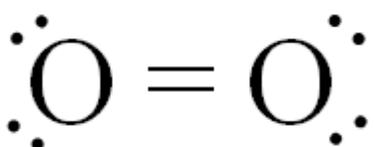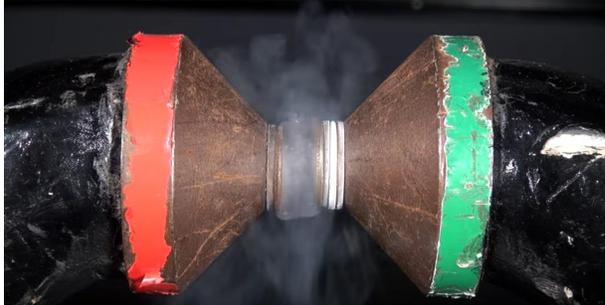# Ch 221 – Summary of Molecular Orbital Theory

I. **Problems With Valence Bond Theory** – does not predict that oxygen has magnetic properties (caused by unpaired electrons, next section)
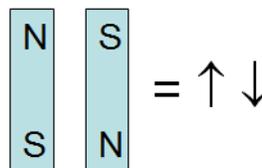

*The Lewis structure of oxygen predicts that all electrons are paired and so should not be magnetic*

Oxygen trapped in a magnetic field
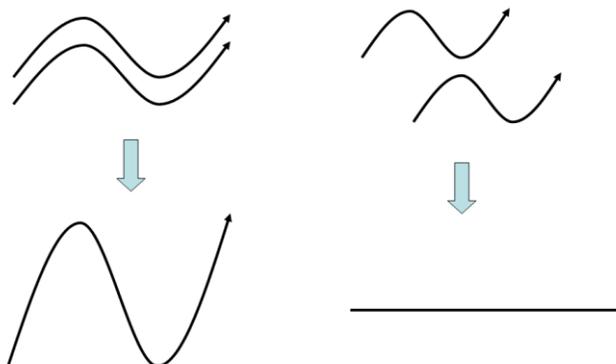
II. **Causes of Magnetism** = unpaired electrons

Diamagnetic materials = all electron spins are "paired", so the magnetic fields cancel out

Zn = [Ar]$3d^{10}4s^2$

$= \uparrow \downarrow$

Paramagnetic materials = unpaired electrons so there is a net magnetism
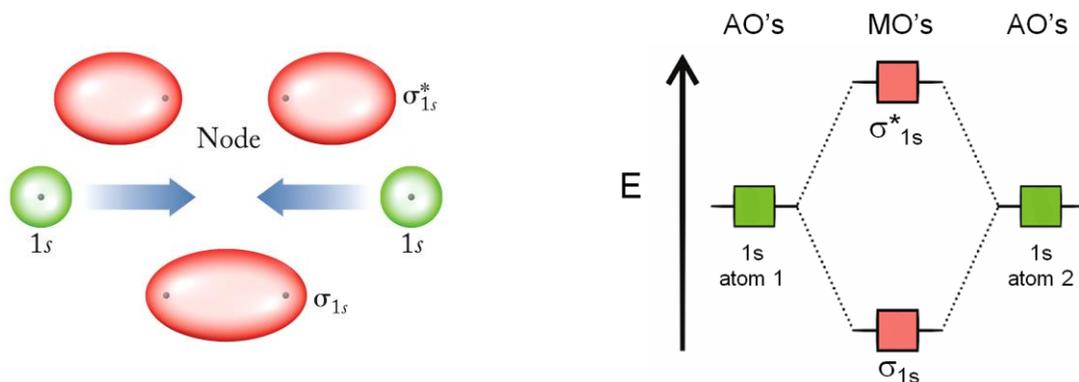
Mn = [Ar]$3d^5 4s^2$

$= \uparrow$
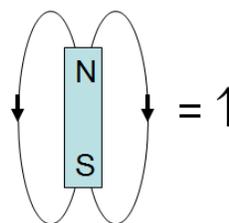
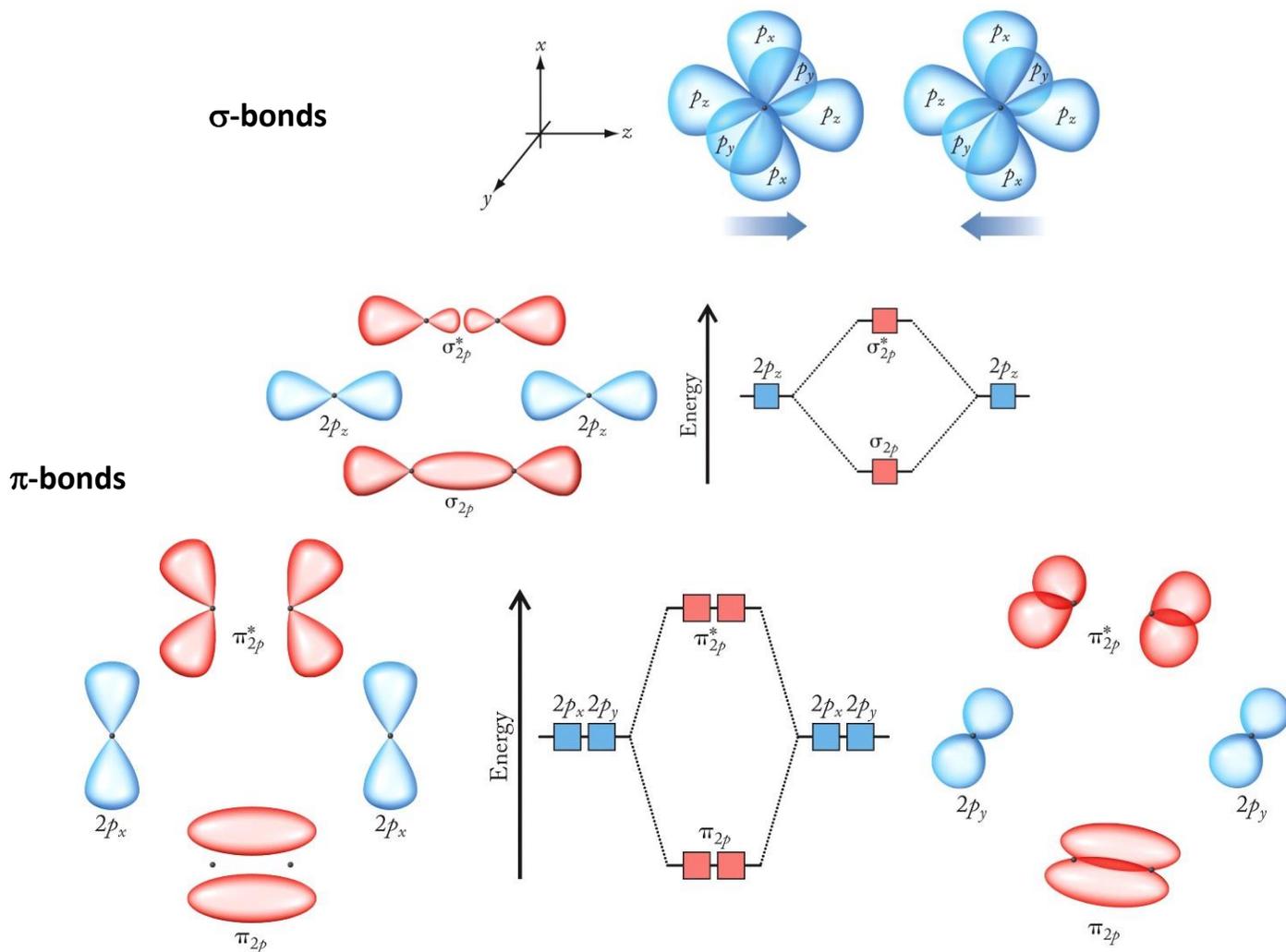III. **Constructive-Destructive Interference** – electrons have wave-like properties

IV. **Molecular Orbitals**: Bonding and Antibonding
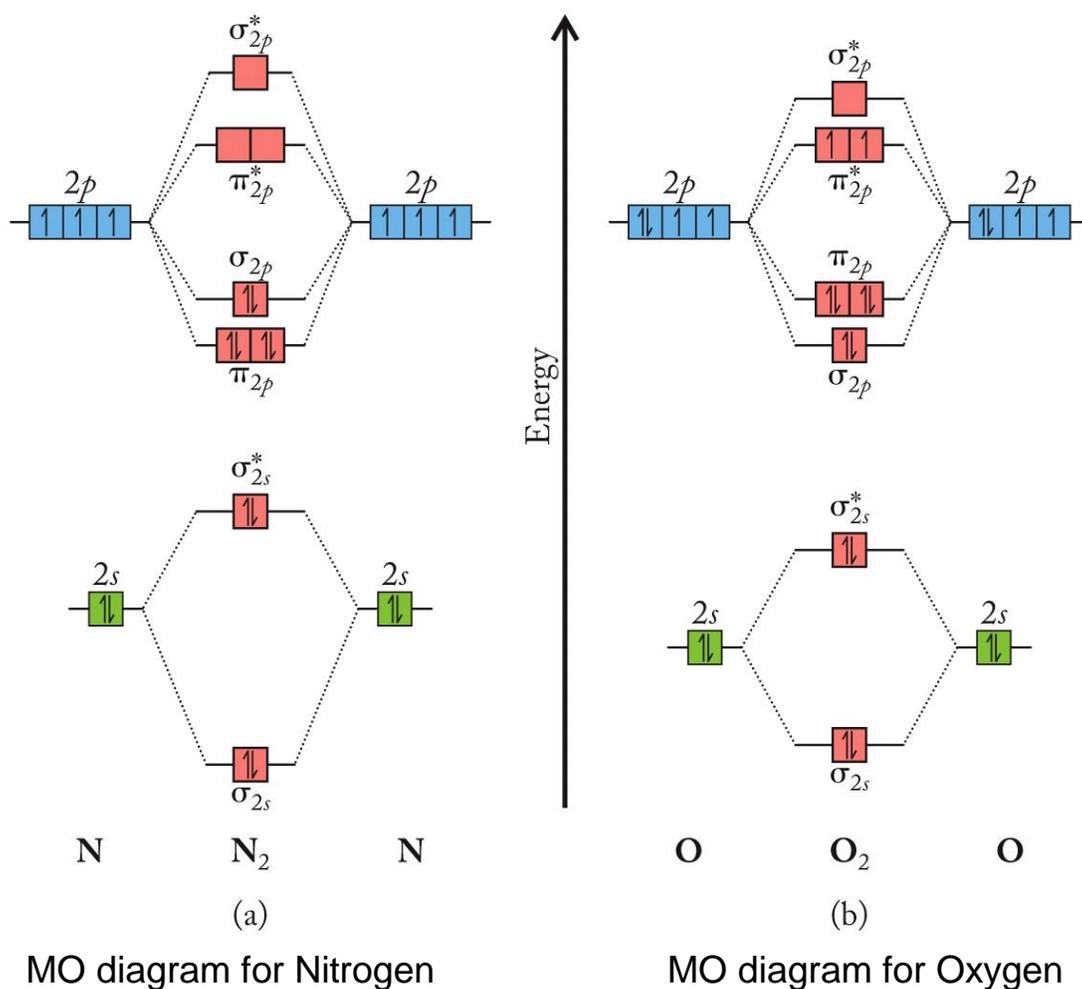
(a) **s-orbitals** = σ bonds (head-to-head overlap)

(b) **p-orbitals** = σ _and_ π bonds (π = side-by-side overlap)

σ-bonds

π-bonds

V. **Rules for filling molecular orbitals** – same as for atoms

(a) **Aufbau Principle** - add electrons to the lowest energy molecular orbitals first
(b) **Pauli Exclusion Principle** – when two electrons share the same orbital the spins must pair up.
(c) **Hund's Rule** – electrons remain unpaired as long as possible (e.g. see the oxygen π^*_{2p} MO's in the diagram below below)

σ^*_{2p}

$2p$ π^*_{2p} $2p$

σ_{2p}

π_{2p}

σ^*_{2s}

$2s$ $2s$

σ_{2s}

N   **N$_2$**   **N**

(a)

MO diagram for Nitrogen

Energy

σ^*_{2p}

$2p$ π^*_{2p} $2p$

π_{2p}

σ_{2p}

σ^*_{2s}

$2s$ $2s$

σ_{2s}

O   **O$_2$**   **O**

(b)

MO diagram for Oxygen

NOTE 1: the σ_{1s} and σ^*_{1s} MO's are not shown because they are all filled and contribute nothing to the *bond order.*
NOTE 2: if the bond order is zero then the molecule dos not exist
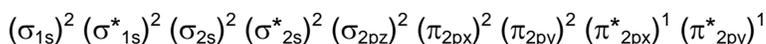
B.O. = ½ (#bonding e's - #anti-bonding e's)

e.g. oxygen (ignoring the σ_{1s} and σ^*_{1s} MO's)

B.O. = ½ (8 - 4) = 2

VI.   **Applications to simple homonuclear diatomics** – be able to:

- fill in the MO diagram (given)
- calculate bond order and predict if the molecule exists or not
- predict any magnetic properties (paramagnetic versus diamagnetic)
- write the molecular electron configuration

e.g. oxygen – MO diagram in previous section. Only the 2px orbital is labelled in the MO diagram but labelled here x,y, and z

$$(\sigma_{1s})^2 \ (\sigma^*_{1s})^2 \ (\sigma_{2s})^2 \ (\sigma^*_{2s})^2 \ (\sigma_{2pz})^2 \ (\pi_{2px})^2 \ (\pi_{2py})^2 \ (\pi^*_{2px})^1 \ (\pi^*_{2py})^1$$

VII.   **Examples for homonuclear diatomics** - Li_2, Be_2, B_2, C_2 and N_2

	Li_2	Be_2	B_2	C_2	N_2
Bond order	1	0	1	2	3
Magnetism	dia	dia	para	dia	dia

NOTE: for Z ≥ 8 the σ_{2p} and π_{2p} MO's switch energies (the MO diagrams will be given)
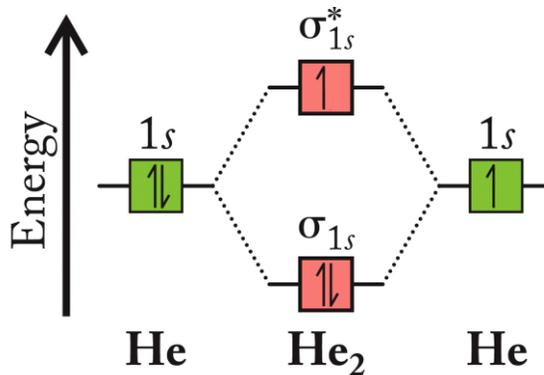

	O_2	F_2	Ne_2
	2	1	0

Examples for ions

(a) **cations**, e.g. He_2^+

- **NOTE 1**: this doesn't mean that each He is +1, it means the molecule is +1 *overall*
- **NOTE 2**: remove an electron from one of the AO's first, and then fill up the MO diagram with the remaining electrons
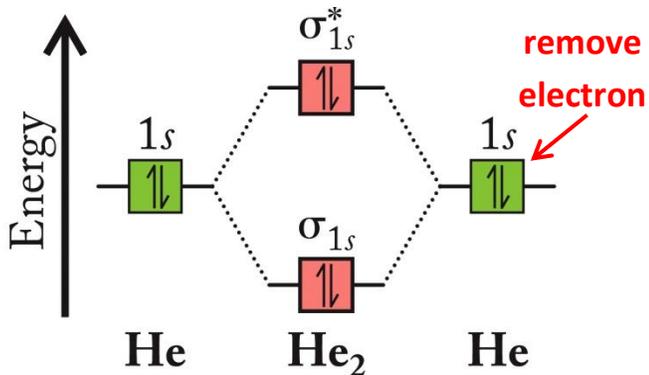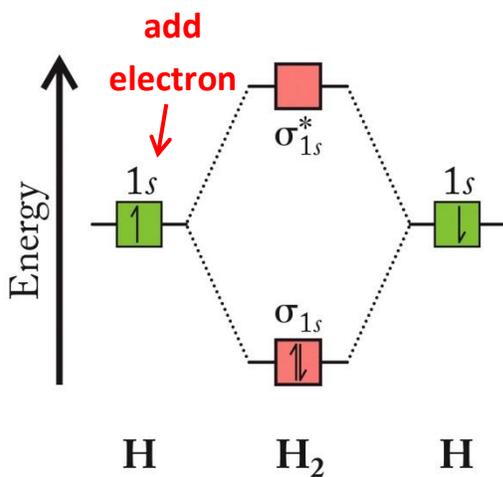

B.O. = ½ (2-2) = 0 (predicts He_2 doesn't exist)
diamagnetic

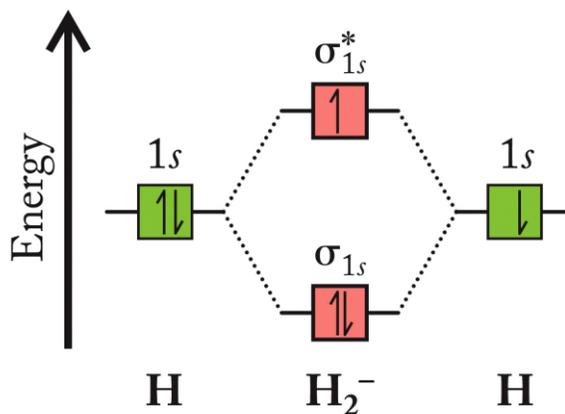B.O. = ½ (2-1) = 0.5 (predicts that He_2^+ exists)
paramagnetic

(b) **anions**, e.g. H_2^-

- Same comments as previously for a cation, except this time ADD an electron to one of the atomic orbitals

B.O. = ½ (2-0) = 1 (exists)
diamagnetic

B.O. = ½ (2-1) = 0.5 (exists)
paramagnetic