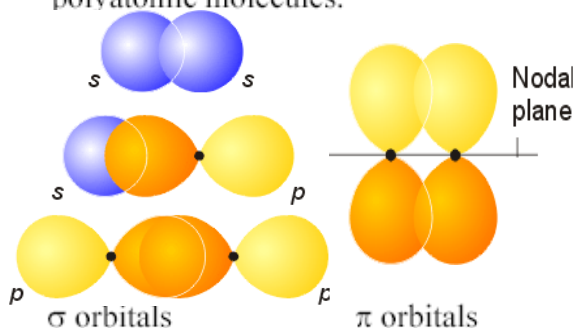


Homonuclear Diatomics

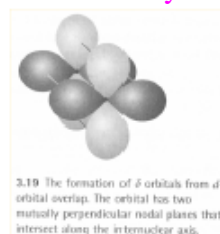
- MOs may be classified according to:
 - Their symmetry around the molecular axis.**
 - Their bonding and antibonding character.**
- $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_y(2p) = \pi_z(2p) < \pi_y^*(2p) = \pi_z^*(2p) < \sigma_{2p}^*$

Classifying orbitals by symmetry

- ◆ Orbitals in diatomics can be classified according to their rotational symmetry characteristics as σ , π or δ . These classifications are strictly only valid for diatomics, but we also use them to describe bonds between pairs of atoms in polyatomic molecules.



dx^2-dy^2 and d_{xy}



δ orbitals
 $[\text{Cl}_4\text{Re} \equiv \text{ReCl}_4]^{2-}$
 Found in quadruply bonded species such as $[\text{Re}_2\text{Cl}_8]^{2-}$

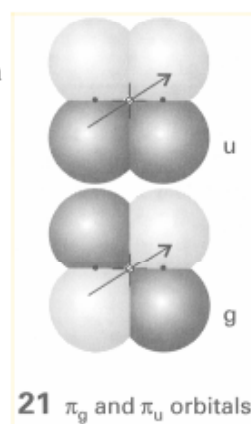
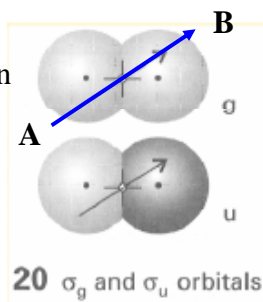
Ungerade or gerade ?

♦ MOs in molecules that are centrosymmetric can be classified as (g) or (u)

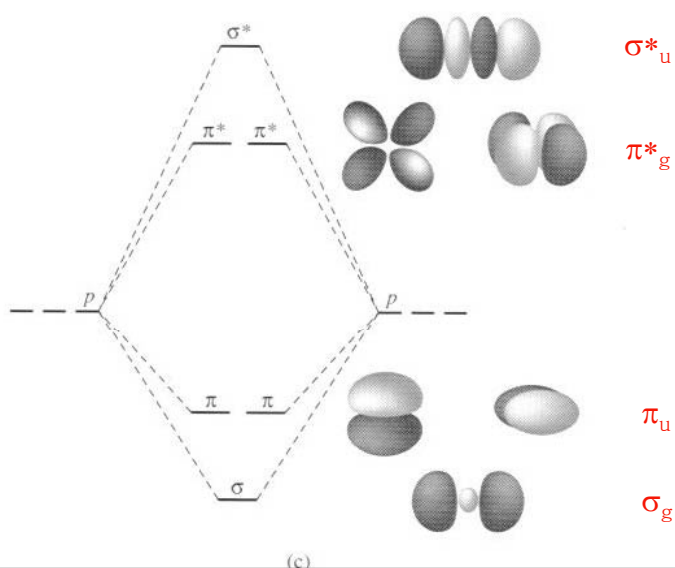
- Useful for predicting spectroscopic transitions etc.
- (g) implies that the wavefunction does not change sign on inversion through the center of the molecule. (u) means that it does change sign

g- identical
under inversion

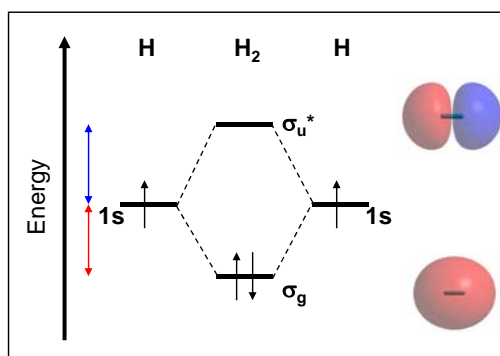
u- not identical



Place labels *g* or *u* in this diagram



First period diatomic molecules



$\sigma 1s^2$

Bond order: 1

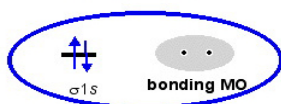
H_2

Bond order = $\frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons})$

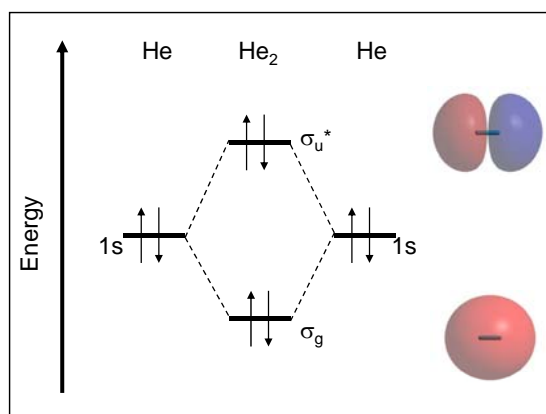
LUMO



HOMO



Diatomic molecules: The bonding in He_2

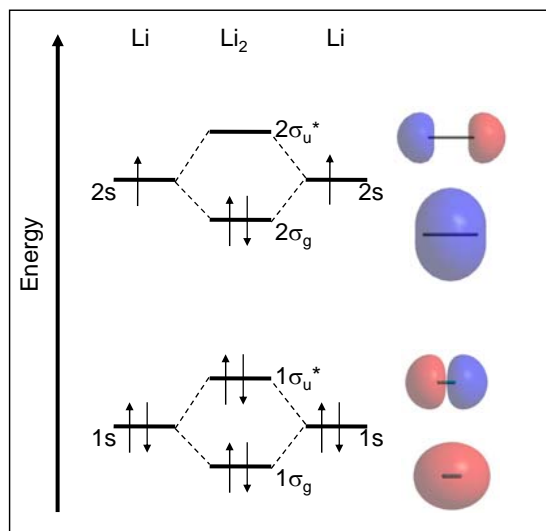


$\sigma 1s^2, \sigma^* 1s^2$

Bond order: 0

Molecular Orbital theory is powerful because it allows us to predict whether molecules should exist or not and it gives us a clear picture of the electronic structure of any hypothetical molecule that we can imagine.

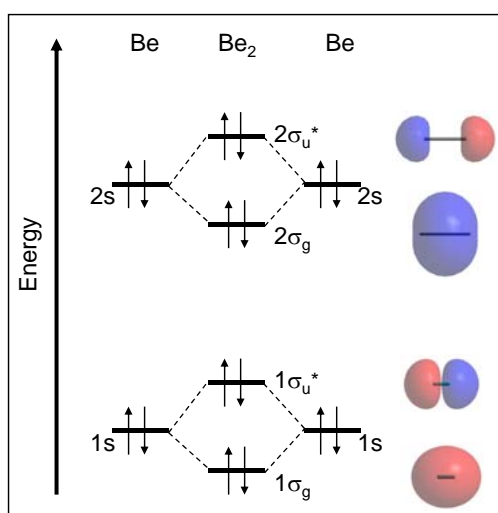
Second period diatomic molecules



$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$

Bond order: 1

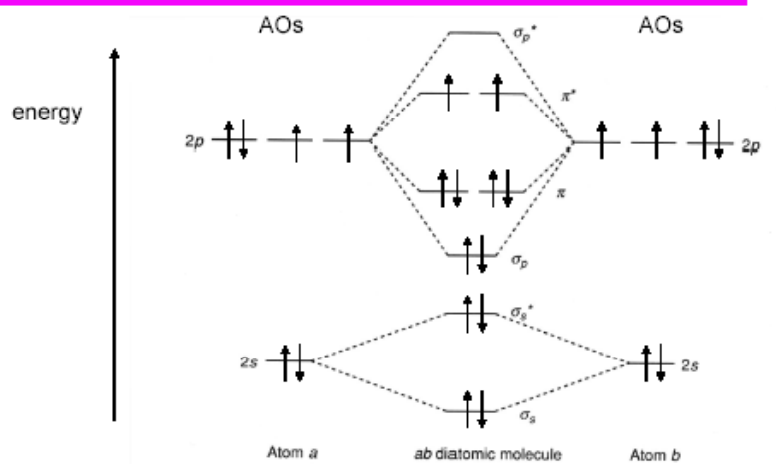
Diatomic molecules: Homonuclear Molecules of the Second Period



$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$

Bond order: 0

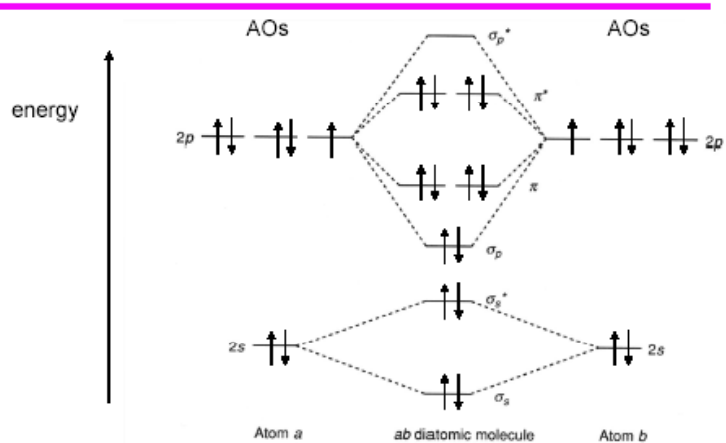
Molecular oxygen



Bond order = 2
2 unpaired electrons → paramagnetic

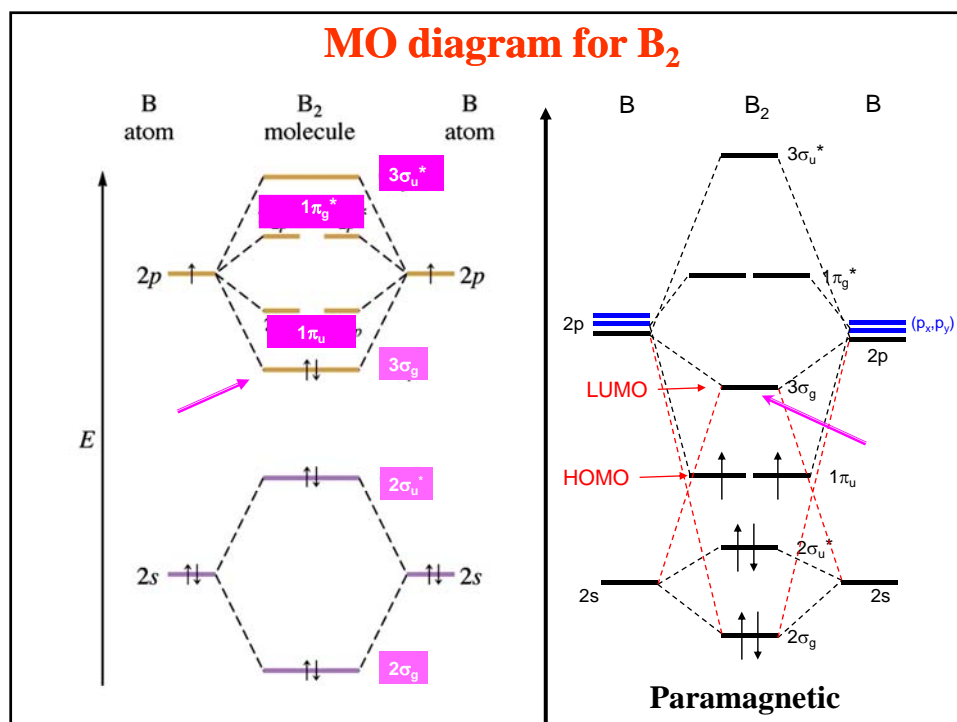
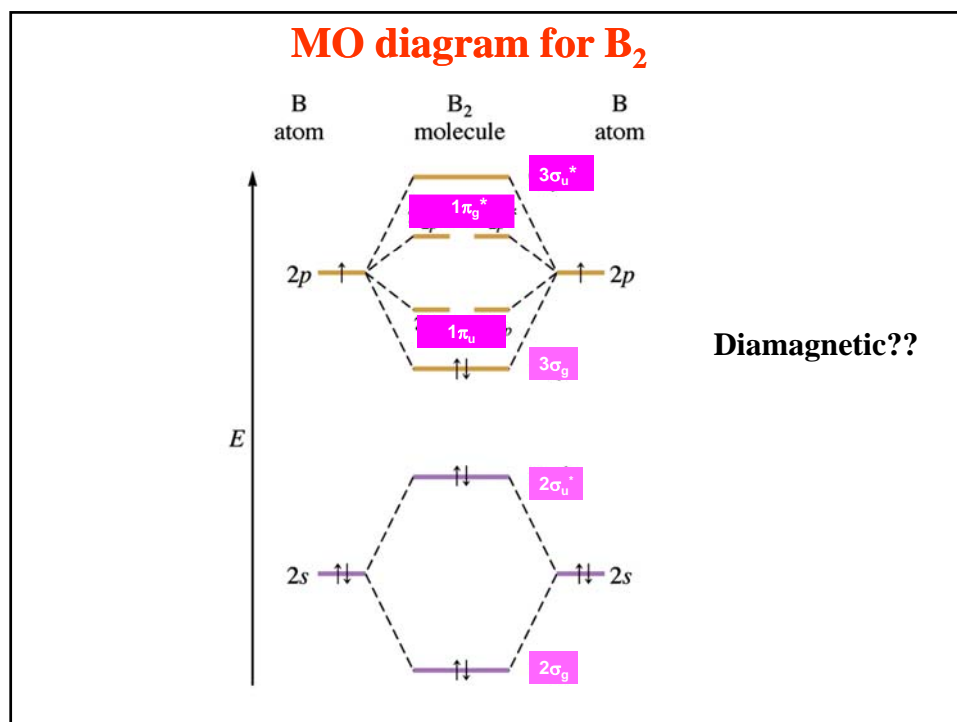
Simplified

Molecular fluorine

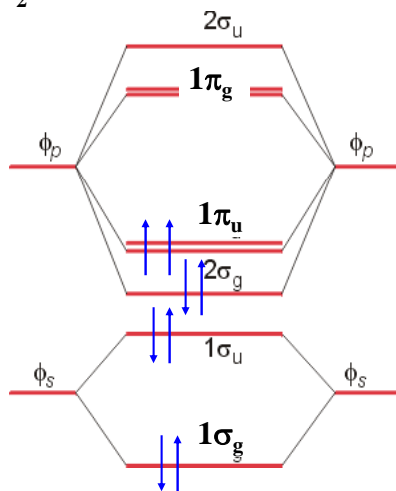


Bond order = 1
0 unpaired electrons → diamagnetic

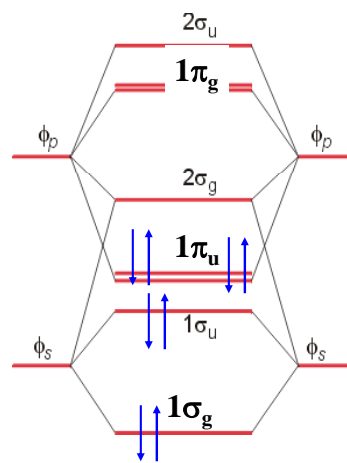
Simplified



C_2

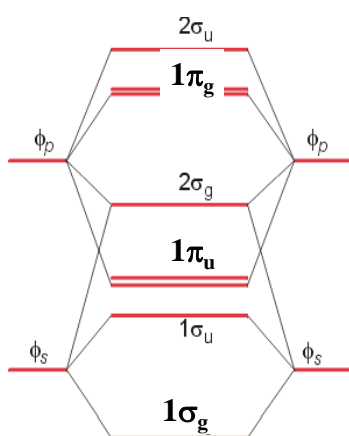


Para~~X~~magnetic ?

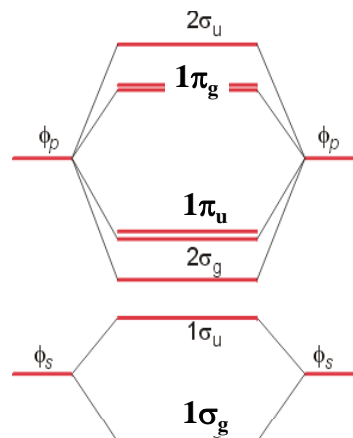


Diamagnetic

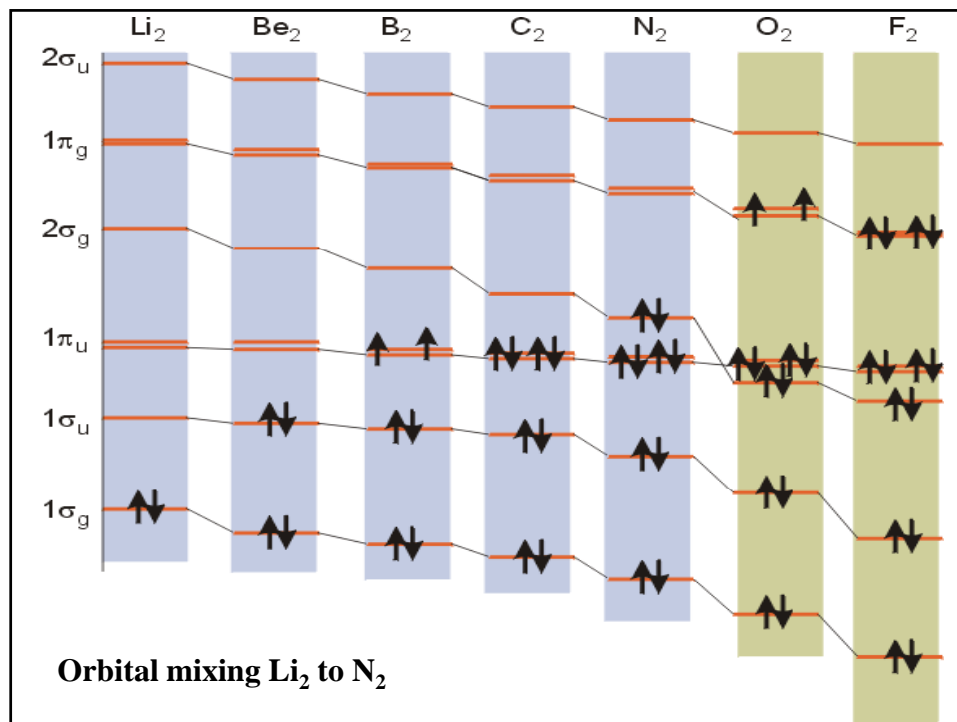
General MO diagrams



Li_2 to N_2



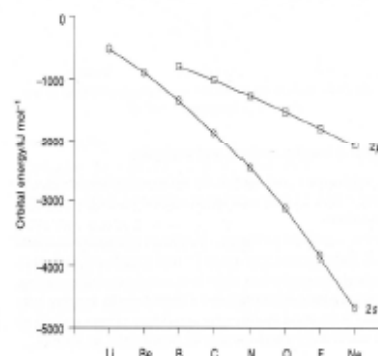
O_2 and F_2



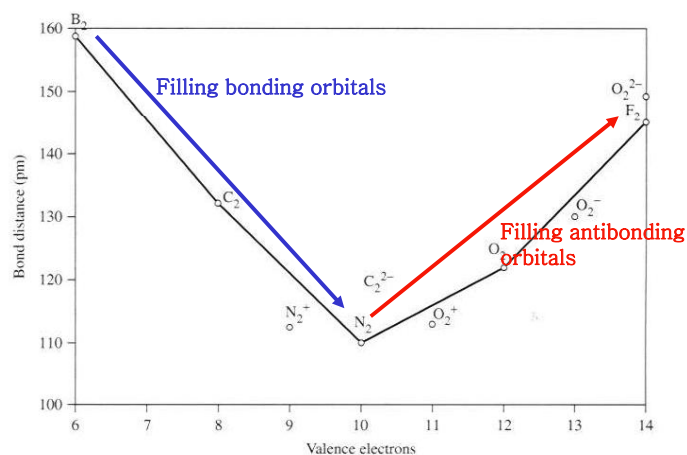
Orbital Mixing

- Orbitals with similar energy interact, if they have the appropriate symmetries
- The σ_{2p} and σ_{2s} orbitals are symmetry related and give rise to two new orbitals, one with higher and one with lower energy

Li : 200 kJ/mol
F : 2500 kJ/mol



Bond lengths in diatomic molecules



Bond Order vs. Bond Length & Energy

Species	Bond order	Bond length/pm	Bond energy/kJ mol ⁻¹
H ₂ ⁺	1/2	105.2	256
H ₂	1	74.1	432
H ₂ ⁻	1/2	—	100–200
He ₂	0	297	0.1*
Li ₂	1	267.3	101
Be ₂	0	—	4
B ₂	1	159	289
C ₂	2	124.25	599
N ₂	3	109.8	942
O ₂	2	<u>120.7</u>	<u>493</u>
O ₂ ⁺	2 1/2	111.6	643
O ₂ ⁻	1 1/2	<u>135</u>	<u>395</u>
O ₂ ²⁻	1	149	—
F ₂	1	141.2	155
Ne ₂	0	310	0.2*

*Van der Waal forces.

Summary

From a basis set of N atomic orbitals, N molecular orbitals are constructed. In Period 2, $N=8$.

The eight orbitals can be classified by symmetry into two sets: 4 σ and 4 π orbitals.

The four π orbitals from one doubly degenerate pair of bonding orbitals and one doubly degenerate pair of antibonding orbitals.

The four σ orbitals span a range of energies, one being strongly bonding and another strongly antibonding, with the remaining two σ orbitals lying between these extremes.

To establish the actual location of the energy levels, it is necessary to use absorption spectroscopy or photoelectron spectroscopy.

Heteronuclear diatomics

- ◆ The contributions to the MO from each of the atoms is unequal
 - $\psi = c_A\phi(A) + c_B\phi(B) + \dots$
- ◆ The more electronegative atom contributes strongly to the bonding orbital
- ◆ The less electronegative atom contributes strongly to the anti-bonding orbital
 - gives rise to polarity

Distance between b-MO and AO

Heteronuclear Diatomics....

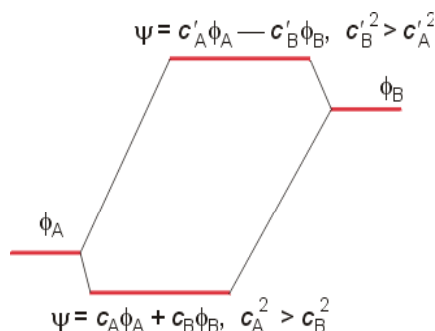
✉ The energy level diagram is not symmetrical.

✉ The bonding MOs are closer to the atomic orbitals which are lower in energy.

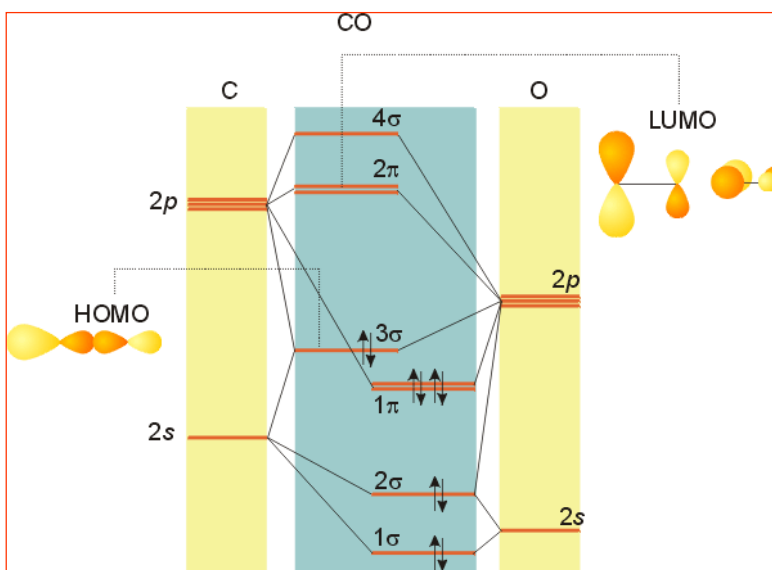
✉ The antibonding MOs are closer to those higher in energy.

c – extent to which each atomic orbitals contribute to MO

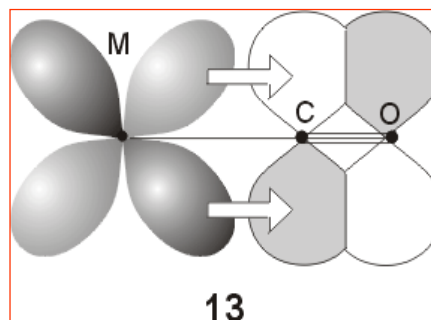
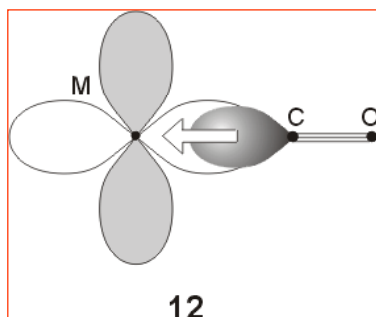
If $c_A > c_B$ the MO is composed principally of ϕ_A



MO of CO



Stabilizing Low Oxidation State: CO Can Do the Job



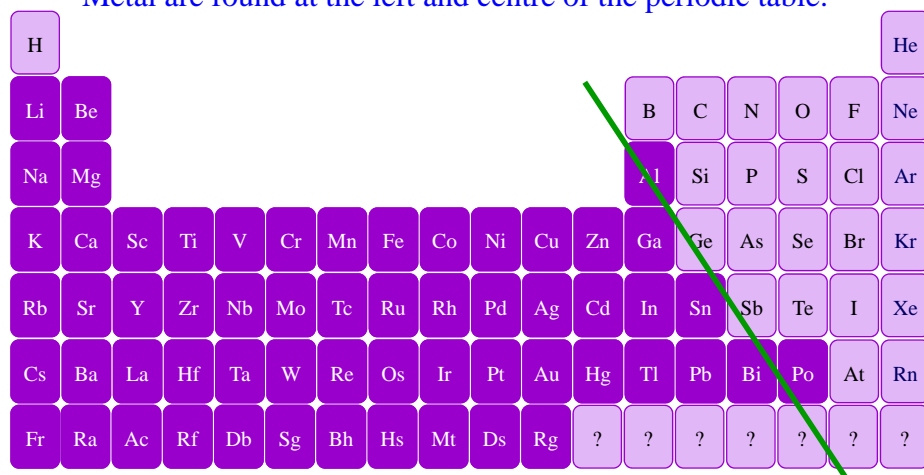
Ni(CO)_4 , $\text{[Fe(CO)}_5\text{]}$, $\text{[Cr(CO)}_6\text{]}$, $\text{[Mn}_2\text{(CO)}_{10}\text{]}$, $\text{[Co}_2\text{(CO)}_8\text{]}$,
 $\text{Na}_2\text{[Fe(CO)}_4\text{]}$, $\text{Na[Mn(CO)}_5\text{]}$

Metallic Bonding



Metals in the periodic table

Metal are found at the left and centre of the periodic table.

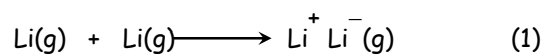


H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	?	?	?	?	?	?	?

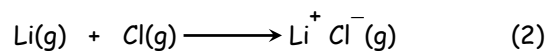
Nature of Metallic Bonding

Not ionic.....

atoms of the same electronegativity



No favourable

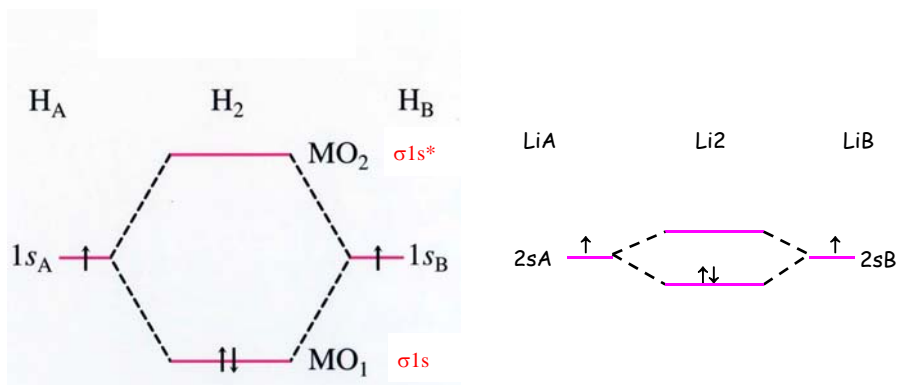


favourable

Not covalent....

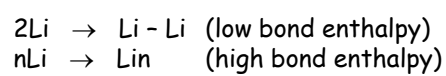
efficiency of orbital overlap decreases as the bonding atoms get larger

MO approach....



Conclusion :

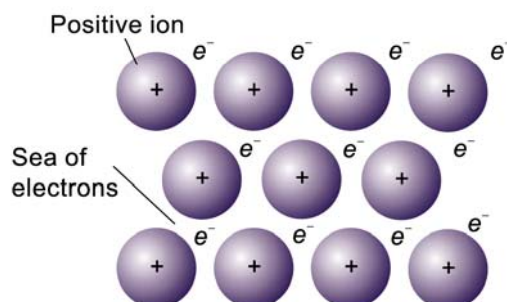
1. Metals tend to form giant structures rather than discrete molecules.



Stronger bonds are formed due to extensive delocalization of valence electrons.

Conclusion...

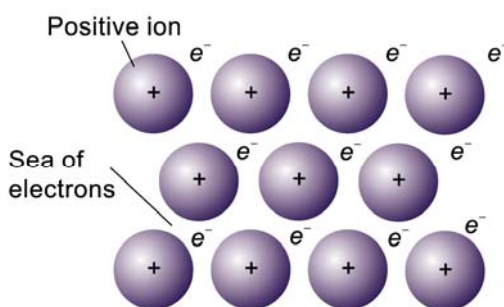
2. The electron-sea model



The valence electrons do not belong to any specific atoms (not localized) but delocalize throughout the whole crystal structure.

Conclusion....

2. The electron-sea model



Mobile e⁻s → electron sea Stationary +ve ions

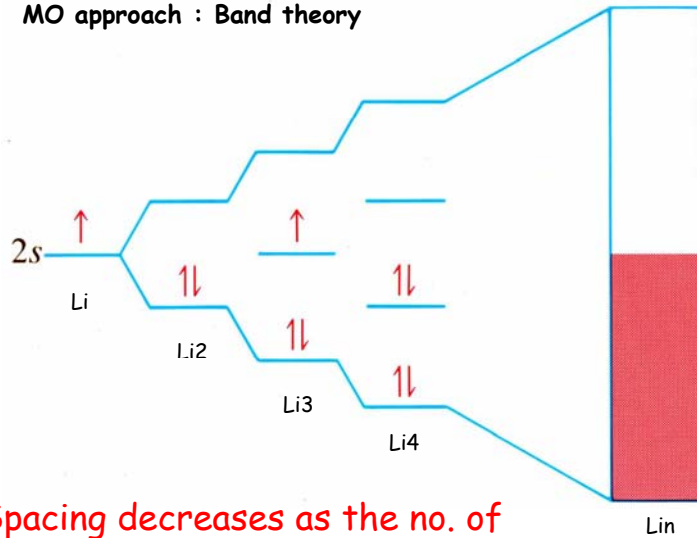
The electrostatic attractive forces between the delocalized electron cloud and the positive ions are called the metallic bonds

Since metallic bonds are non-directional, they exist in significant extent even in molten state.

The boiling points of metals are much higher than the corresponding melting points. E.g. Na m.p. = 97.8 °C ; b.p. = 903.8 °C

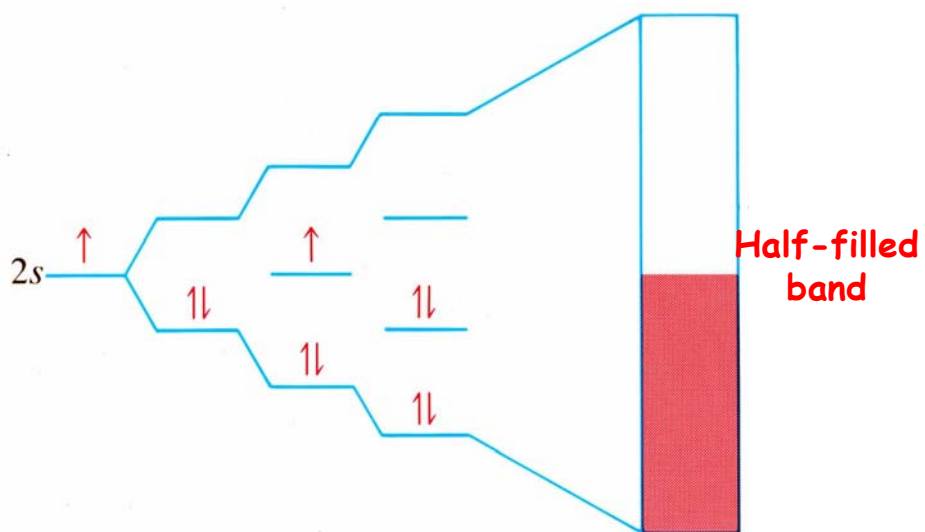
Conclusion : -

3. MO approach : Band theory

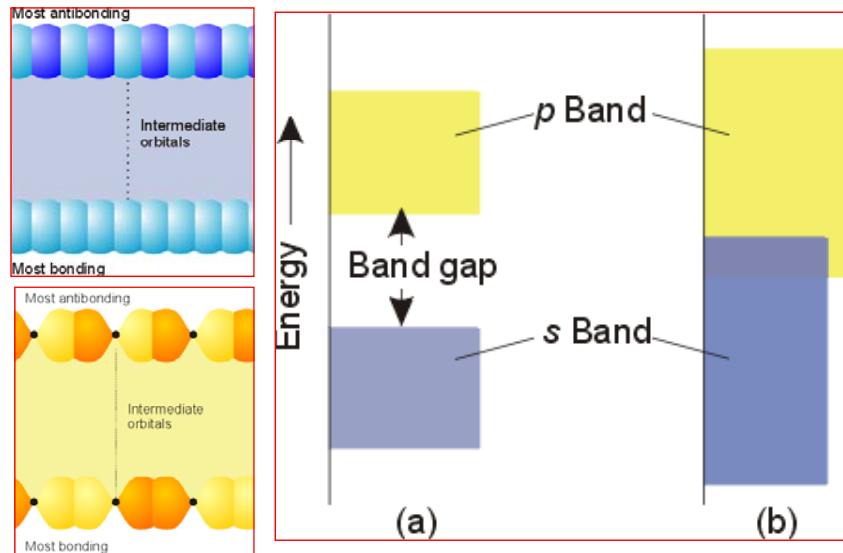


Spacing decreases as the no. of molecular orbitals increases...

Lin : n orbitals overlap \rightarrow continuous band



MOT OF SOLIDS: BAND & BAND GAP

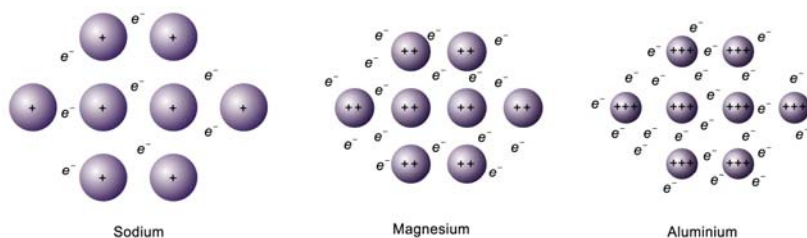


33

The strength of metallic bond can be estimated by
melting point,
boiling point,
enthalpy change of fusion or
enthalpy change of vapourization.

Higher m.p./b.p./ ΔH_{fusion} / ΔH_{vap}
 \Rightarrow stronger metallic bond

3 Factors affecting the strength of metallic bond



The metallic bond strength increases with:

1. decreasing size of the metal atom
(i.e. the metallic radius);
2. increasing number of valence electrons
of the metal atom.

Typical properties of metals

1. High density

Reason: close packing of atoms in metallic crystal (h.c.p./f.c.c. co-ordination number = 12)

Metal	Ni	Cu	Ag	Pb	Hg	Au
Density (g cm^{-3})	8.91	8.94	10.49	10.66	13.53	19.30

Exception : Alkali metals have low densities
(< 1 for Li, Na and K)

- (a) they have more open structures
(b.c.c. /co-ordination number = 8)
- (b) their atomic radii are the highest in their own
Periods.

E.g. Size : Na > Mg > Al

2. High melting point and boiling point

Extensive delocalization of valence electrons \Rightarrow stronger bonds

Bond strength : -

ionic bond \approx covalent bond \approx metallic bond

3. High flexibility

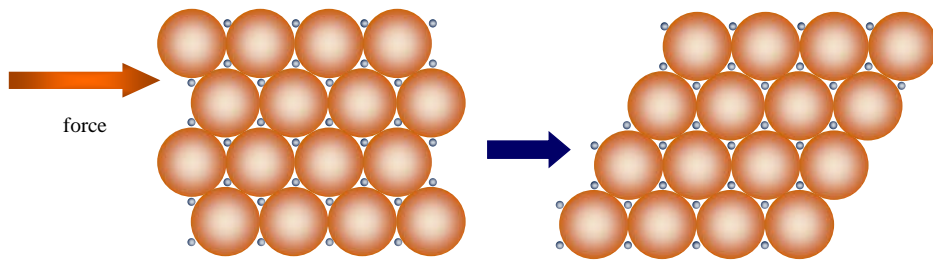
Malleability :

The ability to be deformed under compression

Ductility :

The ability to be deformed under tension

- Metals are usually tough, not brittle. When a metal is hit, the layers of the lattice just slide over each other. The metallic bonds do not break because the electrons are free to move.



This means that metals are:

- **malleable** – they can be bent and pressed into shape;
- **ductile** – they can be drawn out into wires.

Reasons : -

- (a) The presence of layers in the crystal lattice
i.e. the layers can slide over one another under strain
- (b) Metallic bonds are non-directional.
i.e. electrons can take up new positions and reform metallic bond after the deformation

4. Surface Luster

5. High Thermal and Electrical Conductivity

Due to the free movement of delocalized electrons

Silver is the best conductor of electricity and copper is the second best.



Why is copper used instead of silver for electrical wires?

