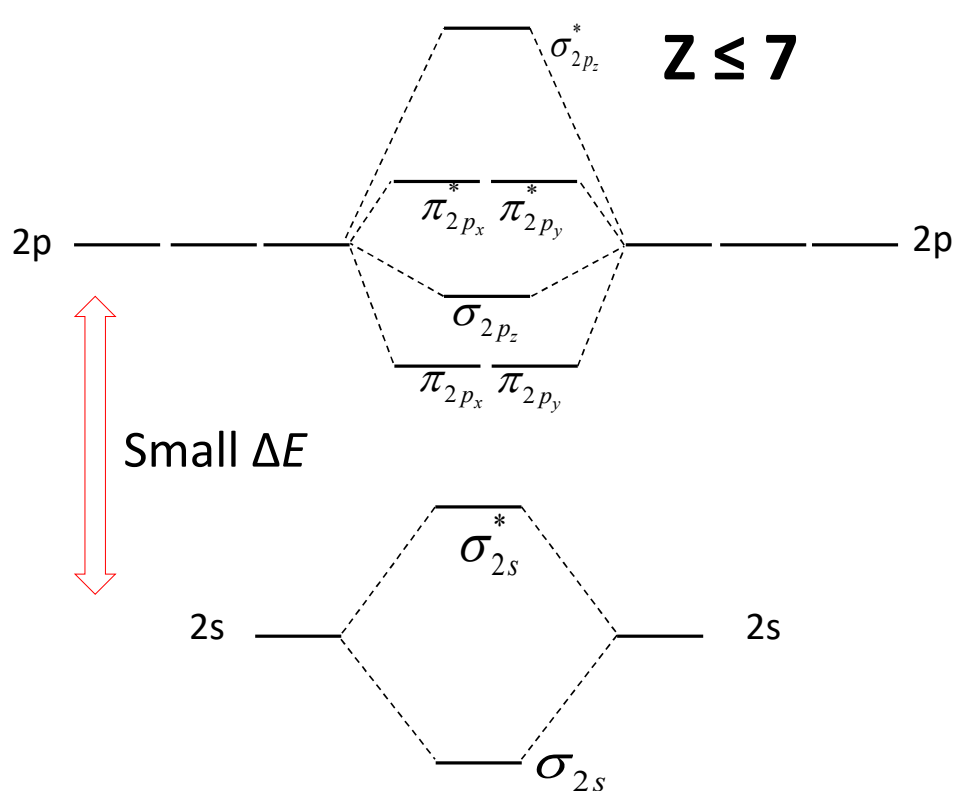
doubly degenerate π and π^* MOs

Can omit MOs for core electrons – just have equal electrons in bonding and antibonding orbitals



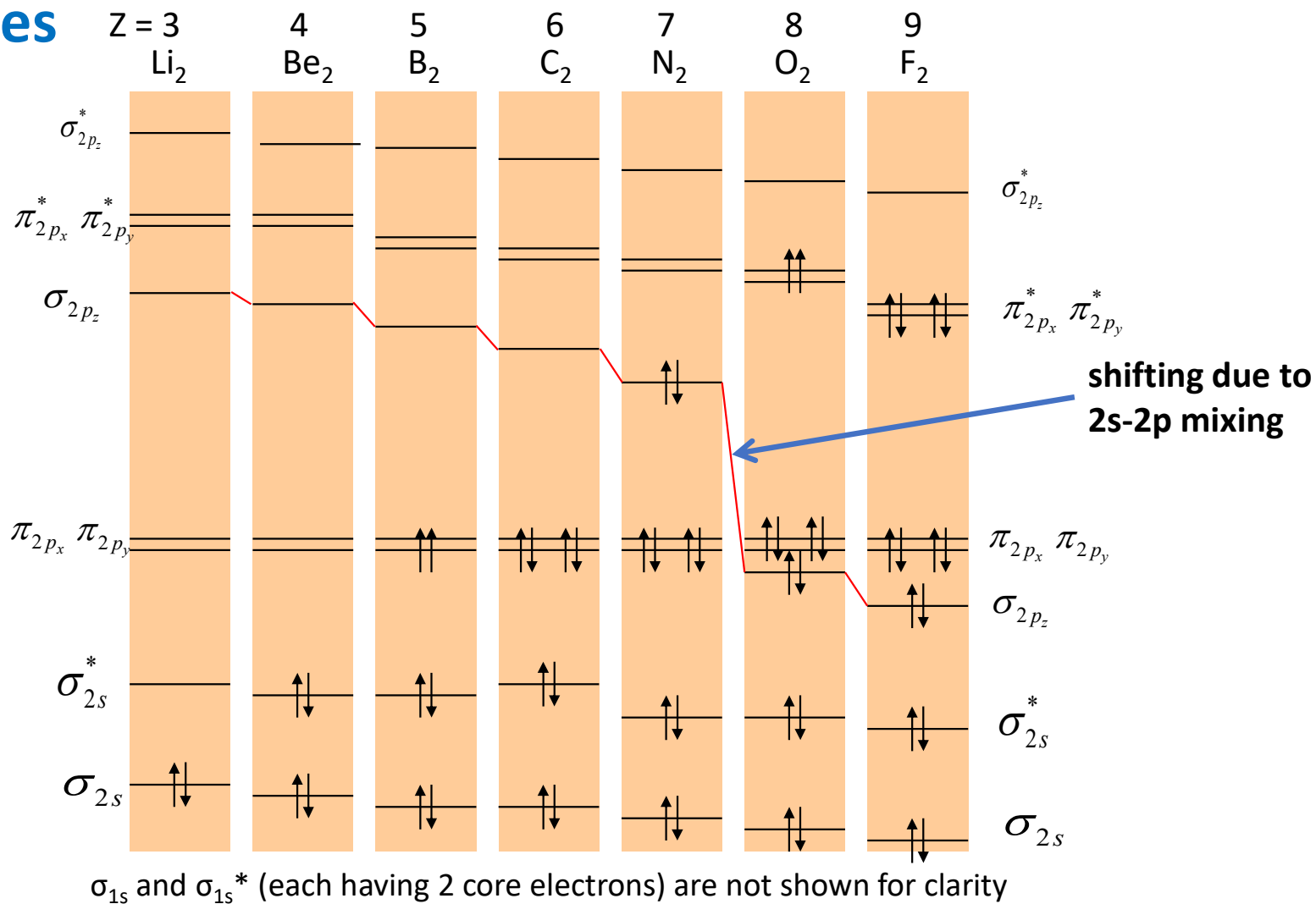
Complication for Lighter Elements ($Z \leq 7$)

- Because σ_{2s} and σ_{2p} MOs occupy the same space (along the bond direction), they interact with each other causing energy levels related to σ_{2p} to shift upwards (interaction called 2s-2p mixing).
- This effect is more pronounced for light elements ($Z \leq 7$) because their 2s and 2p orbitals have smaller energy difference.



Orbital Energies

Can you calculate bond orders and predict their magnetic property?



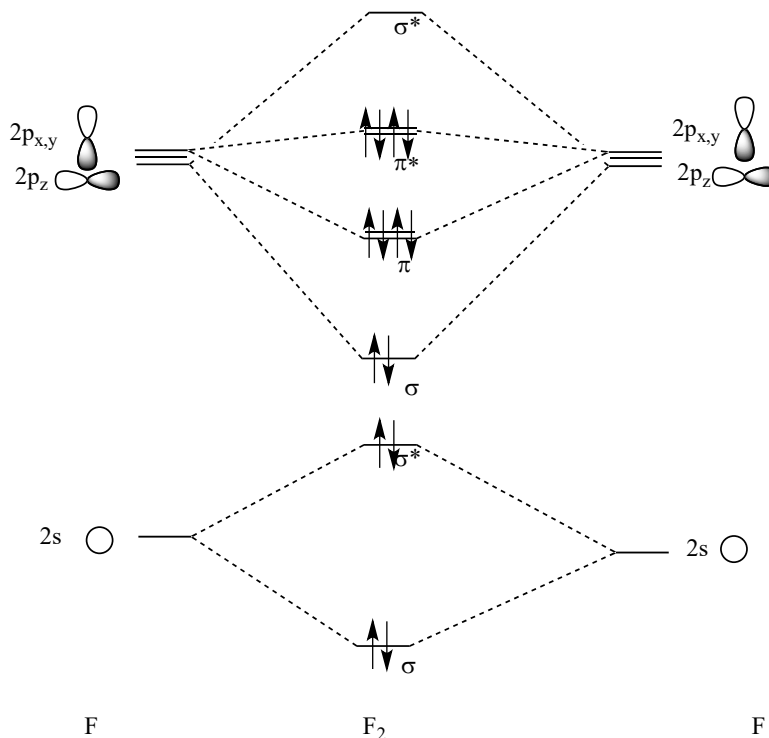
Example 1

The following data show that, removing an electron from N_2 forms an ion with a weaker, longer bond than in the parent molecules, whereas the ion formed from O_2 has a stronger, shorter bond. Can you explain these trends?

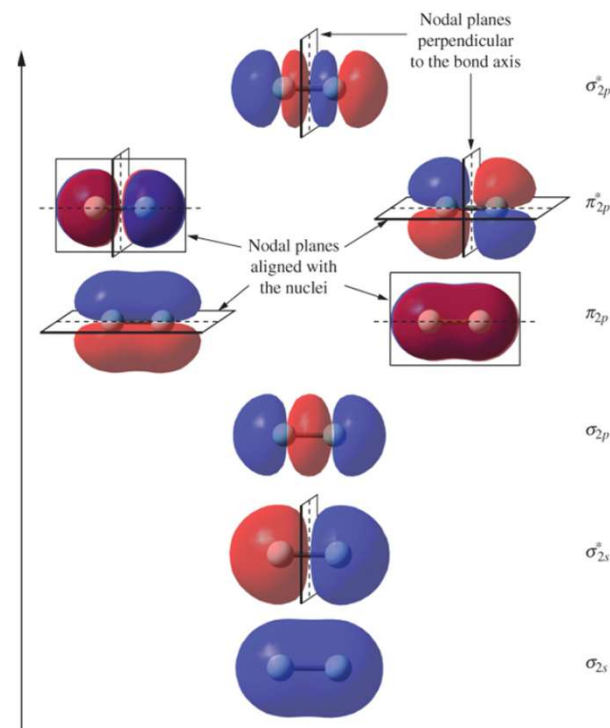
	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

What about lone pairs?

- **Bond order** (# of bond pairs) is determined by the net number of valence electrons in bonding and antibonding MOs. In F_2 , bond order = $(8-6)/2 = 1$ (single bond).
- **Lone pairs** are made from all other valence electrons in bonding and antibonding MOs that are canceled out. # of lone pairs = $12/2 = 6$. Lewis structure for F_2
- **Lewis theory:** lone pairs are localized on atoms.
- **MO theory:** “lone pairs” are shared by the whole molecule.

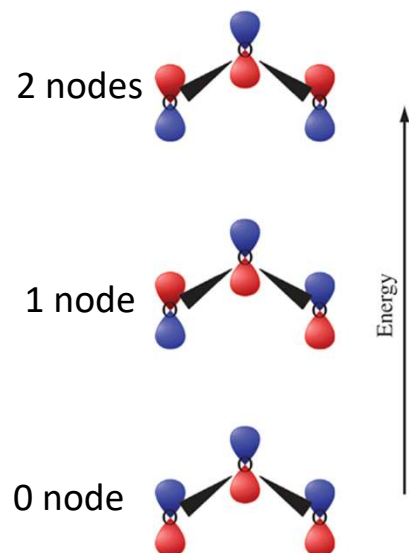
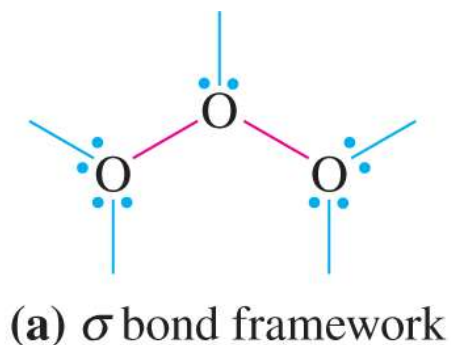
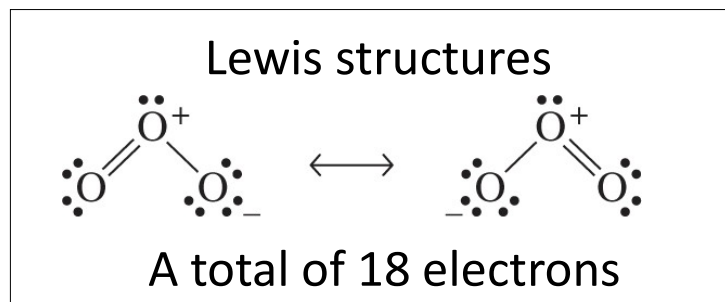


Lewis structure

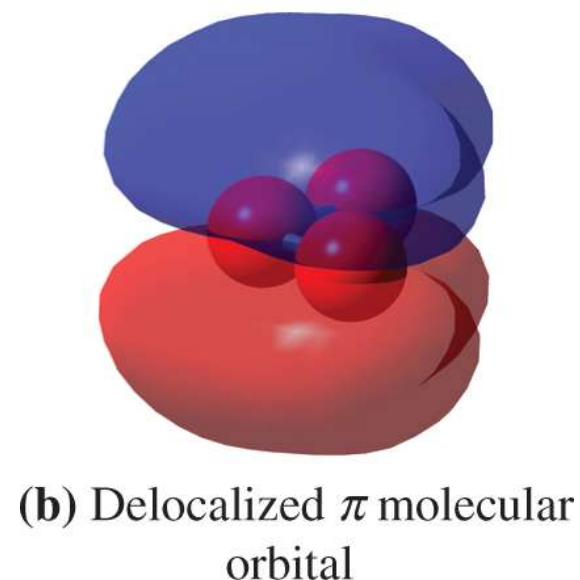
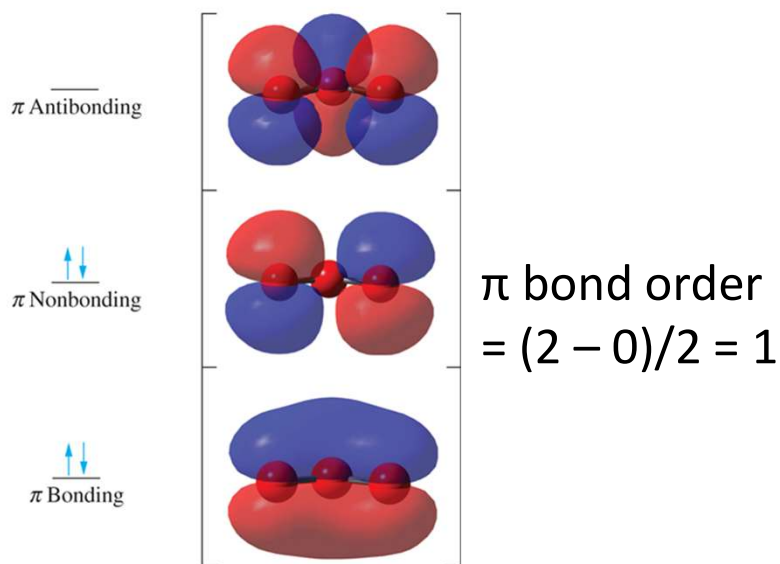


Delocalized Electrons

- **Example:** O_3
- Let's just look at the p orbitals

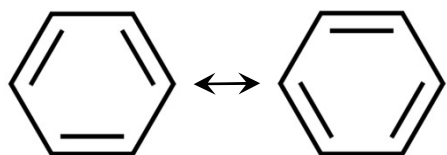


3 unhybridized 2p AOs

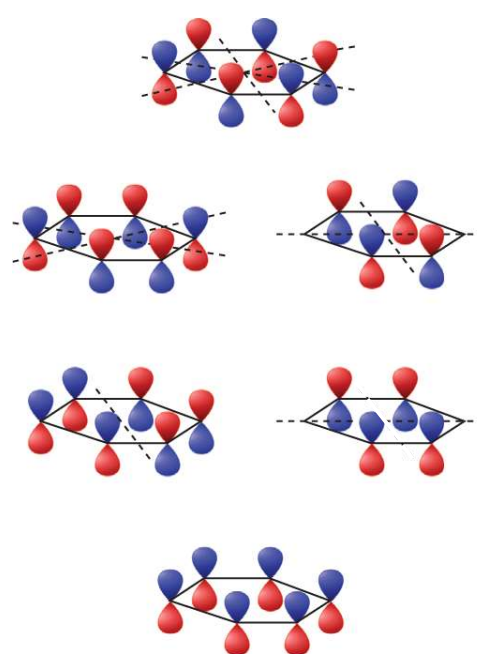


MO Theory & Benzene

MOs show that π electrons are delocalized within the molecule (shared among all 6 carbons).

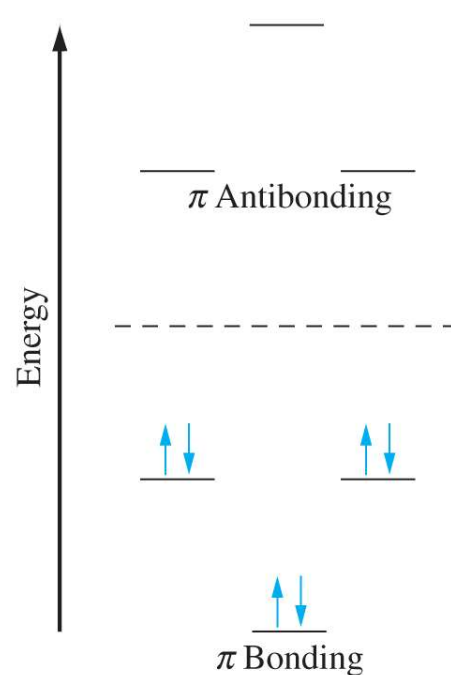


Benzene resonance structures

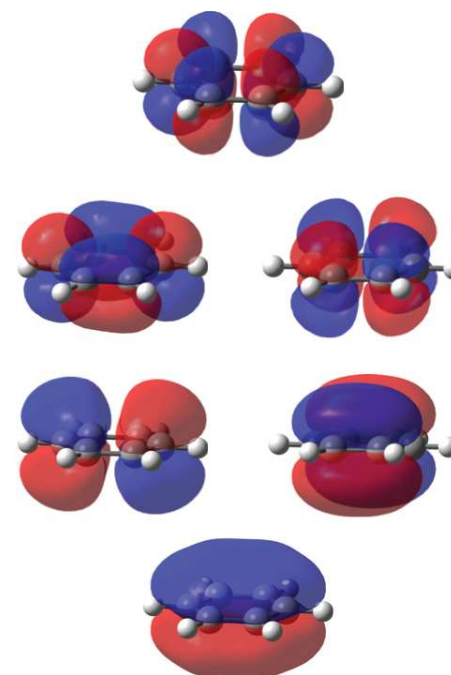


π orbitals of benzene

(a)



(b)

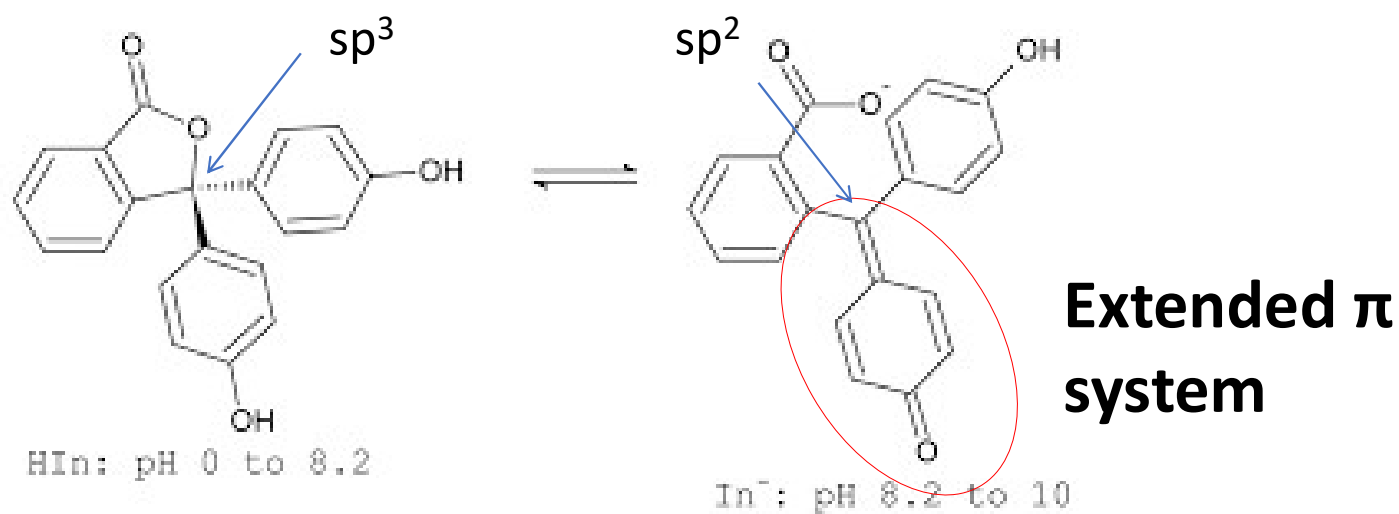


Computed π orbitals

(c)

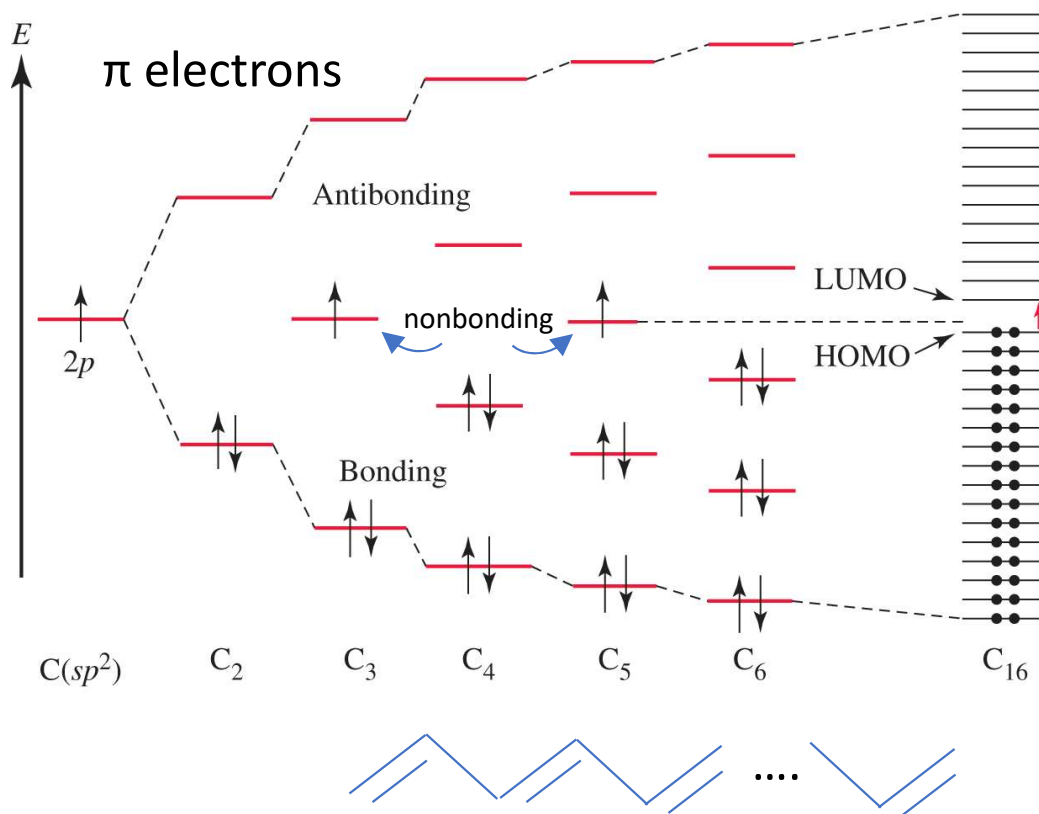
$$\pi \text{ bond order} = (6 - 0)/2 = 3$$

Phenolphthalein



Extended π Systems

Most organic compounds are colorless, because the HOMO-LUMO gap is in the UV region. However, when the extended π system is large enough, this gap can be decreased to visible, giving rise to color of compound.



LUMO=Lowest Unoccupied MO

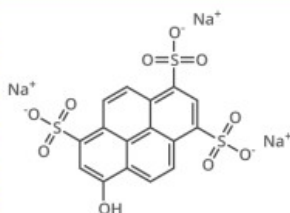
HOMO=Highest Occupied MO

THE CHEMISTRY OF HIGHLIGHTER COLOURS

HIGHLIGHTERS COME IN A RANGE OF COLOURS. THIS GRAPHIC SHOWS A SELECTION OF COMPOUNDS THAT CAN BE USED TO IMPART THESE COLOURS TO THE INK.



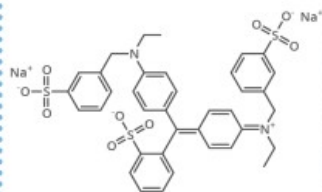
Yellow



PYRANINE - SOLVENT GREEN 7
(Pyrene dye)

Pyranine, a pyrene dye, is the dye commonly used in yellow highlighters. Another compound that can be utilised is fluorescein. By mixing a pyrene dye with a triphenylmethane dye, a green ink can also be obtained.

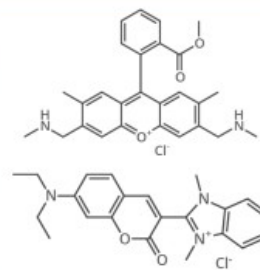
Blue



ACID BLUE 9
(Triphenylmethane dye)

A triphenylmethane dye such as Acid Blue 9 is commonly used to achieve a blue ink colour; it is used in combination with a colour-brightening compound, for example an anionic stilbene derivative.

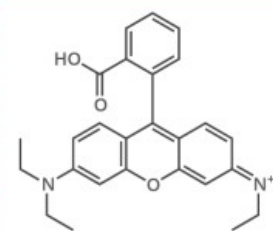
Orange



BASONYL RED 485 (TOP) & BASIC YELLOW 40
(Xanthene dye and Coumarin dye)

A mix of a xanthene dye and a coumarin dye is required to achieve an orange colour.

Pink



SOLVENT RED 49
(Rhodamine dye)

A rhodamine dye can be used to impart a pink colour to the highlighter ink. A rhodamine dye can also be combined with a triphenylmethane dye in order to produce a purple-coloured highlighter.



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<https://www.compoundchem.com/2015/01/22/highlighters/>