

Inorganic Chemistry

Books to Refer:

1. Inorganic Chemistry by Shriver & Atkins
2. Inorganic Chemistry by James E. Huheey
3. WILEY Engineering Chemistry – 2nd Ed. 2013
4. Solid State Chemistry: An introduction, 4th Ed., CRC Press.; Moore and Smart.

Inorganic Syllabus

Chapter-1:	Bonding and Coordination Chemistry
Chapter-2:	Organometallics and Catalysis
Chapter-3:	Redox chemistry
Chapter-4:	Materials Chemistry

- **Bonding and Coordination Chemistry:** Bonding in homo- (Li_2 to $\text{N}_2 \text{O}_2$ and F_2) and heterodinuclear (only CO). CFT and application of CFT. From Laboratory to Living Systems. Spectroscopic, magnetic, functional properties of new age coordination compounds, and Hemoglobin. (5 lectures)
- **Organometallics and Catalysis:** Metal carbonyls. Oxidative addition and reductive elimination, insertion and elimination reactions. Hydrogenation (Wilkinson's catalyst), Carbonylation (Monsanto Process) (3 lectures)
- **Redox chemistry:** Diagrammatic representation and use of Latimer and Frost diagram. Applications of redox chemistry in energy storage (primary and secondary batteries). (3 lectures)
- **Materials Chemistry:** Metal oxides, spinel, superconductor, and boron nitride. (1-2 lectures)

Important Instruction

- Must attend all the Regular and Tutorial classes

Mode of Evaluation

- **3 (Three) Assignments:** Detail instruction will be sent
- **One Online Test for Inorganic** (through moodle platform)

Tutorial Classes

- Online platform: Googlemeet
- Separate link will be shared by TA

What to do in Tutorial Classes?

Doubt clearing/additional discussion/Question-Answer

Section	Day and Time	TA's name	TA's email id
15 (A+B)			
15 (C+D)			
16 (A+B)			
16 (C+D)			

What is Inorganic Chemistry? Why to read? Role in real life?

MODERN PERIODIC TABLE OF THE ELEMENTS LONG FORM

Groups	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A
Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H HYDROGEN								BORON	CARBON	NITROGEN	OXYGEN	FLUORINE					HELIUM
2	Li LITHIUM	Be BERYLLIUM							B	C	N	O	F					He NEON
3	Na SODIUM	Mg MAGNESIUM												Al ALUMINUM	Si SILICON	P PHOSPHORUS	S SLUPHUR	Cl CHLORINE
4	K POTASSIUM	Ca CALCIUM	Sc SCANDIUM	Ti TITANIUM	V VANADIUM	Cr CHROMIUM	Mn MANGANESE	Fe IRON	Co COBALT	Ni NICKEL	Cu COPPER	Zn ZINC	Ga GALLIUM	Ge GERMANIUM	As ARSENIC	Se SELENIUM	Br BROMINE	Kr KRYPTON
5	Rb RUBIDIUM	Sr STRONTIUM	Y YTTRIUM	Nb ZIRCONIUM	Mo NIOBIUM	Tc MOLYBDENUM	Tn TECHNETIUM	Ru RUTHENIUM	Rh RHODIUM	Pd PALLADIUM	Ag SILVER	Cd CADMIUM	In INDIUM	Tl TELLURIUM	Sb ANTIMONY	Te IODINE	Xe XENON	
6	Cs CESIUM	Ba BARIUM	La LANTHANUM	Hf HAFNIUM	Ta TANTALUM	W TUNGSTEN	Rhenium	Os OSMIUM	Ir IRIDUM	Pt PLATINUM	Gold	Mercury	Th THALLIUM	Pb LEAD	Bi BISMUTH	Po POLONIUM	At ASTATINE	Rn RADON
7	Fr FRANCIUM	Ra RADIUM	Ac ACTINIUM	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Metasternum	Darmstadtium	Unununium	Ununtrium	Ununpentium	Ununhexium	Ununseptium	Uuo UNNOCTIUM	Uuu UNUNOCTIUM	
	INDEX																	
	Atomic Number Density (g/cm³) Atomic Radius Molting Point (°C) Symbol Electron Structure	Atomic Weight Electro First Ionization Energy Oxidation State Year of Discovery Name																
	Solids are shown in Gases are shown in Liquids are shown in Synthetic elements are shown in () indicates most stable isotope Radioactive elements are marked by	Black Red Green Orange Radiation symbol																

Chemical Bonding

- Two existing theories,
- Molecular Orbital Theory (MOT)
- Valence Bond Theory (VBT)

Molecular Orbital Theory

- MOT starts with the idea that the quantum mechanical principles applied to atoms may be applied equally well to the molecules.

MOT: We can write the following principles

- ✉ Describe Each electron in a molecule by a certain wave function Ψ - Molecular Orbital (MO).
- ✉ Each Ψ is defined by certain quantum numbers, which govern its energy and its shape.
- ✉ Each Ψ is associated with a definite energy value.
- ✉ Each electron has a spin, $\pm \frac{1}{2}$ and labeled by its spin quantum number m_s .
- ✉ When building the molecule- Aufbau Principle (Building Principle) - Pauli Exclusion Principle.

Simplest possible molecule: H_2^+ : 2 nuclei and 1 electron.

- Let the two nuclei be labeled as A and B & wave functions as Ψ_A & Ψ_B .
- Since the complete MO has characteristics separately possessed by Ψ_A and Ψ_B ,
 - $\Psi = C_A \Psi_A + C_B \Psi_B$
 - or $\Psi = N(\Psi_A + \lambda \Psi_B)$
- $\lambda = C_B/C_A$, and N - normalization constant

This method is known as Linear Combination of Atomic Orbitals or LCAO

- Ψ_A and Ψ_B are same atomic orbitals except for their different origin.
- By symmetry Ψ_A and Ψ_B must appear with equal weight and we can therefore write
- $\lambda^2 = 1$, or $\lambda = \pm 1$
 - Therefore, the two allowed MO's are
 - $\Psi = \Psi_A \pm \Psi_B$

For $\Psi_A + \Psi_B$
we can now calculate the energy

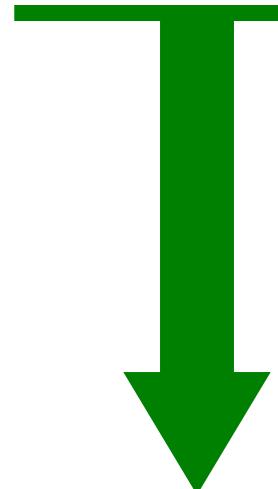
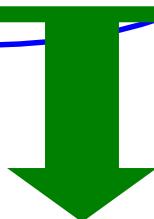
- From Variation Theorem we can write the energy function as
- $E = \langle \Psi_A + \Psi_B | H | \Psi_A + \Psi_B \rangle / \langle \Psi_A + \Psi_B | \Psi_A + \Psi_B \rangle$

Looking at the numerator:

$$E = \underbrace{\langle \Psi_A + \Psi_B | H | \Psi_A + \Psi_B \rangle}_{\text{Numerator}} / \langle \Psi_A + \Psi_B | \Psi_A + \Psi_B \rangle$$

- $\langle \Psi_A + \Psi_B | H | \Psi_A + \Psi_B \rangle = \langle \Psi_A | H | \Psi_A \rangle +$
- $\langle \Psi_B | H | \Psi_B \rangle +$
- $\langle \Psi_A | H | \Psi_B \rangle +$
- $\langle \Psi_B | H | \Psi_A \rangle$
- $= \langle \Psi_A | H | \Psi_A \rangle + \langle \Psi_B | H | \Psi_B \rangle + 2\langle \Psi_A | H | \Psi_B \rangle$

$$= \langle \Psi_A | H | \Psi_A \rangle + \langle \Psi_B | H | \Psi_B \rangle + 2 \langle \Psi_A | H | \Psi_B \rangle$$



ground state energy of a hydrogen atom. let us call this as E_A

$$\langle \Psi_A | H | \Psi_B \rangle = \langle \Psi_B | H | \Psi_A \rangle = \beta$$

β = resonance integral

\therefore Numerator = $2E_A + 2\beta$

Looking at the denominator:

$$E = \frac{\langle \Psi_A + \Psi_B | H | \Psi_A + \Psi_B \rangle}{\langle \Psi_A + \Psi_B | \Psi_A + \Psi_B \rangle}$$

- $\langle \Psi_A + \Psi_B | \Psi_A + \Psi_B \rangle = \langle \Psi_A | \Psi_A \rangle +$
- $\qquad\qquad\qquad \langle \Psi_B | \Psi_B \rangle +$
- $\qquad\qquad\qquad \langle \Psi_A | \Psi_B \rangle +$
- $\qquad\qquad\qquad \langle \Psi_B | \Psi_A \rangle$
- $= \langle \Psi_A | \Psi_A \rangle + \langle \Psi_B | \Psi_B \rangle + 2\langle \Psi_A | \Psi_B \rangle$

$$= \langle \Psi_A | \Psi_A \rangle + \langle \Psi_B | \Psi_B \rangle + 2\langle \Psi_A | \Psi_B \rangle$$

Ψ_A and Ψ_B are normalized,
so $\langle \Psi_A | \Psi_A \rangle = \langle \Psi_B | \Psi_B \rangle = 1$

$\langle \Psi_A | \Psi_B \rangle = \langle \Psi_B | \Psi_A \rangle = S,$
 $S = \text{Overlap integral.}$

$\therefore \text{Denominator} = 2(1 + S)$

Summing Up . . .

$$E = \frac{\langle \Psi_A + \Psi_B | H | \Psi_A + \Psi_B \rangle}{\langle \Psi_A + \Psi_B | \Psi_A + \Psi_B \rangle}$$


Numerator = $2E_A + 2\beta$

Denominator = $2(1 + S)$

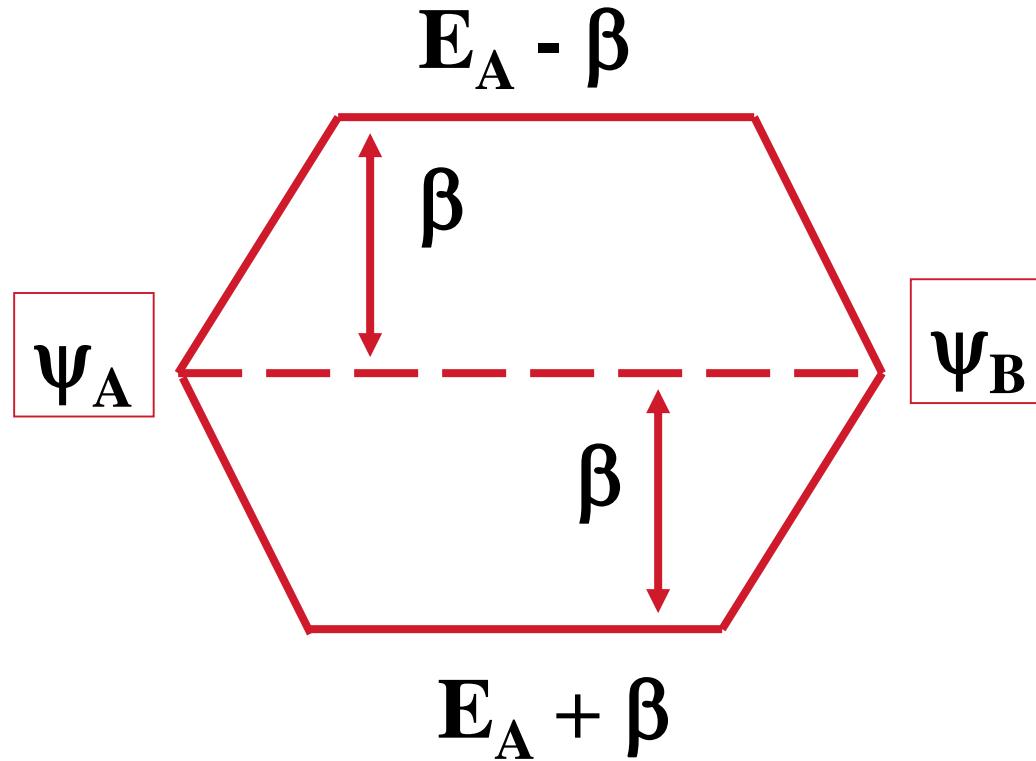
$$E_+ = (E_A + \beta) / (1 + S)$$

Also $E_- = (E_A - \beta) / (1 - S)$

$$E_{\pm} = E_A \pm \beta$$

S is very small
 \therefore Neglect S

Energy level diagram



Linear combination of atomic orbitals

Rules for linear combination.....

1. Atomic orbitals must be roughly of the same energy.
2. The orbital must overlap one another as much as possible- atoms must be close enough for effective overlap.
3. In order to produce bonding and antibonding MOs, either the symmetry of two atomic orbital must remain unchanged when rotated about the internuclear line or both atomic orbitals must change symmetry in identical manner.

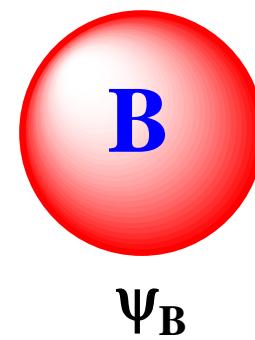
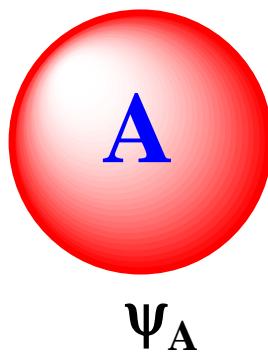
Rules for the use of MOs

- * When two AOs mix, two MOs will be produced
- * Each orbital can have a total of two electrons (Pauli principle)
- * Lowest energy orbitals are filled first (Aufbau principle)
- * Unpaired electrons have parallel spin (Hund's rule)

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

Linear Combination of Atomic Orbitals (LCAO)

The wave function for the molecular orbitals can be approximated by taking linear combinations of atomic orbitals.



$$\Psi_{AB} = N(c_A \Psi_A + c_B \Psi_B)$$

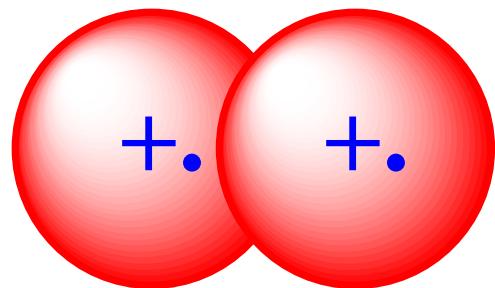
c – extent to which each AO contributes to the MO

$$\Psi_{AB}^2 = (c_A^2 \Psi_A^2 + 2c_A c_B \Psi_A \Psi_B + c_B^2 \Psi_B^2)$$

Probability density

Overlap integral

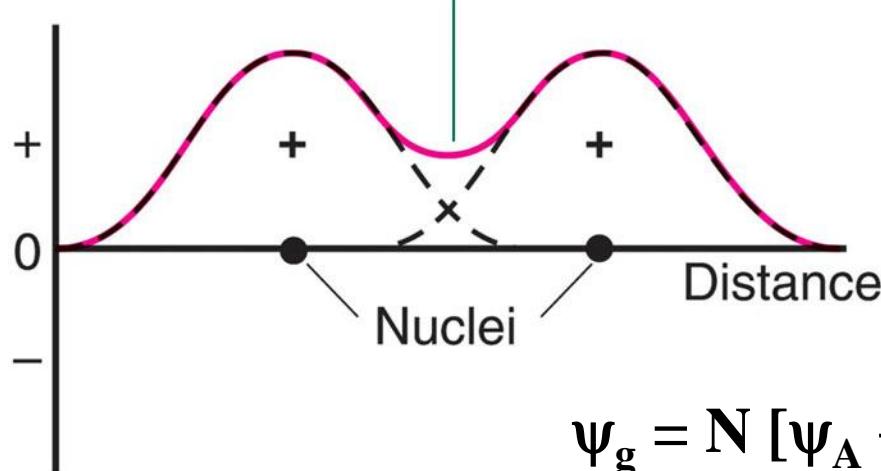
Constructive interference



$$c_A = c_B = 1$$

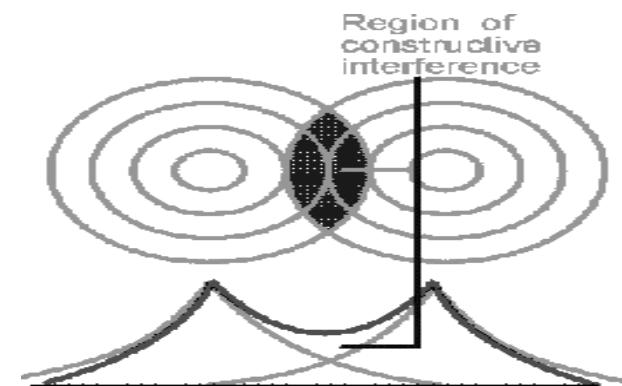
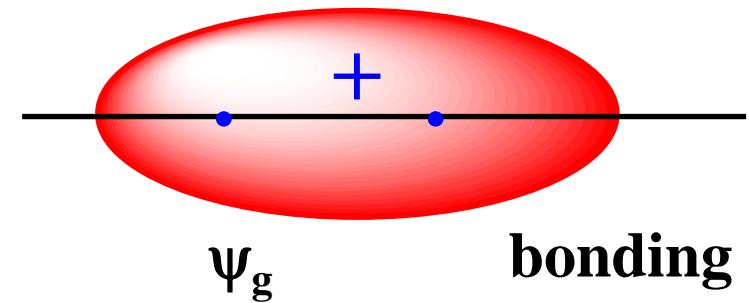
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Waves reinforce



$$\Psi_g = N [\Psi_A + \Psi_B]$$

Amplitudes of wave functions added



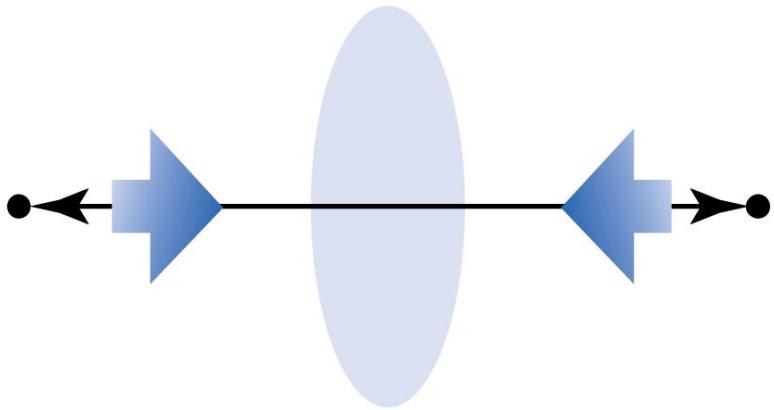
What holds the molecule together?

- ◆ There is nothing magic about the molecule being bonded
 - Electrons preferentially spend time between the two nuclei. They act as electrostatic “glue”

$$\Psi_{AB}^2 = (c_A^2 \Psi_A^2 + 2c_A c_B \Psi_A \Psi_B + c_B^2 \Psi_B^2)$$

electron density on original atoms,

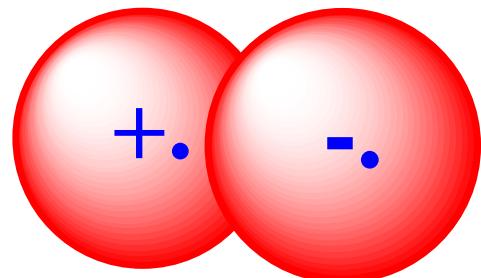
density between atoms



The accumulation of electron density between the nuclei put the electron in a position where it interacts strongly with both nuclei.

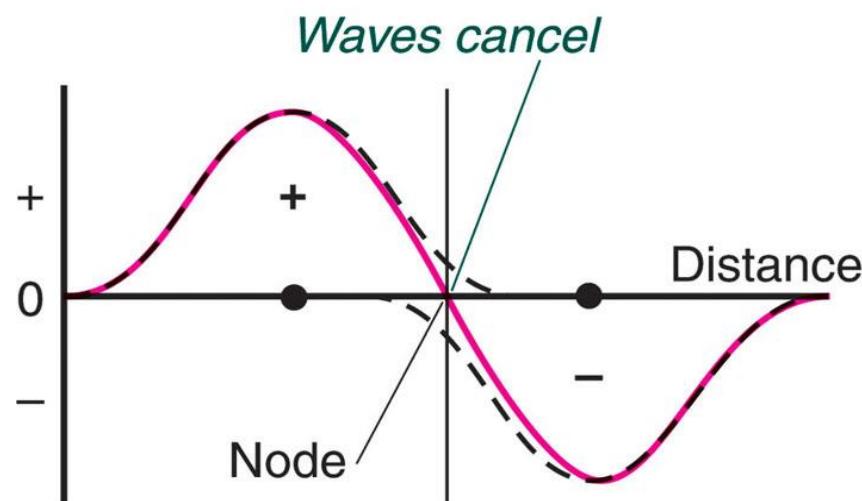
Nuclei are shielded from each other

The energy of the molecule is lower

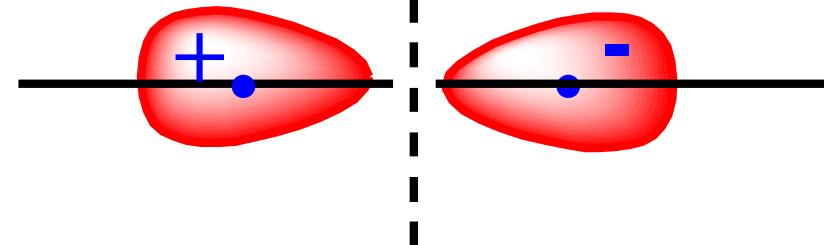


$$c_A = +1, c_B = -1$$

$$\Psi_u = N [\Psi_A - \Psi_B]$$



Amplitudes of wave functions subtracted.



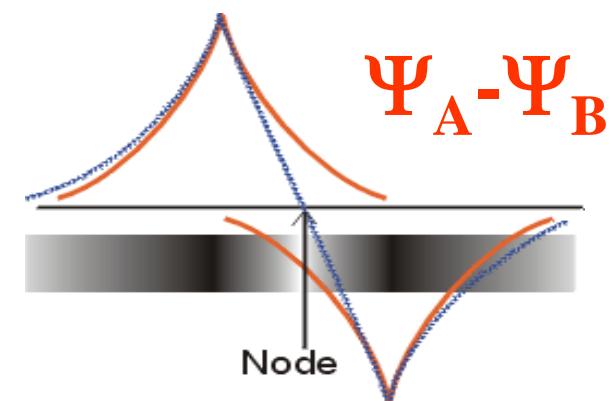
$$\Psi_u$$

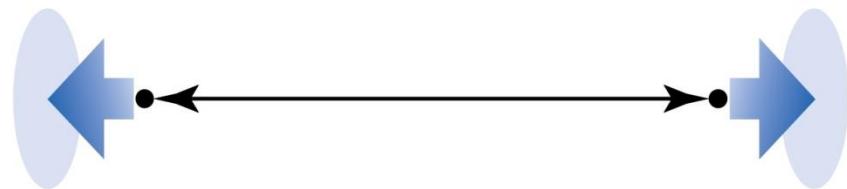
antibonding

Destructive interference

Nodal plane perpendicular to the H-H bond axis (en density = 0)

Energy of the en in this orbital is higher.





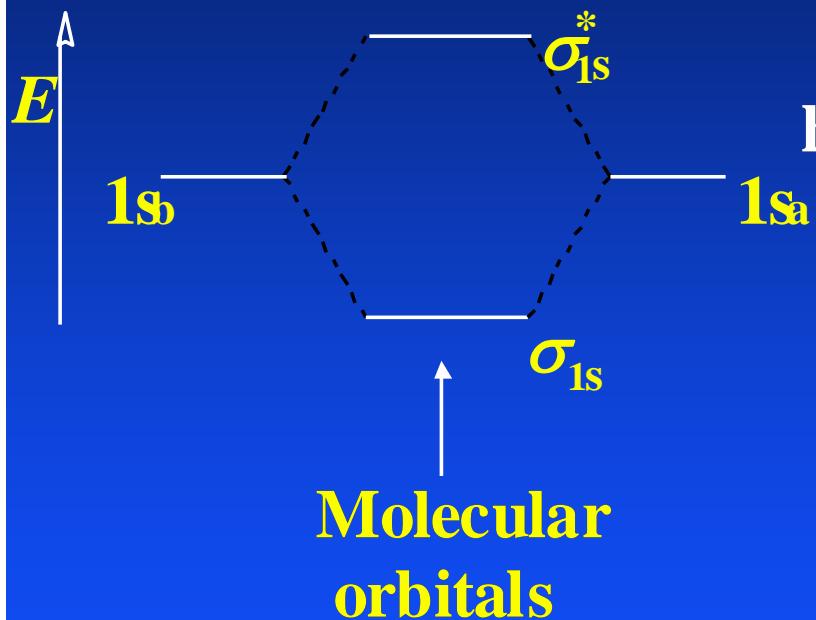
(b)

■ The electron is excluded from internuclear region → destabilizing

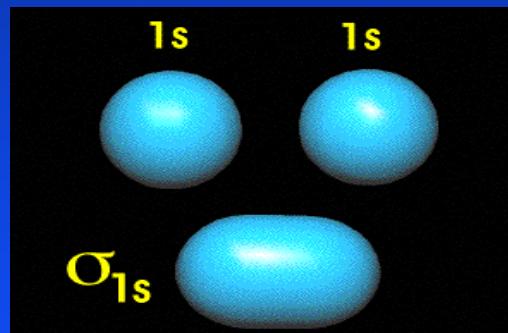
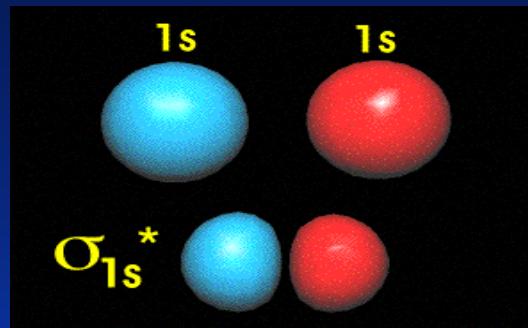
Antibonding

When 2 atomic orbitals combine there are 2 resultant orbitals.

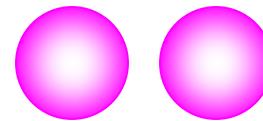
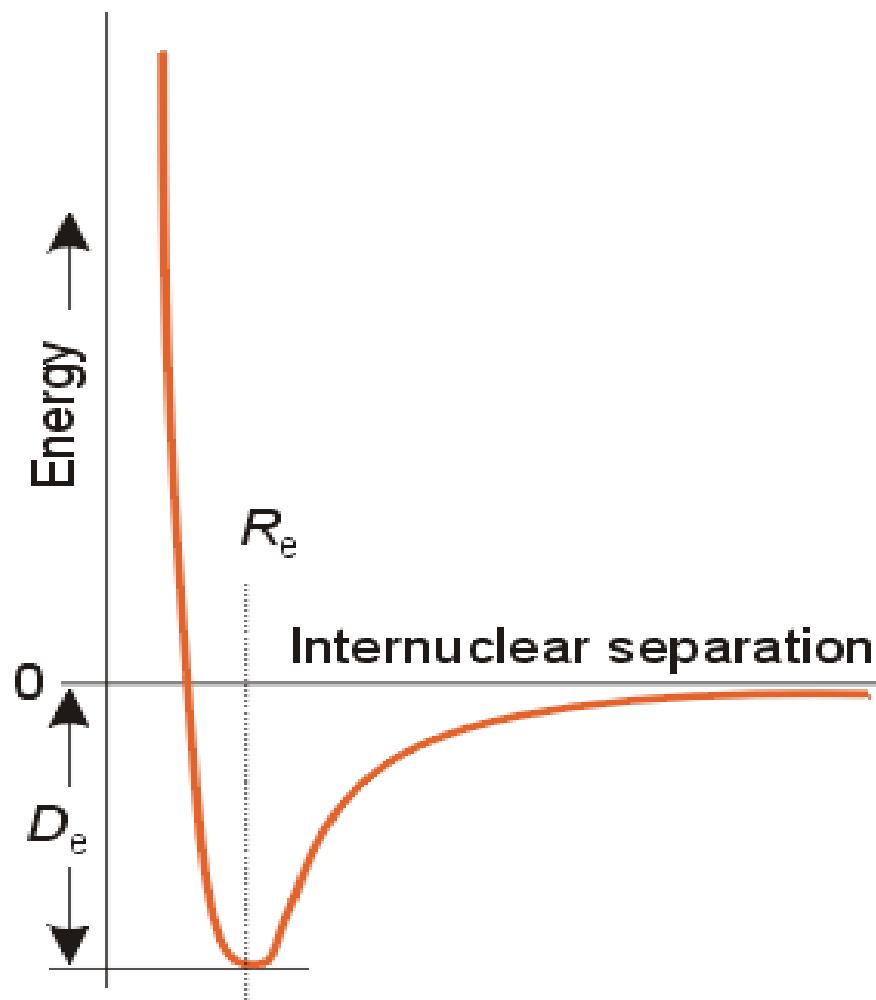
Eg. s orbitals



high energy antibonding orbital



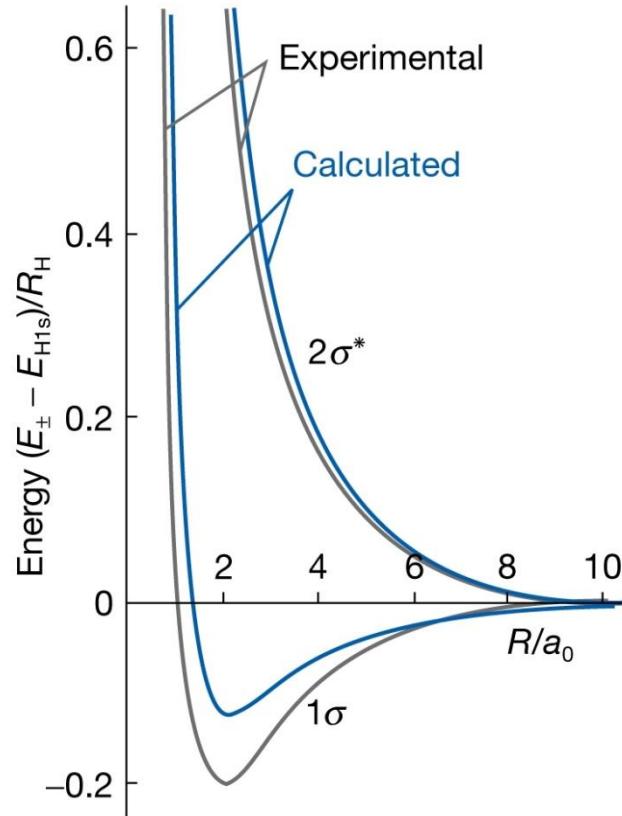
low energy bonding orbital



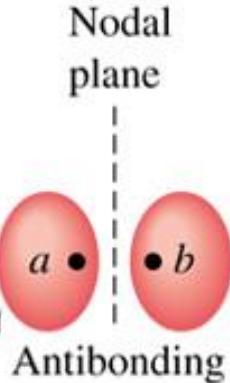
Molecular potential energy curve shows the variation of the molecular energy with internuclear separation.

Looking at the Energy Profile

- Bonding orbital
- called *1s orbital*
- *s electron*
- The energy of 1s orbital decreases as R decreases
- However at small separation, repulsion becomes large
- There is a minimum in potential energy curve



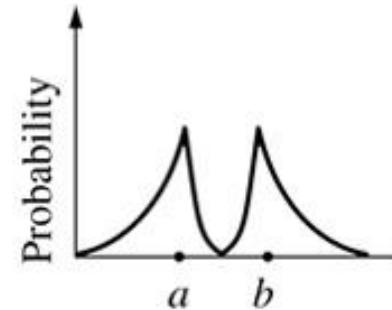
$1s_a$ and $1s_b$



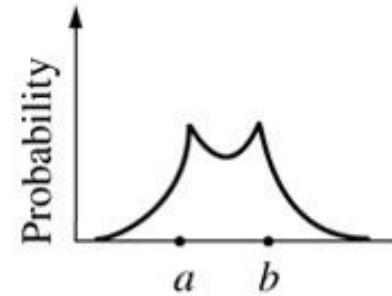
LCAO of n A.O \Rightarrow n M.O

1s orbitals of
two widely
separated
hydrogen atoms

Molecular orbitals
of H_2 molecule



σ_{1s}^*



σ_{1s}

Electron charge
density (probability)
along a line joining two
hydrogen nuclei: a and b

Energy
level
diagram

H_2

11.4 eV

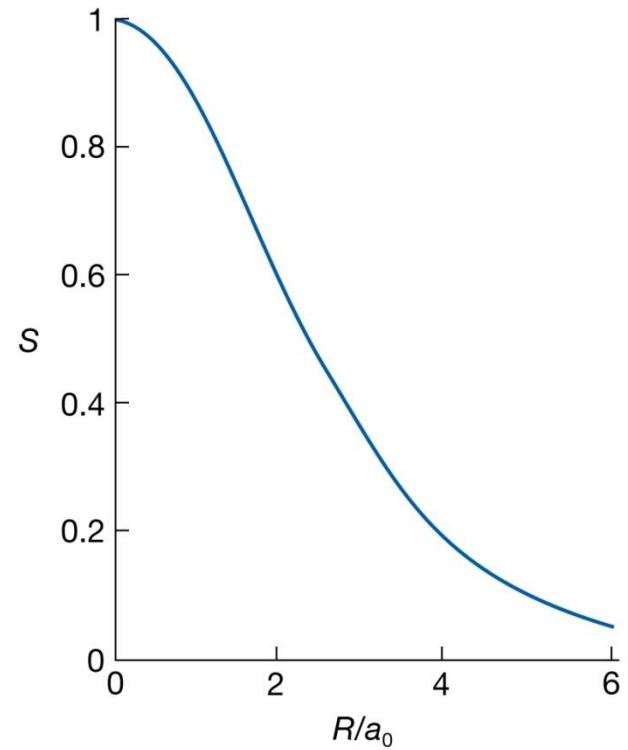
109 nm

Location of
Bonding orbital
4.5 eV

The overlap integral

■ The extent to which two atomic orbitals on different atom overlaps : the overlap integral

$$S = \int \psi_A^* \psi_B d\tau$$



$S > 0$ Bonding

$S < 0$ anti

- The extent to which orbitals overlap can be evaluated using an overlap integral S .
 - $S = 0$ indicates that the orbitals do not overlap/interact with one another
 - S depends on the symmetry of the orbital

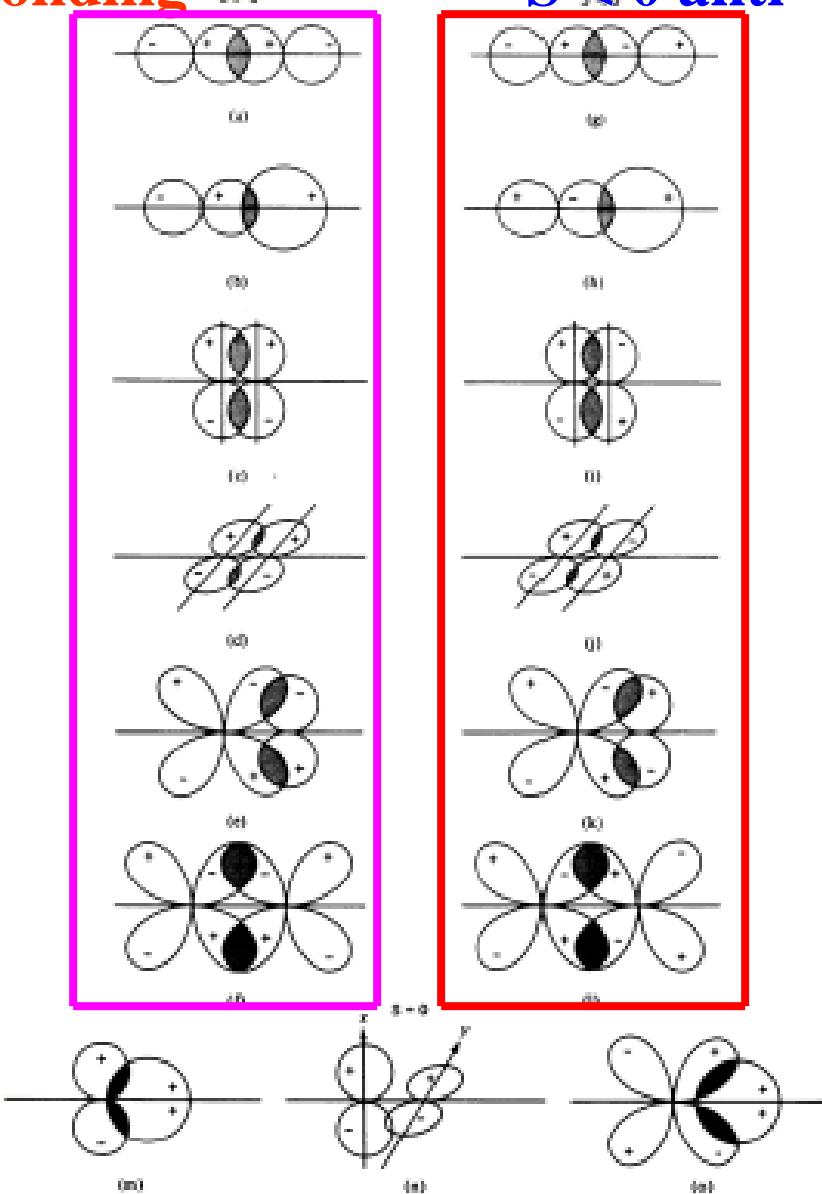


Fig. 5.8 Arrangement of atomic orbitals resulting in positive (a-f), negative (g-i), and zero (j-l) overlap.

Bond strength depends on the degree of overlap

$S = 0$ nonbonding

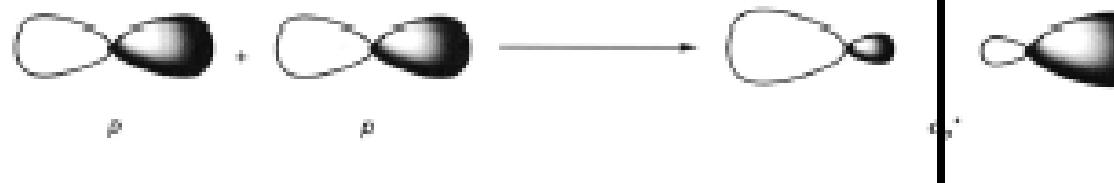
Linear combinations of p_z orbitals

- ◆ Addition of two p_z AOs results a bonding σ_p MO, subtraction will give an *antibonding* σ_p* MO with a nodal plane perpendicular to the bond axis

$$\Psi_{\sigma} = \frac{1}{\sqrt{2}} [\Psi_{2p_z}(H_a) + \Psi_{2p_z}(H_b)]$$

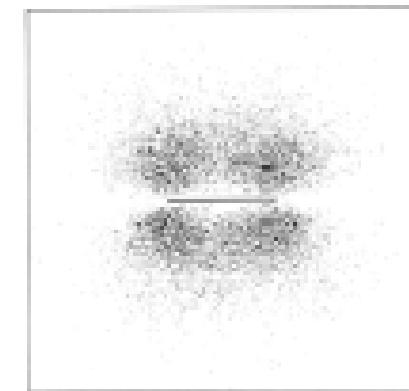
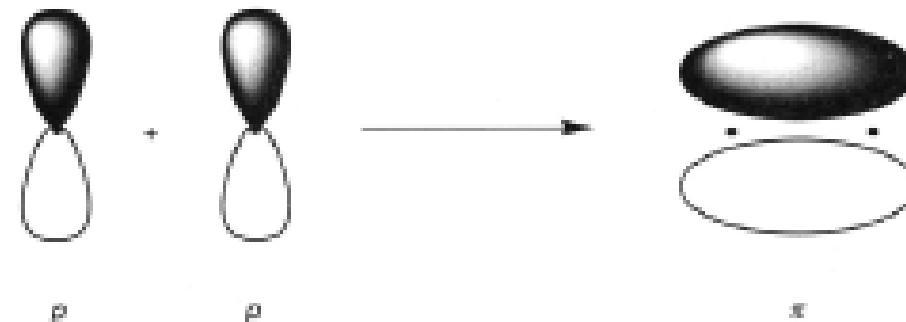


$$\Psi_{\sigma^*} = \frac{1}{\sqrt{2}} [\Psi_{2p_z}(H_a) - \Psi_{2p_z}(H_b)]$$

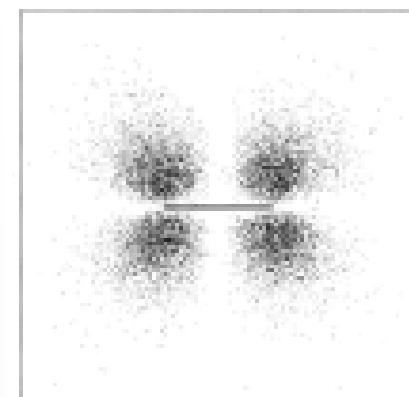
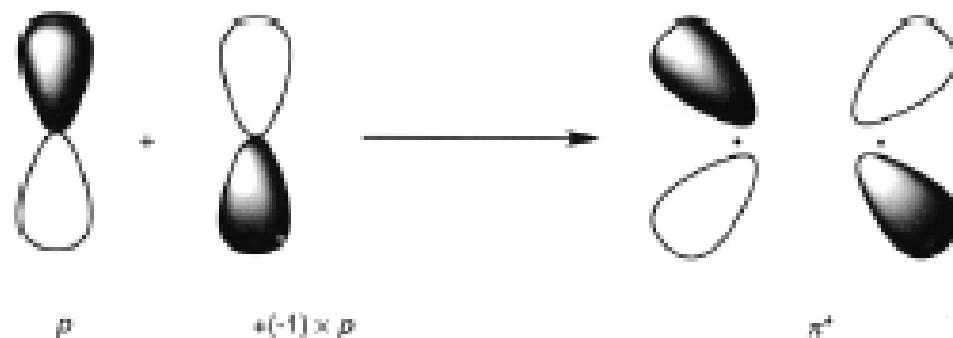


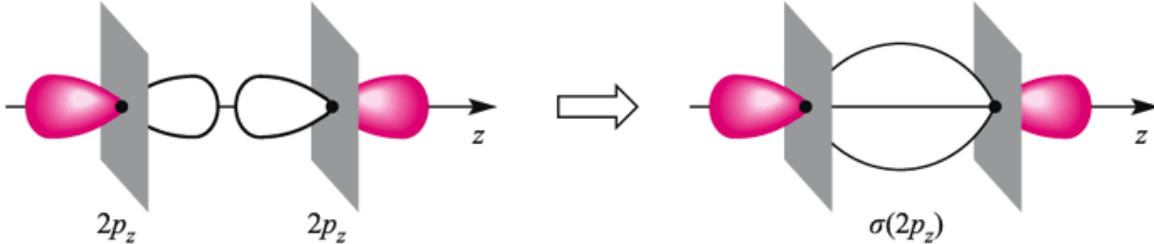
Linear combinations of p_x and p_y orbitals

- ◆ Addition of two p_x (or p_y) AOs results a bonding π_p MO containing a nodal plane along the bond axis:

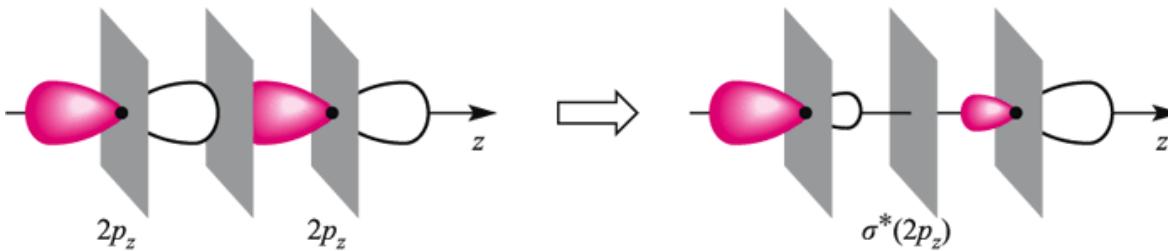


- ◆ Subtraction results an *antibonding* π_p^* MO with *two* nodal planes: one plane *perpendicular* and one *parallel* to the bond axis

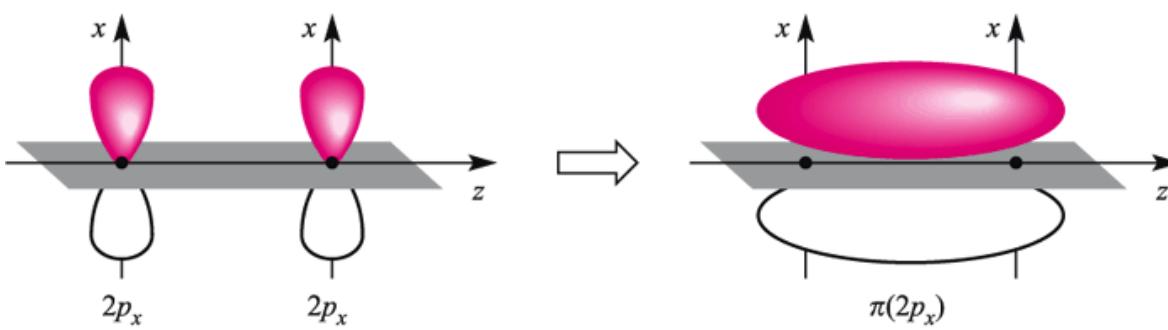




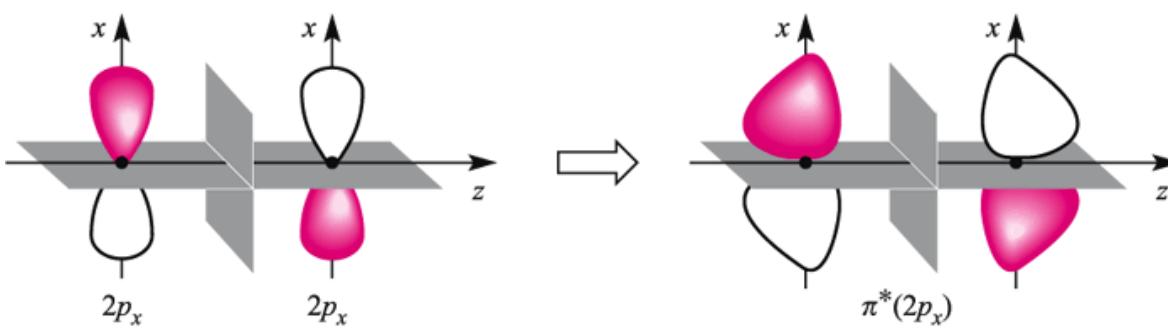
(a)



(b)



(c)



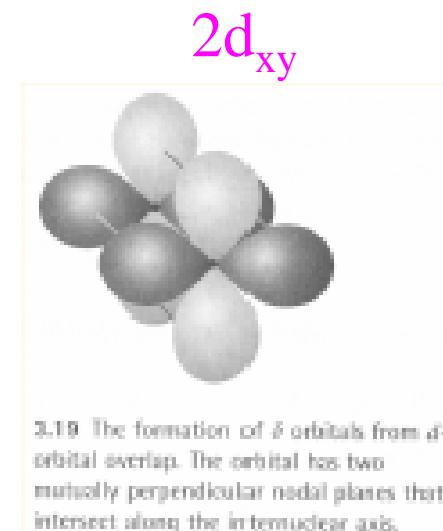
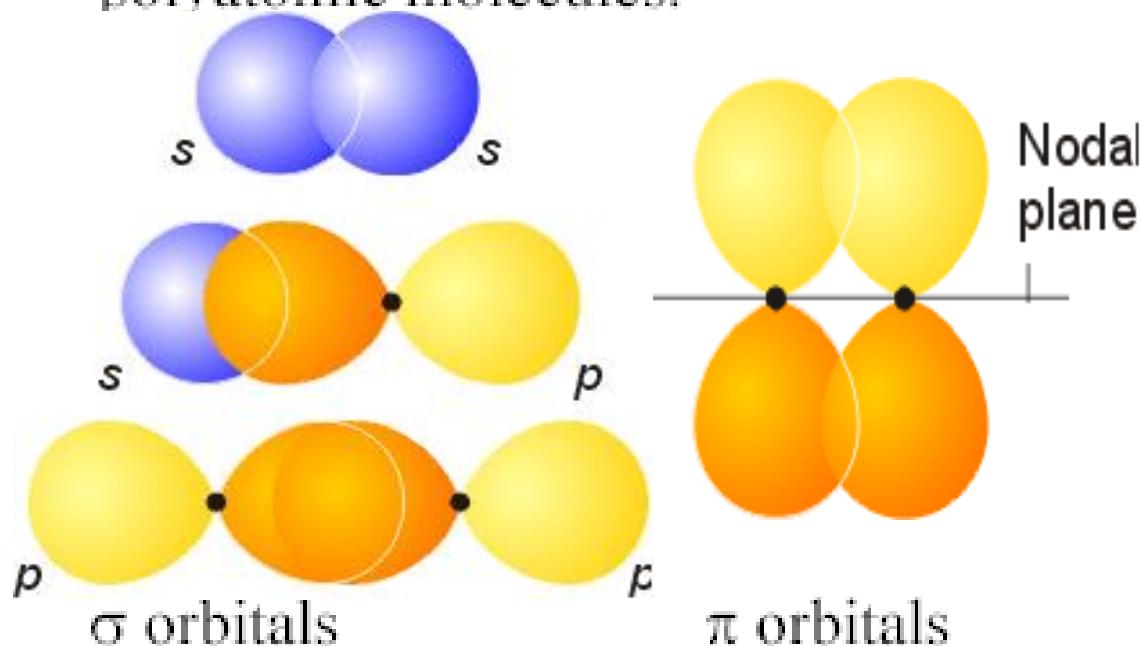
(d)

Homonuclear Diatomics

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

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.



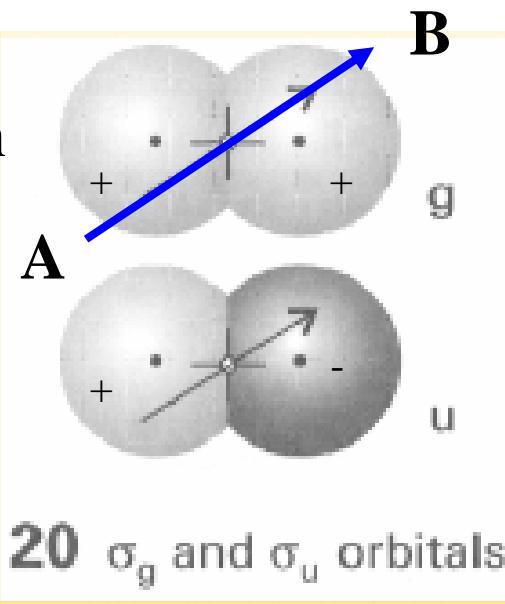
3.19 The formation of δ orbitals from d -orbital overlap. The orbital has two mutually perpendicular nodal planes that intersect along the internuclear axis.

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

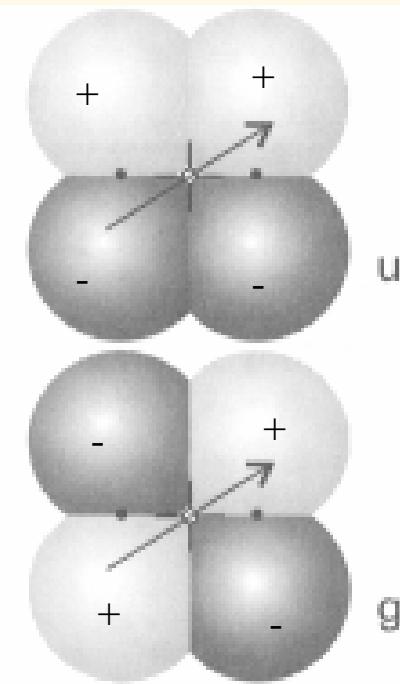
Ungerade or gerade ?

- 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

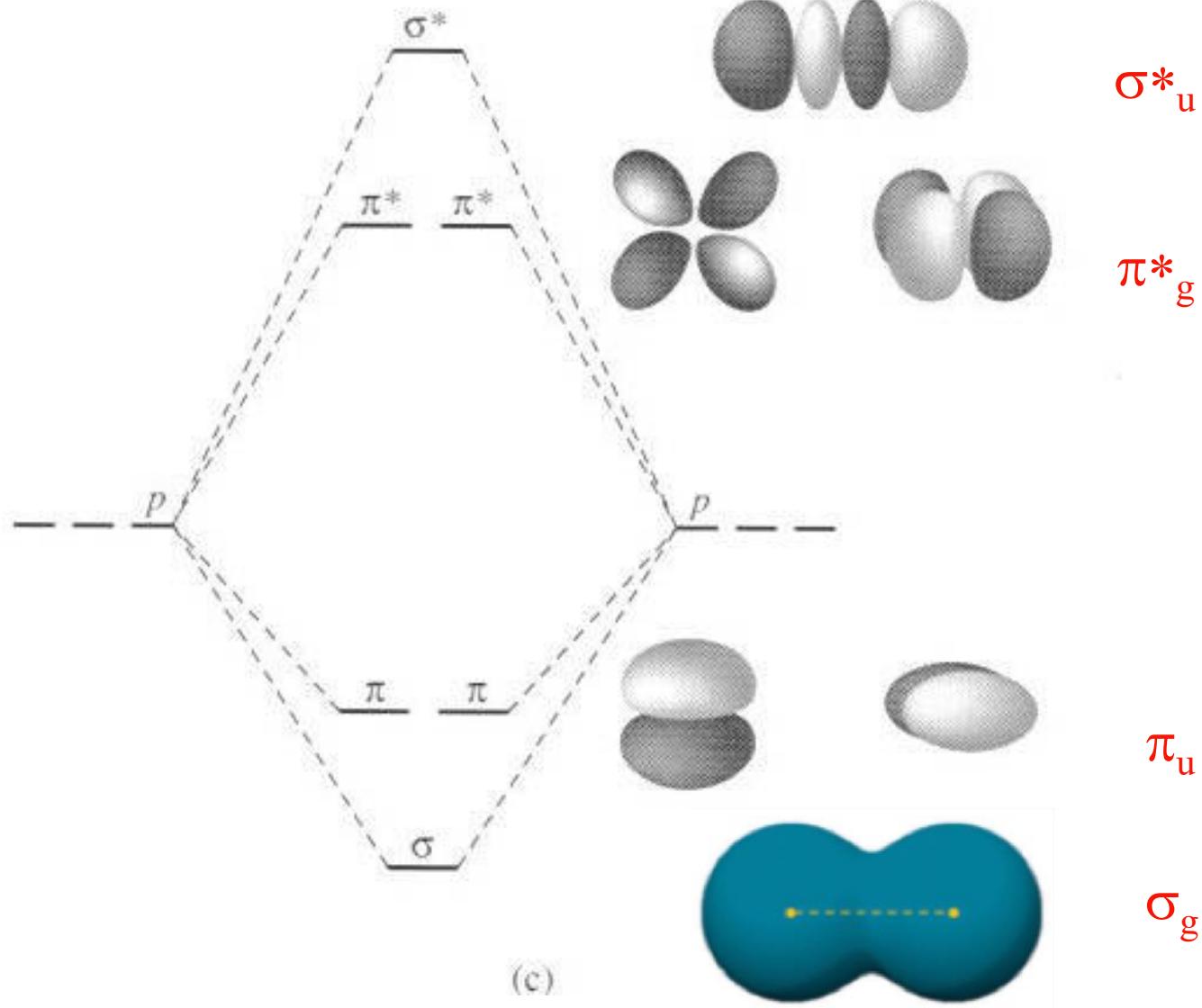
g- identical
under inversion



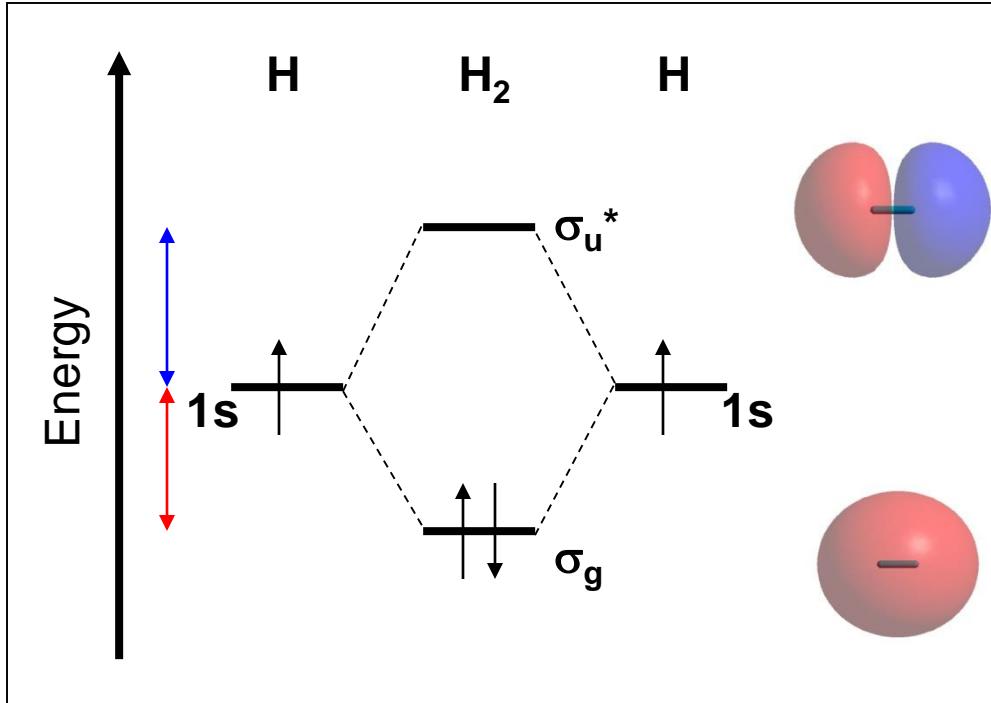
u- not identical



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

$\sigma^* 1s$

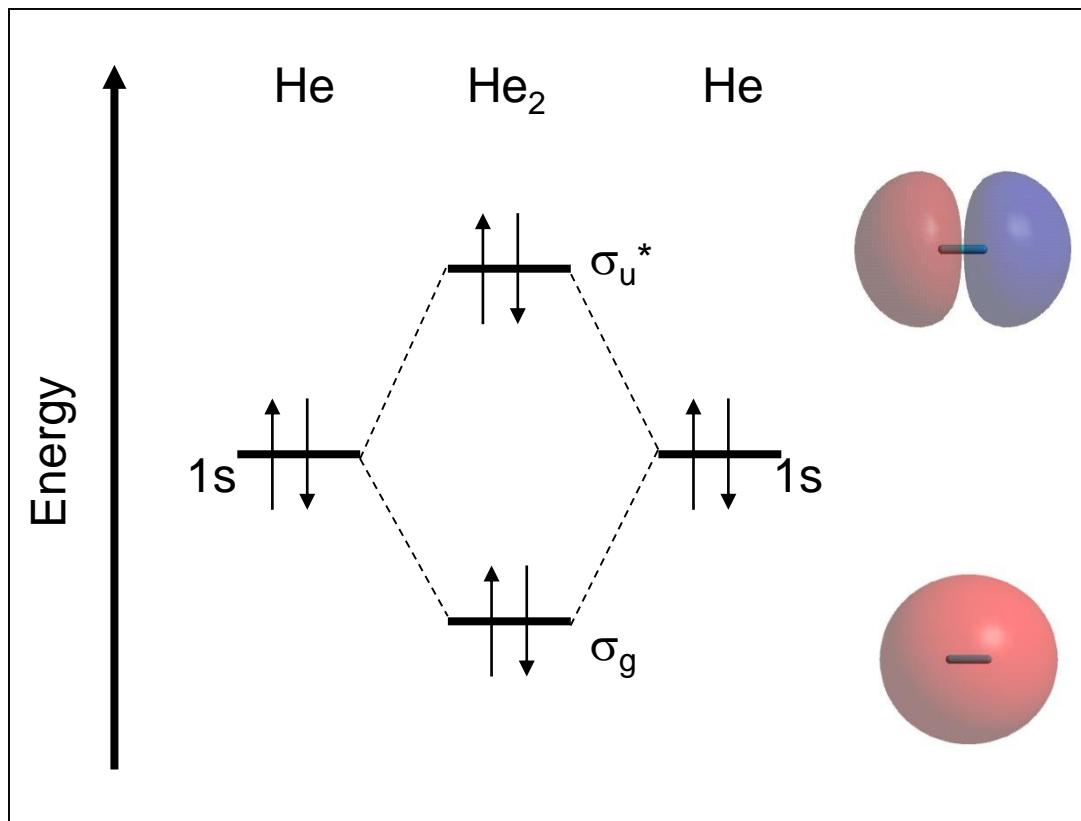
antibonding

HOMO

$\uparrow \downarrow$

$\sigma 1s$ bonding MO

Diatomc molecules: The bonding in He_2

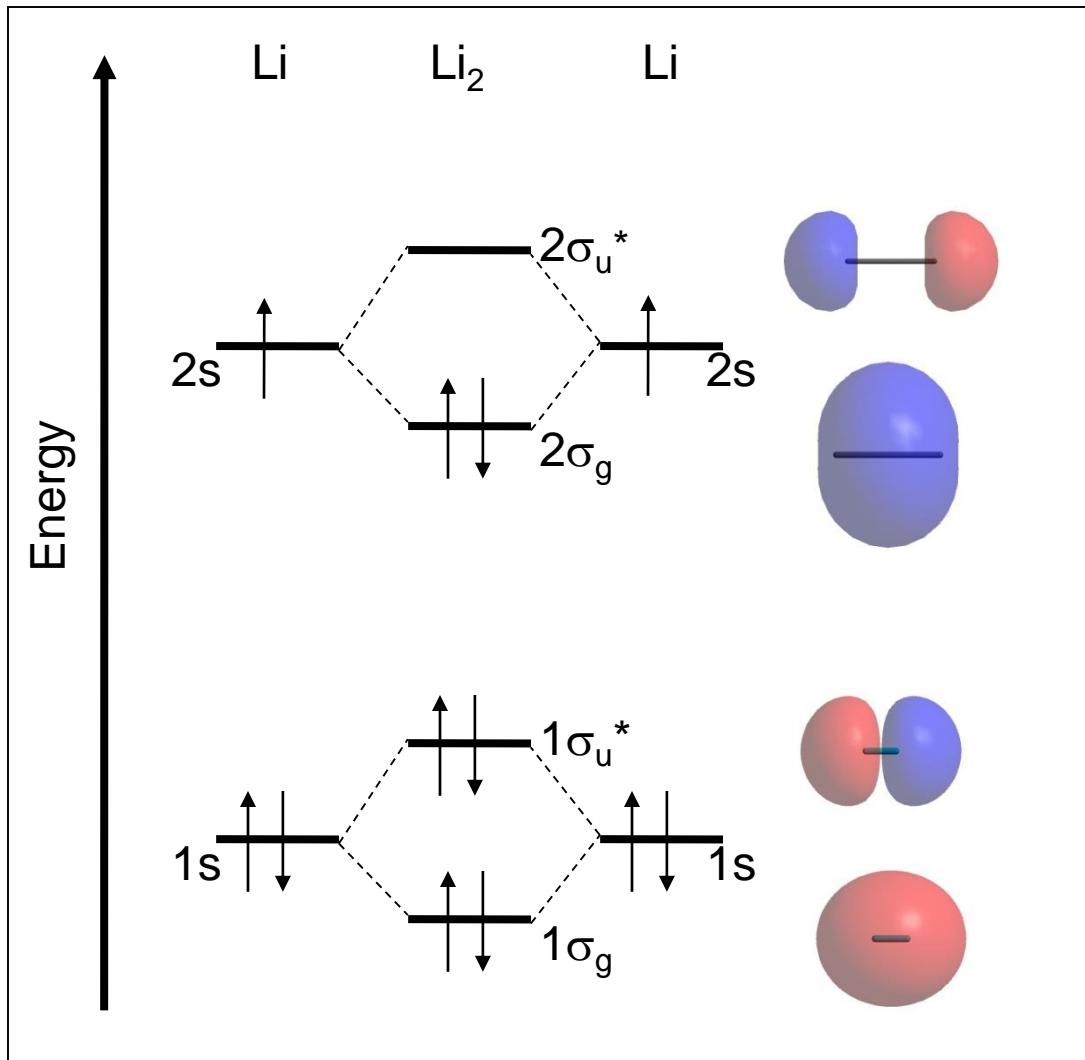


$\sigma 1s^2, \sigma^* 1s^2$

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.

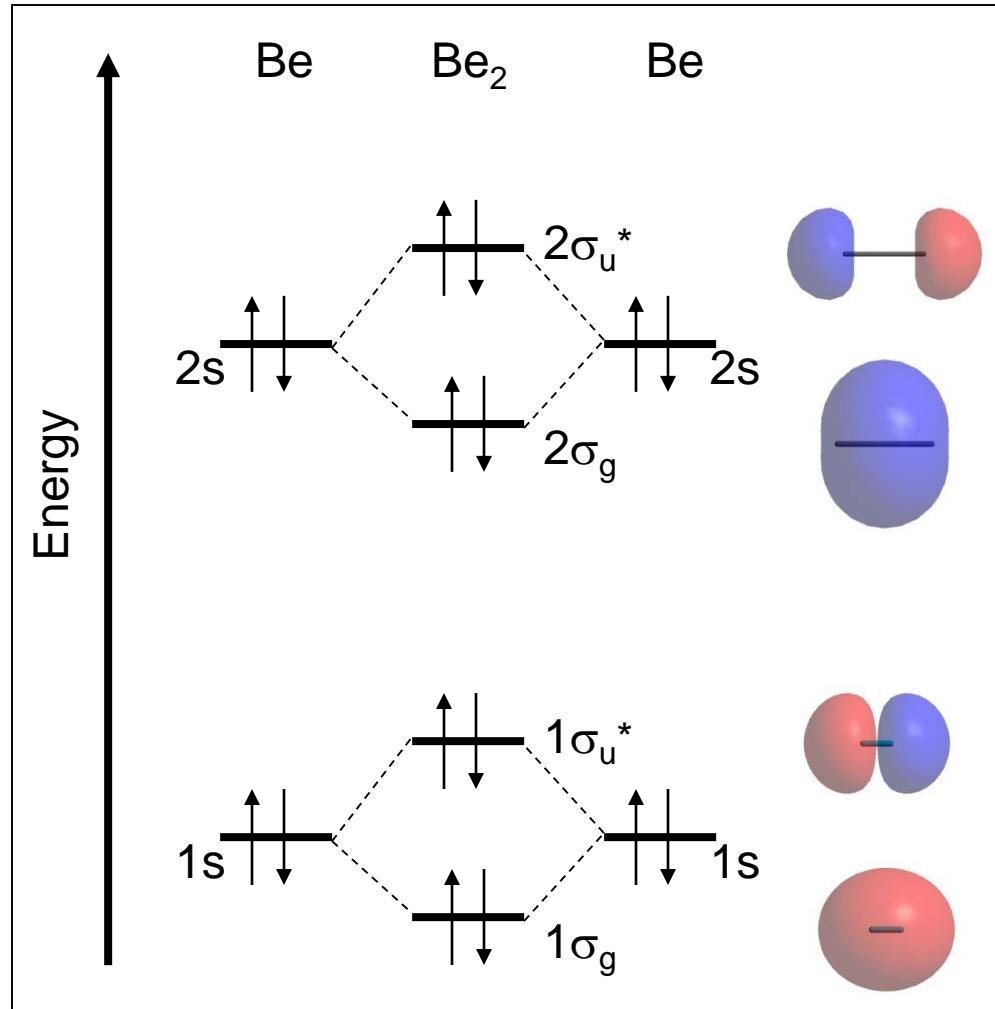
Second period diatomic molecules



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

Bond order: 1

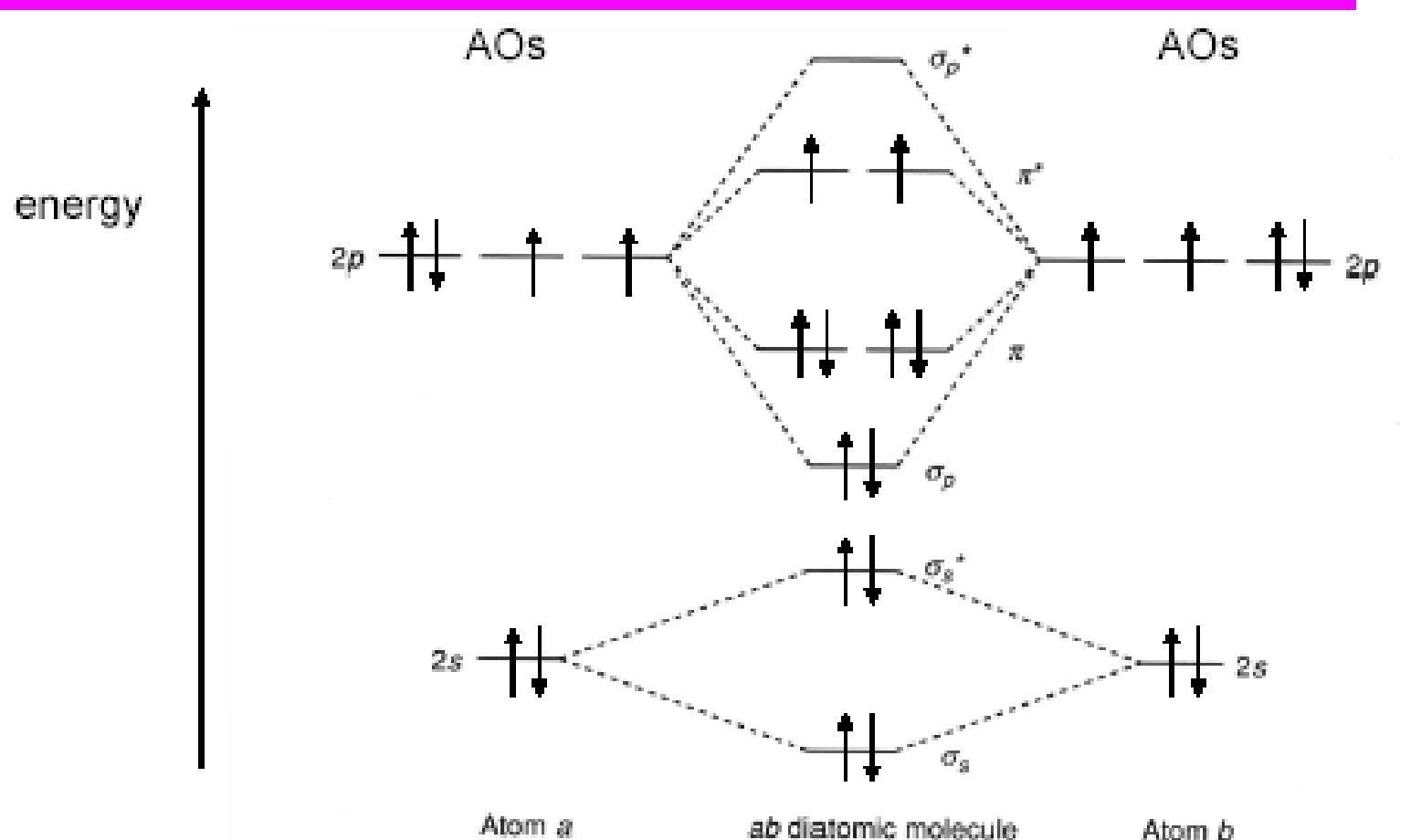
Diatomc molecules: Homonuclear Molecules of the Second Period



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

Bond order: 0

Molecular oxygen

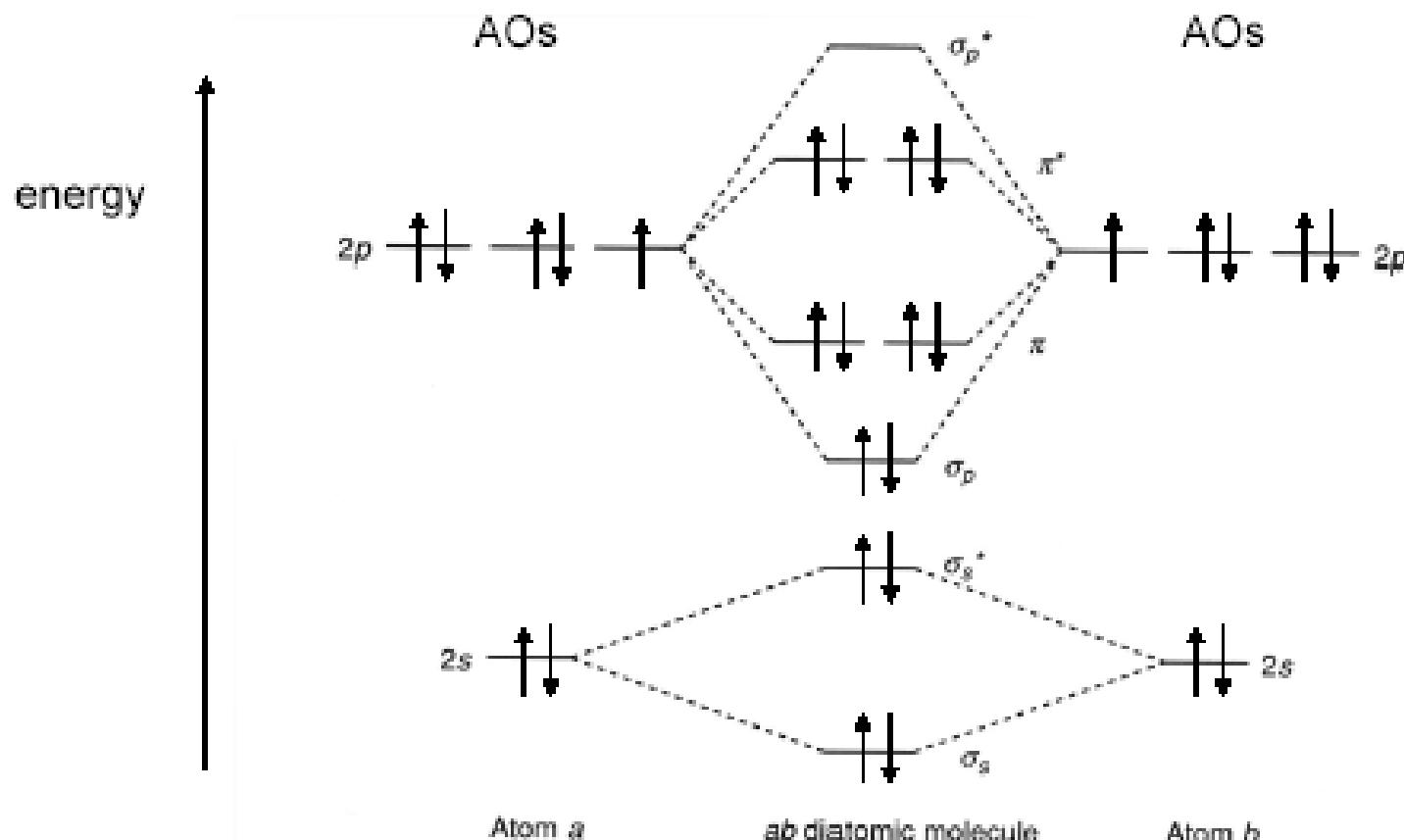


Bond order = 2

2 unpaired electrons \rightarrow paramagnetic

Simplified

Molecular fluorine

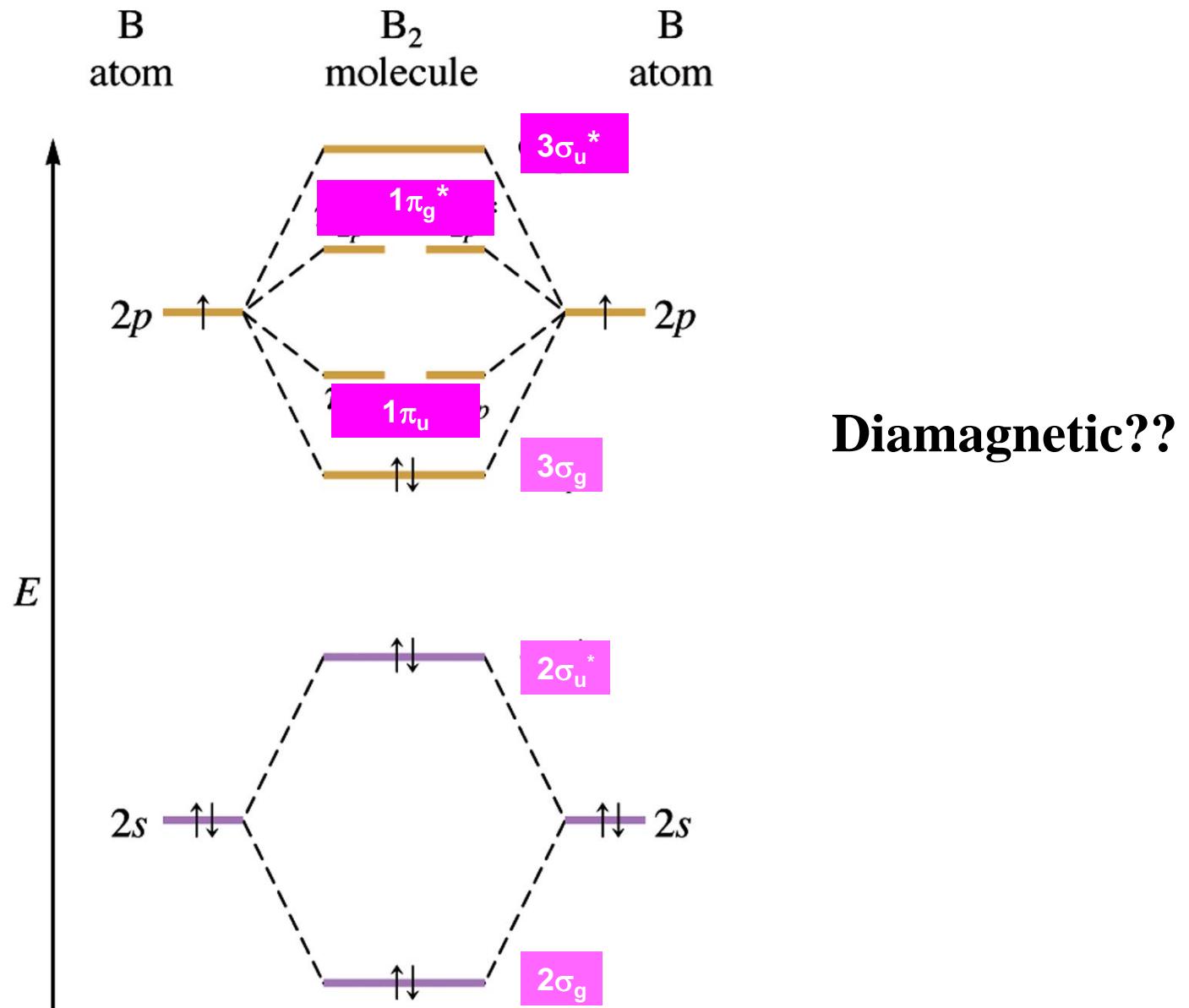


Bond order = 1

0 unpaired electrons → diamagnetic

Simplified

MO diagram for B_2

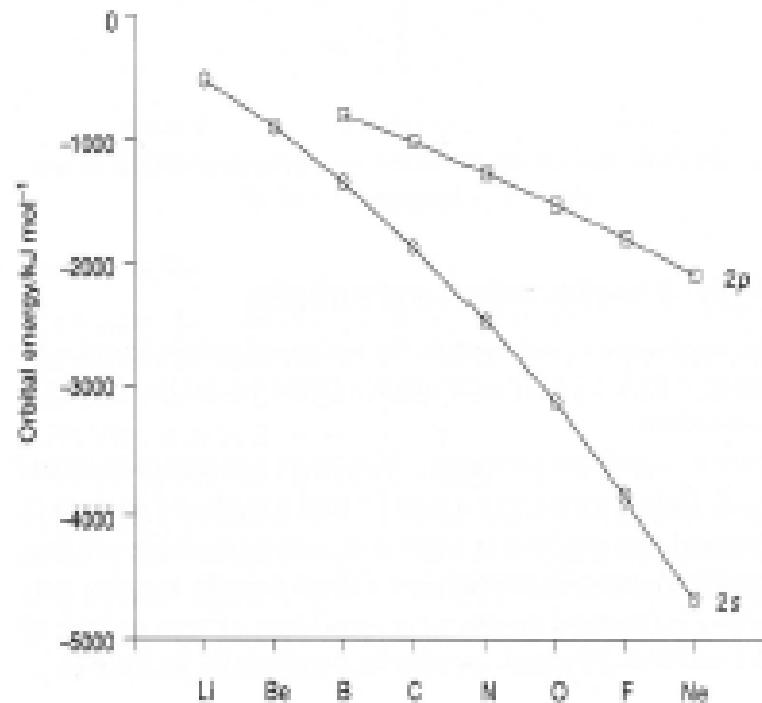


Orbital Mixing

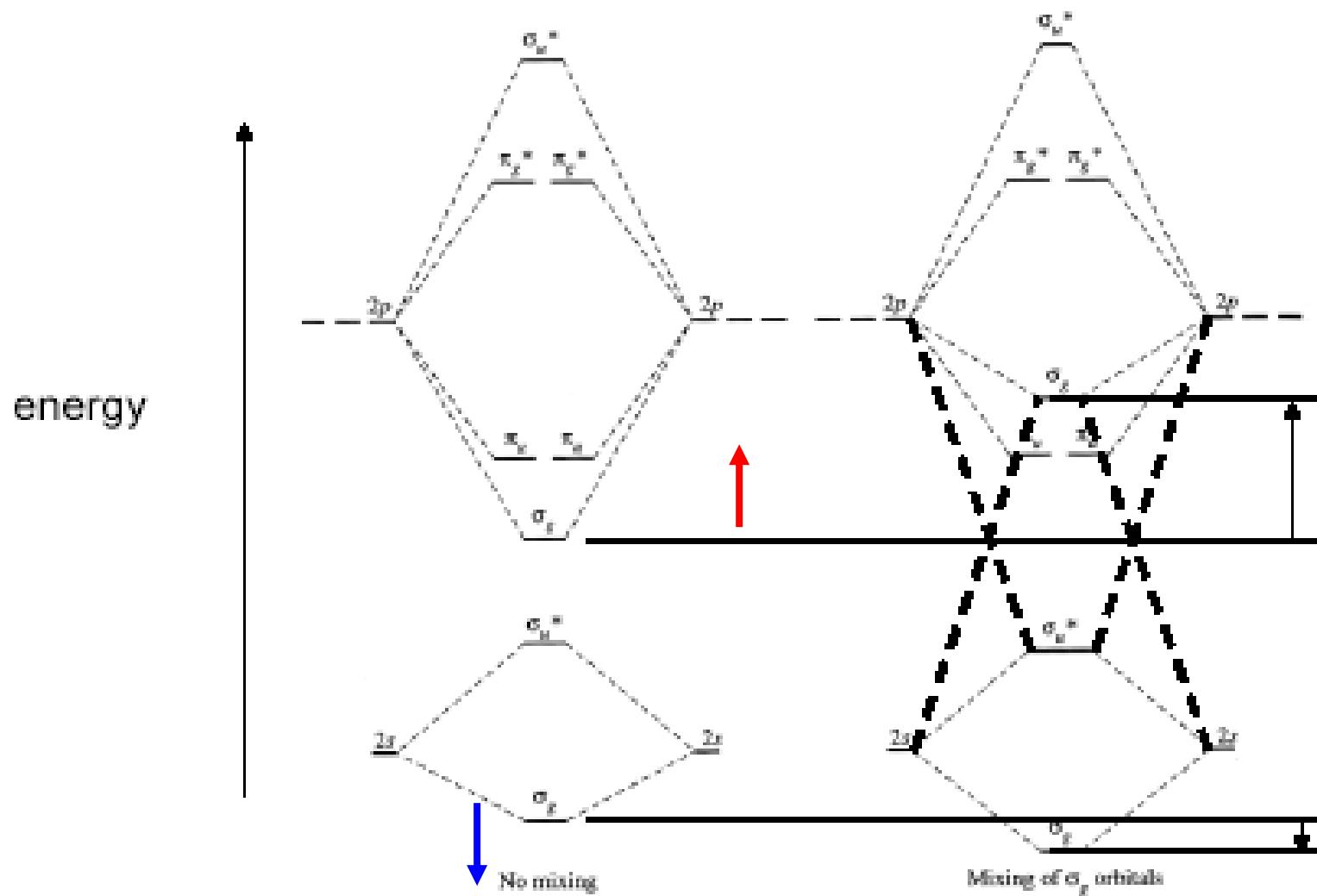
- ◆ Orbitals with similar energy interact, if they have the appropriate symmetries
- ◆ The σ_{2p} and σ_{2s} orbitals are symmetry related and give rise to two new orbitals, one with higher and one with lower energy

Li : 200 kJ/mol

F: 2500 kJ/mol

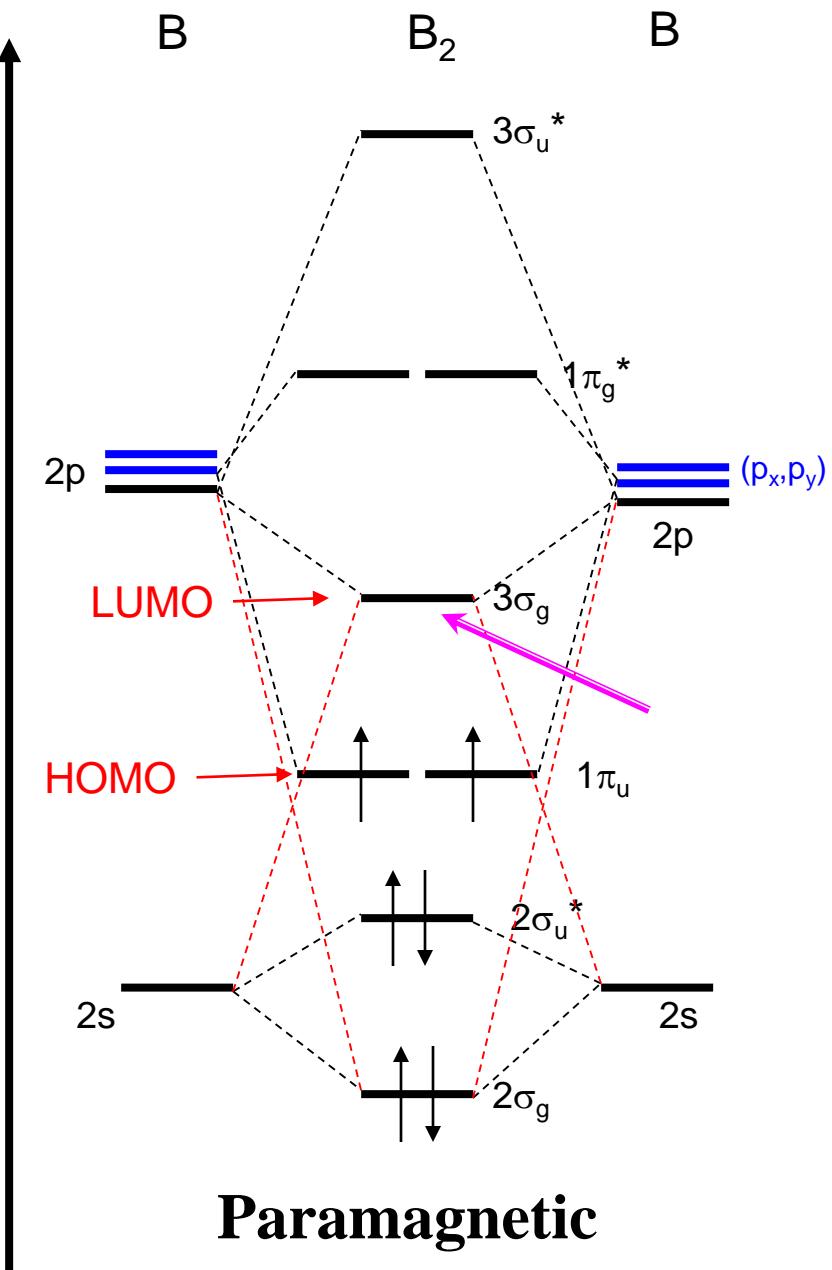
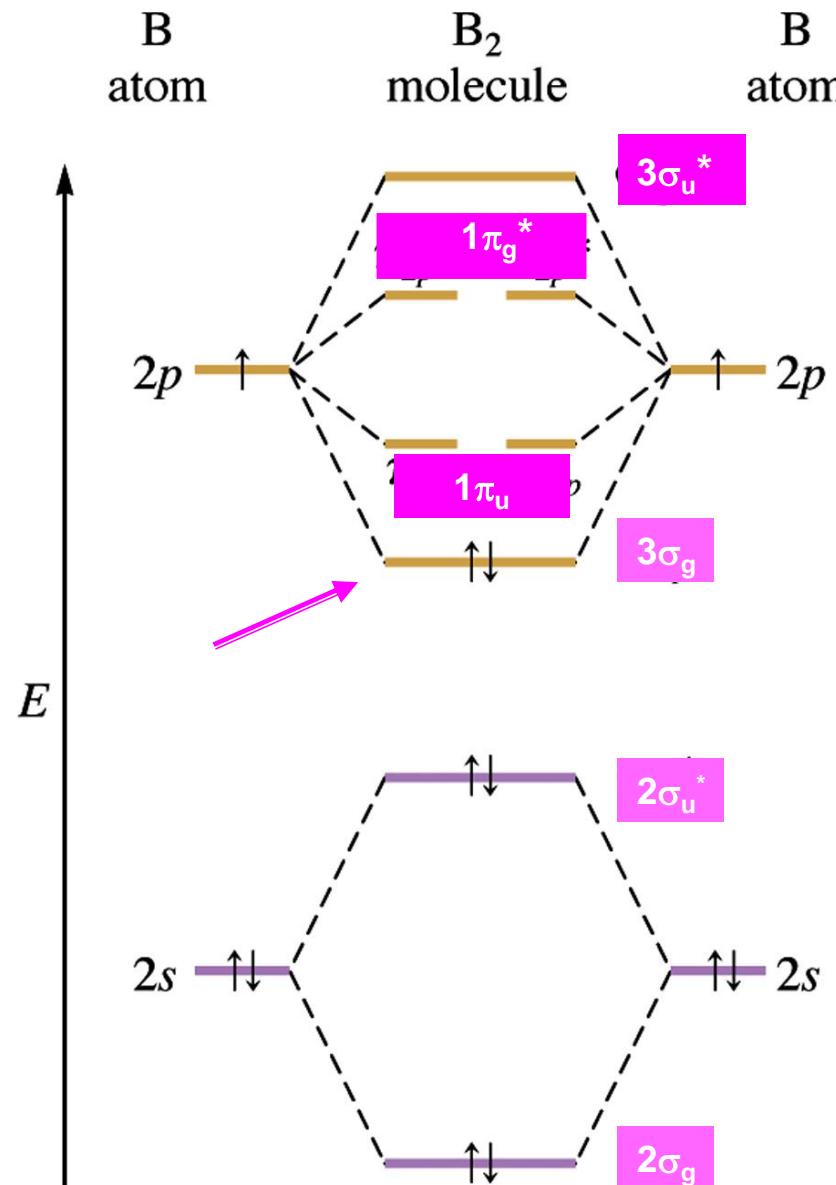


Effect of orbital mixing

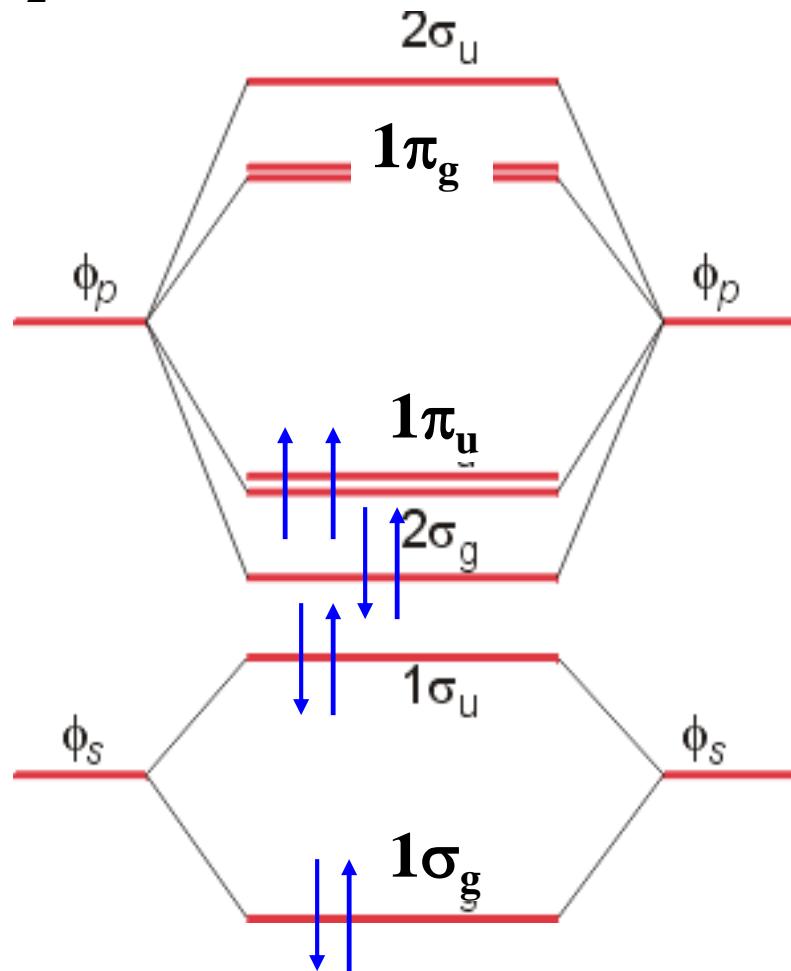


Same symmetry, energy mix-the one with higher energy moves higher and the one with lower energy moves lower

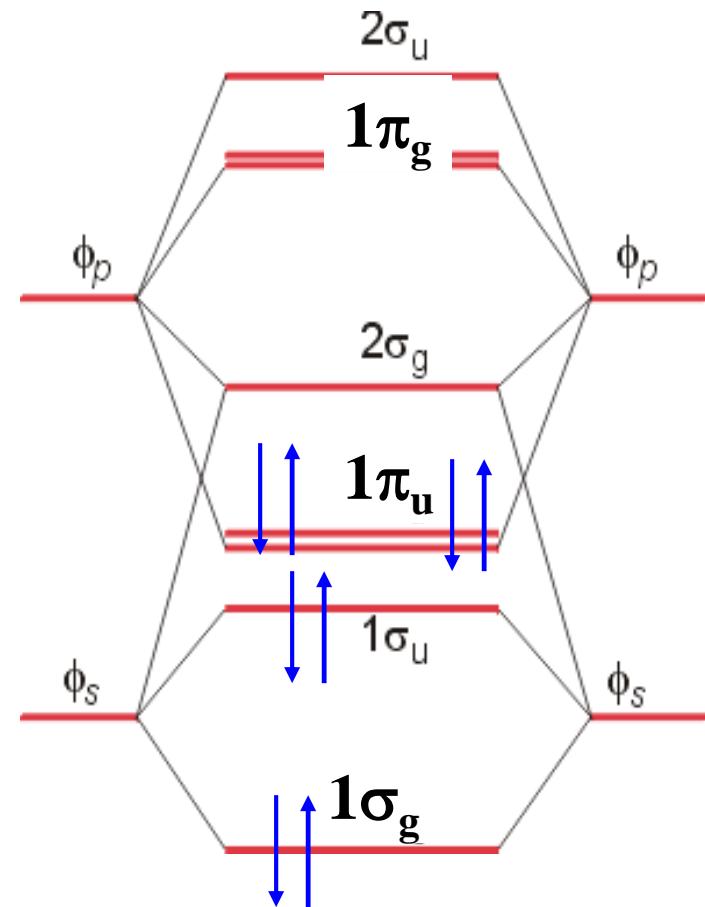
MO diagram for B_2



C_2

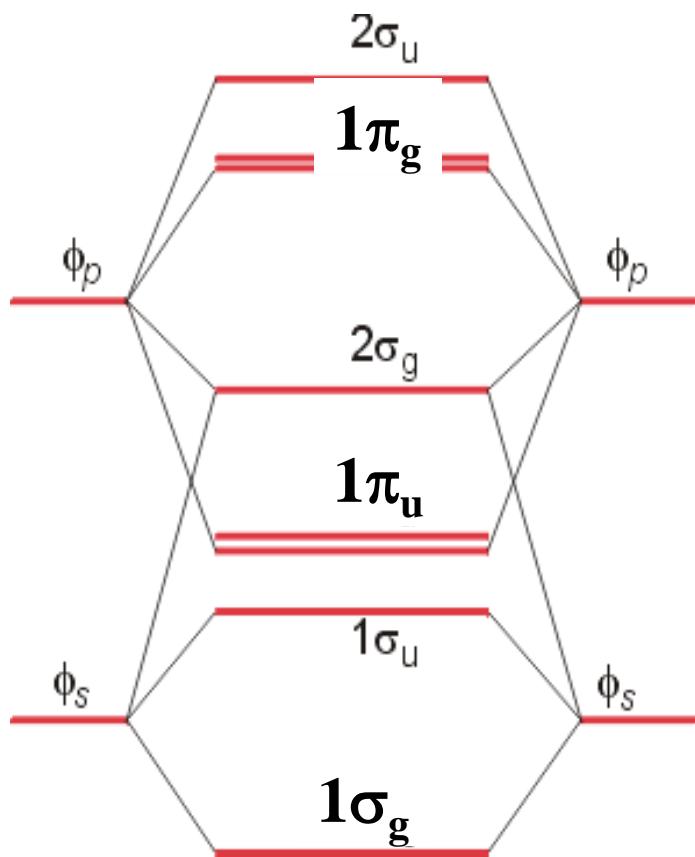


Paramagnetic ?

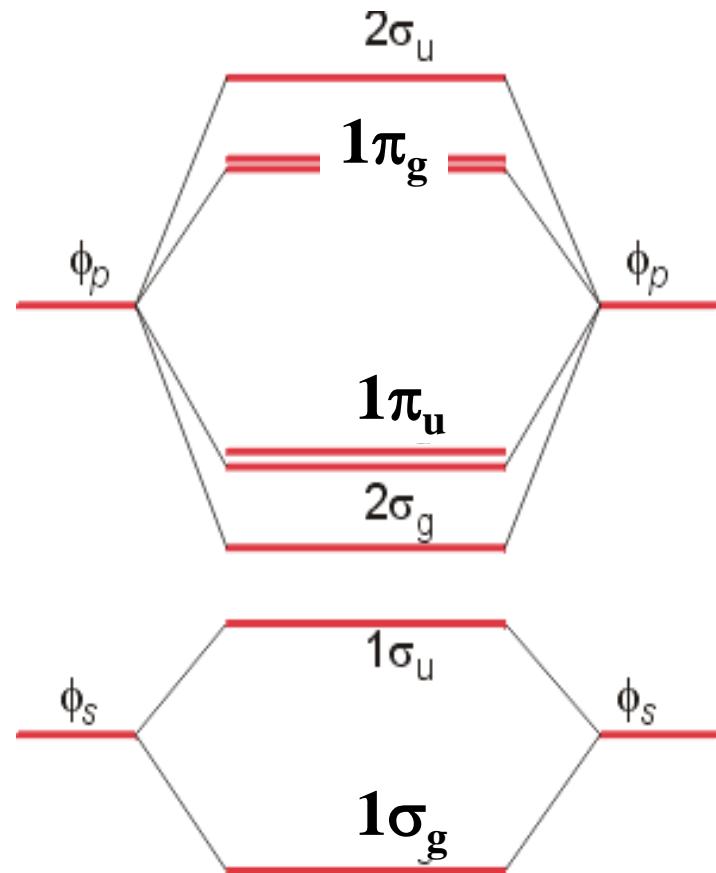


Diamagnetic

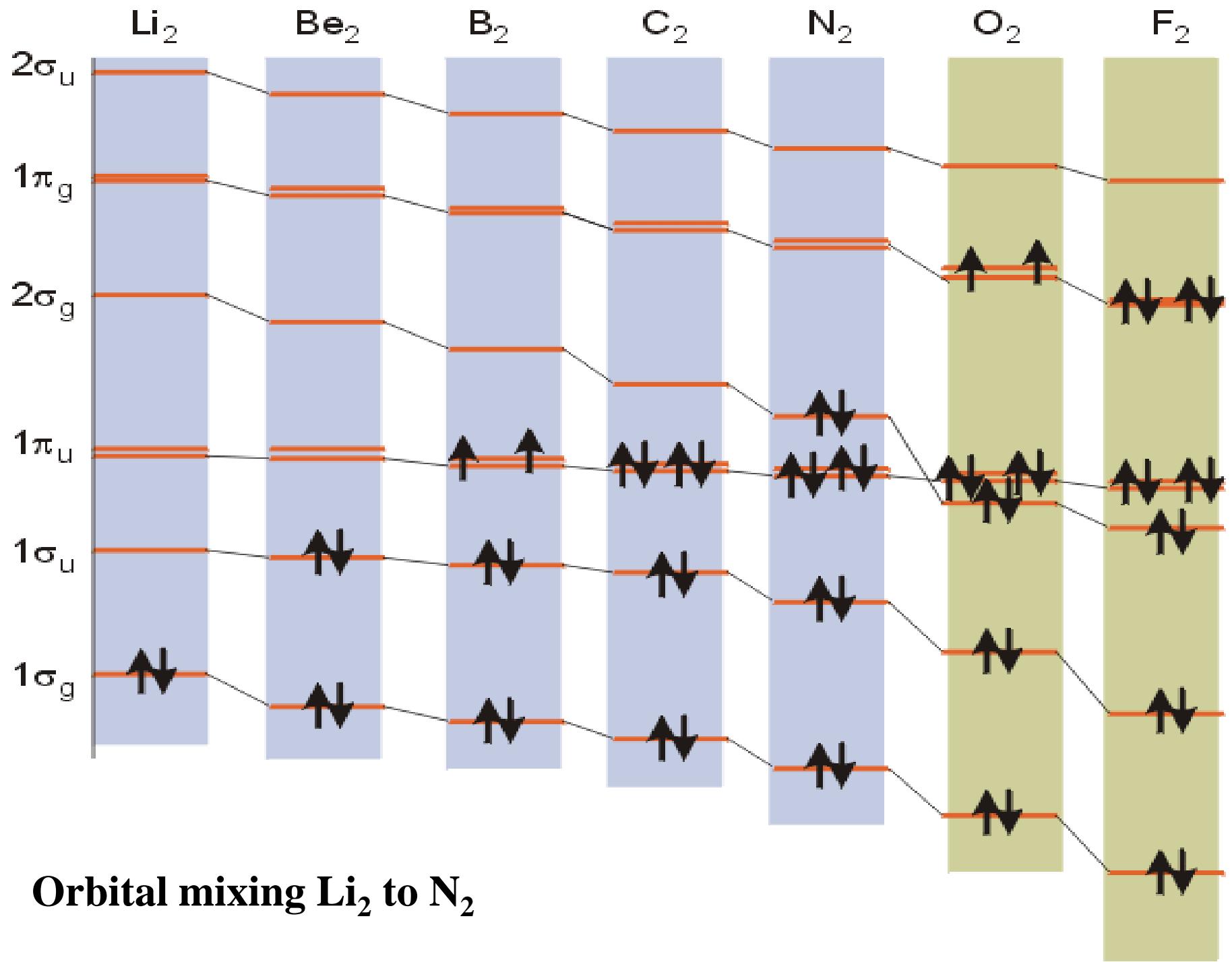
General MO diagrams



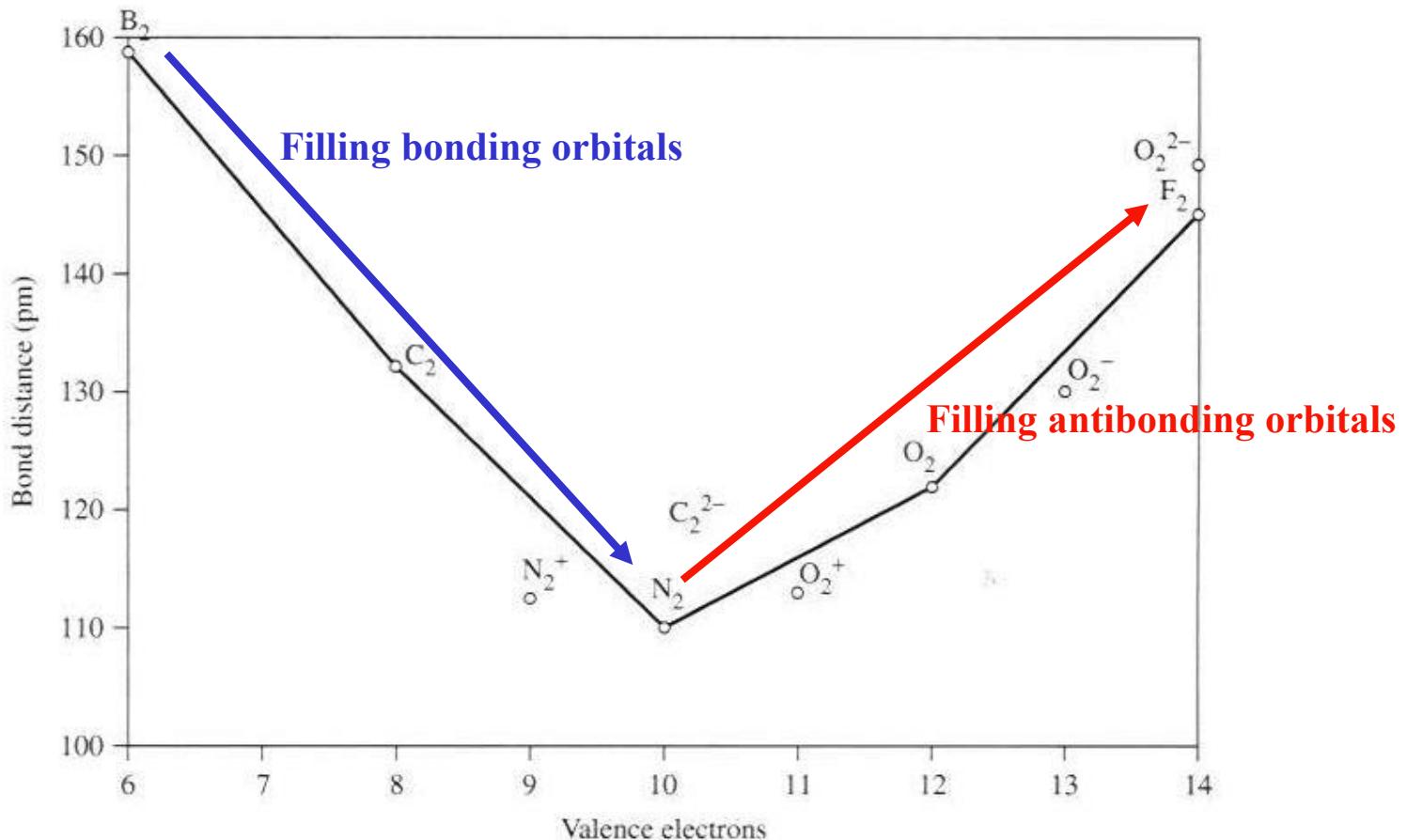
Li_2 to N_2



O_2 and F_2



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	120.7	493
O ₂ ⁺	2 1/2	111.6	643
O ₂ ⁻	1 1/2	135	395
O ₂ ²⁻	1	149	—
F ₂	1	141.2	155
Ne ₂	0	310	0.2*

*Van der Waal forces.

Hetronuclear 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

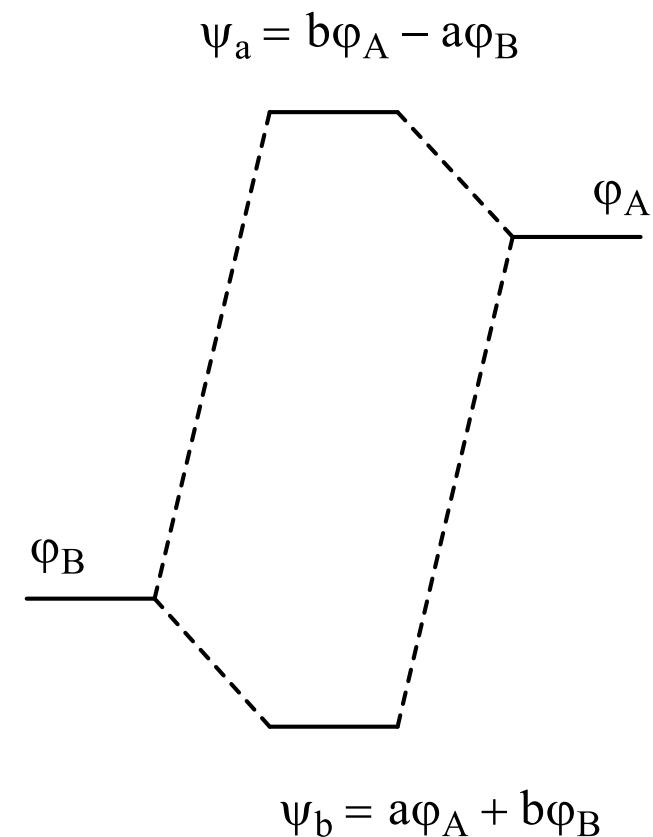
Heteronuclear Diatomics....

✉ 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.

a or b – extent to which each atomic orbitals contribute to MO.



If atom B is more electronegative than atom A, where $b > a$;

HF

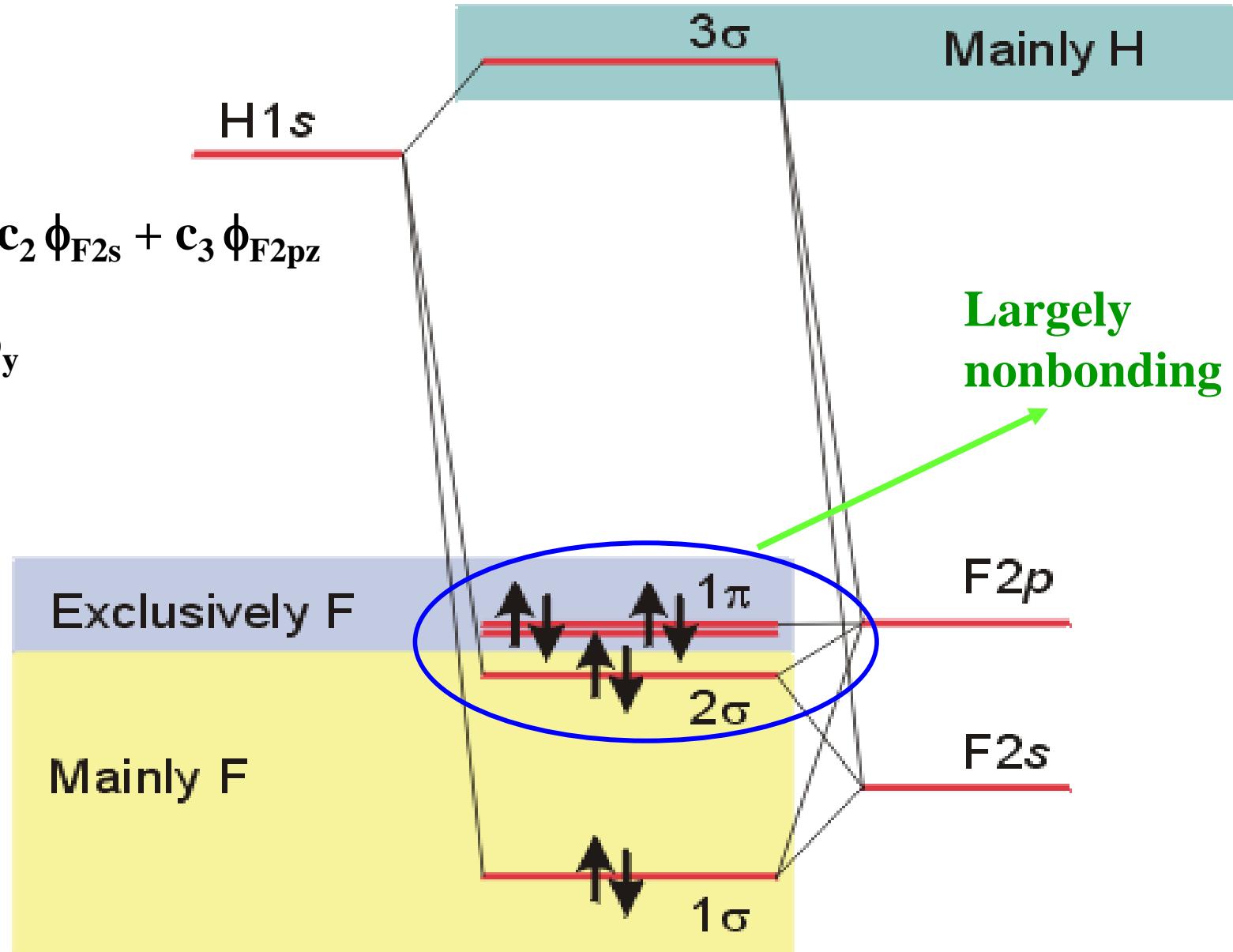
1s 1
2s, 2p 7

$$\psi = c_1 \phi_{H1s} + c_2 \phi_{F2s} + c_3 \phi_{F2pz}$$

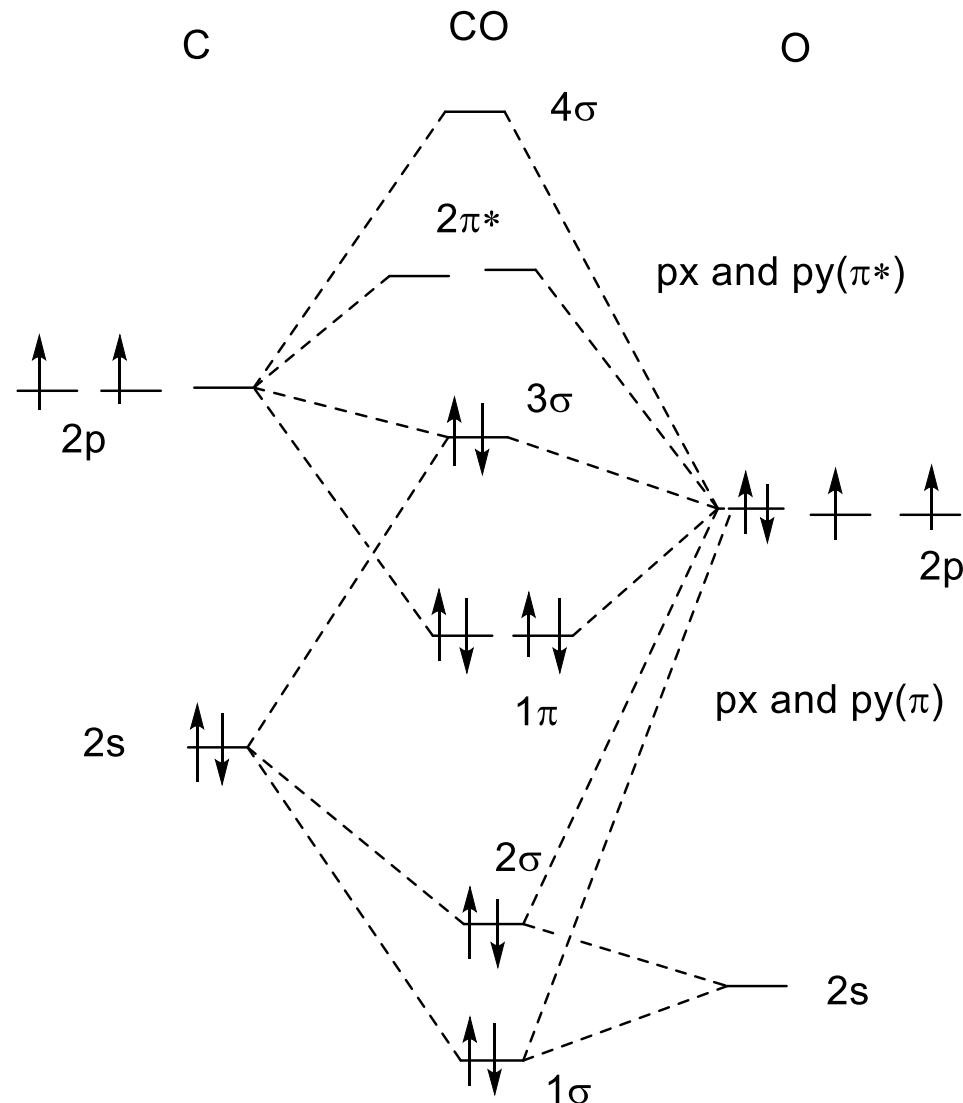
2p_x and 2p_y

1σ² 2σ² 1π⁴

Polar



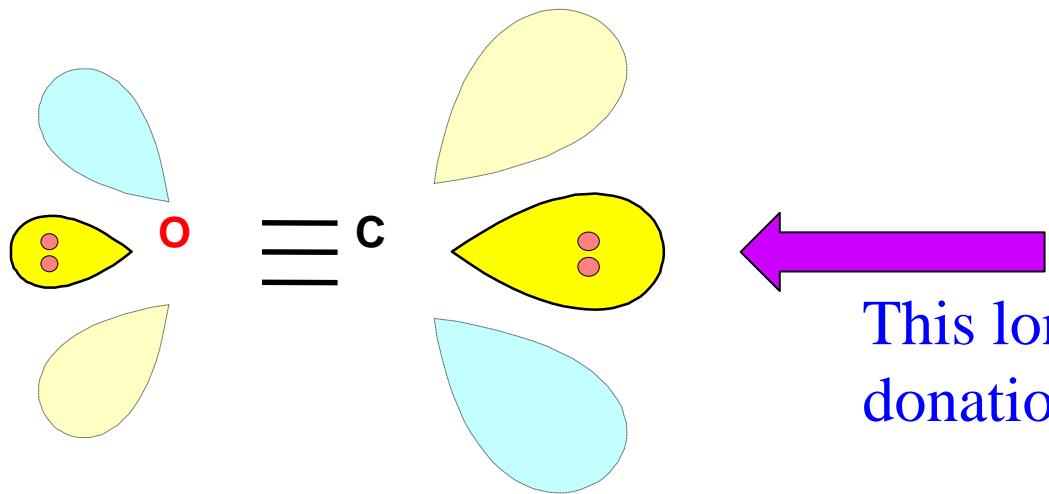
MO of CO



1σ and 3σ are essentially nonbonding and bond order is 3.

CO is a very good ligand!

How does it act?



This lone pair is available for donation to act as ligand.