Molecular Bond Theory

Short comings of the localized electron model:

electrons are not really localized

so the concept of resonance was added

no direct information about bond energies

Molecular Orbital Model

useful for explaining molecular:

- electron distribution
- energy of electrons
- color
- magnetic properties
  - *paramagnetism*
  - *diamagnetism*

Molecular Orbitals (MO's)

result from interaction of atomic orbitals (AO's)of the bonding atoms

Remember: quantum mechanics focuses on the wave nature of electrons

(δ) sigma Bonding

two atomic orbitals (AO's) overlap end to end to form two δ molecular orbitals (MO's)

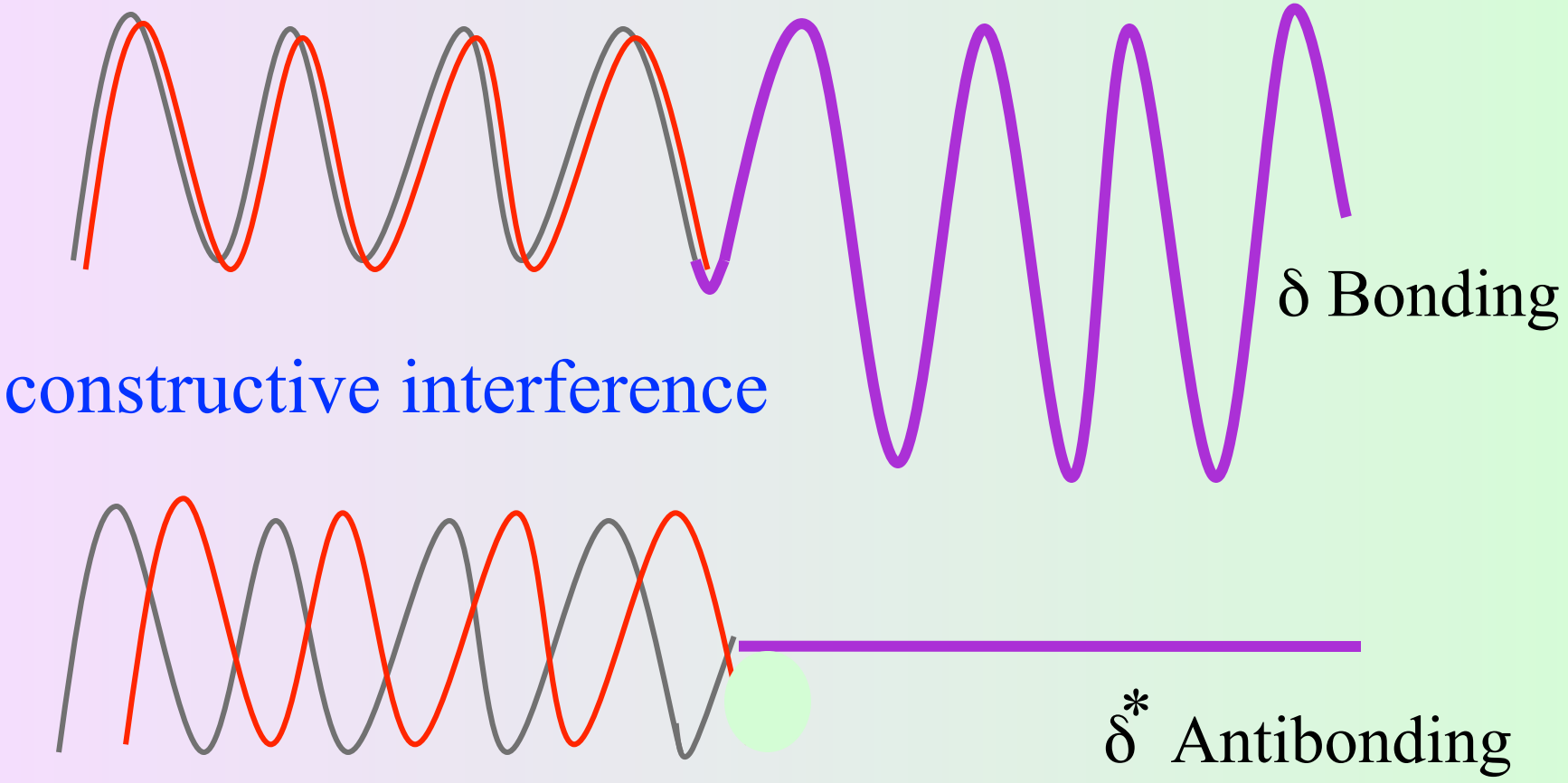
a

δ Bonding Orbital

and

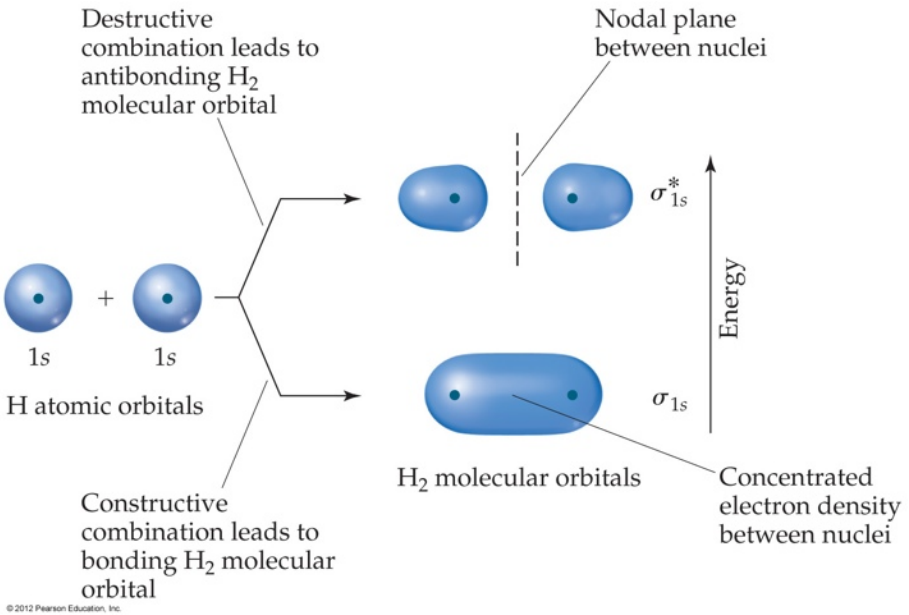
δ^* Antibonding Orbital

Wave interactions



Molecular-Orbital (MO) Theory

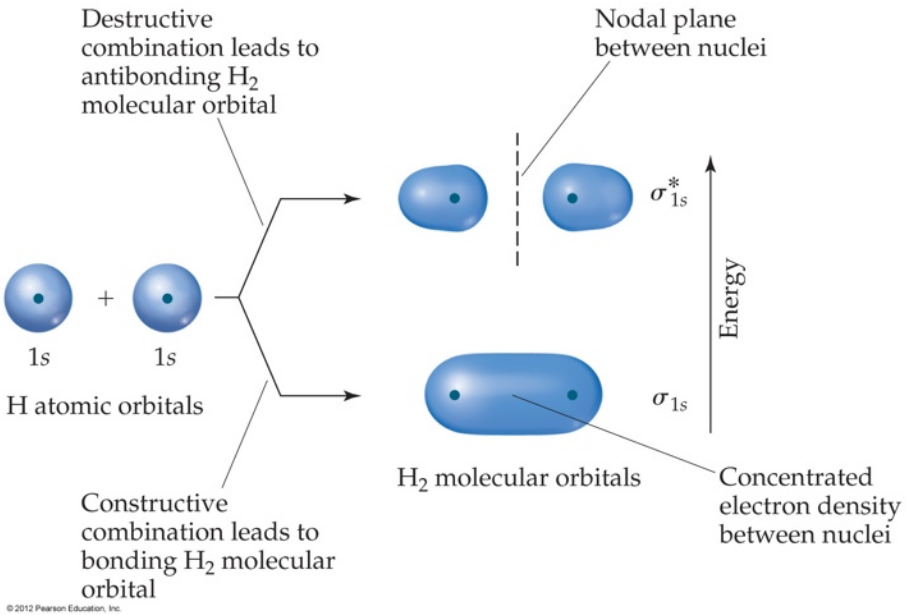
- In MO theory, we invoke the wave nature of electrons.
- If waves interact constructively, the resulting orbital is lower in energy: a bonding molecular orbital.



Molecular Geometries and Bonding

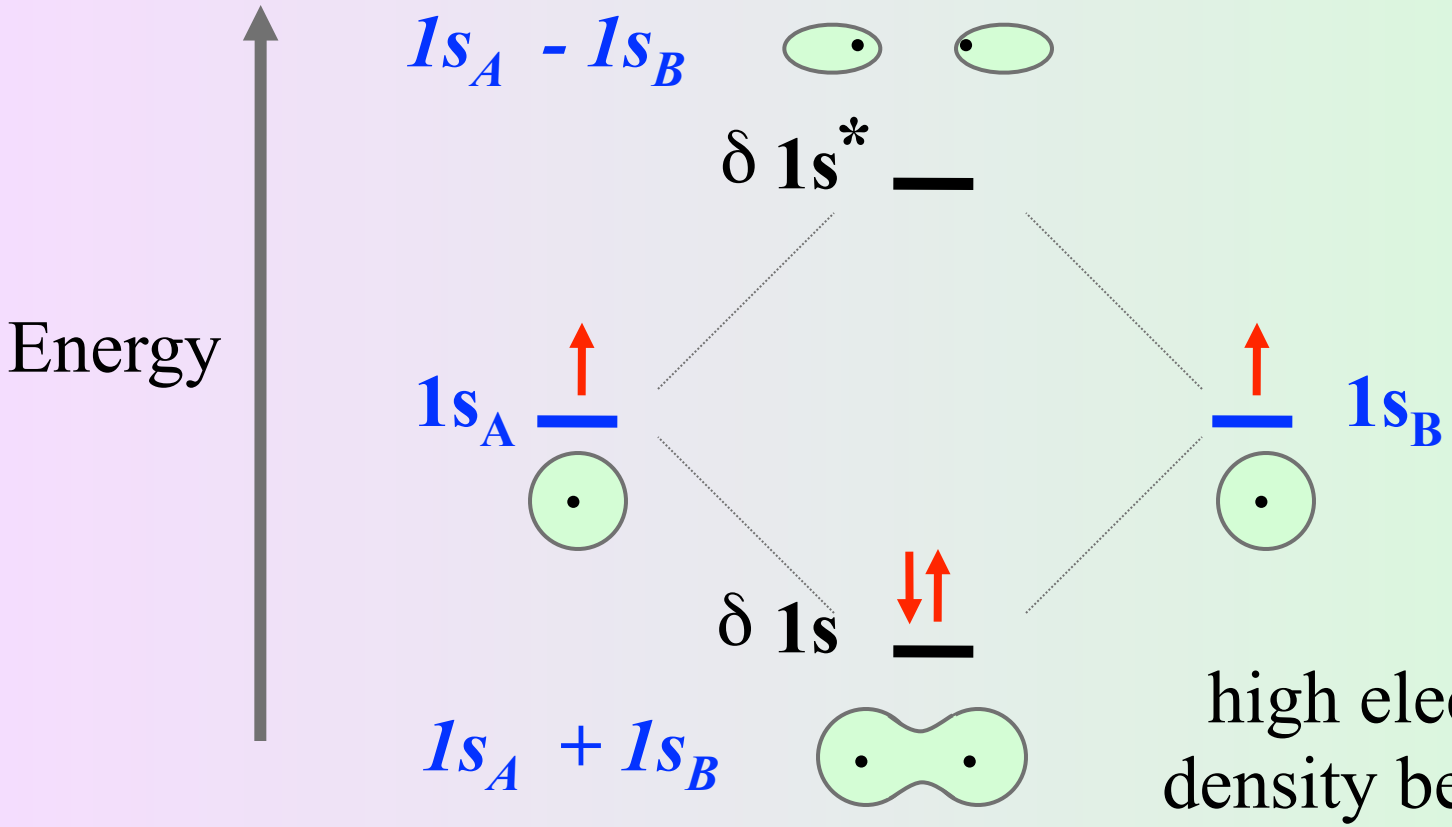
Molecular-Orbital (MO) Theory

If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.



δ sigma Bonding (H_2)

electron density is zero between the nuclei



high electron density between the nuclei

δ Bonding Orbitals

have lower potential energy than the bonding atomic orbitals

δ^* Antibonding Orbitals

have higher potential energy than the bonding atomic orbitals

low electron density leaves only repulsion between the nuclei

Molecular Orbital Electron Configurations

We assign electrons to MO,s using the same rules we used to determine atomic electron configurations.

aufbau principle

Pauli exclusion principle

Hund's rule

the number of MO's formed is always equal to the number of atomic orbitals combined

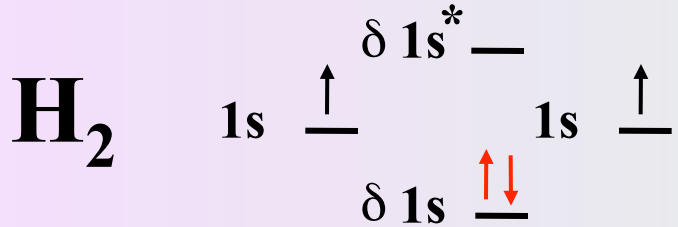
Bond Order

$$= \frac{1}{2}\left(\begin{array}{l}\text{number of electrons in}\\ \text{bonding MO's}\end{array} - \begin{array}{l}\text{number of electrons}\\ \text{in antibonding MO's}\end{array}\right)$$

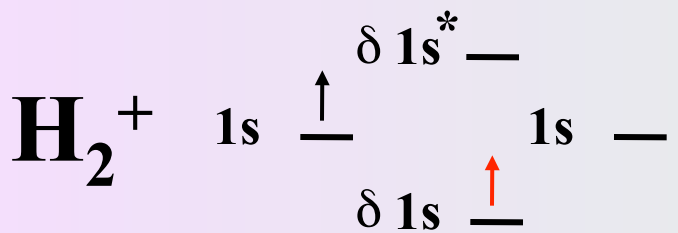
used to predict the relative stability's of proposed molecules

zero or a negative value means the bond has no stability

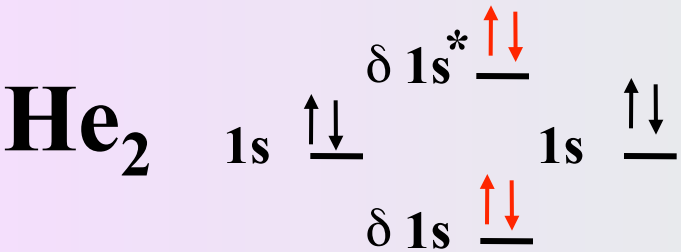
Bond Order



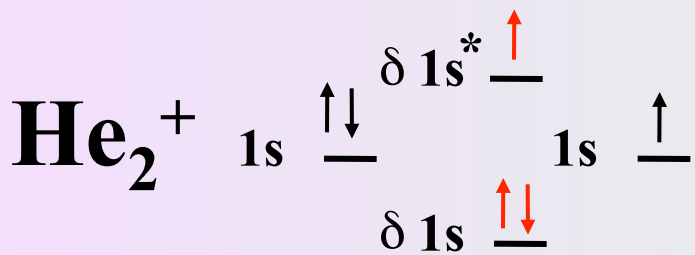
$1/2(2 - 0) = 1$



$1/2(1 - 0) = 1/2$



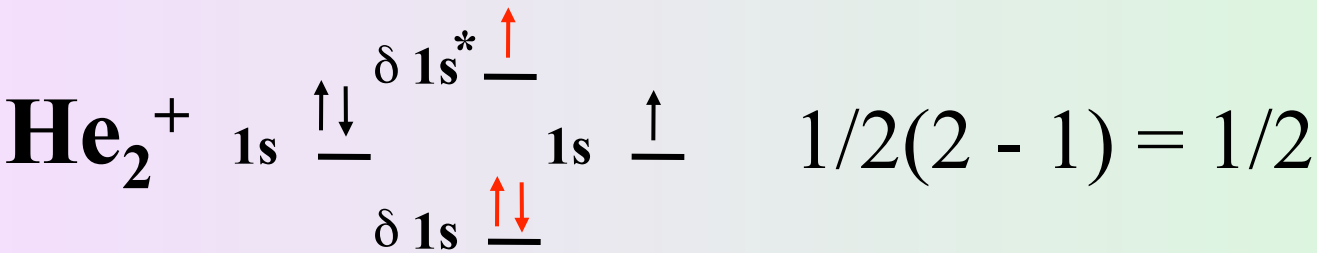
$1/2(2 - 2) = 0$



$1/2(2 - 1) = 1/2$

Bond Order

more stable due to less nuclear and electron repulsion



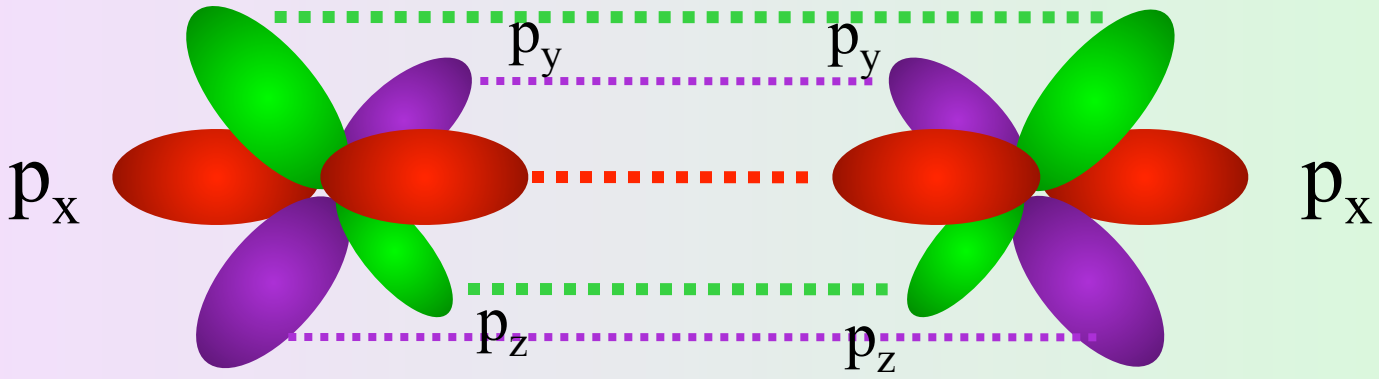
Homonuclear Diatomic Molecules of the Second Period

(π) Pi Bonds

two atomic orbitals overlap from side by side positions along the internuclear axis to form Bonding and Antibonding π Orbitals

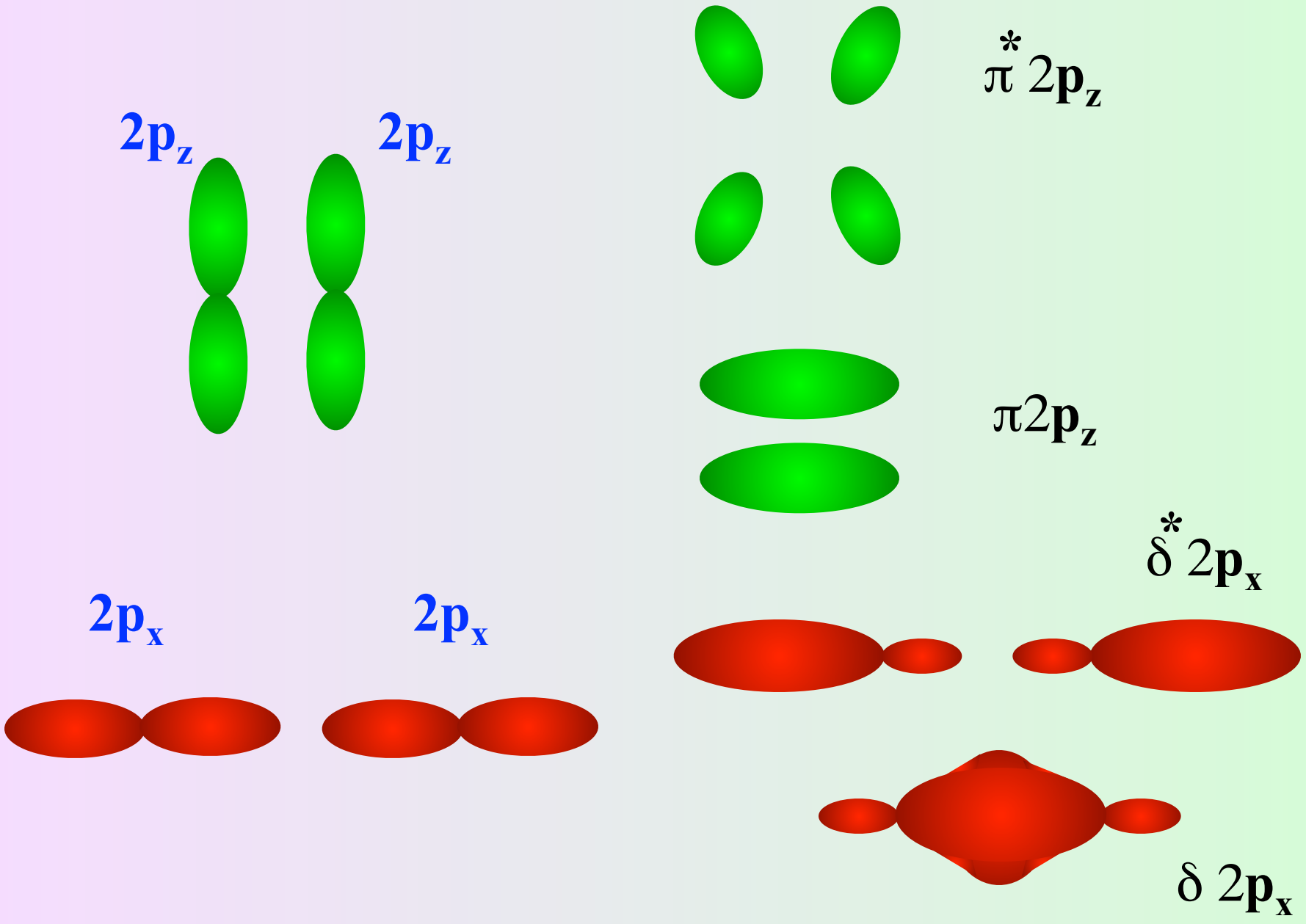
electron density is located above and below the inter nuclear axis

Three P orbitals for each element in the second period all of which interact form:

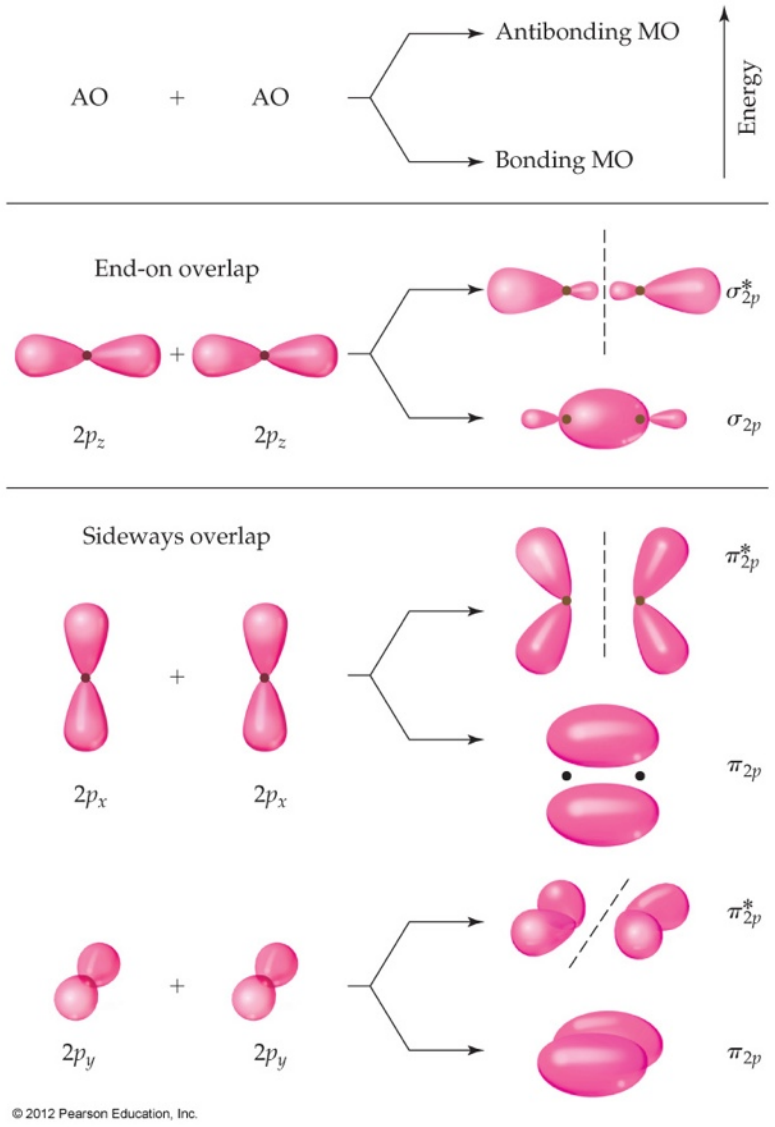


two sigma bonds δ p_x and $\delta^* p_x$

four Pi bonds π p_y , $\pi^* p_y$ and πp_z , $\pi^* p_z$


$2p_z$
$2p_z$
$\pi^* 2p_z$
$\pi 2p_z$
$2p_x$
$2p_x$
$\delta^* 2p_x$
$\delta\ 2p_x$

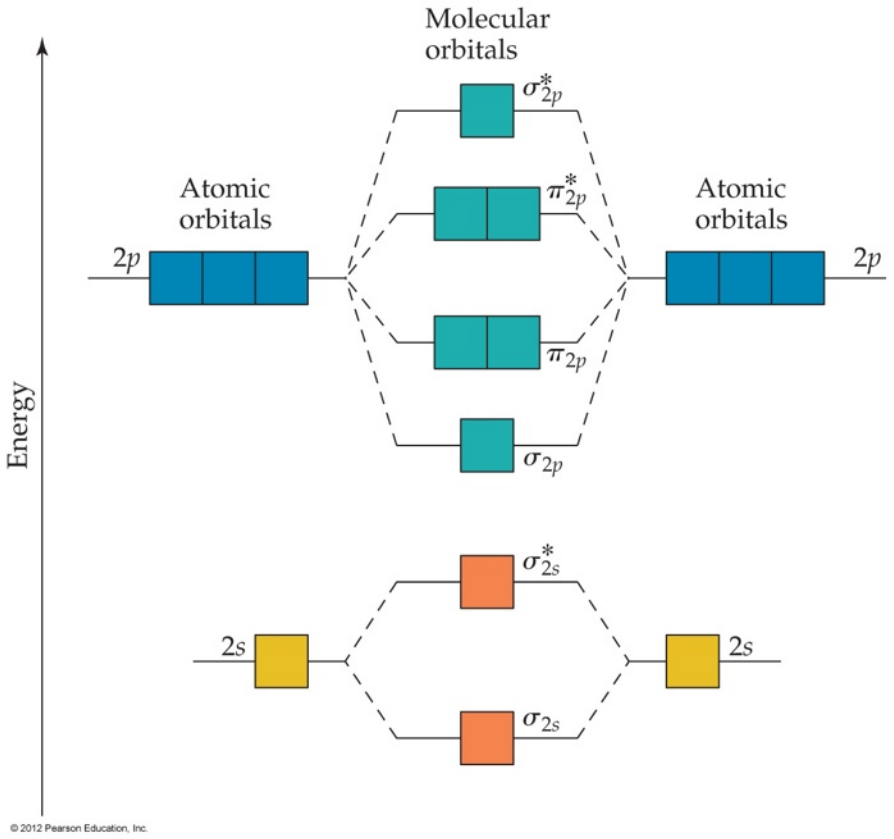
MO Theory



- For atoms with both *s* and *p* orbitals, there are two types of interactions:
  - The *s* and the *p* orbitals that face each other overlap in σ fashion.
  - The other two sets of *p* orbitals overlap in π fashion.

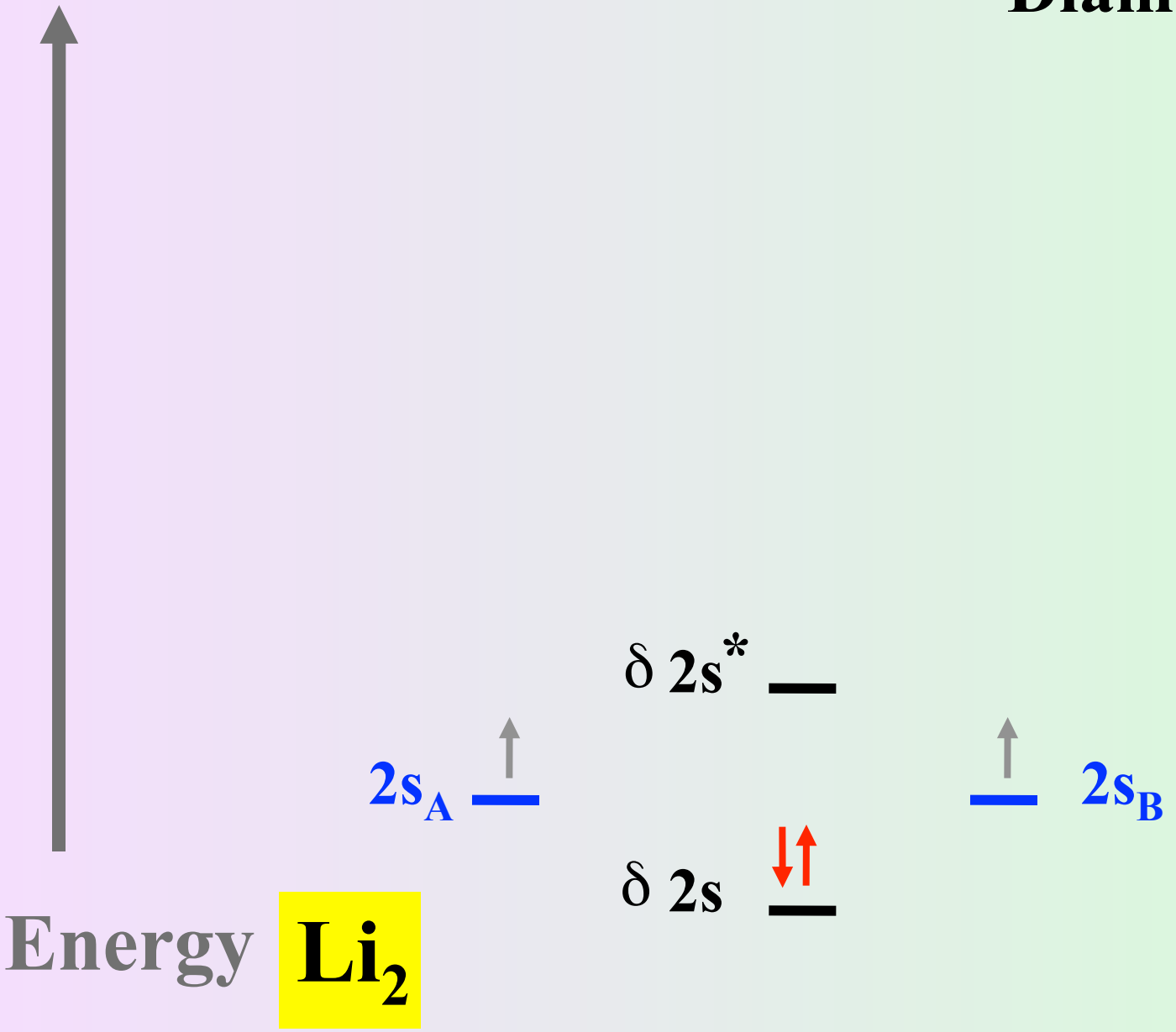
MO Theory

- The resulting MO diagram looks like this (Fig. 9.41).
- There are both σ and π bonding molecular orbitals and σ^* and π^* antibonding molecular orbitals.

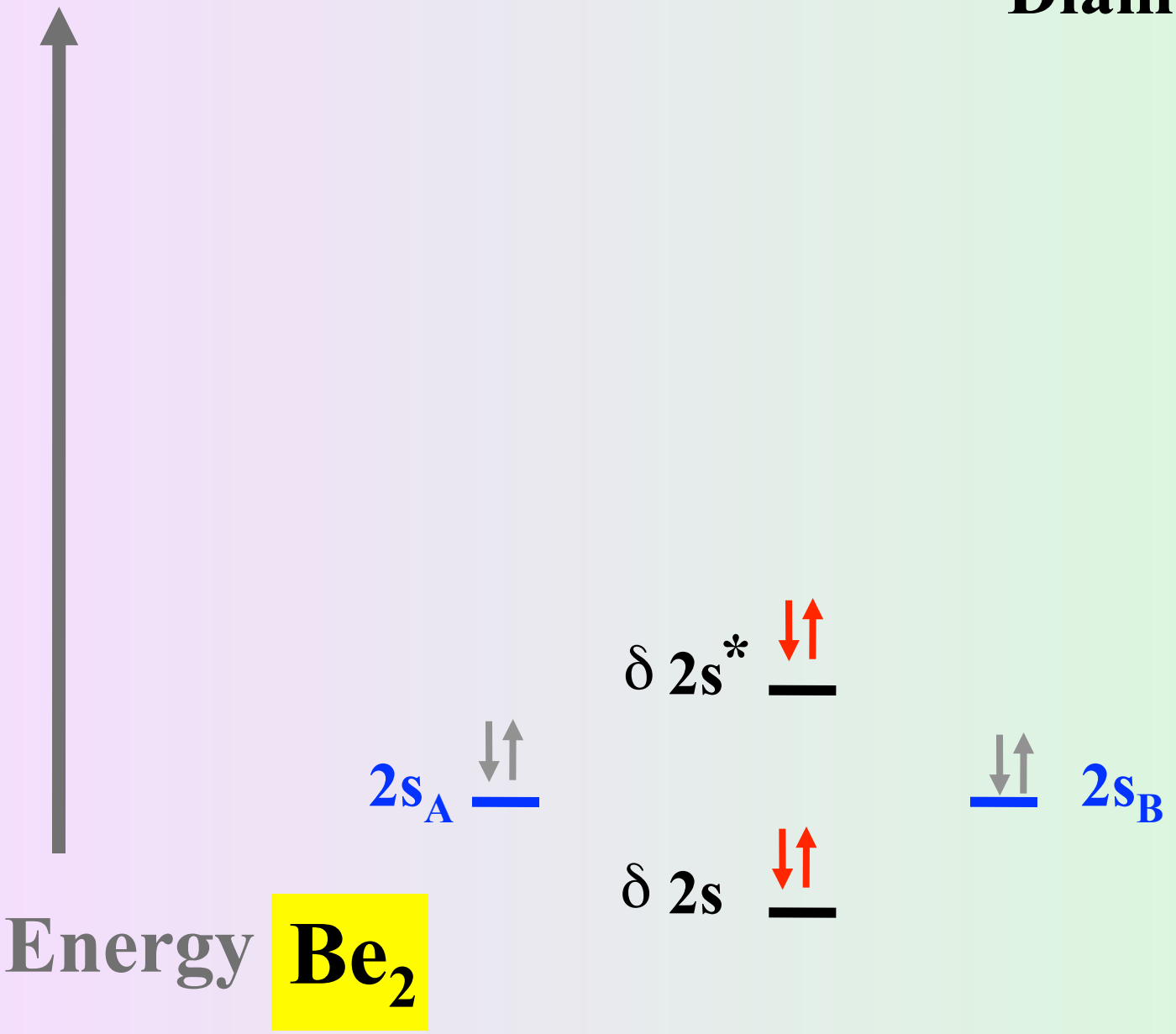


Molecular Geometries and Bonding

Diamagnetic

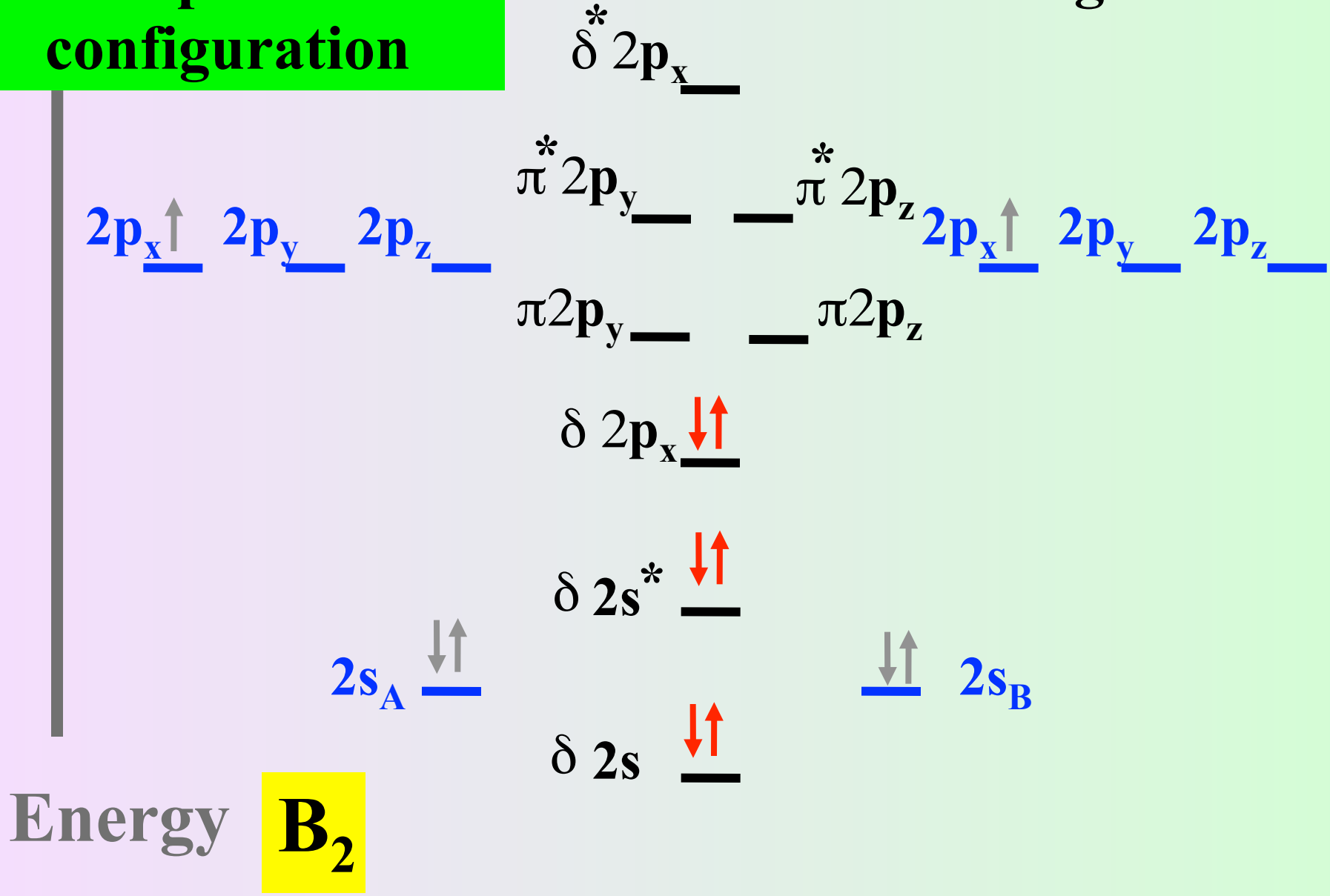


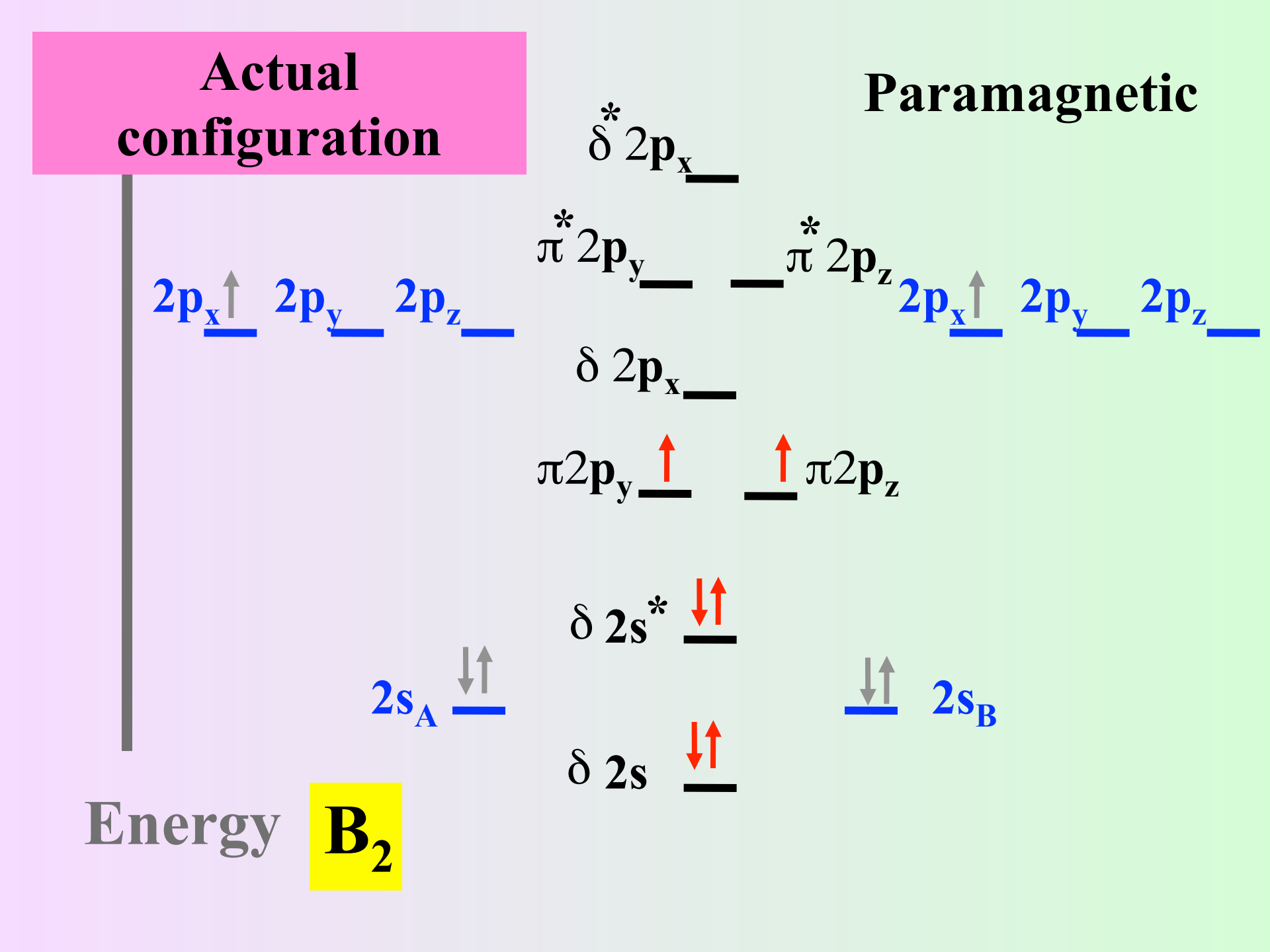
Diamagnetic



Expected configuration

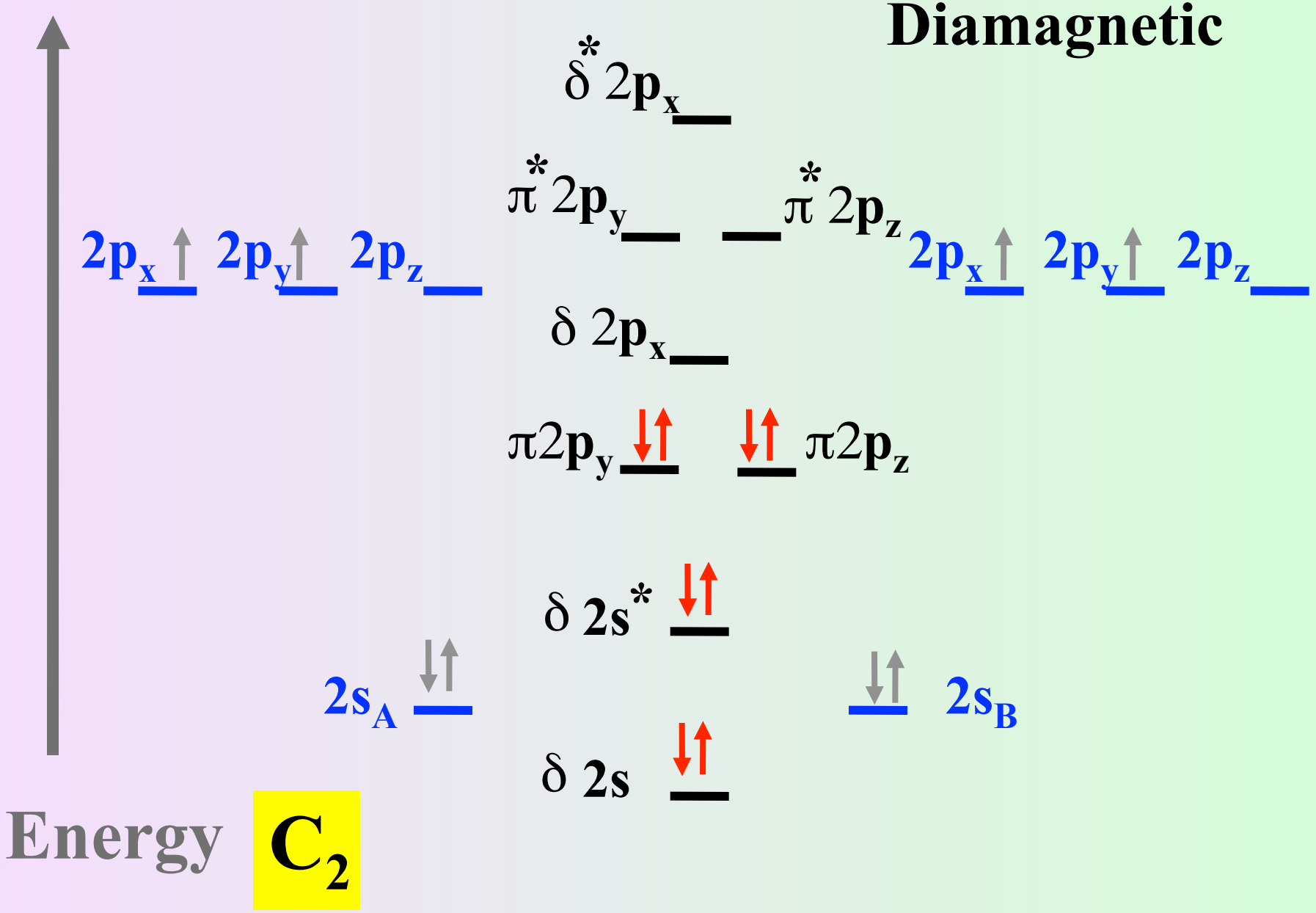
Diamagnetic

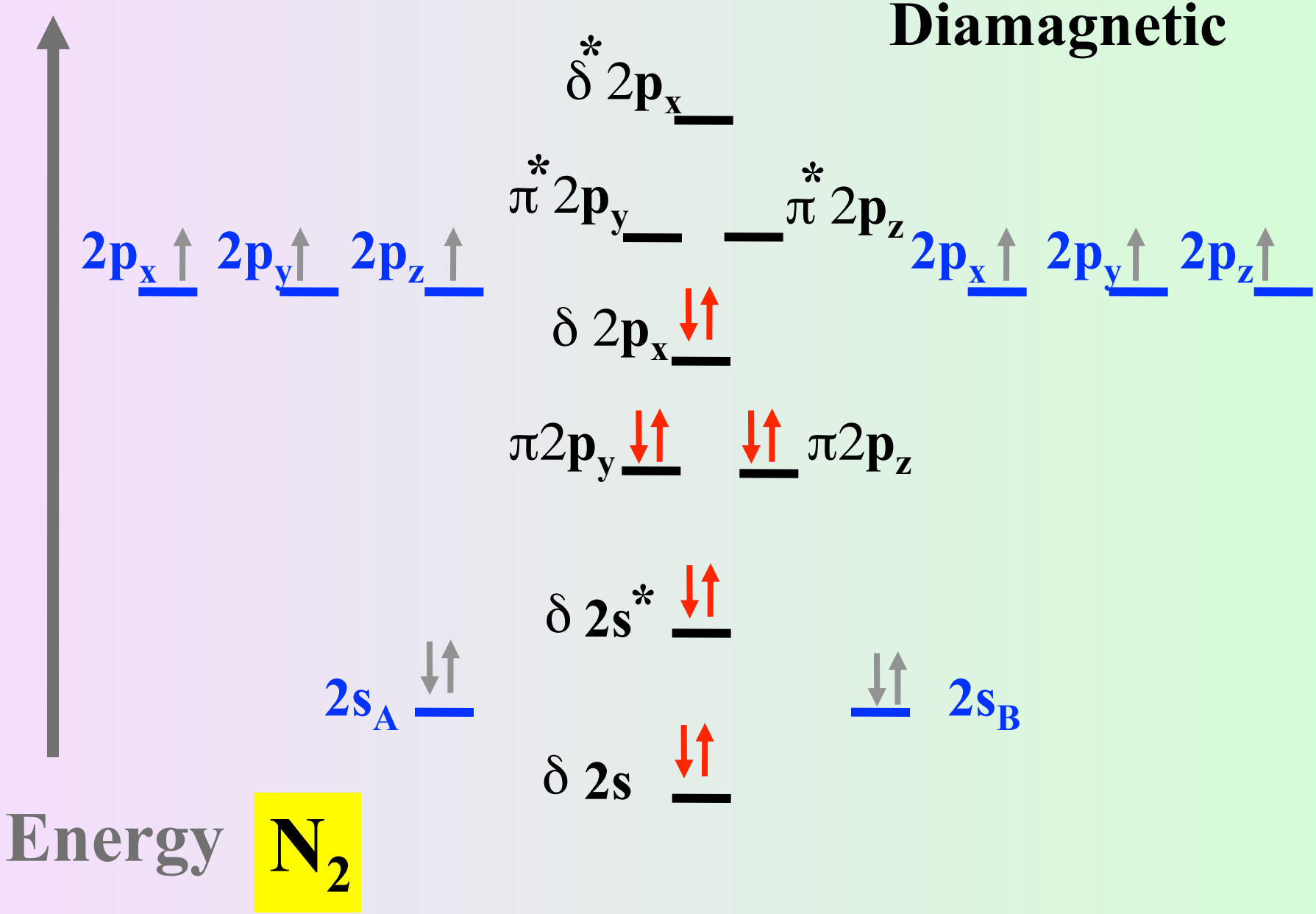



Actual configuration
Paramagnetic
δ* 2p_x
π* 2p_y
π* 2p_z
2p_x 2p_y 2p_z
2p_x 2p_y 2p_z
δ 2p_x
π2p_y
π2p_z
δ 2s*
2s_A
2s_B
δ 2s
Energy
B2

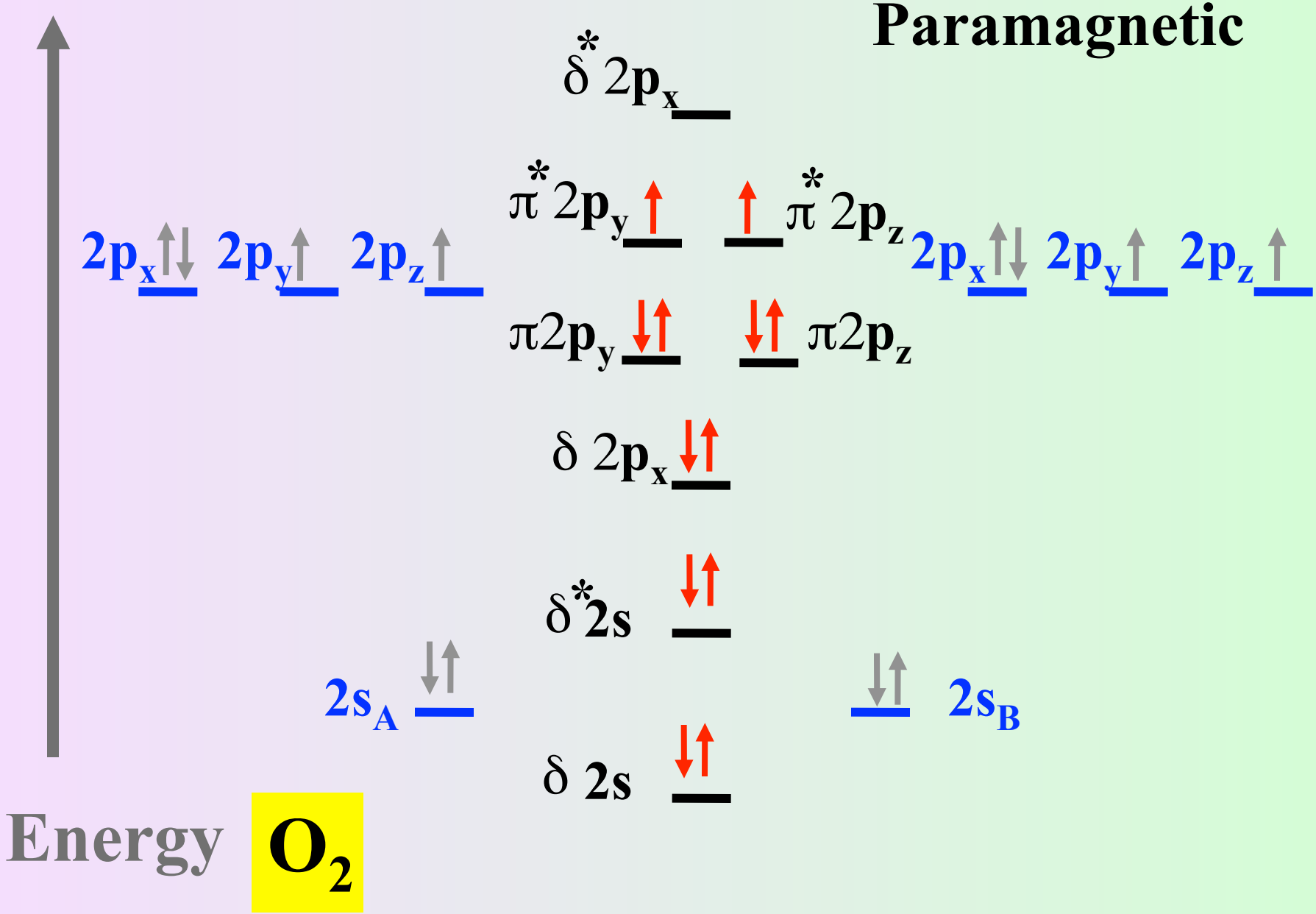
The δ $2p_x$ bond concentrates electrons in the same area as the 2s sigma bonds. This increases repulsion's and raises the potential energy of the electrons

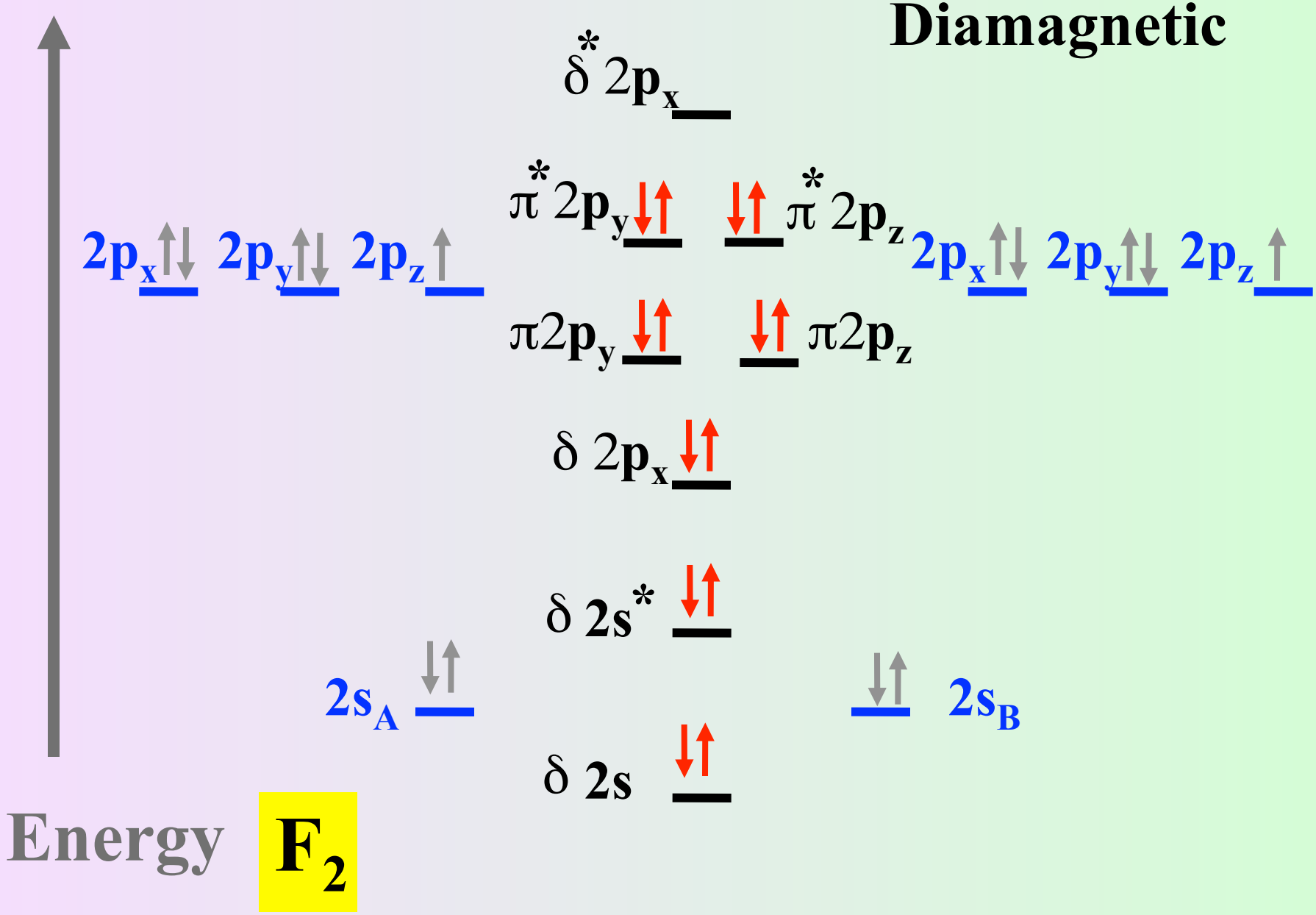
The $\pi 2p_y$ and the $\pi 2p_z$ MO's are lower in energy because they exist the outside the internuclear zone


Diamagnetic
δ* 2p_x
π* 2p_y
π* 2p_z
2p_x 2p_y 2p_z
2p_x 2p_y 2p_z
δ 2p_x
π2p_y
π2p_z
δ 2s*
2s_A
2s_B
δ 2s
Energy
C2

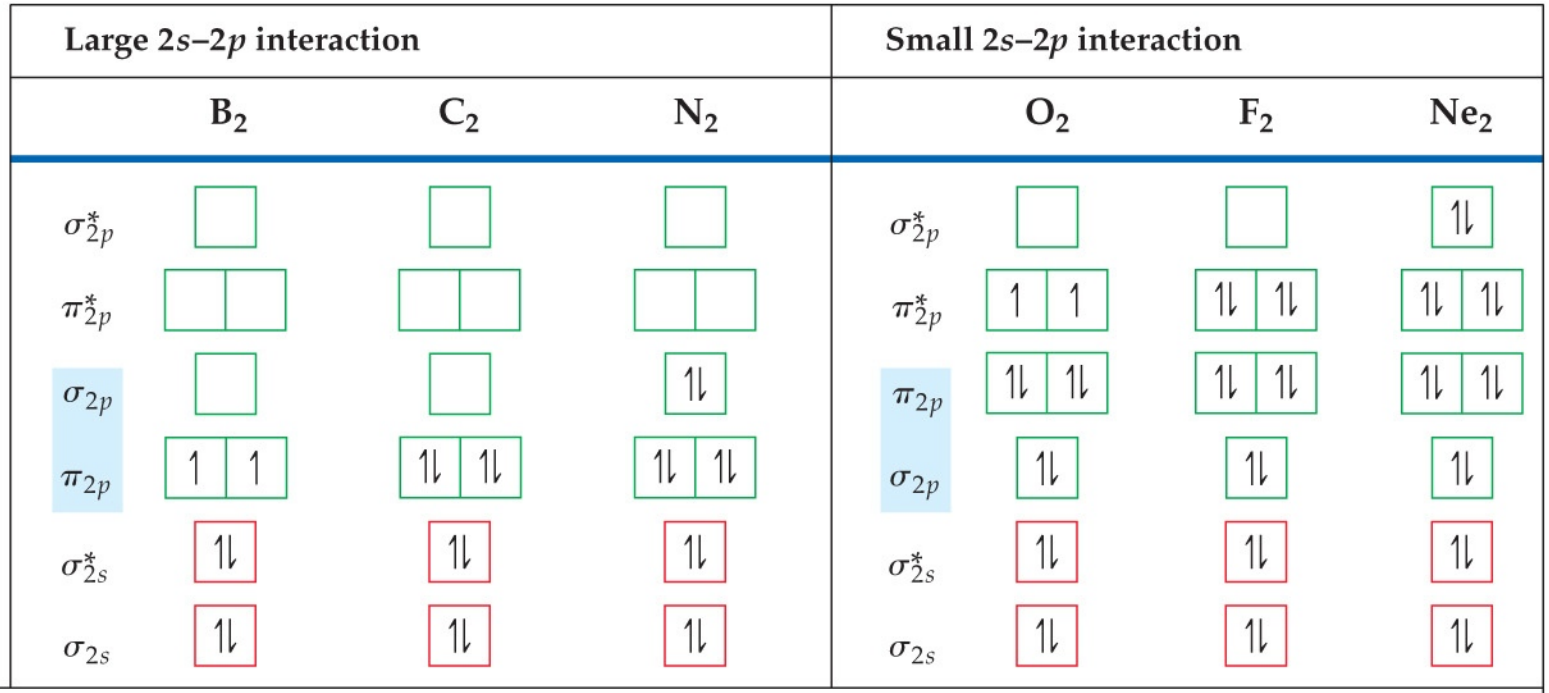

Diamagnetic
δ* 2p_x
π* 2p_y
π* 2p_z
2p_x 2p_y 2p_z
2p_x 2p_y 2p_z
δ 2p_x
π2p_y
π2p_z
δ 2s*
2s_A
2s_B
δ 2s
Energy
N2

The repulsion's between the $\delta 2p_x$ bond and 2s sigma bonds decreases from left to right in the second period. As a result the $\delta 2p_x$ bond is lower in energy then the $\pi 2p_y$ and the $\pi 2p_z$ for the O_2 and F_2 electron configuration


Paramagnetic
δ* 2p_x
π* 2p_y
π* 2p_z
2p_x 2p_y 2p_z
2p_x 2p_y 2p_z
π2p_y
π2p_z
δ 2p_x
δ* 2s
2s_A
2s_B
δ 2s
Energy
O_2


Diamagnetic
δ* 2p_x
π* 2p_y
π* 2p_z
2p_x 2p_y 2p_z
2p_x 2p_y 2p_z
π2p_y
π2p_z
δ 2p_x
δ 2s*
2s_A
2s_B
δ 2s
Energy
F2

Second-Row MO Diagrams



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Molecular Geometries and Bonding