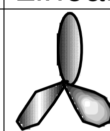
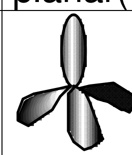
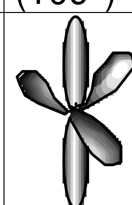
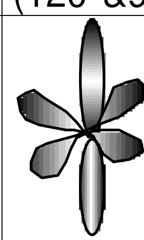
UNIT III

Chemical Bonding

There are two basic approaches to chemical bonding based on the results of quantum mechanics. These are the Valence Bond Theory (VB) and the Molecular Orbital theory (MO).

1) Valence Bond Theory: Here individual atoms come together to form a covalent bond. When two atoms get together to form a covalent bond, an atomic orbital of one atom **overlaps** with an atomic orbital of another atom. That is, two orbitals share same common region in space. The pair of electrons are shared between the two atoms in this region of overlap. **The greater the overlap, the stronger the bond**. The region of space formed by the overlapping orbitals has a maximum capacity of **two electrons** that must have opposite spins as the Pauli exclusion principle prescribes.The valence Bond theory required the introduction of **hybrid orbitals** which would lead to the most overlap that satisfies the observed molecular shapes.

Types of Hybrid Orbitals:

Pure atomic orbital of the central atom	Hybrid orbitals of the central atom	Number of hybrid orbitals	Shape of hybrid orbitals
s, p	sp	2	 Linear (180°)
s,p_x,p_y	sp^2	3	 Trigonal planar(120°)
s,p_x,p_y,p_z	sp^3	4	 Tetrahedral (109°)
s,p_x,p_y,p_z,d	sp^3d or dsp^3	5	 Trigonal Bipyramid (120°&90°)
s,p_x,p_y,p_z,d,d	sp^3d^2 or d^2sp^3	6	 Octahedral (90°)

Exercise : Use the Valence-Bond theory to explain the bonding in each of the following:

1) CH_4

We need to draw the **electron-dot structure** so that we can **predict the geometry of the groups of electrons around the central atom**. Hence, we predict the **type of hybrid orbitals** employed for bonding by the central atom.

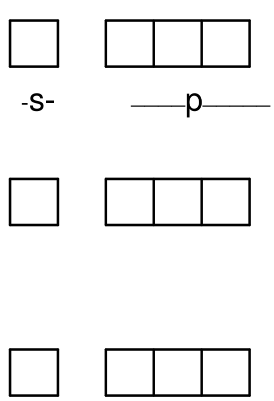
a) Electron-dot structure:

b) **Number** of groups of electrons is ______________.

c) The **geometry** of the groups of electrons is _______________.

d) The only orbitals that extend towards the corners of a tetarhedral are _________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of _________________° with each other.

e) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals. These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms. Recall that the greater the region of overlap, the stronger (and most stable) the bond.



(ground state)

(excited state)

2) NH_3

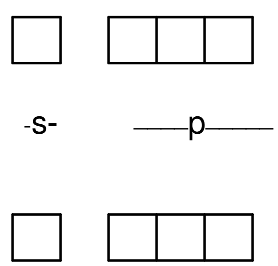
a) Electron-dot structure:

b) **Number** of groups of electrons is ______________.

c) The **geometry** of the groups of electrons is _______________.

d) The only orbitals that extend towards the corners of a tetrahedral are _________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of _________________° with each other.

e) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals . These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms.Recall that the greater the region of overlap, the stronger (and most stable) the bond.



(ground state)

Questions:1) Which orbital is occupied by the nonbonding pair of electrons?
Answer: _______

2) The actual bond angle is 107°. Explain the deviation of the bond angle from the typical 109° expected for the above geometry?________

3) H_2O

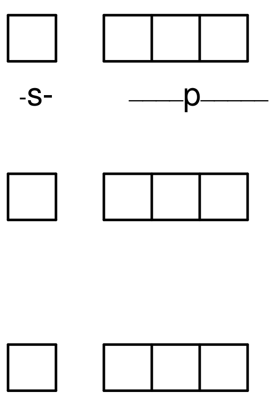
a) Electron-dot structure:

b) **Number** of groups of electrons is ______________.

c) The **geometry** of the groups of electrons is _______________.

d) The only orbitals that extend towards the corners of a tetrahedral are _________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of _________________° with each other.

e) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals. These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms. Recall that the greater the region of overlap, the stronger (and most stable) the bond.



(ground state)

(excited state)

Questions: 1) What are the orbitals occupied by the lone-pairs of electrons?Ans_________The actual bond angle is 104° . Explain the deviation of the bond angle from the typical 109° expected . Answer: ____

4) SF_4

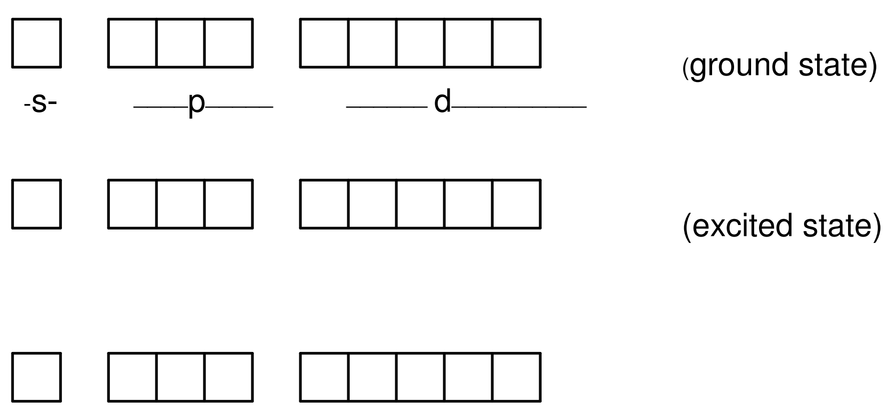
a) Electron-dot structure:

b) **Number** of groups of electrons is ______________.

c) The **geometry** of the groups of electrons is _______________.

d) The only orbitals that extend towards the corners of the above predicted geometry are _________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of _________________° with each other.

e) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals. These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms. Recall that the greater the region of overlap, the stronger (and most stable) the bond.



5) SF_6

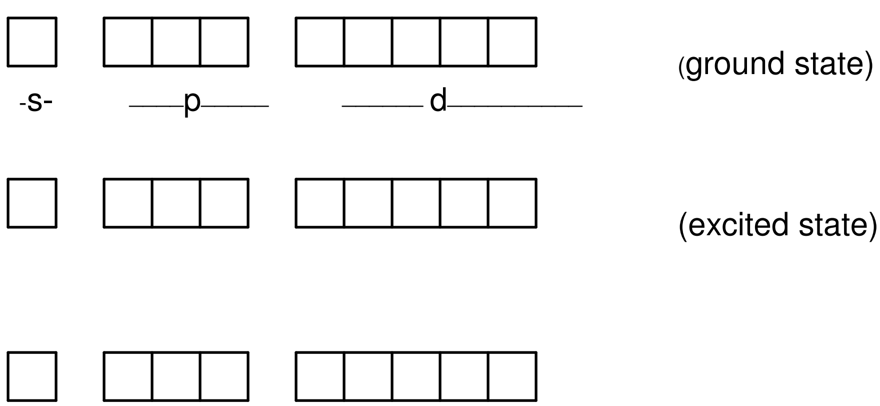
a) Electron-dot structure:

b) **Number** of groups of electrons is _______________.

c) The **geometry** of the groups of electrons is ________________.

d) The only orbitals that extend towards the corners of the above predicted geometry are __________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of __________________° with each other.

e) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals. These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms. Recall that the greater the region of overlap, the stronger (and most stable) the bond.



Types of Covalent Bonds and the Valence Bond Description of Multiple Bonding

A sigma bond (σ - bond) is a covalent bond formed by the overlap of two atomic orbitals whose axis coincide. That is, end-to-end overlap of the orbitals on neighboring atoms.

A Pi bond (π-bond) is a covalent bond formed by the overlap of two atomic orbitals whose axes are parallel. That is, side-to-side overlap.

Exercise: Use the Valence Bond model to explain the bonding in the following molecules:

1) C_2H_6

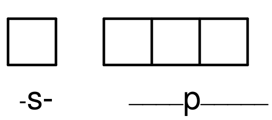
a) Electron-dot structure:

b) **Number** of groups of electrons is ______________.

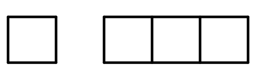
c) The **geometry** of the groups of electrons is _______________.

d) The only orbitals that extend towards the corners of the above predicted geometry are _________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of _________________° with each other.

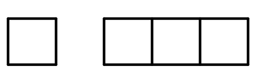
e) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals. These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms. Recall that the greater the region of overlap, the stronger (and most stable) the bond.



(ground state)



(excited state)



2) C_2H_4

a) Electron-dot structure:

b) **Number** of groups of electrons is ______________.

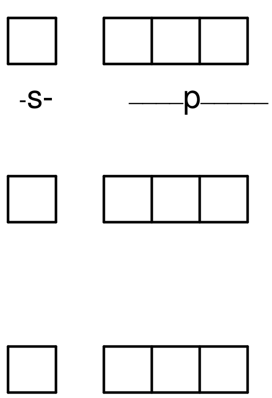
c) The **geometry** of the groups of electrons is _______________.

d) i) How **σ** -bonds are present around each carbon atom? Ans: ___

ii) How many π-bonds are present around each carbon atom? Ans: ___

e) The only orbitals that extend towards the corners of the above predicted geometry are _________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of _________________° with each other.

f) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals. These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms. Recall that the greater the region of overlap, the stronger (and most stable) the bond.



(ground state)

(excited state)

3) C_2H_2

a) Electron-dot structure:

b) **Number** of groups of electrons is ______________.

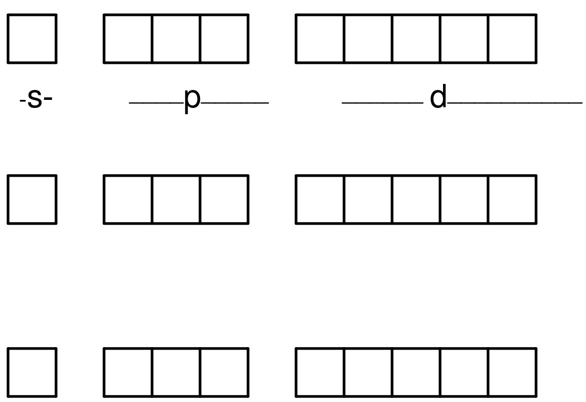
c) The **geometry** of the groups of electrons is _______________.

d) i) How many **σ** -bonds are present around each carbon atom? Ans: _____

ii) How many π-bonds are present around each carbon atom? Ans: ____

e) The only orbitals that extend towards the corners of the above predicted geometry are _________________ **hybrid orbitals**. These hybrid orbitals make an **angle** of _________________° with each other.

f) Draw the **electron- box diagram** showing the transformation of pure atomic orbitals of the central atom into hybrid orbitals . These will be the new orbitals on the central atom that will overlap with the atomic orbitals of the surrounding atoms. Recall that the greater the region of overlap, the stronger (and most stable) the bond.

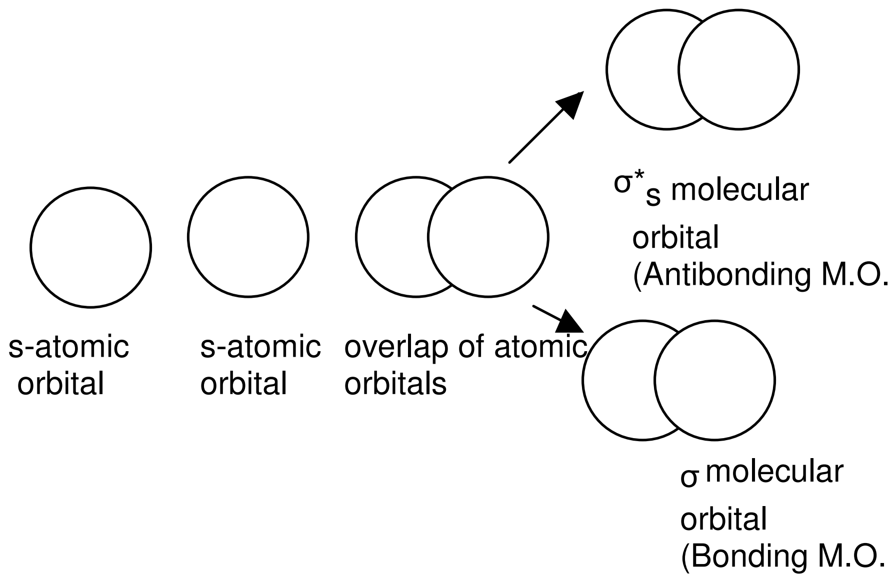


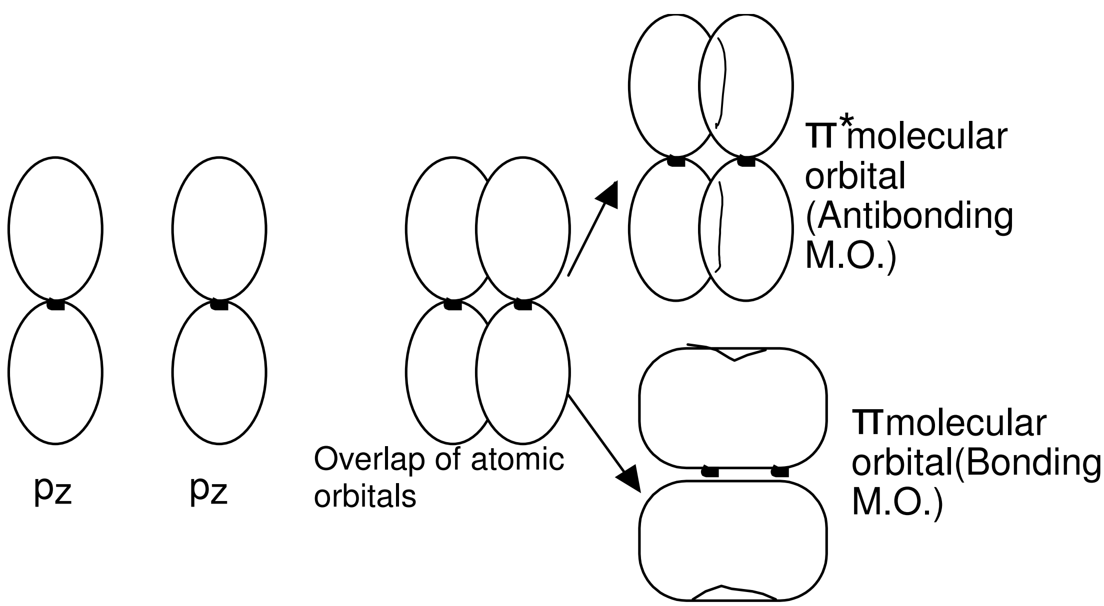
(ground state)

(excited state)

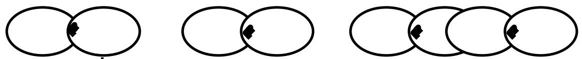
2) Molecular Orbital Theory:
The previous-- **localized electron**-- model is great for interpreting the structure and bonding of molecules. But the model does not deal effectively with molecules containing double bonds, so the concept of resonance was introduced. Also, the model does not deal effectively with molecules containing unpaired electrons. Another model often used to describe bonding is the molecular orbital model which views a molecule as a set of positive nuclei with orbitals **extending** over the entire molecule (that is **delocalized** molecular orbitals). Molecular orbitals have many of the same characteristics as atomic orbitals. Each molecular orbital can hold two electrons of opposite spins.

The Following Diagram Illustrates the Formation of Molecular Orbitals from the Combination of Atomic Orbitals:



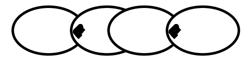


The formation of sigma molecular orbitals from the combination of p_x atomic orbitals (σ_{px}):

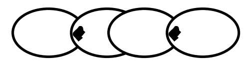


p_x atomic orbital

px atomic orbital



σ*px molecular orbital(Antibonding M.O.



σpx molecular orbital(Bonding M.O.)

Exercise:Draw a diagram illustrating the formation of Pi molecular orbitals from the combination of p_y atomic orbitals:

Exercise: (a)Will an s-orbital of one atom and a p_x orbital of another atom combine to form molecular orbitals?Answer: _____Draw contour diagrams for the molecular orbitals formed.

b) Will an s-orbital of one atom combine with a p_z atomic orbital of another atom to form molecular orbitals? Answer_____ Justify your answer using illustrative diagram(s).________

Exercise: Draw the Molecular Orbital energy level diagram for the homonuclear diatomic molecules and ions given below.

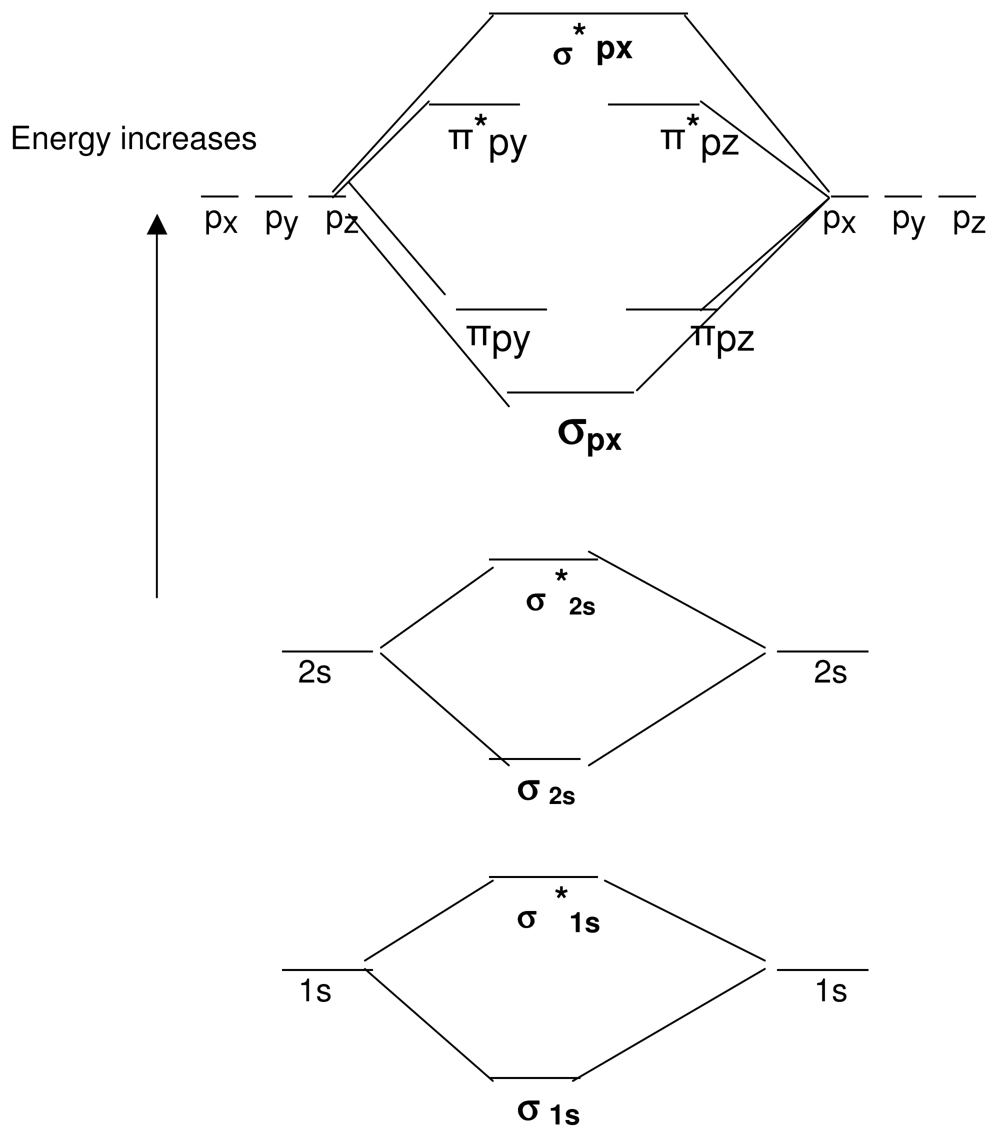
a) Calculate the bond order.
b) Predict whether the molecule or ion exist or not.
c) Predict the magnetic property.
d) Write the electronic configuration.

i) H_2

ii) He_2

iii) He_2^+

MO energy level Scheme for a homonuclear diatomic molecule or ion.



Exercise: a)Draw the MO energy level scheme for the N_2 molecule.

b) Calculate the bond order for the N_2 molecule. Hence, predict if it exists or not.

c) If it does exist, predict its magnetic property.

d) Write the electronic configuration for N_2.

Answer:

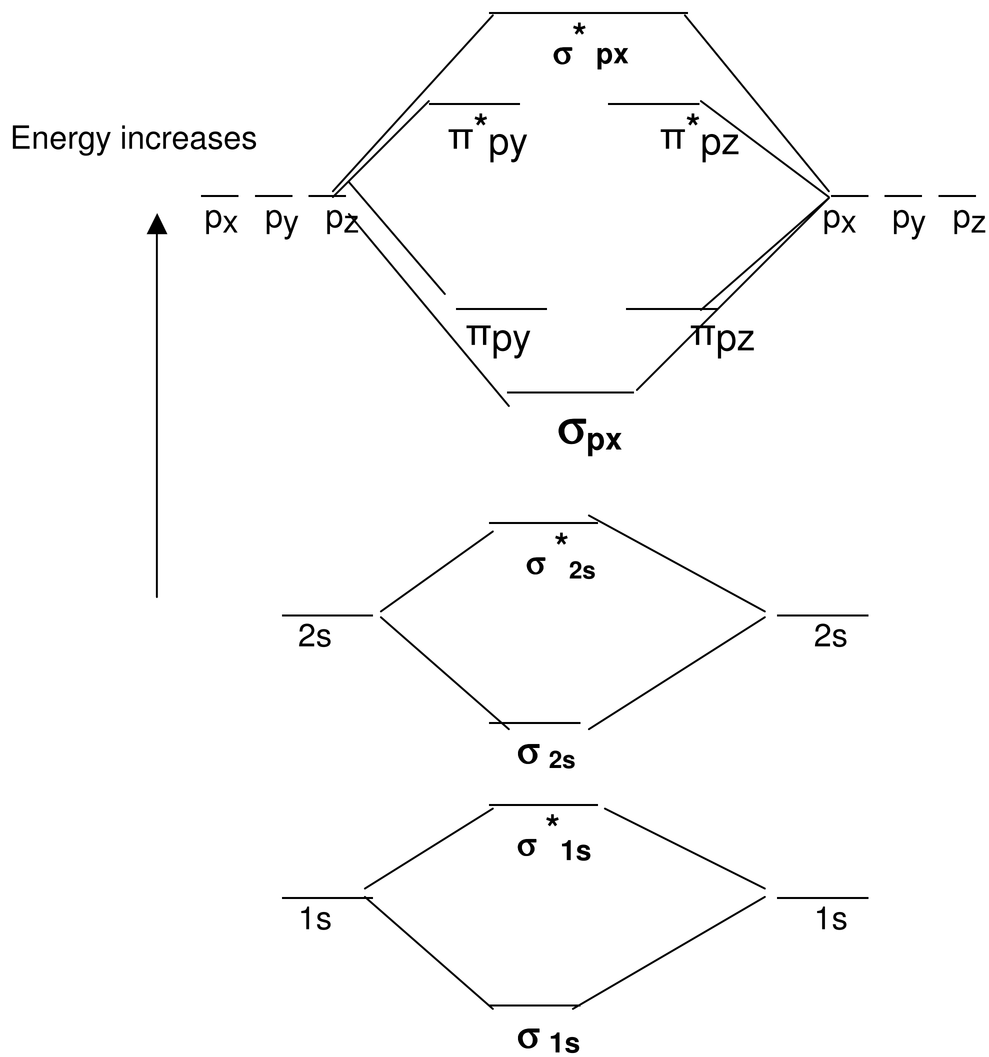
Exercise: a)Draw the MO energy level scheme for the N_2^+ ion.

b)Calculate the bond order of the N_2^+ ion. Hence, predict if N_2^+ exists or not.

c) If it does exist, predict its magnetic property.

d) Write the electronic configuration for N_2^+.

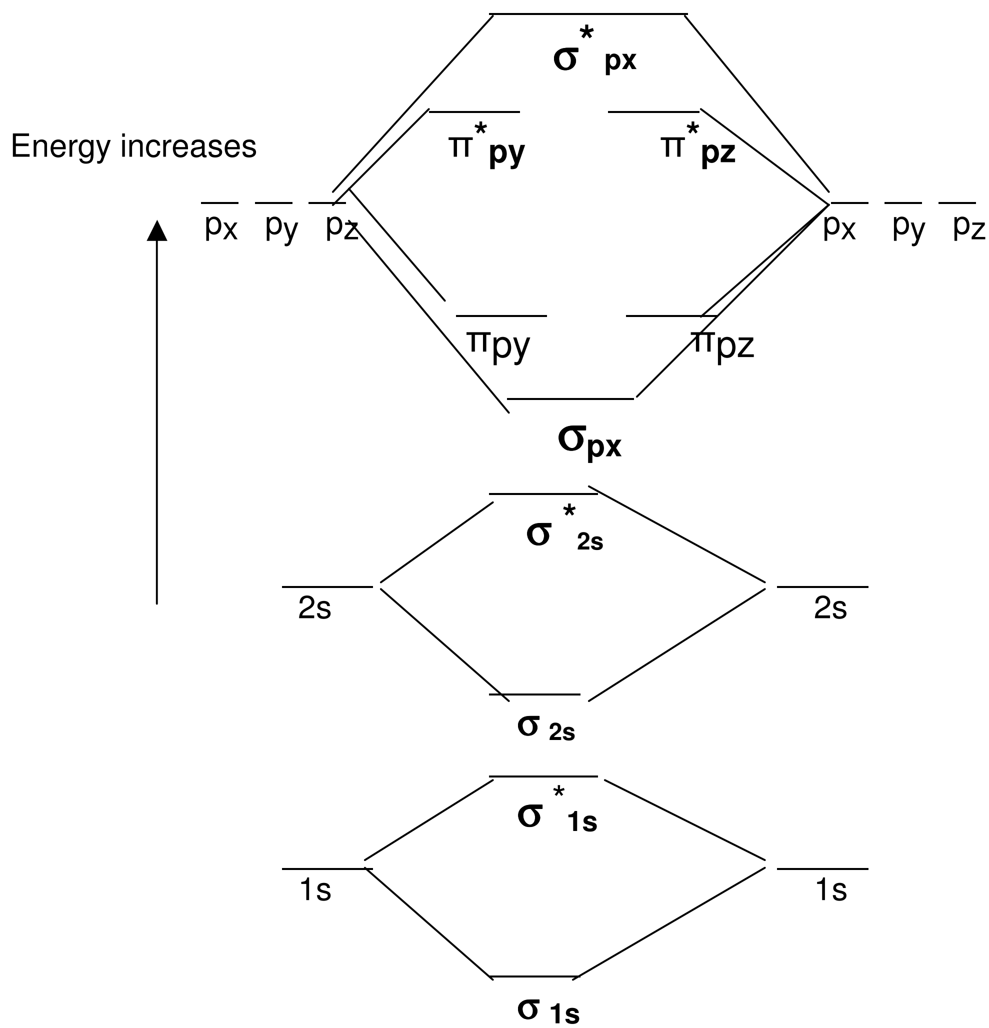
e) Compare the bond length and strength of N_2 to N_2^+



Answer:
b)
c)
d)
e)

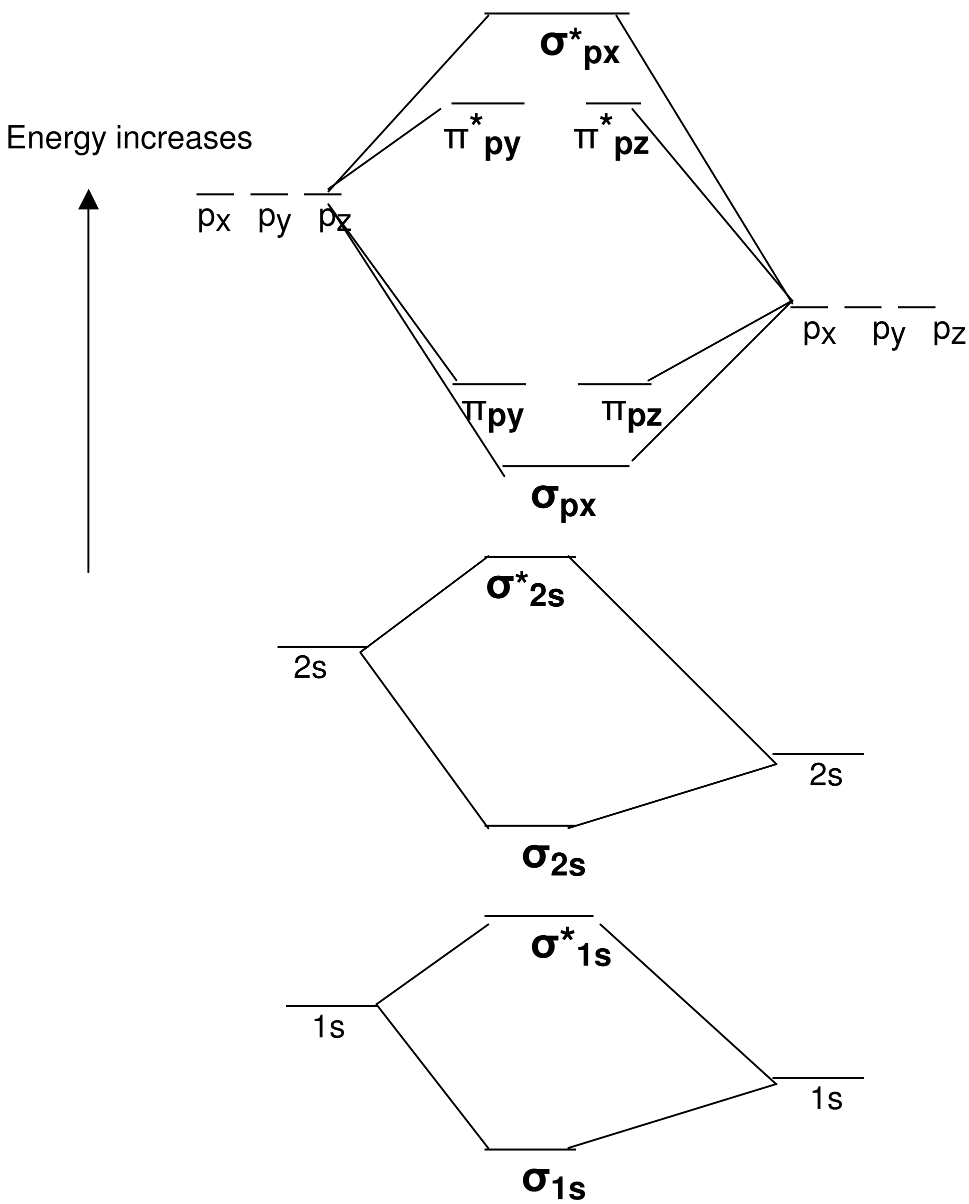
Exercise: Compare the bond order deduced from the MO model to that deduced from drawing the electron-dot structure.

Exercise: a)Draw the MO energy level scheme for the O_2 molecule.
b) Calculate the bond order for O_2. Hence, predict whether O_2 exists or not.
c) If it does exist, predict its magnetic property.
d) Write the electronic configuration for O_2.
e) Compare the bond length and strength of O_2 to O_2^{2-} .



Answer:
b)
c)
d)
e)
Notice that N_2^{2-} would have the same electronic configuration as O_2, since they are **isoelectronic**.
Exercise: Compare the bond order of O_2 deduced from the MO model to that deduced from drawing the electron-dot structure. Could you have predicted the magnetic property of O_2 from the electron-dot structure?

MO energy level Scheme for a hetronuclear diatomic molecule or ion.



Exercise: a)Draw the MO energy level scheme for the NO molecule.

b) Calculate the bond order of the NO molecule. Hence, predict whether it exists or not.

c) If it does exist, predict its magnetic property.

d) Write the electronic configuration for NO .

e) Draw the electron- dot structure for NO**.**

Answer:

b)

c)

d)

e)