

Molecular Bond Theory

Shortcomings 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

(σ) sigma Bonding

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

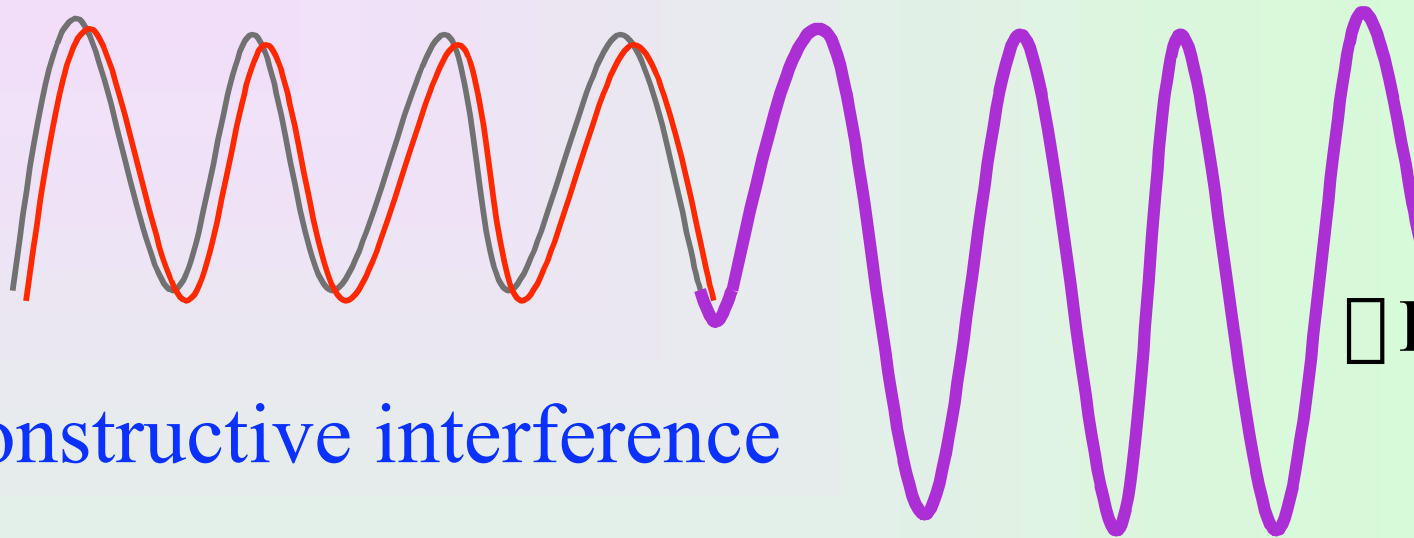
a

σ Bonding Orbital

and

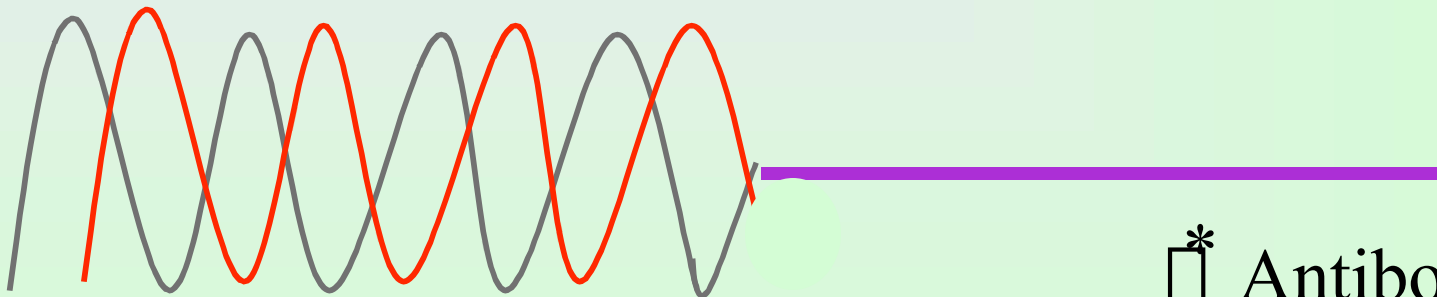
σ^* Antibonding Orbital

Wave interactions



□ Bonding

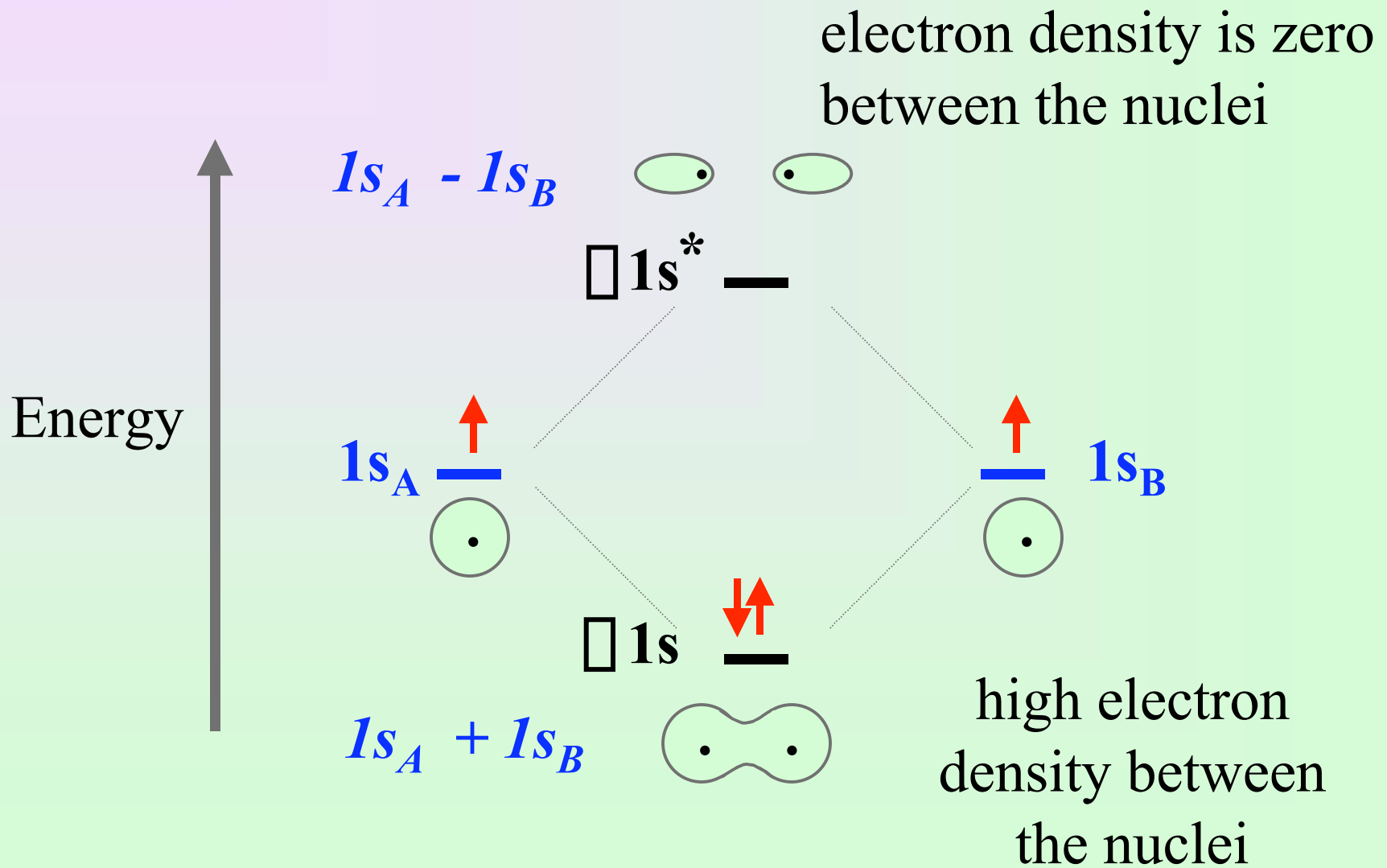
constructive interference



□* Antibonding

destructive interference

□ sigma Bonding (H₂)



□ Bonding Orbitals

have lower potential energy than the bonding atomic orbitals

□* 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

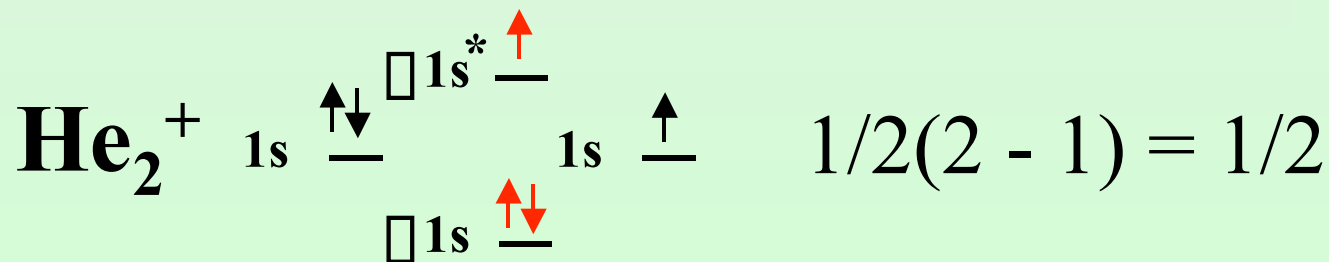
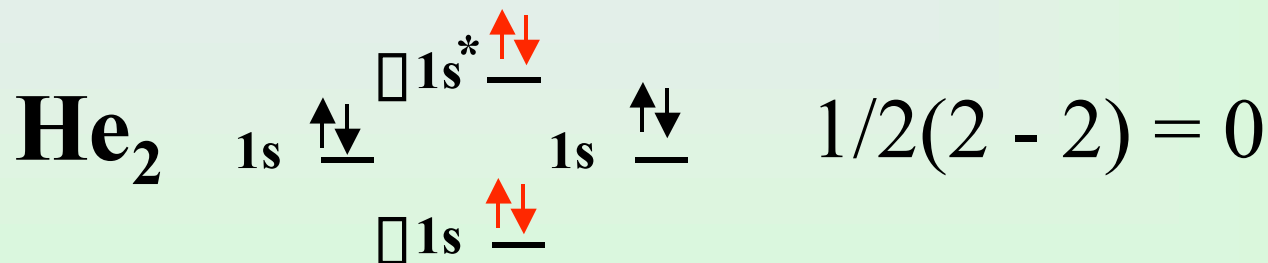
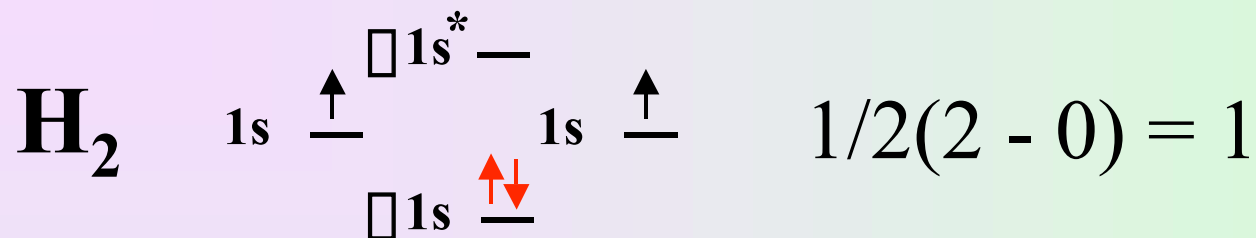
Bond Order

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

used to predict the relative stability's of proposed molecules

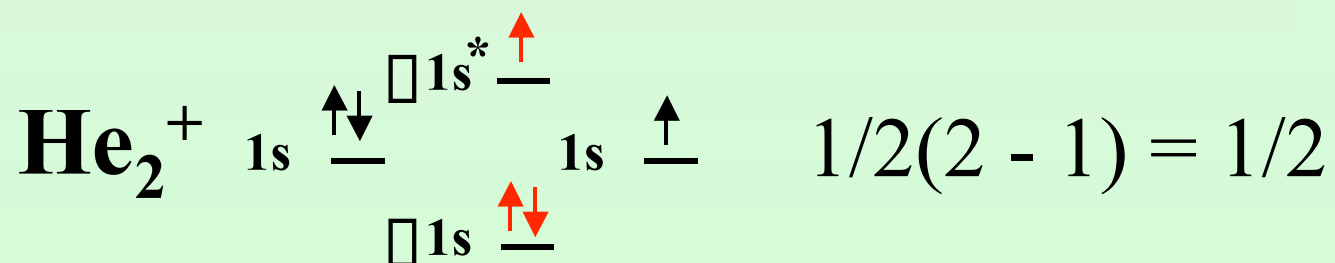
zero or a negative value means the bond has no stability

Bond Order



Bond Order

more stable due to less nuclear
and electron repulsion



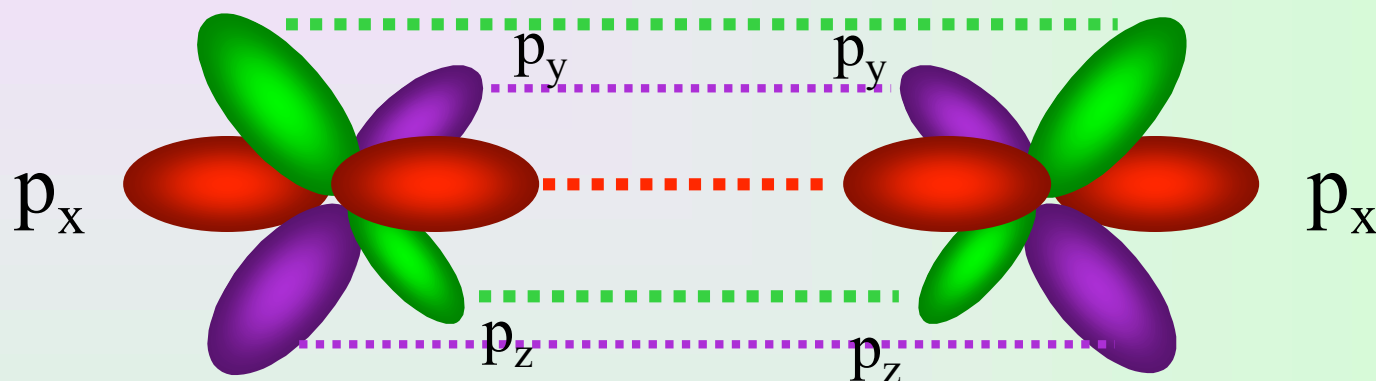
Homonuclear Diatomic Molecules of the Second Period

(π) Pi Bonds

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

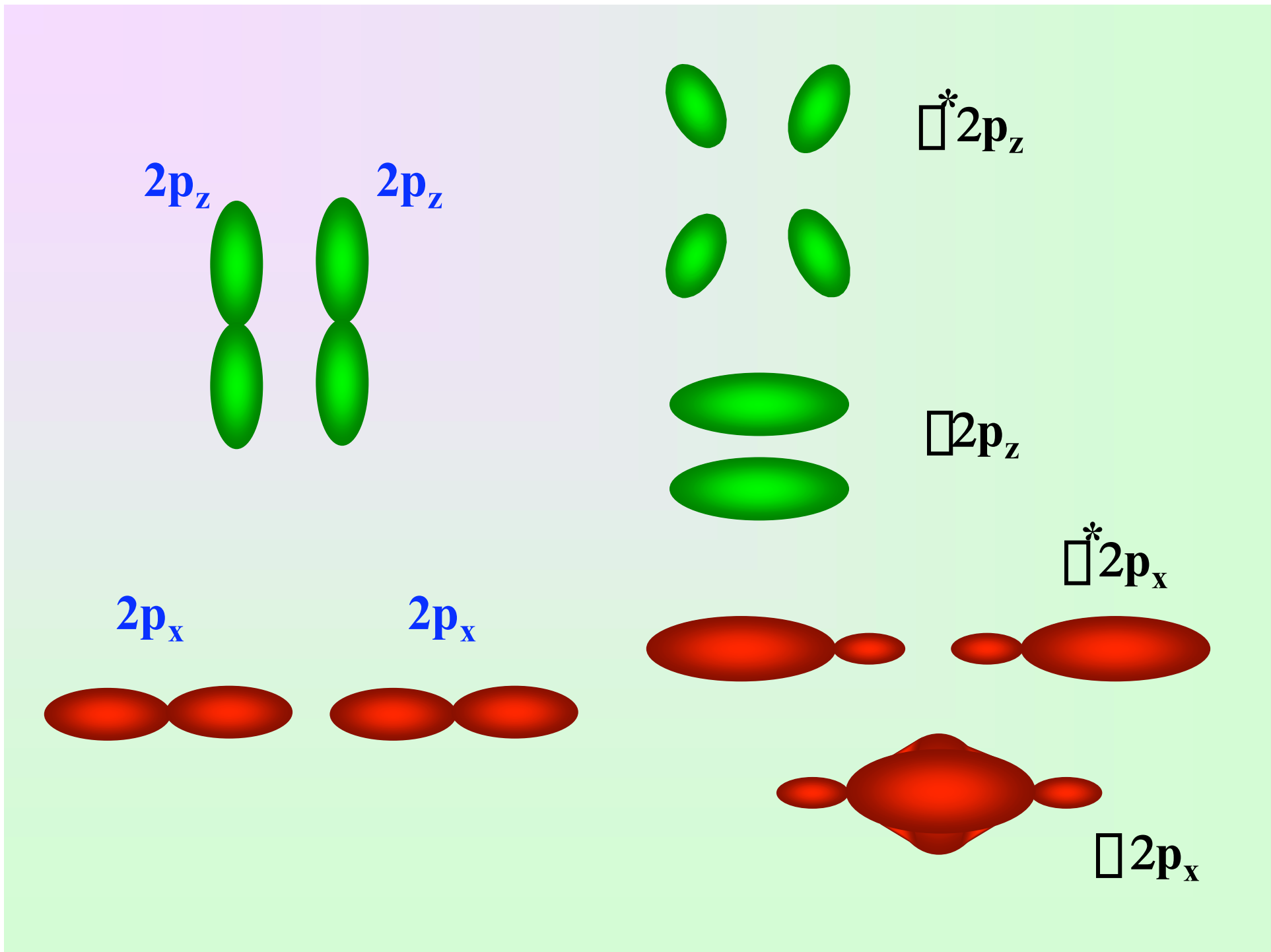
electron density is located above and below the inter nuclear axis

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

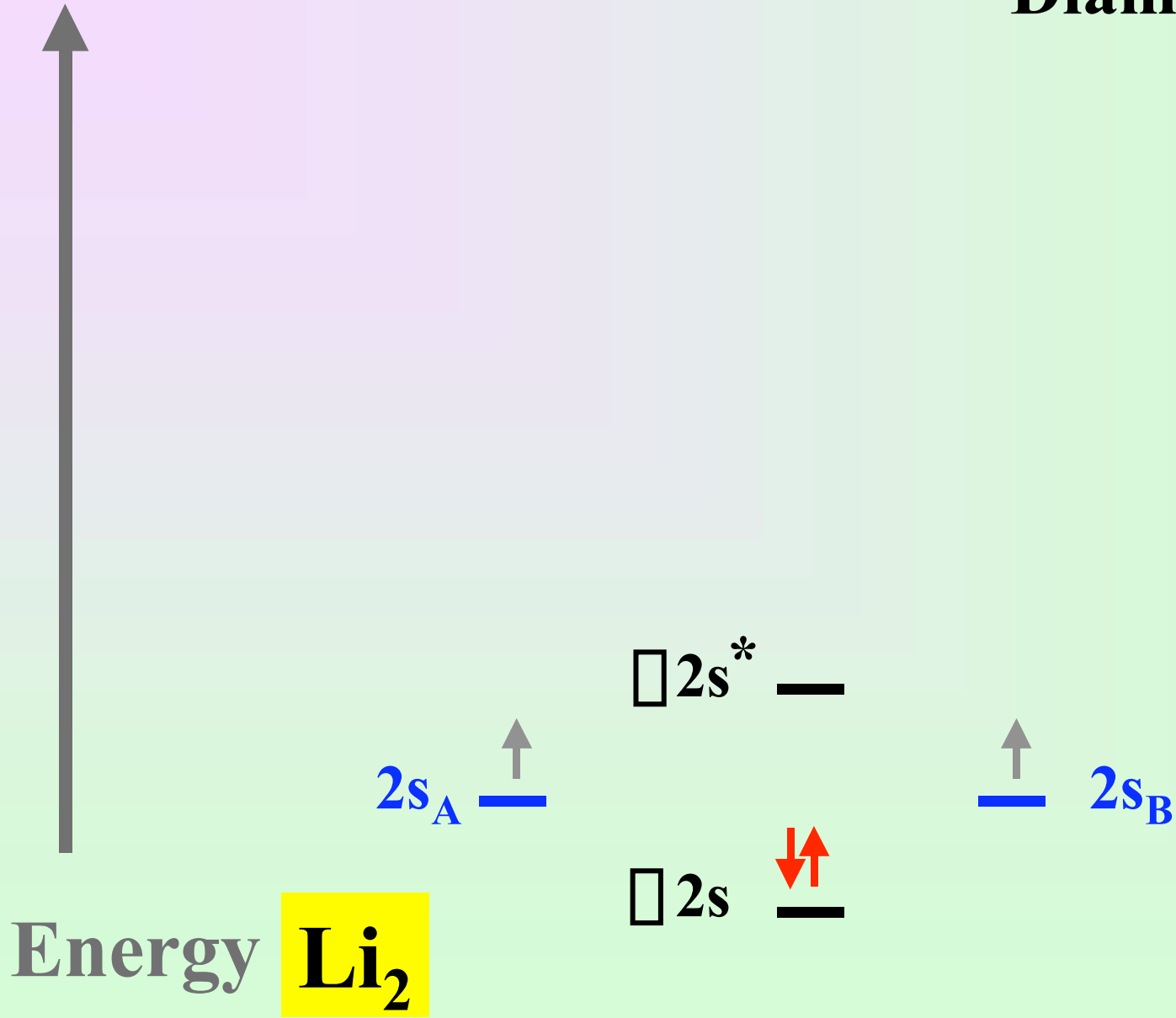


two sigma bonds $\square p_x$ and $\square p_x^*$

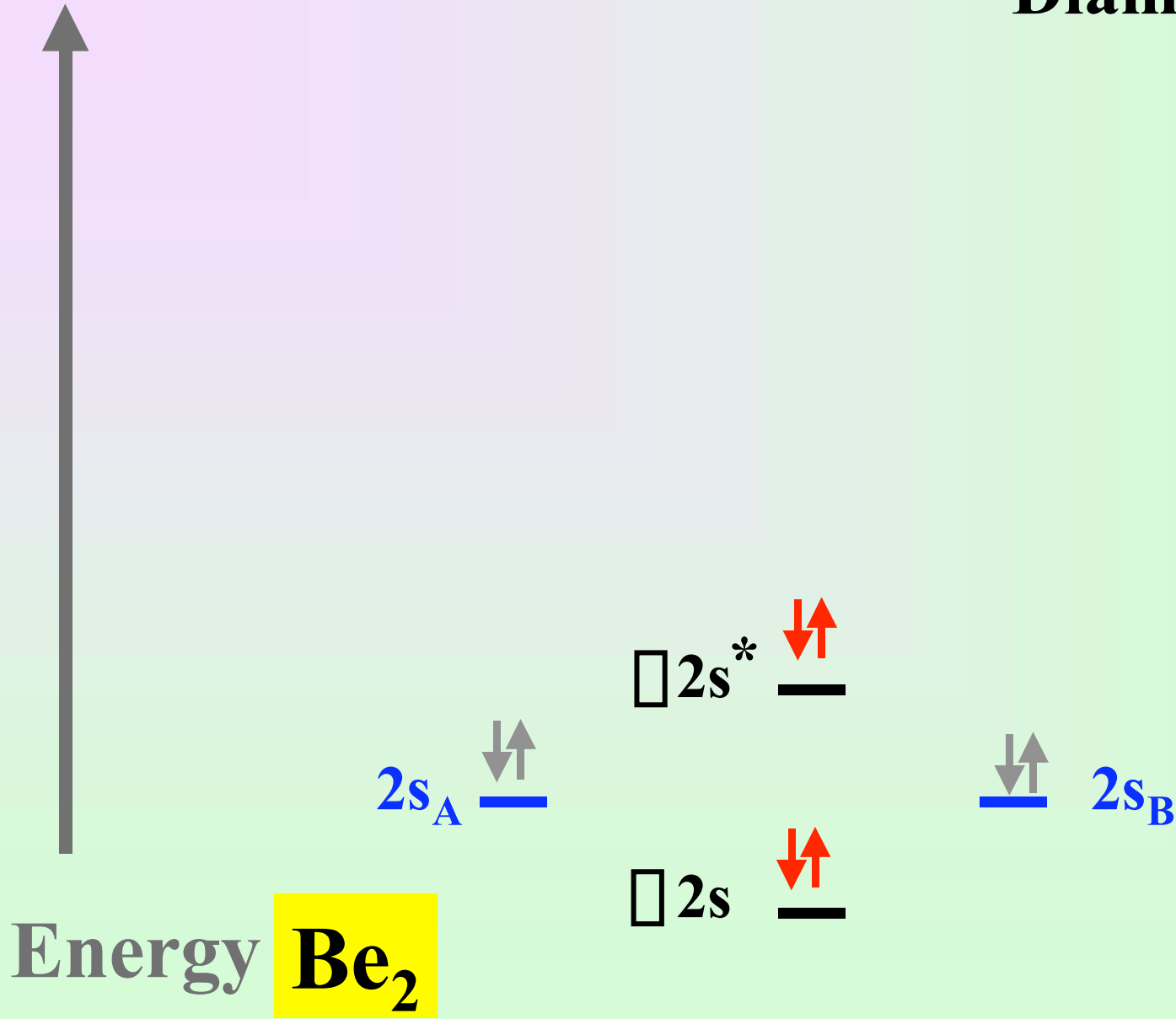
four Pi bonds $\square p_y, \square p_y^*$ and $\square p_z, \square p_z^*$



Diamagnetic

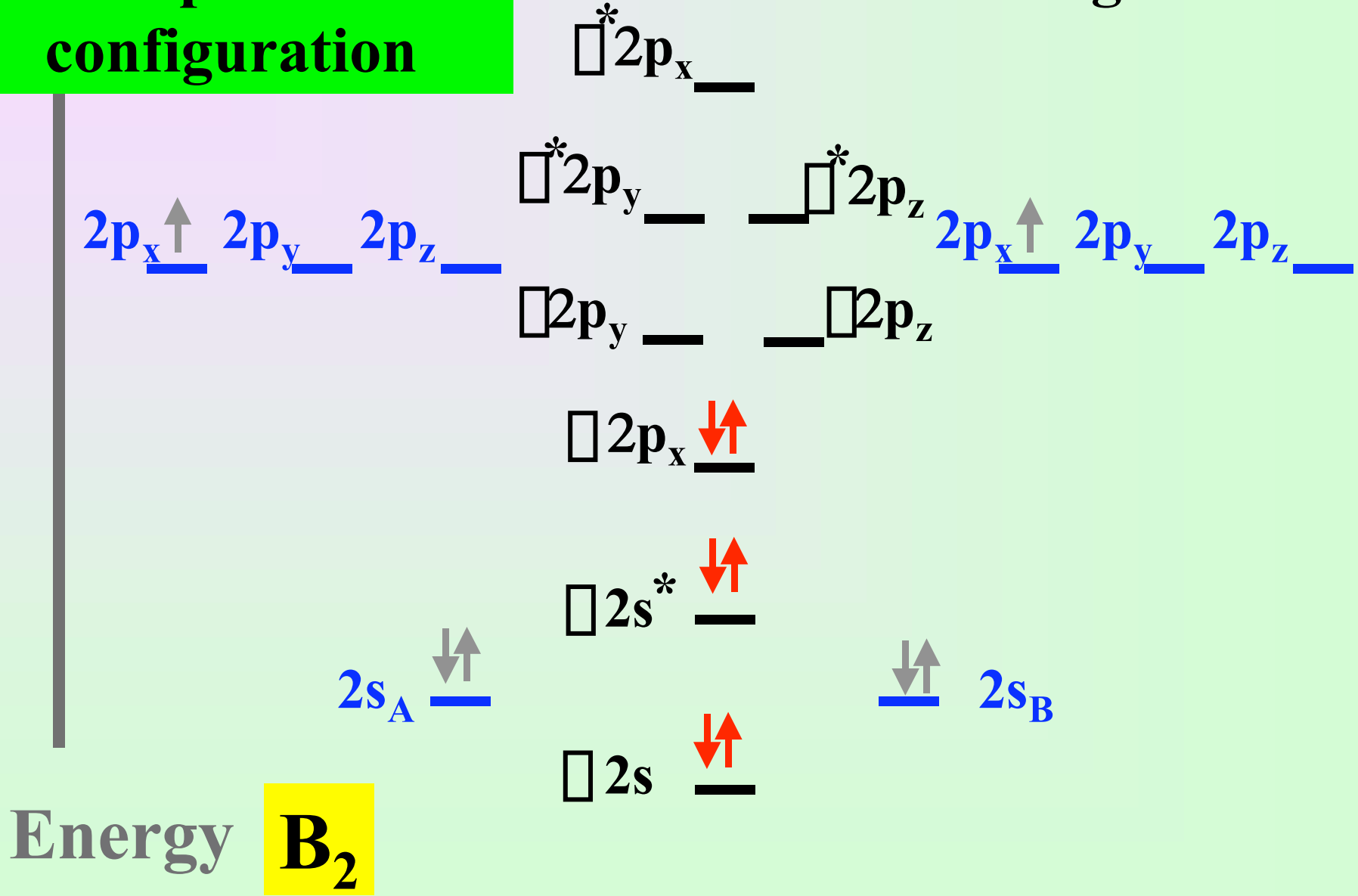


Diamagnetic



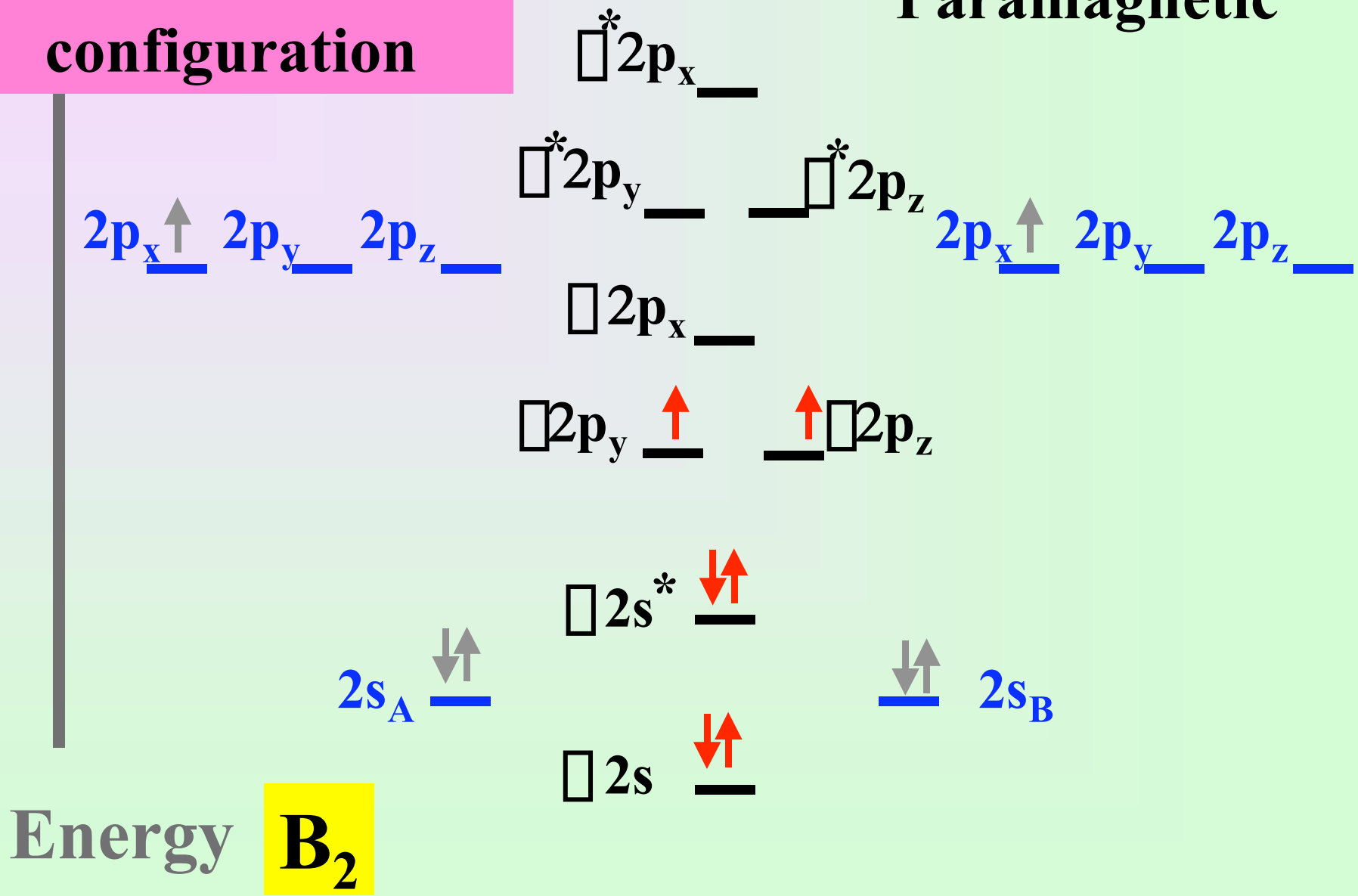
Expected configuration

Diamagnetic



**Actual
configuration**

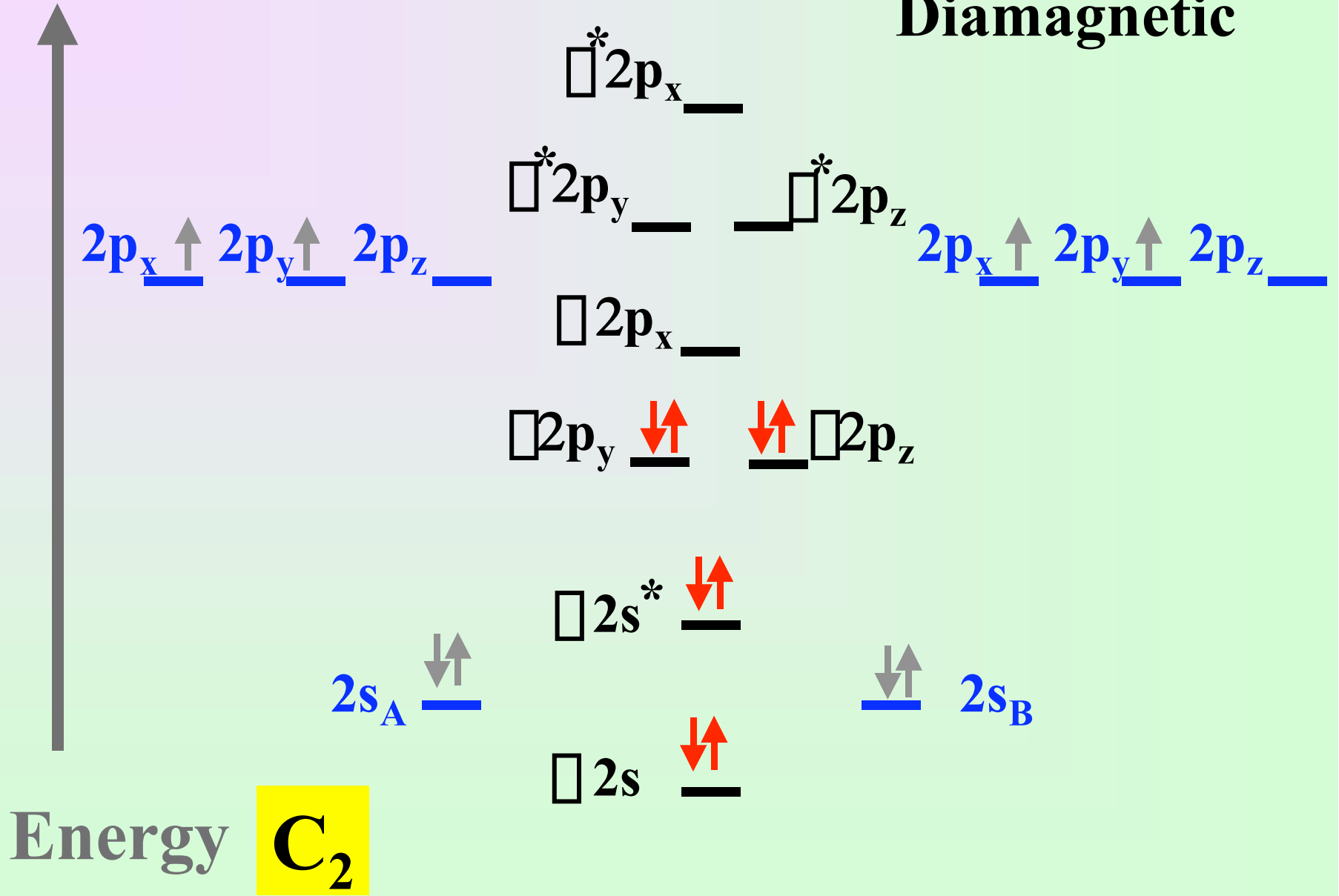
Paramagnetic



The σ_{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

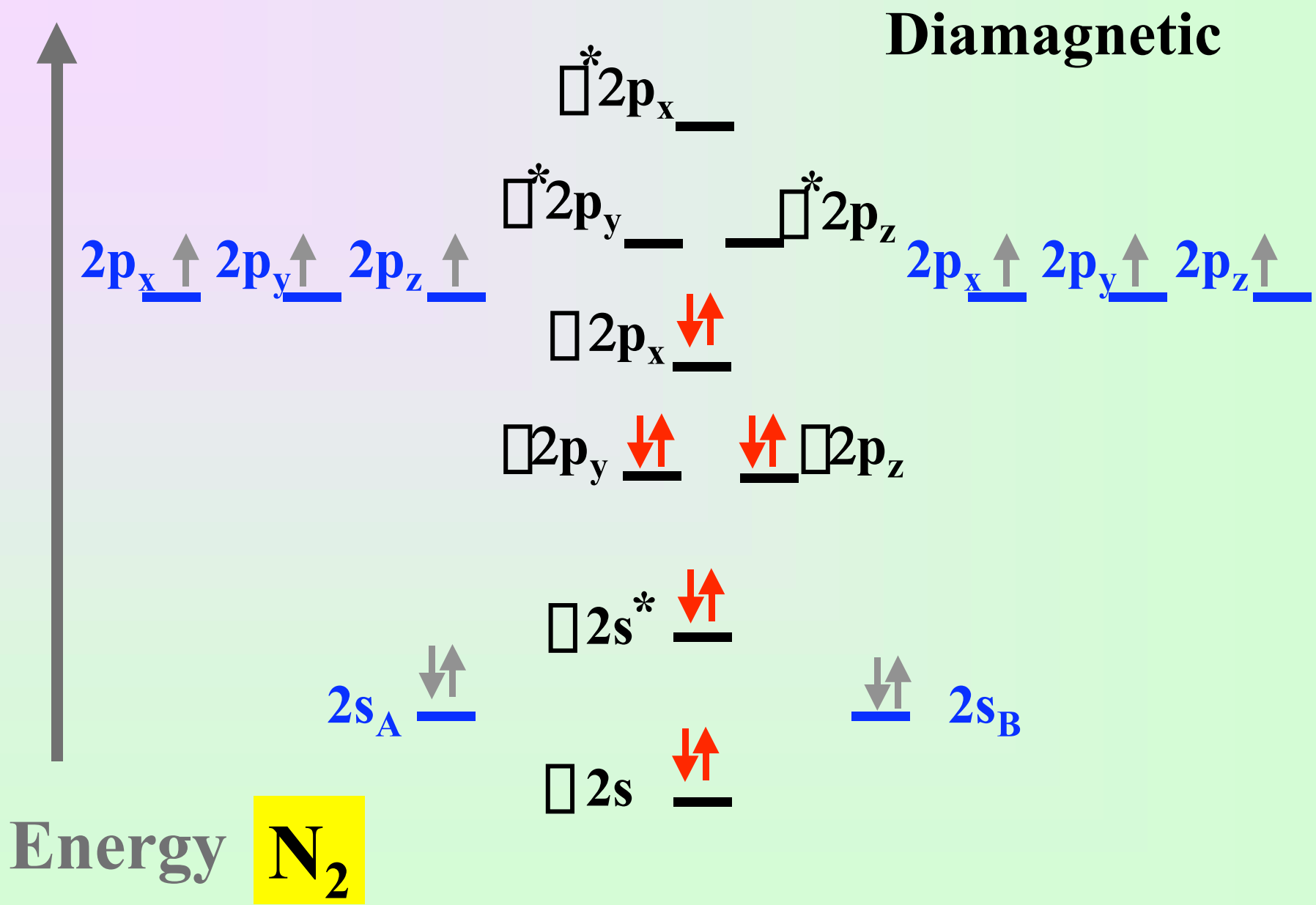
The σ_{2p_y} and the σ_{2p_z} MO's are lower in energy because they exist the outside the internuclear zone

Diamagnetic

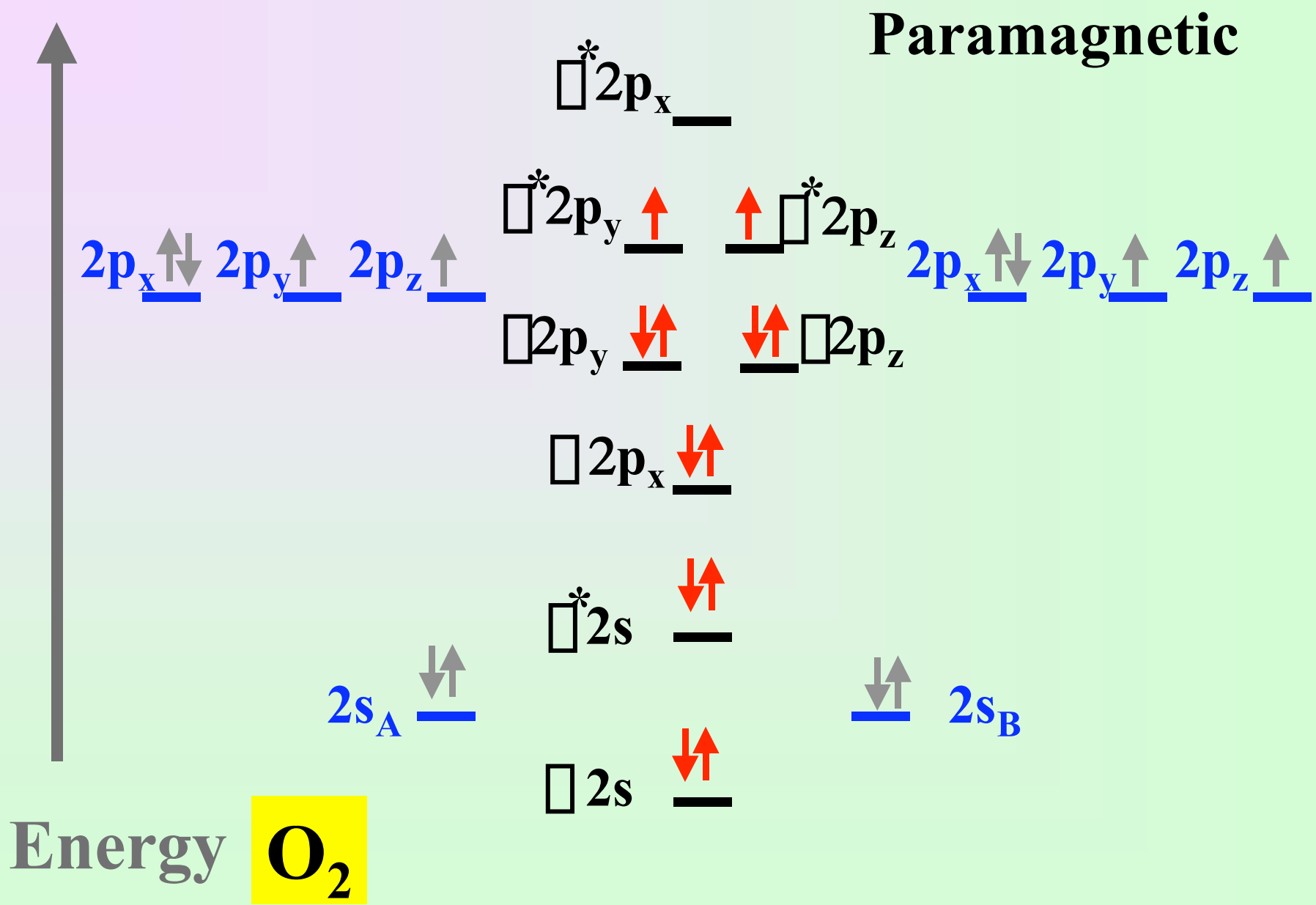


Energy

C₂



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



Diamagnetic

