

MOLECULAR ORBITAL THEORY (MOT)

Principles of Molecular Orbital Theory

Similar to atomic orbitals, molecular orbitals are wave functions, giving the probability of finding an electron in certain regions of a molecule. Each molecular orbital can only have 2 electrons, each with an opposite spin.

The fundamental principles involved in the molecular orbital theory:

- (i) The orbitals must have similar energy;
- (ii) The orbitals must overlap to a considerable extent.
- (iii) The orbitals must have the same symmetry about the molecular axis.

To produce the set of orbitals for a molecule, we add together the valence atomic wave functions for the bonded atoms in the molecule.

Atomic wave functions can have either plus or minus phases, this means the value of the wave function is either positive or negative.

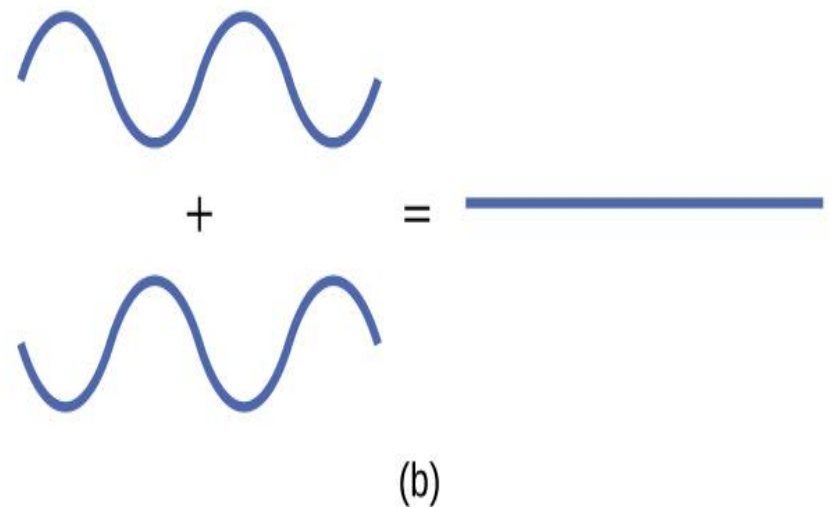
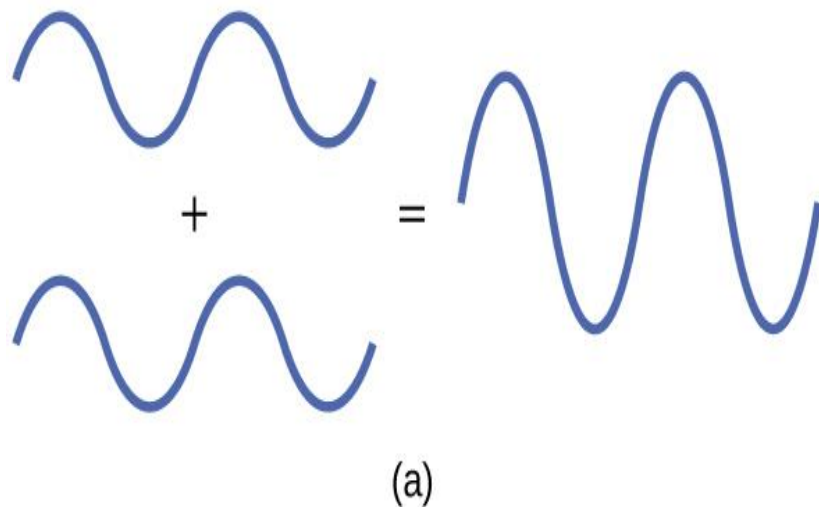


Figure. (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

Bonding, antibonding, and nonbonding MOs

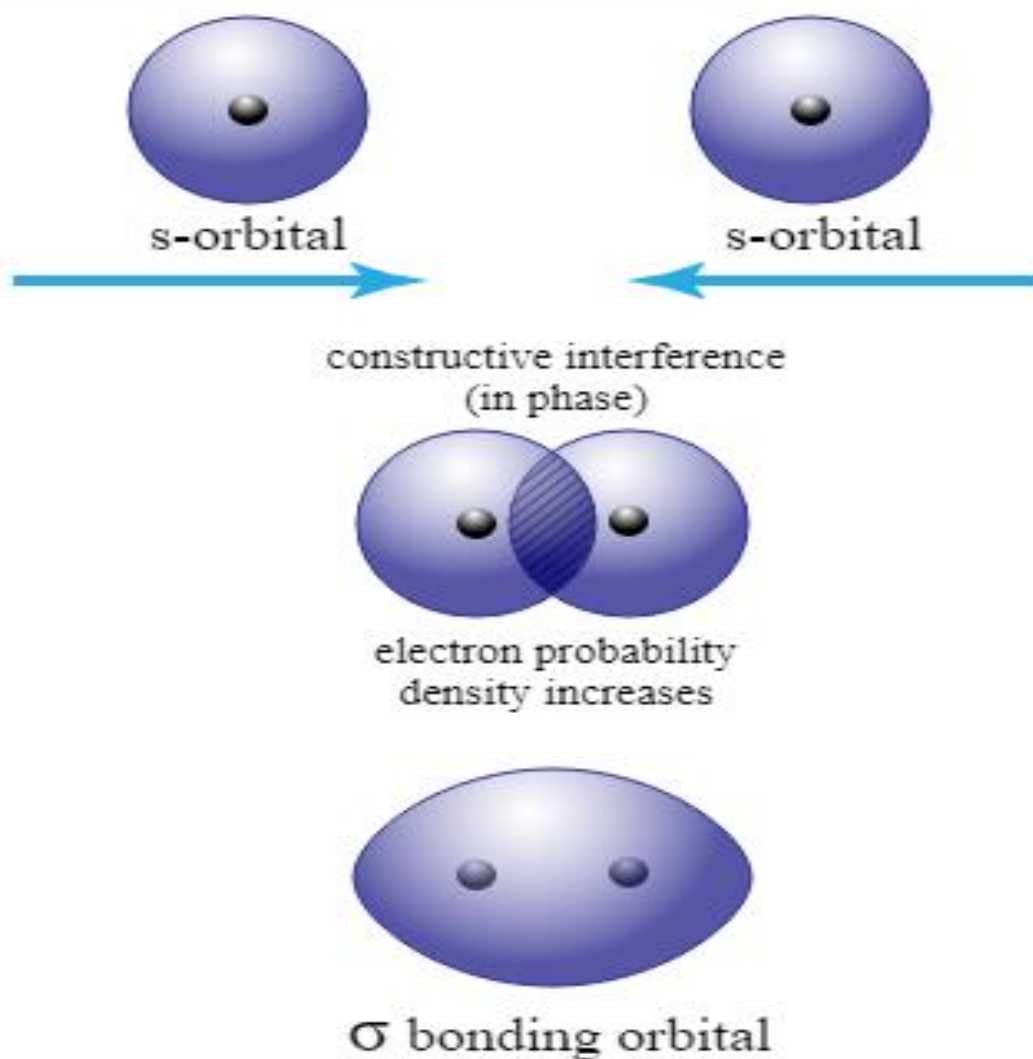
When atomic orbitals interact, the resulting molecular orbital can be of three types: bonding, antibonding, and nonbonding.

Bonding MOs:

1. Bonding orbitals are the molecular orbitals when there is constructive interactions (atomic orbital with same sign of the wave function ψ) occurs between the atomic orbitals in a molecule and leads to increase in electron density between the nuclei.

2. Bonding MOs are lower in energy than the atomic orbitals that combine to produce them.

Sigma Bond Formation s - orbitals



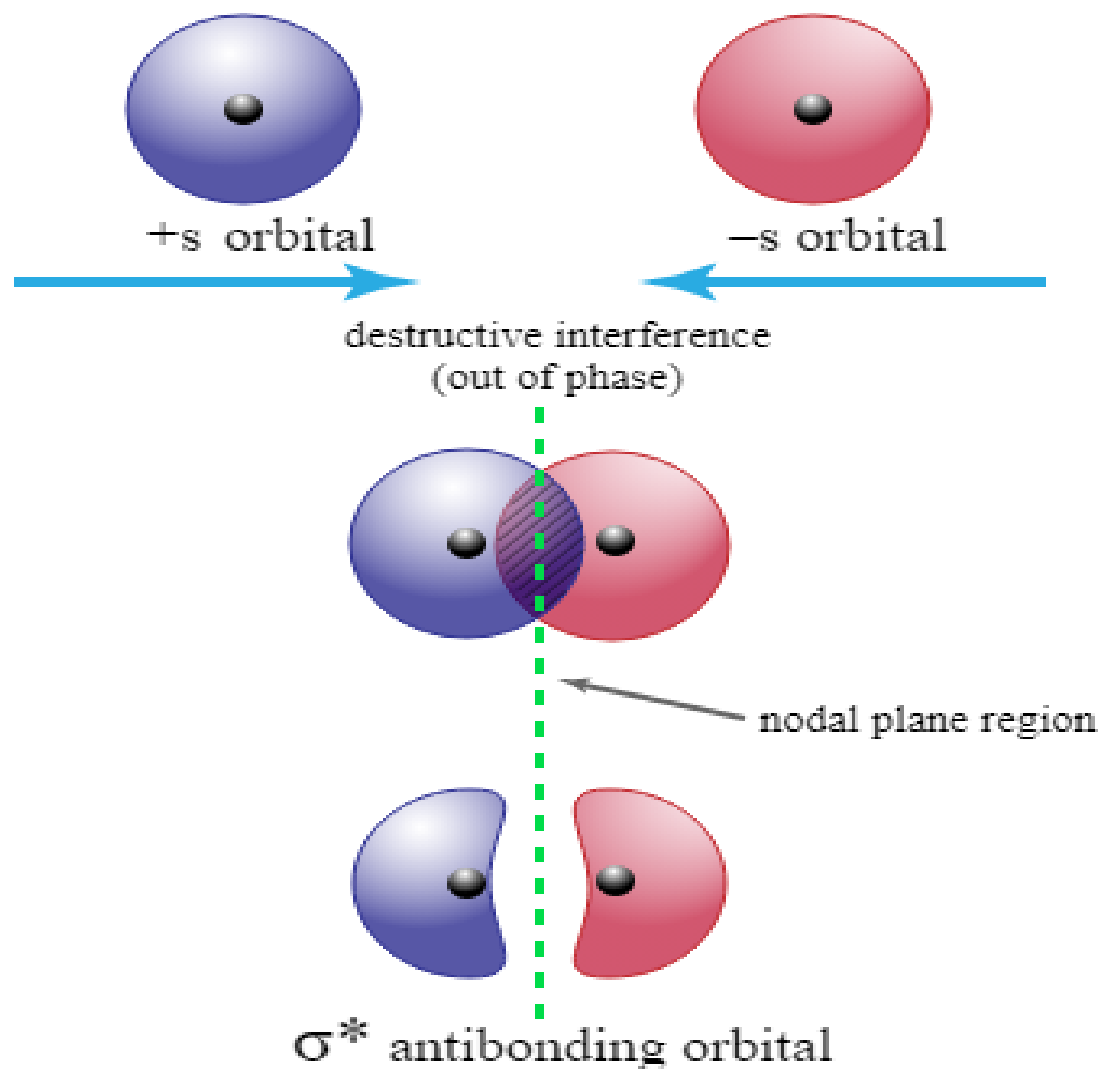
Antibonding MOs:

1. Antibonding orbitals are the molecular orbitals when there is destructive interactions (atomic orbital with opposite sign of the wave function ψ) occurs between the atomic orbitals in a molecule and leads to decrease in electron density between the nuclei and increase in density away from the nuclei.

2. Antibonding MOs are higher in energy than the atomic orbitals that combine to produce them.

3. It also contains a node and it tries to unstabilise the molecule.

sigma antibond formation s - orbitals

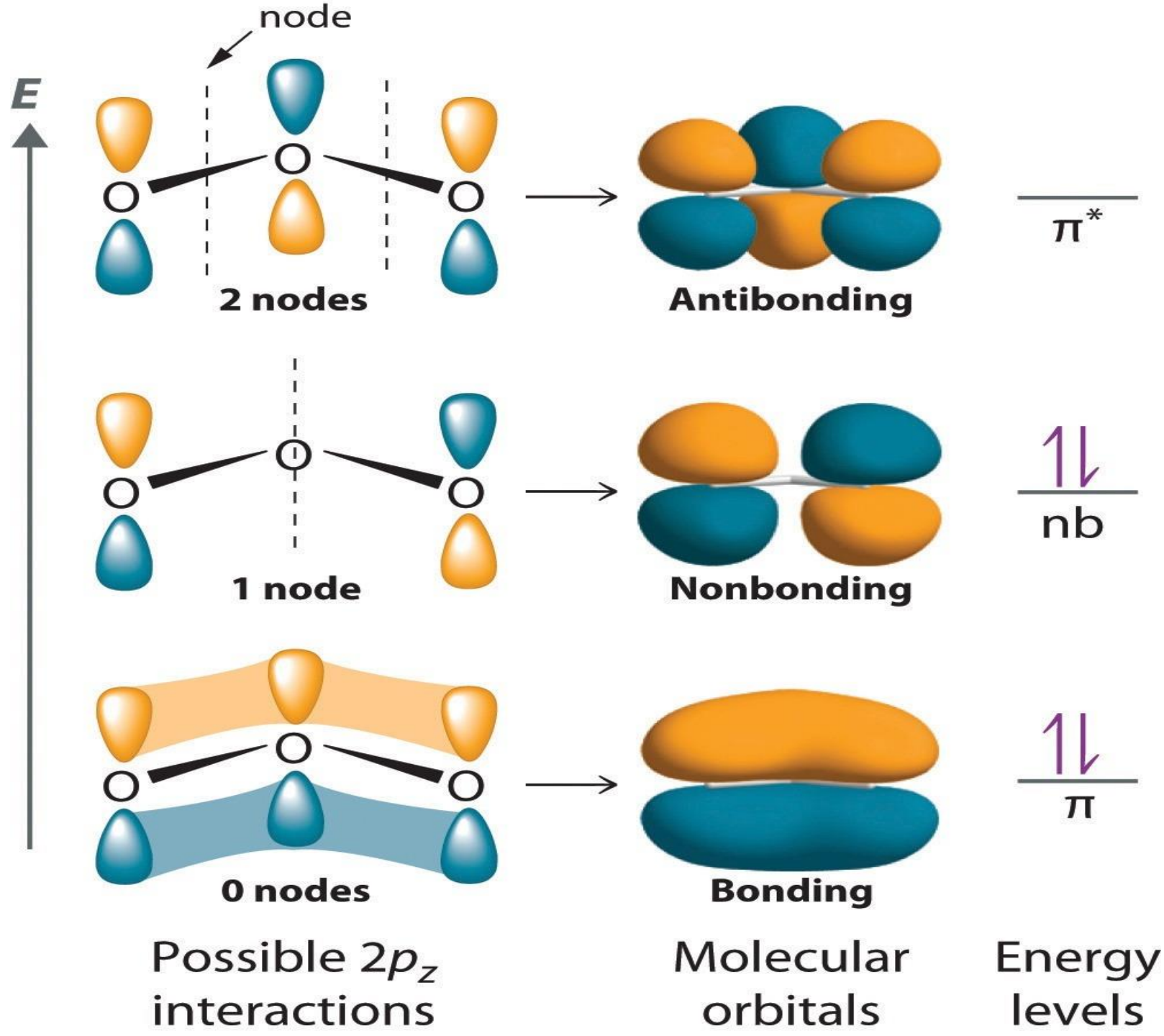


Nonbonding MOs:

1. Nonbonding MOs are the result of no interaction between atomic orbitals because symmetry does not match with any other atomic orbital of the molecule.
2. Nonbonding MOs have the same energy as the atomic orbitals of one of the atoms in the molecule.

3. Occupation of electrons in non bonding orbital neither increases nor decreases the bond order between the involved atoms.

4. The energy level of a non-bonding orbital is typically in between the valence shell bonding orbital and the antibonding orbital.



Magnetism: Diamagnetic and Paramagnetic properties

Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals.

Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first.

Electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins.

Diamagnetism

phenomenon in which a material is not magnetic itself but is repelled by a magnetic field; it occurs when there are only paired electrons present.

Paramagnetism

phenomenon in which a material is not magnetic itself but is attracted to a magnetic field; it occurs when there are unpaired electrons present.

Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field.

Bond Order

In molecular orbital theory, bond order is defined as half of the difference between the number of bonding and anti-bonding electrons. **Bond order = [(Number of electrons in bonding molecular orbitals) - (Number of electrons in anti-bonding molecular orbitals)]/2.**

Bond order suggest the no of bonds between two atoms. If it is coming out as 0 this means there is no bond between two atoms. This means they exist as monoatomic molecules.

σ bonding orbital

Bonding molecular orbital formed by in-phase overlap of atomic orbital along the axis of the bond, in which the electron density is found in between the nuclei.

σ^* bonding orbital

Antibonding molecular orbital formed by out-of-phase overlap of atomic orbital along the axis of the bond, generating a node between the nuclei.

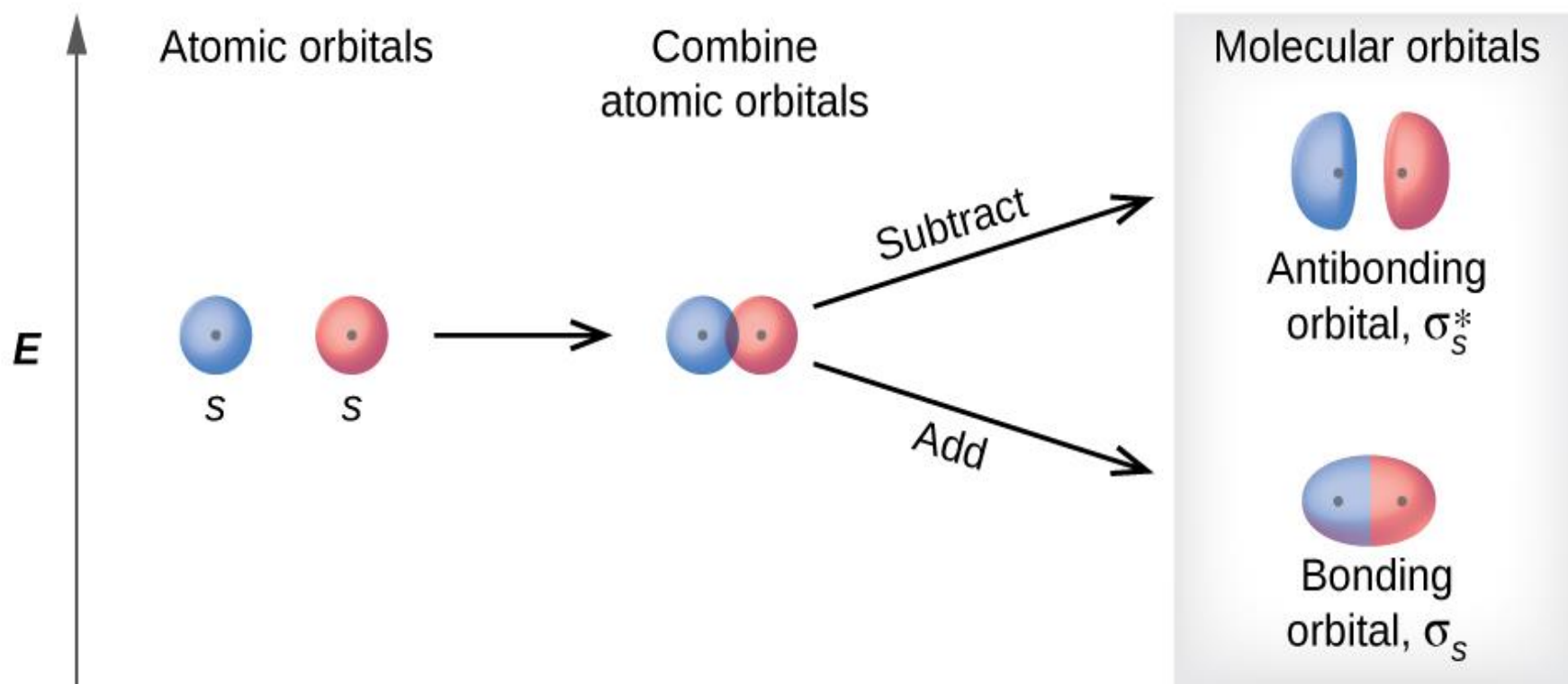


Figure. Sigma (σ) and sigma-star (σ^*) molecular orbitals are formed by the combination of two s atomic orbitals. The (.) signs indicate the locations of nuclei.

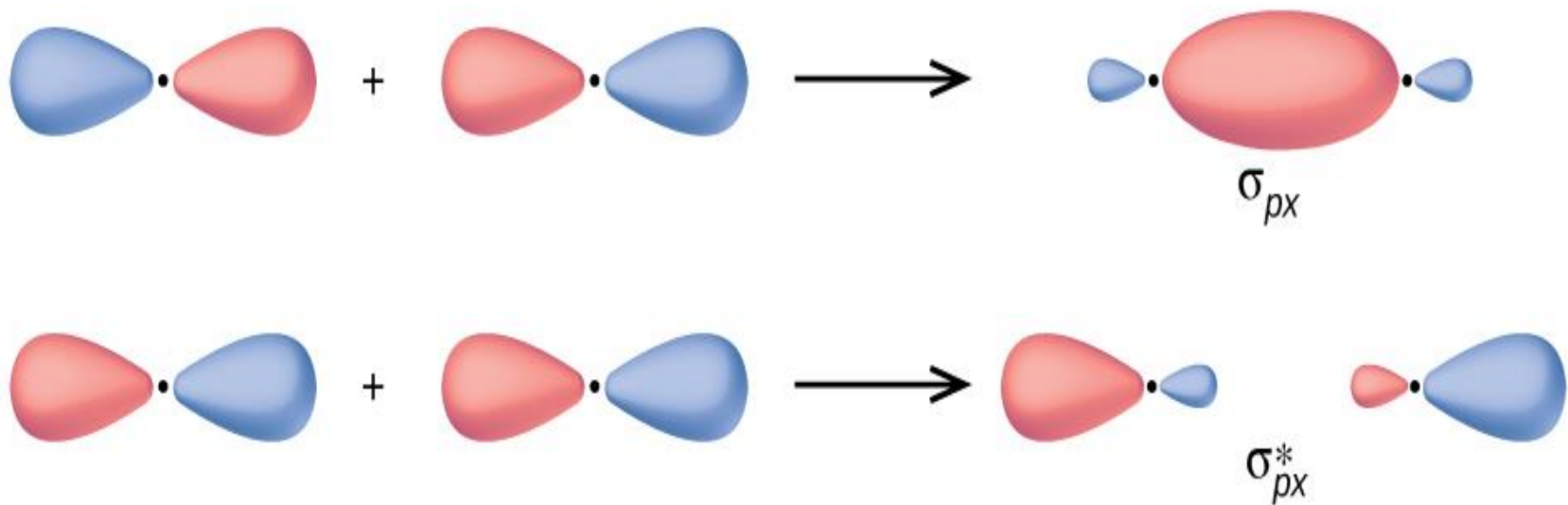


Figure. Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^* .

π bonding orbital

Molecular orbital formed by in-phase side-by-side overlap of atomic orbitals, in which the electron density is found on opposite sides of the internuclear axis.

π^* bonding orbital

Antibonding molecular orbital formed by out of phase side-by-side overlap of atomic orbitals, in which the electron density is found on both sides of the internuclear axis, and there is a node between the nuclei.

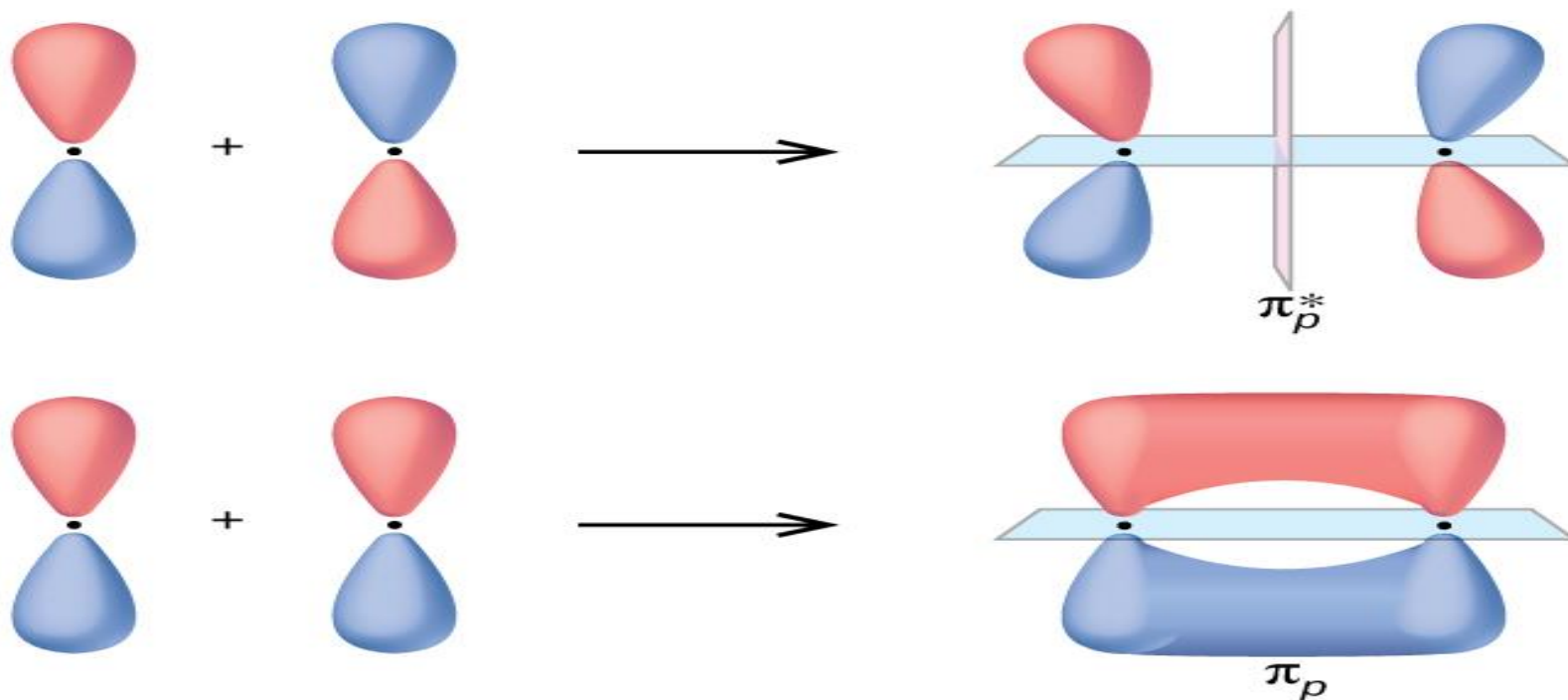
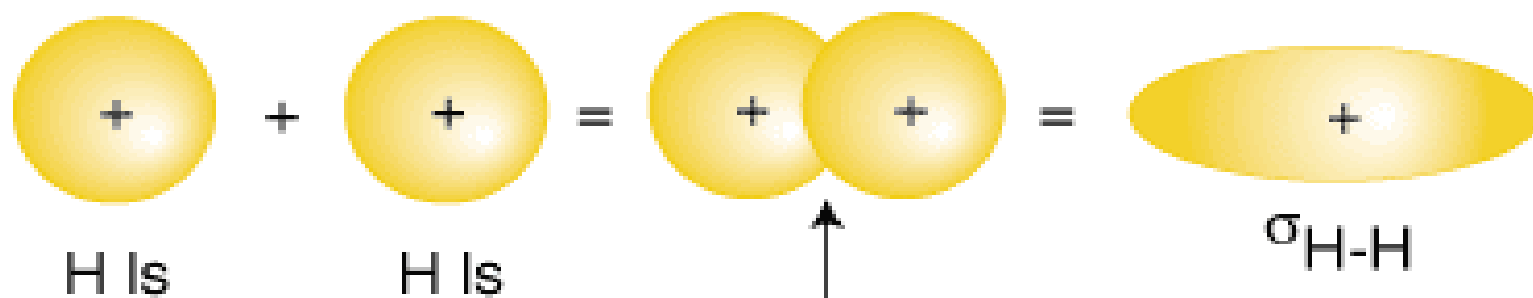


Figure. Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

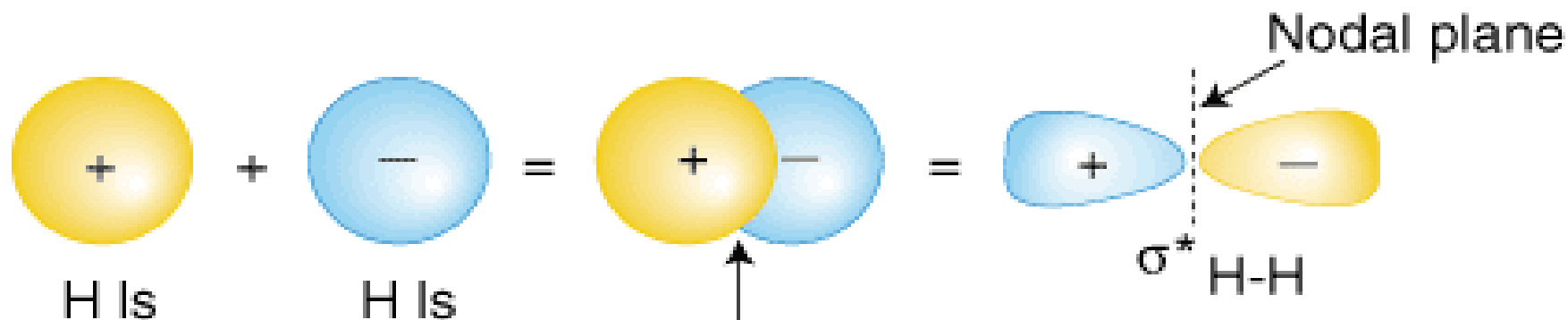
Examples

For example taking the simplest molecule hydrogen, H_2 . To produce the molecular orbitals for hydrogen, addition of the valence atomic wave-functions results the molecular orbitals for hydrogen.

There are two ways to add the wave functions, either both in-phase (either both plus or both minus) or out-of-phase (one plus and the other minus).



Constructive
overlap



Destructive
overlap

Fig. shows how atomic wave functions can be added together to produce molecular orbitals.

The in-phase overlap produces bonding molecular orbital and build-up of electron density between the two nuclei which results a lowering of energy for that orbital.

Electrons in this orbital spend most of their time in the region directly between the two nuclei.

The out of phase overlap produce antibonding molecular orbital and, shows a decrease in electron density between the nuclei and reaching a value of zero at the midpoint between the nuclei where there is a nodal plane.

Due to the decrease in electron density between the nuclei, the anti-bonding orbital is higher in energy than both the bonding orbitals and the parent orbitals.

Electrons which are placed in a bonding molecular orbital are known as bonding electrons and signify attraction.

Electrons which are placed in an anti-bonding molecular orbital are known as anti-bonding electrons and signify repulsion.

Orbital correlation diagram for H_2 , is given as:

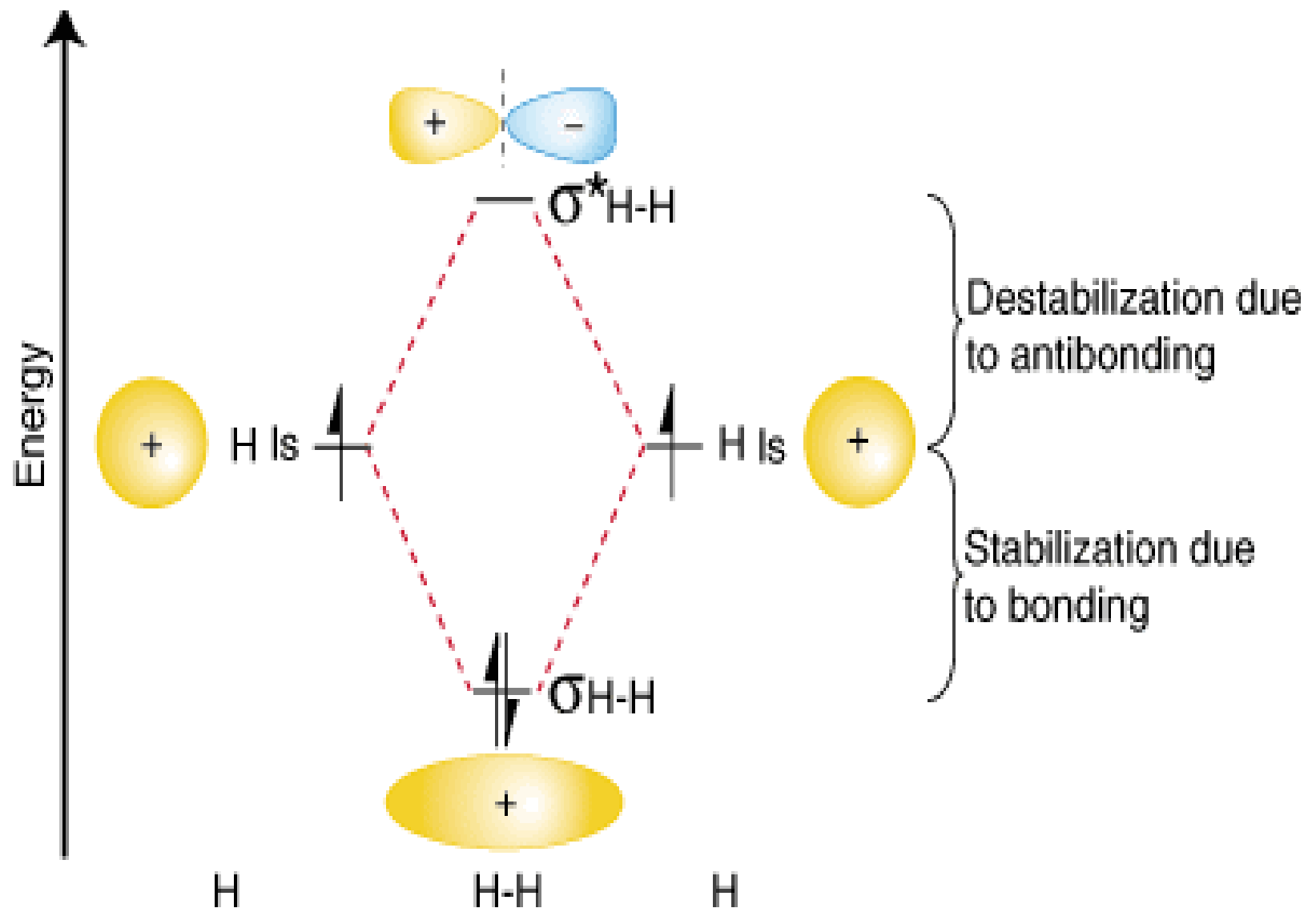


Figure: An orbital correlation diagram for hydrogen

The orbitals of the separated atoms are written on either side of the diagram as horizontal lines, at heights denoting their relative energies.

The electrons in each atomic orbital are represented by arrows.

In the middle of the diagram, the molecular orbitals of the molecule of interest are written.

Dashed lines connect the parent atomic orbitals with the daughter molecular orbitals.

In general, bonding molecular orbitals are lower in energy than either of their parent atomic orbitals. Similarly, anti-bonding orbitals are higher in energy than either of its parent atomic orbitals.

The amount of stabilization of the bonding orbital must equal the amount of destabilization of the anti-bonding orbital, as shown above.

Bond order of H₂

Bond order

Bond order = $\frac{1}{2}$ (e in bonding MO - e in anti bonding MO)

For H₂, bond order = $\frac{1}{2}$ (2-0) = 1, which means H₂ has only one bond. The anti bonding orbital is empty. Thus, H₂ is a stable molecule.

Again, in the MO, there is no unpaired electron, so H₂ is diamagnetic.

Bonding in Helium

An orbital correlation diagram for He_2 is provided in :

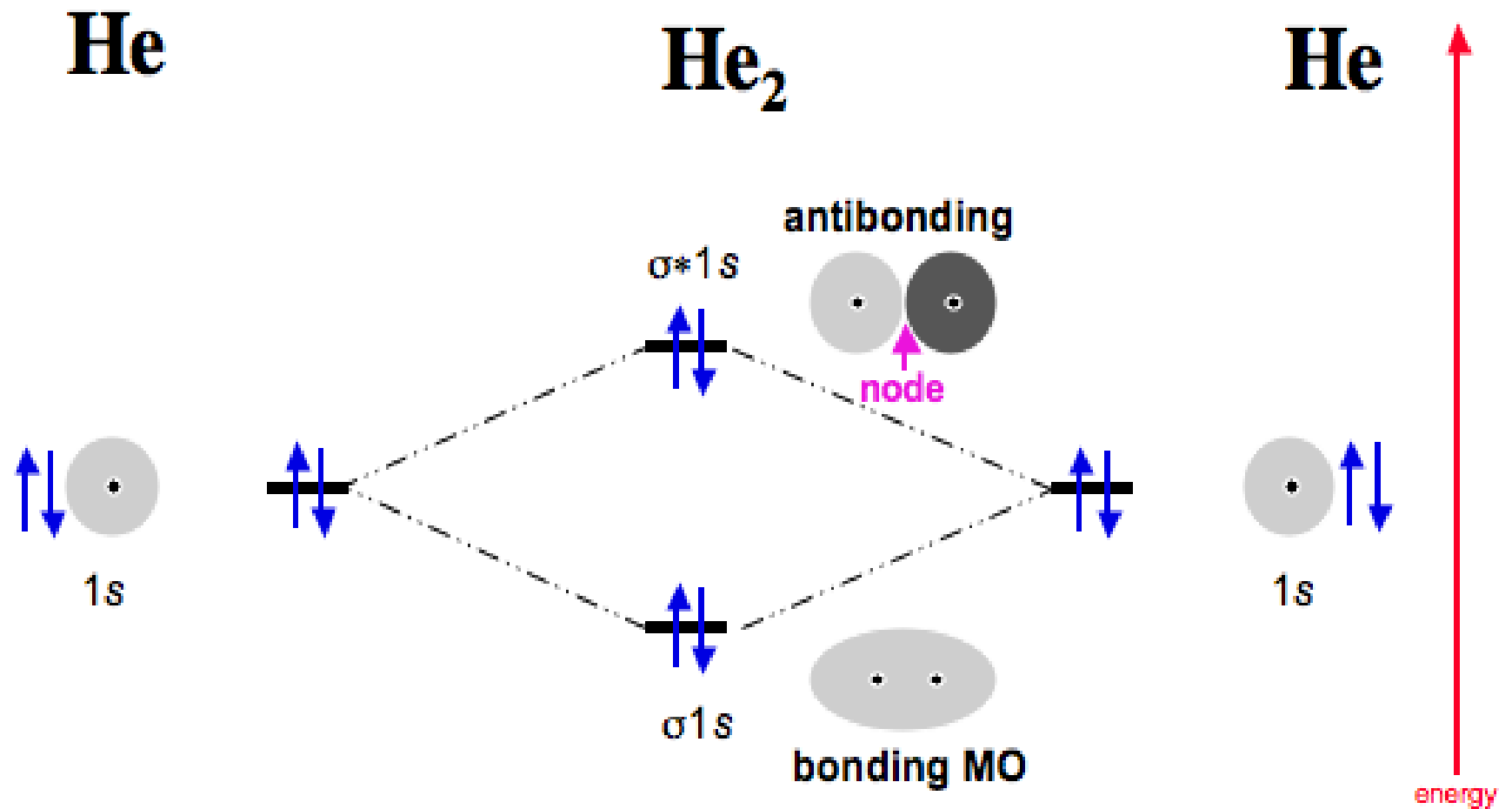


Figure : An orbital correlation diagram for a hypothetical He-He molecule

From the orbital correlation diagram above, it is notice that the amount of stabilization due to bonding is equal to the amount of destabilization due to anti-bonding, because there are two electrons in the bonding orbital and two electrons in the anti-bonding orbital.

The total energy of an He_2 molecule would be essentially the same as the energy of a pair of isolated helium atoms, and there would be nothing to hold the helium atoms together to form a molecule.

The fact that an He_2 molecule is neither more nor less stable than a pair of isolated helium atoms.

Therefore, there is no net stabilization due to bonding . So the He_2 molecule will not exist in nature.

Bond order of He

Bond Order =(Electrons in bonding molecular orbitals - electrons in antibonding molecular orbitals) /2

Bond Order =Nb-Na/2

Bond Order =2-2/2=0

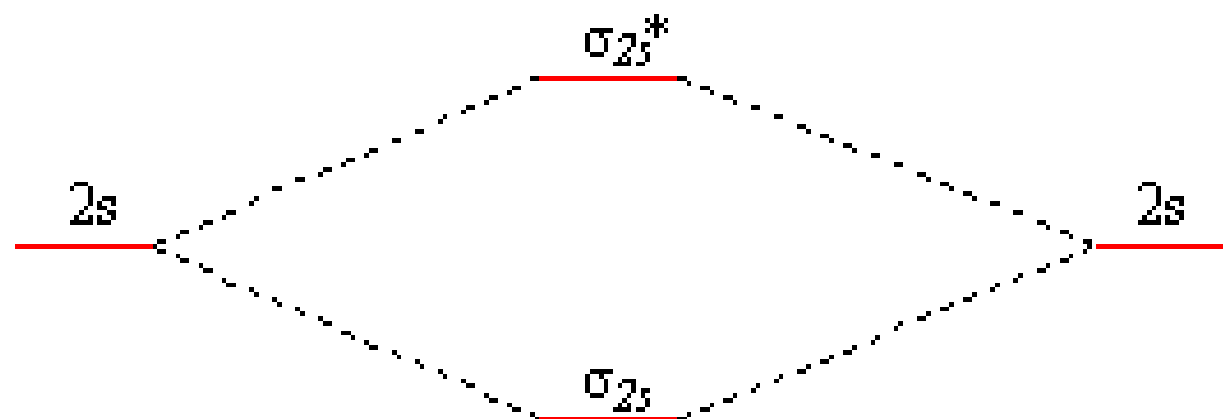
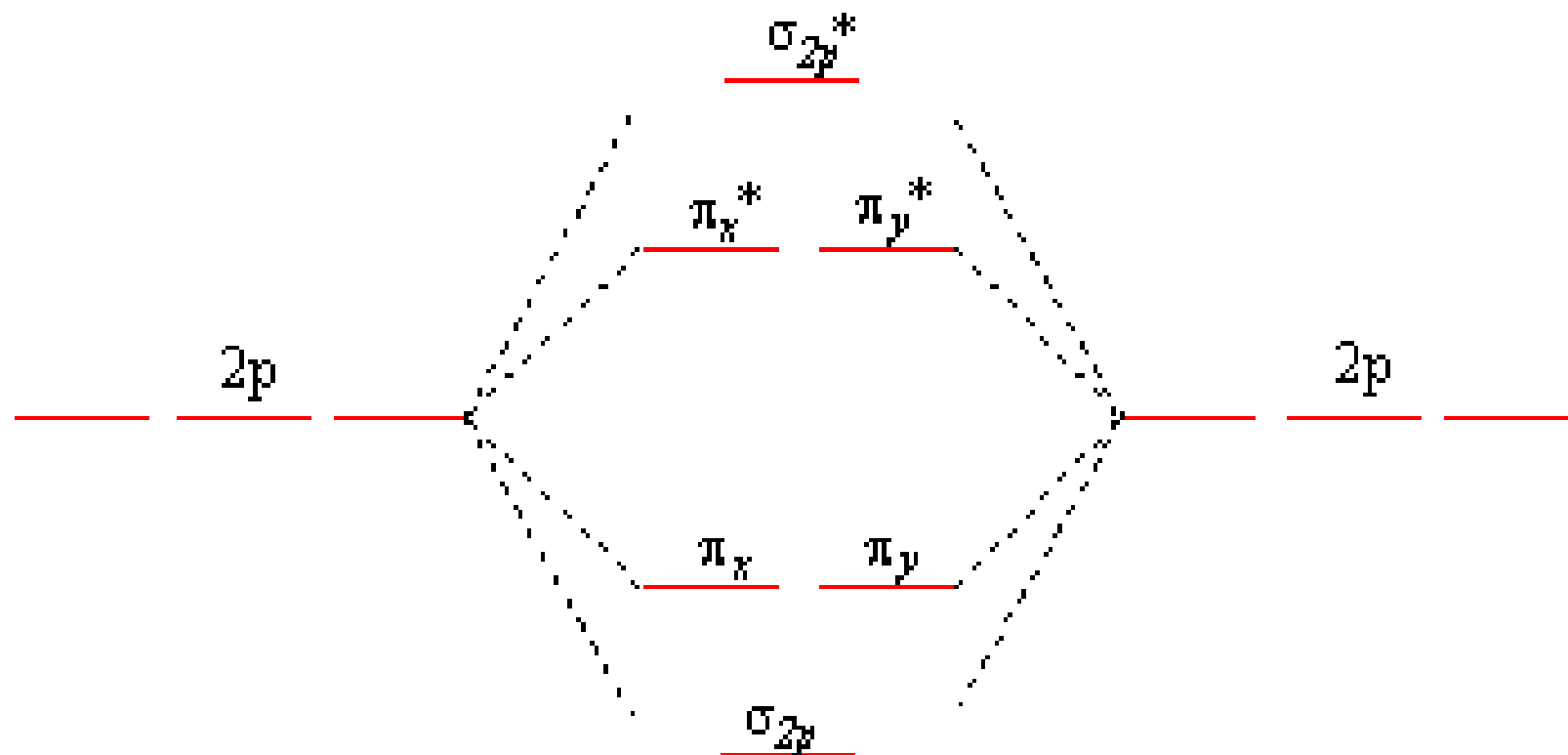
The bond order calculation shows that there will be a bond order of zero for the He_2 molecule. Hence helium is a noble gas and does not form covalent compounds.

Molecular Orbitals of the Second Energy Level

The interaction of four valence atomic orbitals on one atom ($2s$, $2p_x$, $2p_y$ and $2p_z$) with a set of four atomic orbitals on another atom leads to the formation of a total of eight molecular orbitals: σ_{2s} , σ_{2s}^* , σ_{2p} , σ_{2p}^* , π_x , π_y , π_x^* , and π_y^* .

There is a significant difference between the energies of the $2s$ and $2p$ orbitals on an atom. As a result, the σ_{2s} and σ_{2s}^* orbitals both lie at lower energies than the σ_{2p} , σ_{2p}^* , π_x , π_y , π_x^* , and π_y^* orbitals.

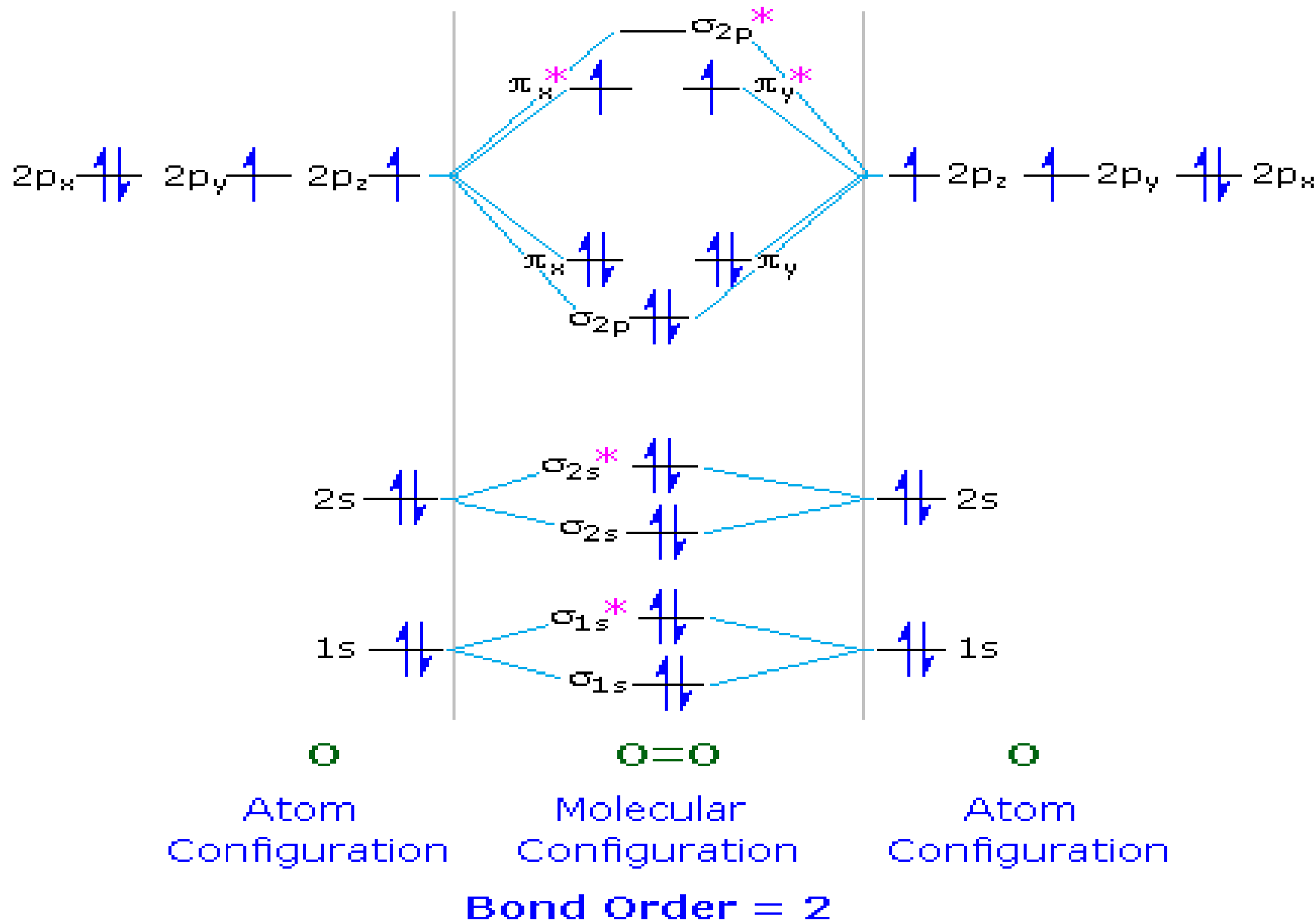
σ_{2p} orbital lies at a lower energy than the π_x and π_y orbitals, and the σ_{2p}^* orbital lies at higher energy than the π_x^* and π_y^* orbitals, as shown in the figure below.



MO diagram of O₂

This molecule has sixteen electrons. The atomic orbitals combine to produce the following molecular orbital diagram:

Energy ↑



Bond order of O₂

Bond order is given as (number of Bonding electrons - number of anti bonding electrons)/2

$$\text{Thus BO} = (10 - 6) / 2$$

$$= 4 / 2$$

$$= 2$$

Why is O₂ paramagnetic?

According to molecular orbital Theory (MOT), there is 1 unpaired electron in the π_{2px} antibonding orbital and another unpaired electron in π_{2py} antibonding orbital.

As molecules containing unpaired electrons are strongly attracted by magnetic field, hence oxygen has paramagnetic nature.

in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure .

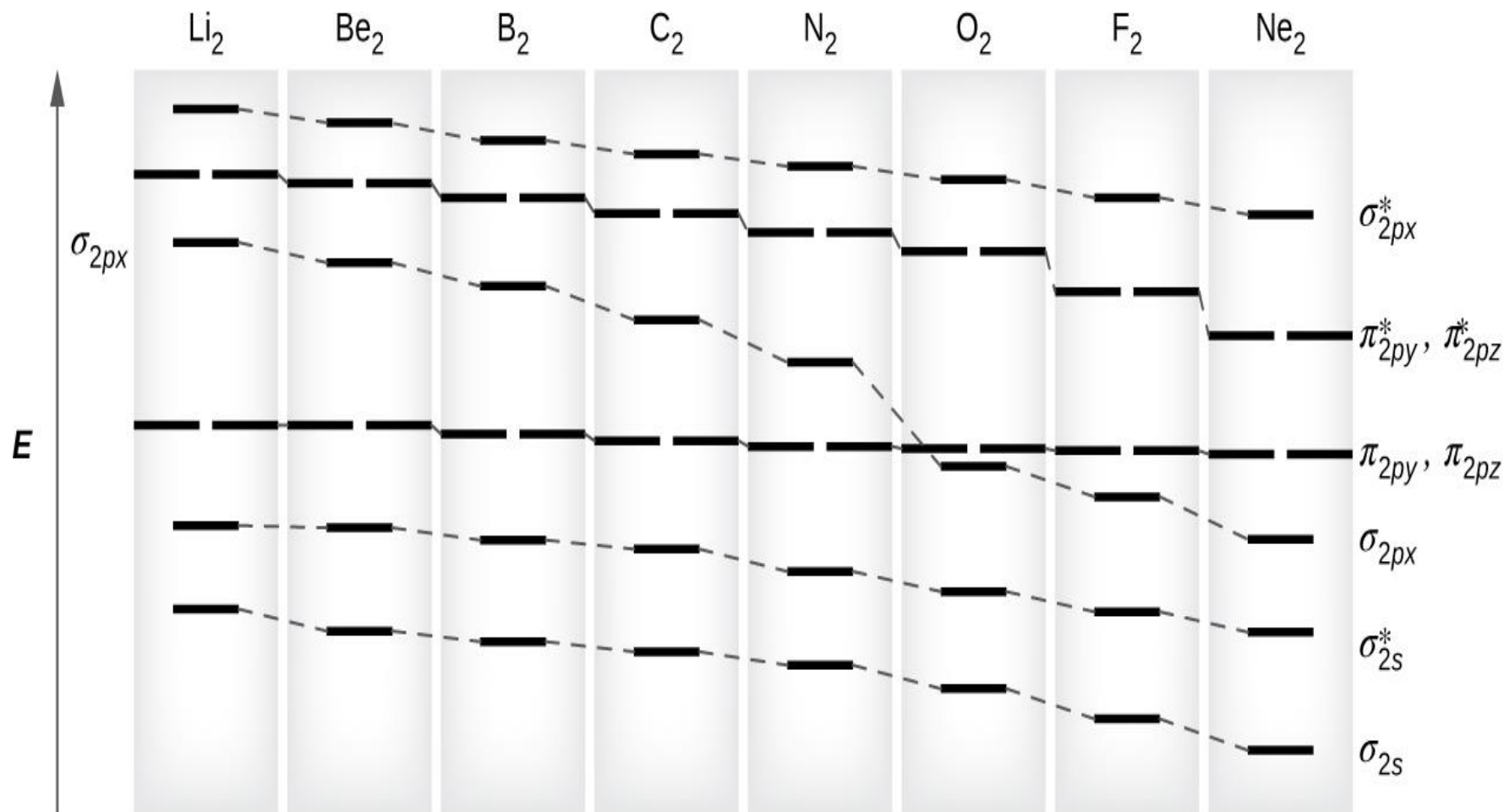


Figure. This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2 , the order of the orbitals changes.

for atoms with three or fewer electrons in the p orbitals (Li through N) there is a different pattern, in which the σ_p orbital is higher in energy than the π_p set.

This switch in orbital ordering occurs because of a phenomenon called **s-p mixing**. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals.

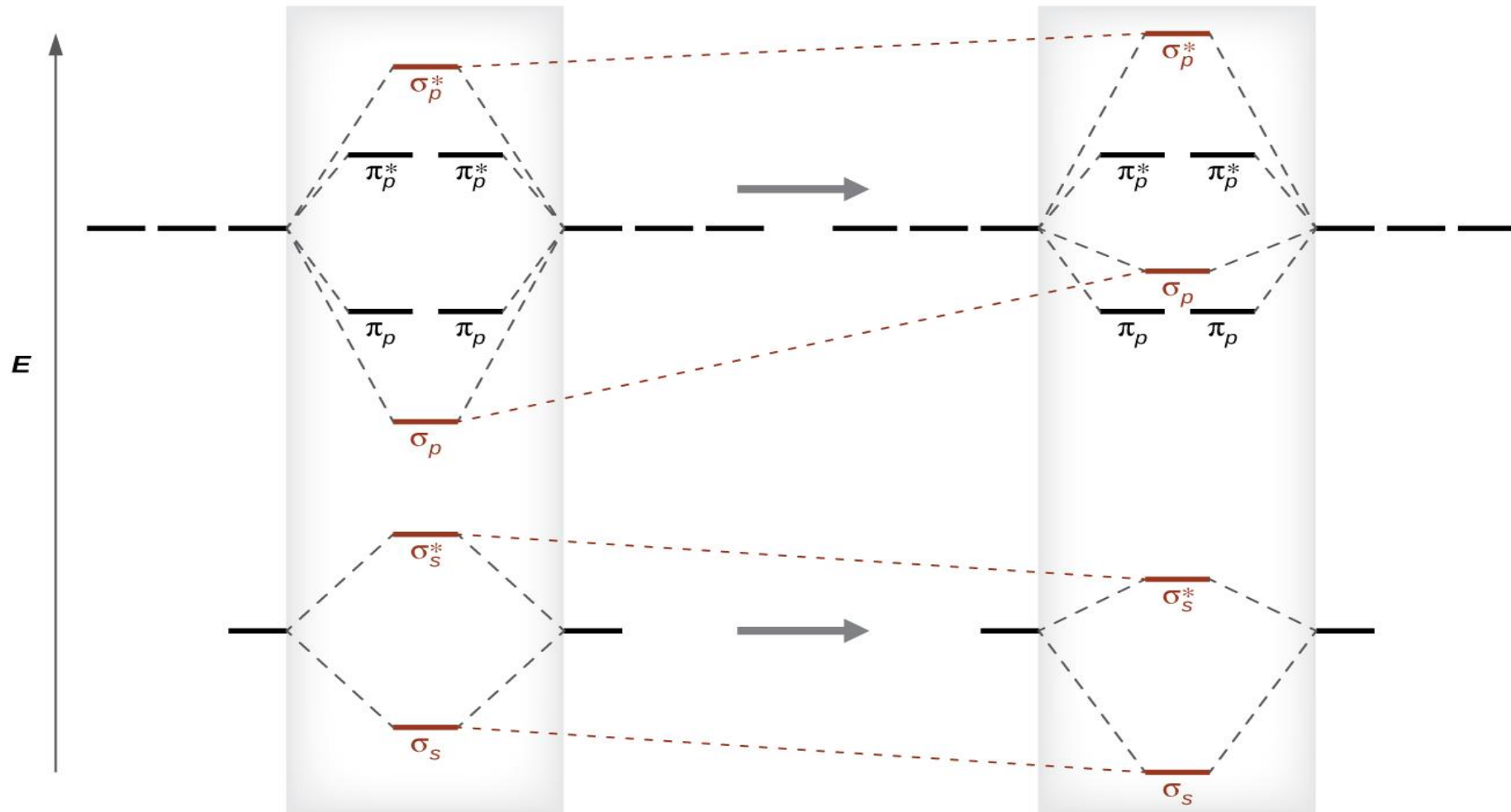


Figure. Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p^* orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

s-p mixing occurs when the s and p orbitals have similar energies.

When a single p orbital contains a pair of electrons, the act of pairing the electrons raises the energy of the orbital.

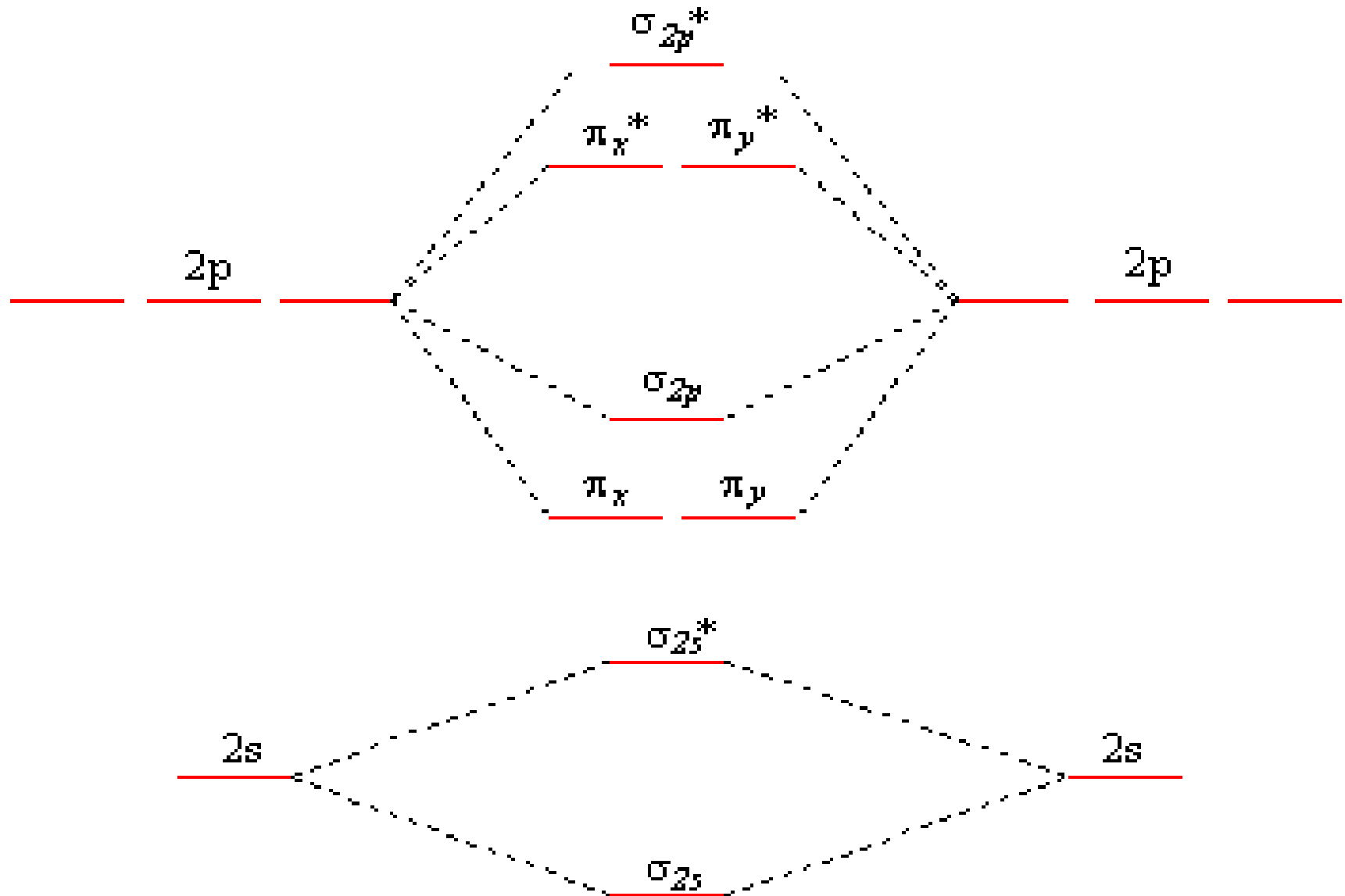
Thus the $2p$ orbitals for O, F, and Ne are higher in energy than the $2p$ orbitals for Li, Be, B, C, and N.

Because of this, O_2 , F_2 , and N_2 only have negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in (Figure).

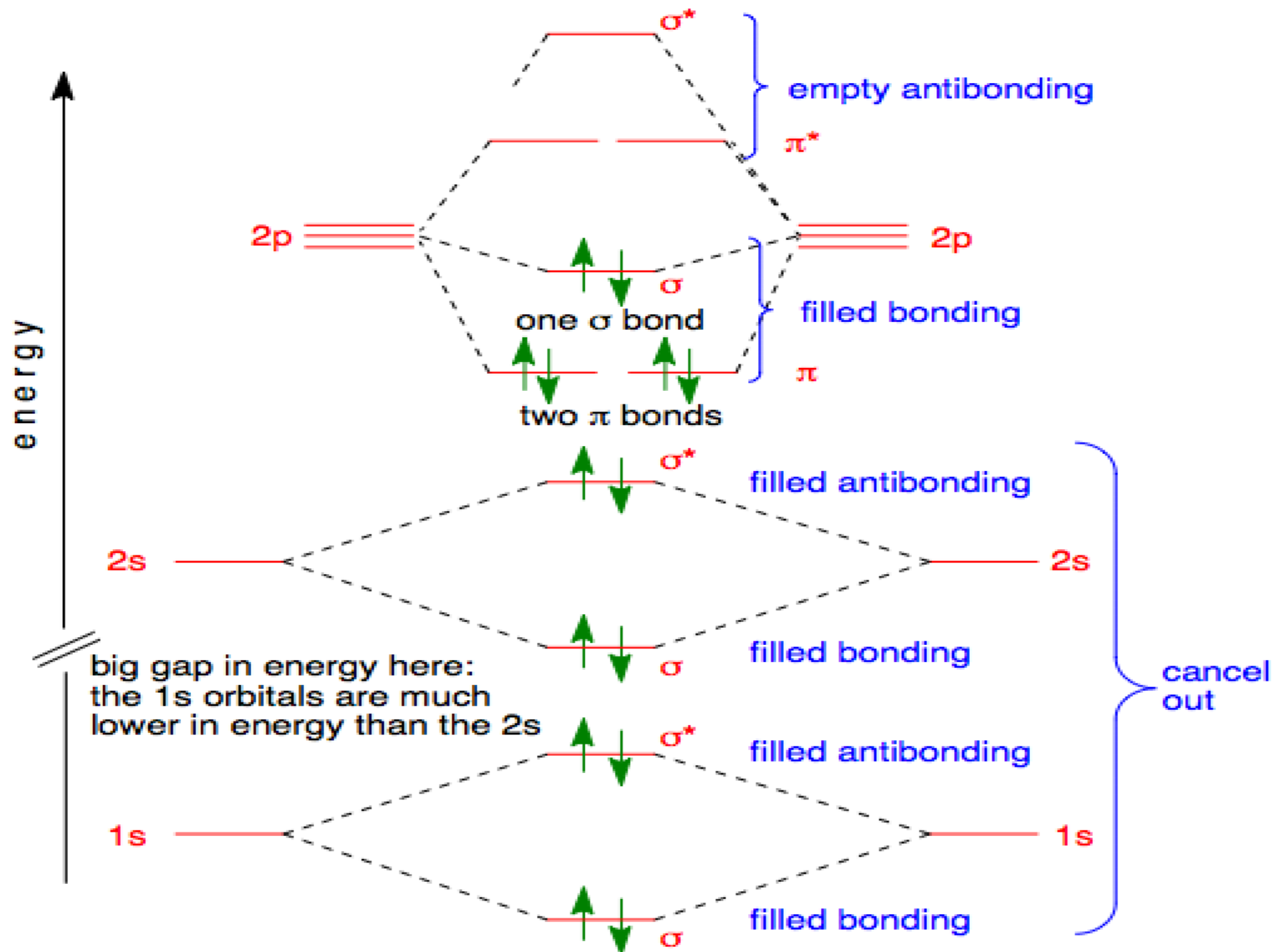
All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

MO diagram of N₂

N_2 are best described by a model, as shown in the figure below.



This molecule has fourteen electrons. The atomic orbitals combine to produce the following molecular orbital diagram:



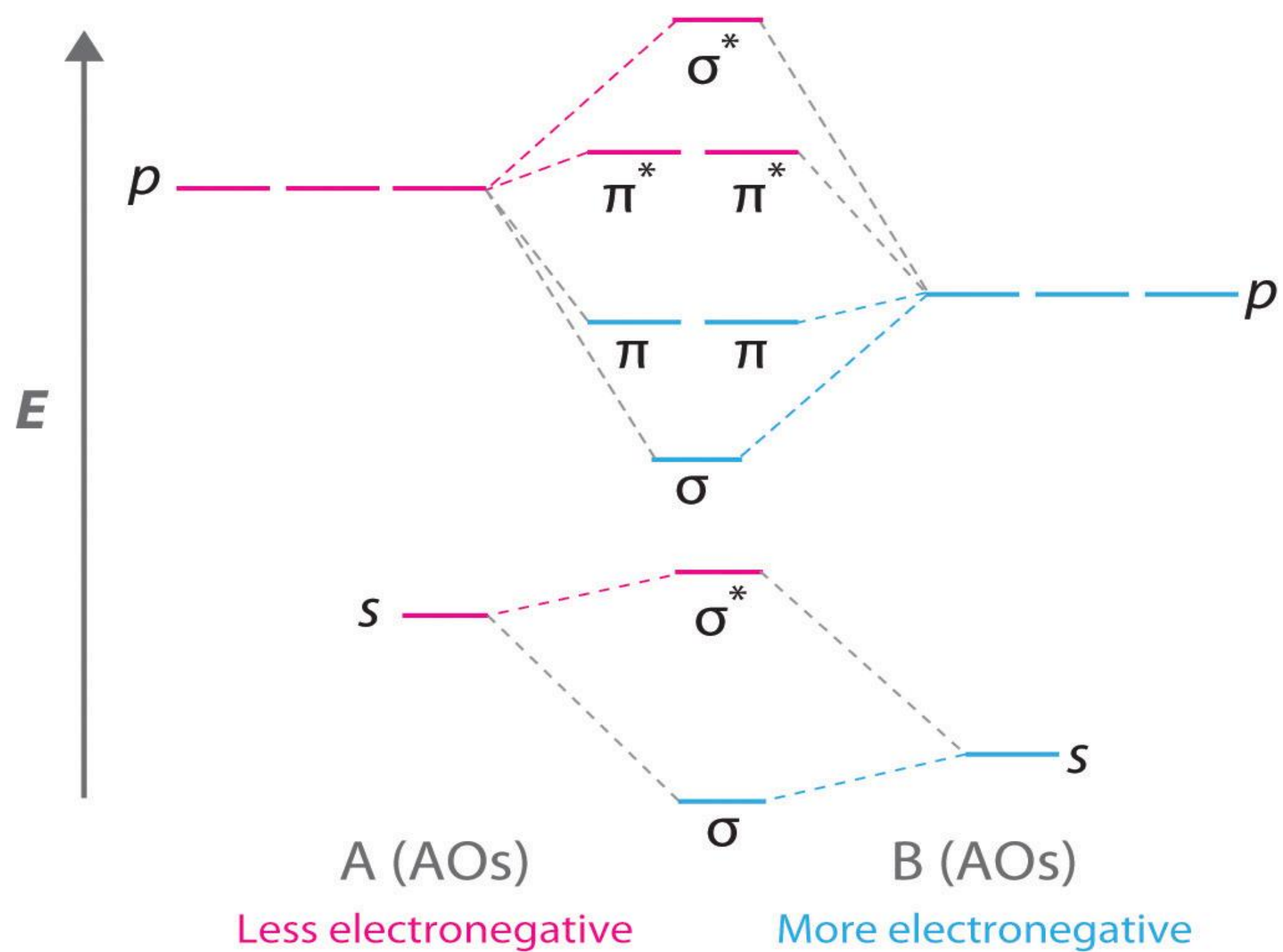
Unlike O_2 , the σ_{2p} and π_{2p} orbitals are switched in energy

Bond order of N₂

Bond order is given as (number of Bonding electrons - number of anti bonding electrons)/2

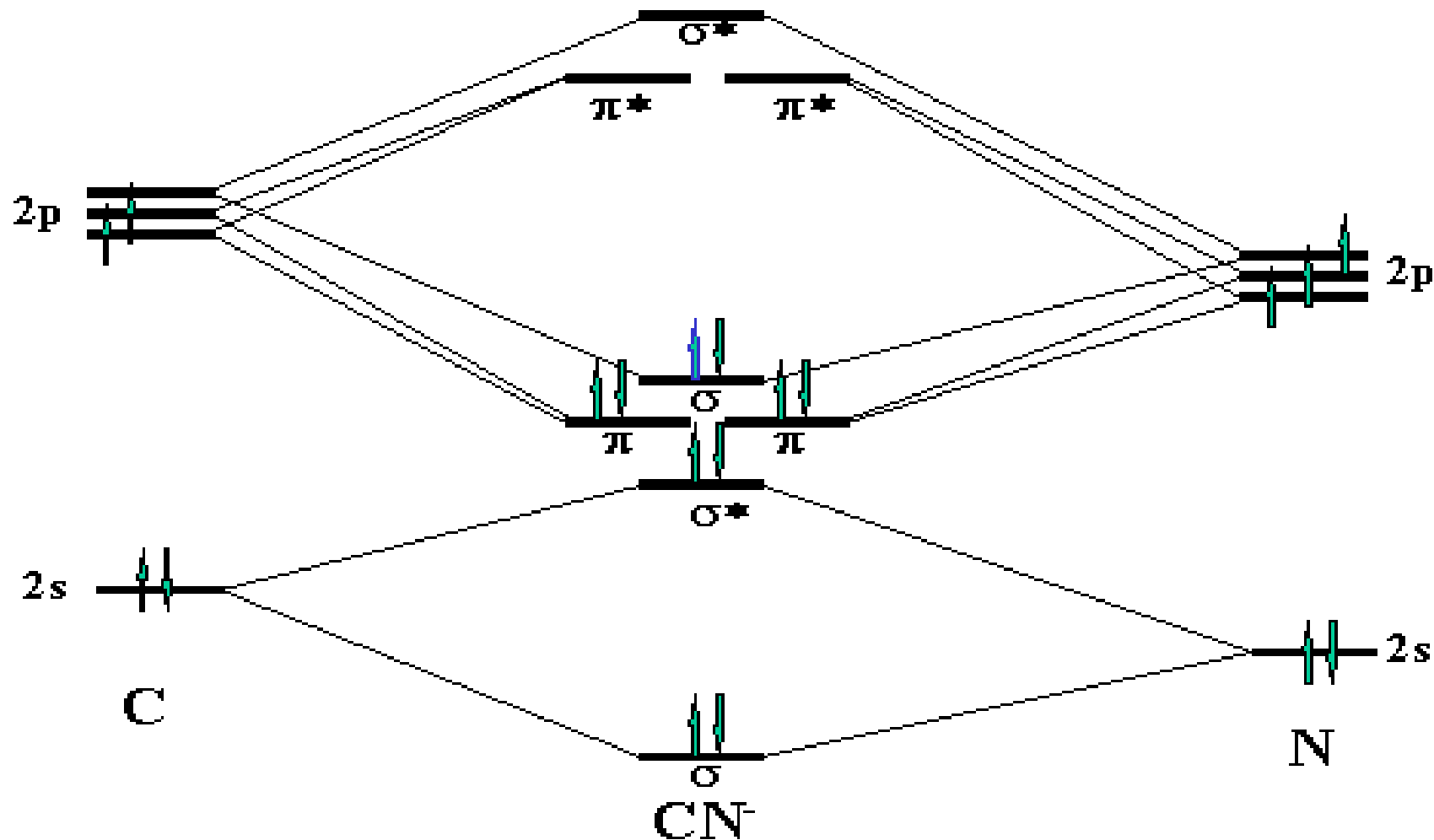
$$\text{Thus BO} = (10 - 4) / 2 = 3$$

MO diagram of heteronuclear diatomic molecule



Molecular Orbital Diagram of CN^-

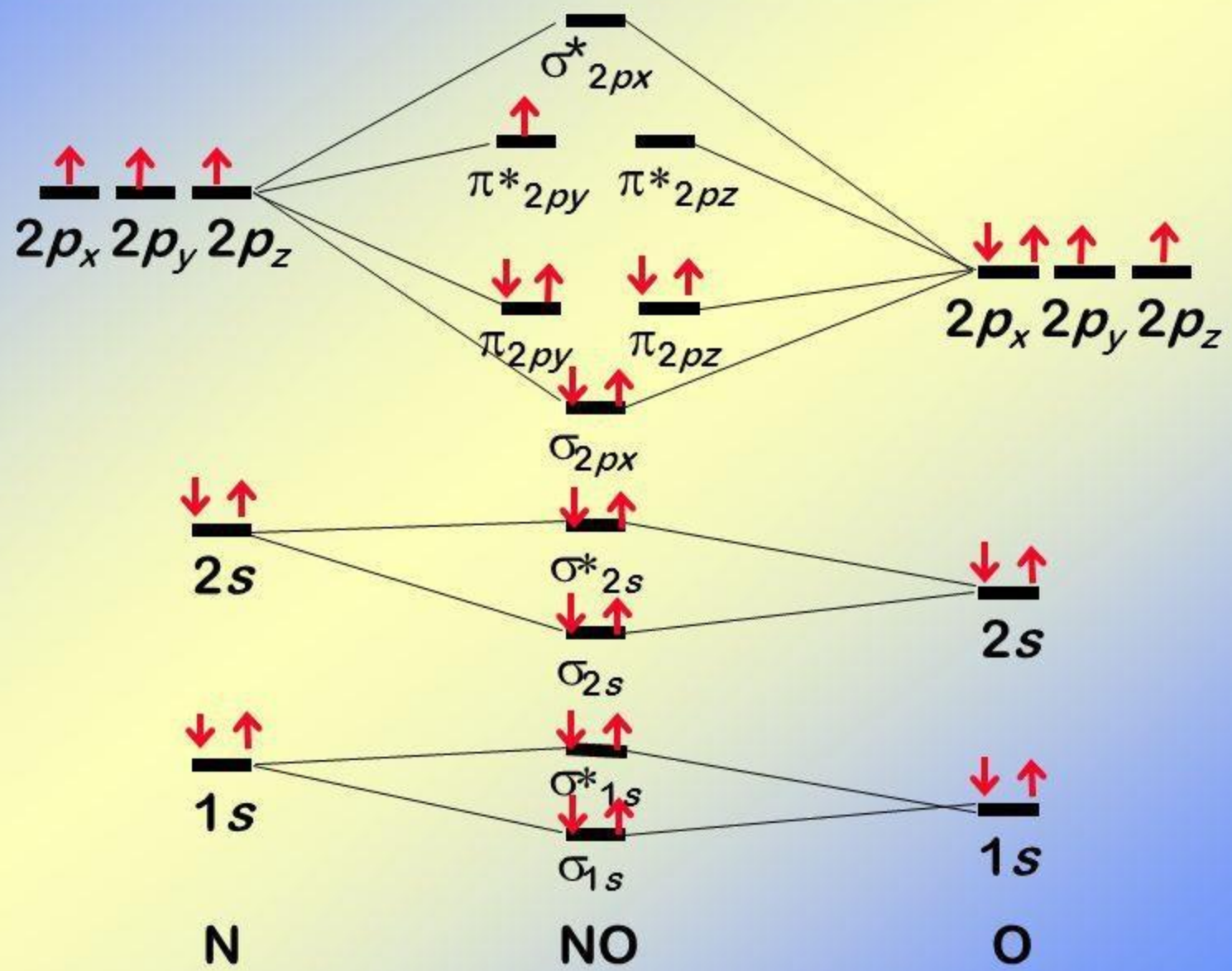
Nitrogen is more electronegative than Carbon (due to higher nuclear charge), thus, the atomic orbitals of N should be lower in energy than those of C. In the diagram shown below, only the orbitals of the 2nd shell are shown. Only the valence electrons are considered: C has 4 and N has 5. The CN⁻ ion has an additional electron (shown in blue) because of its charge:



The bond order of CN^- is 3. Since all the electrons are paired, this ion should be diamagnetic.

MO diagram of NO

MO diagram for NO



Bond order of NO

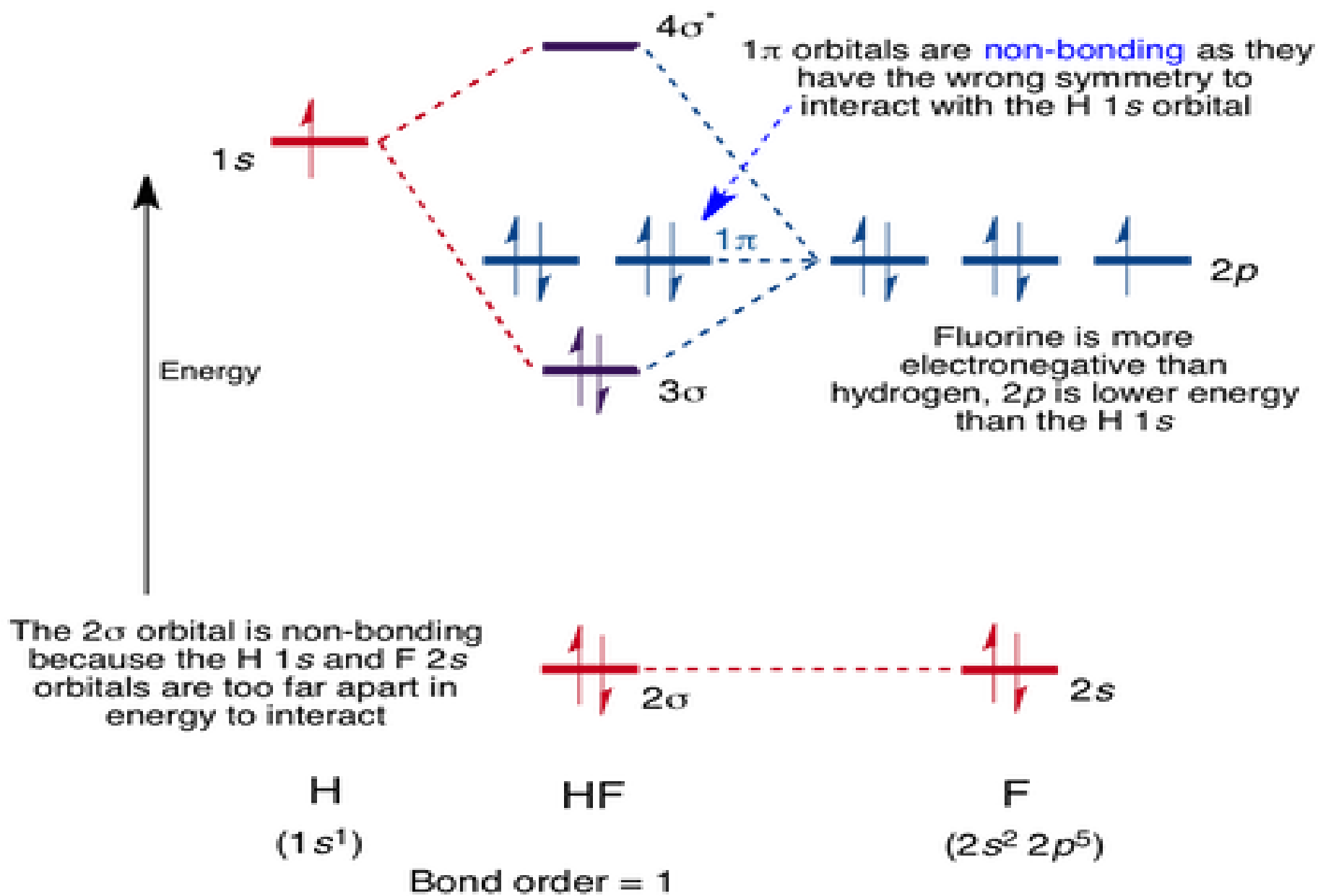
According to molecular orbital theory –

Bond order = $\frac{1}{2}(\text{no. of BMO} - \text{no. of anti ABMO})$

$$\frac{1}{2}(10 - 5) = 2.5$$

This is how we get bond order as 2.5

MO in HF



Molecular orbital diagram of HF

Fluorine is the more electronegative atom, so its orbitals will be lower in energy.

Hydrogen has only 1 electron in the 1s orbital available for bonding.

Fluorine atom has filled 2s orbital and 5 electrons in 2p orbitals.

Fluorine's 2s orbital is too low in energy for the Hydrogen atom to bond with it, so it is down by itself at the bottom as a non-bonding orbital.

Hydrogen's 1s orbital will combine with Fluorine's singly occupied 2p orbital, to create the $\sigma(sp)$ bonding molecular orbital and $\sigma^*(sp)$ antibonding molecular orbital.

The bonding molecular orbital is fully filled with two electrons.

The antibonding molecular orbital remain at the top. This one is empty. (If it were full, no bond would exist between H-F.)

The rest of the electrons(Fluorine's two other filled p orbitals) remain in their atomic orbitals.

Because they're already filled, they're going to be non-bonding. They go between the bonding and antibonding molecular orbitals made previously.

Bond order of HF

Bond order is given as (number of Bonding electrons - number of anti bonding electrons)/2

$$\text{Thus BO} = (2 - 0) / 2$$

$$= 2 / 2$$

$$= 1$$