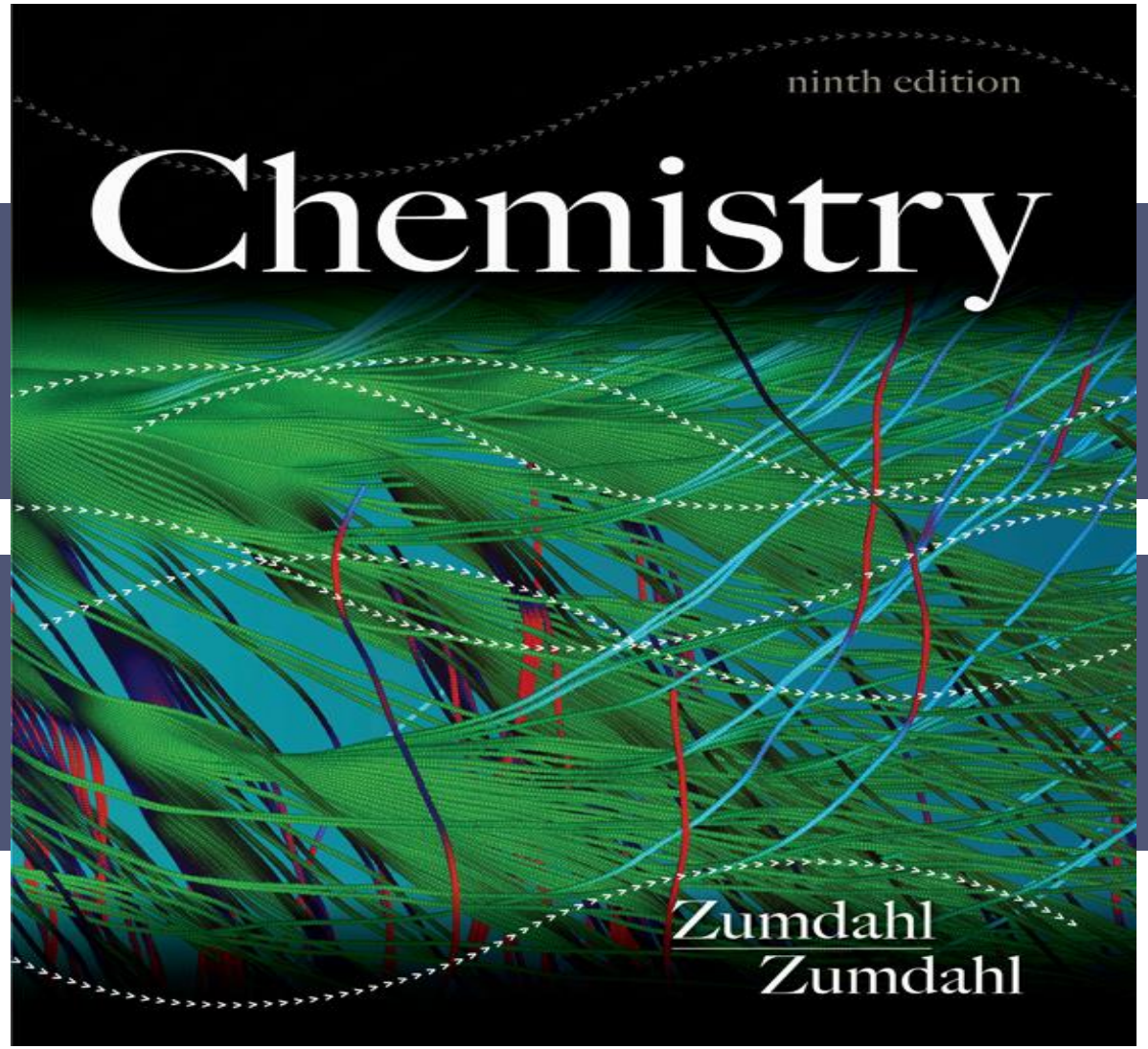


Chapter 9

Covalent Bonding: Orbitals

The Nature of Chemical Bonding

The Nature of Chemical Bonding

There are many types of experiments we can perform to determine the fundamental nature of chemical bonding in materials. For example:

- we can study physical properties such as melting point, hardness, and electrical and thermal conductivity.
- We can also study solubility characteristics and the properties of the resulting solutions.
- To determine the charge distribution in a molecule,
- we can study its behavior in an electric field.
- We can obtain information about the strength of a bonding interaction by measuring the **bond energy,** which is the energy required to break the bond

The Nature of Chemical Bonding

Types of chemical bonds

- Ionic: electrons are transferred to form ions
- Covalent: equal sharing of electrons
- Polar covalent: unequal electron sharing
- Metallic Bonding.

The Nature of Covalent Bonding

Will look into the following concerning **Covalent Bonding**

- The Valence Bond Theory,
- Hybridization and molecular shapes.
- Simple Molecular Orbital Theory,
- Overlap Integral for Simple Diatomic Molecules.

THEORIES OF COVALENT BONDING

1. **Lewis Theory**
   - Show how the valence electron pairs are arranged among the atoms in a molecule or polyatomic ion.
   - The ***Lewis structure (or Lewis formula)***- is two-dimensional structural formula consists of electron-dot symbols that depict each atom and its neighbors, the bonding pairs that hold them together, and the lone pairs that fill each atom's outer level (valence shell) - **octet rule**
2. **Valence Shell Electron Pair Repulsion (VSEPR) Theory and Molecular Geometry**
   - Based on the idea that electron pairs will be arranged around a central atom in a way that minimizes the electron repulsions
   - Can be used to predict the geometric structure of most molecules
   - The theory predicts the shape of covalent compounds in which valence shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing the electron pair repulsion

The Valence Bond Theory (VBT) and Orbital Hybridization

History

- The **Valence Bond Theory** (VBT) was proposed by Heitler & London to explain the formation of **covalent bond quantitatively using *quantum mechanics.***
- Later on, Linus Pauling improved this theory by introducing the concept of **hybridization**.
- At present Valence Bond Theory is one of the two quantum mechanical theories used to describe covalent bond formation and the electronic structure of molecules

The Valence Bond Theory

The main postulates of this theory are as follows:

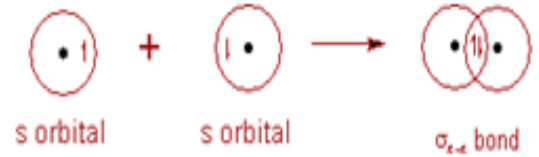
- A covalent bond is formed by the ***overlapping of two half filled valence atomic orbitals***of two different atoms
- The electrons in the overlapping orbitals get paired & confined between the nuclei of two atoms.
- The electron density **between two bonded atoms** increases due to overlapping. **This confers stability to the molecule.**
- The greater the extent of overlapping, **stronger is the bond formed.**
- The direction of the covalent bond is along the region of overlapping of the atomic orbitals **i.e., covalent bond is directional.**
- Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond (σ-bond) and a pi bond (π-bond).

There are two types of covalent bonds based on the pattern of overlapping as follows:

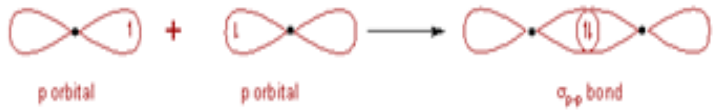
(i) Sigma (σ)-bond

- The covalent bond formed due to overlapping of atomic orbital along the inter nucleus axis is called σ-bond.
- Electron pair is shared in an area centered on a line running *between* the atoms
- This **head-on overlap** of orbitals is referred to as a sigma bond.
- It is a stronger bond and cylindrically symmetrical.
- Depending on the types of orbitals overlapping, the σ-bond is divided into following types:

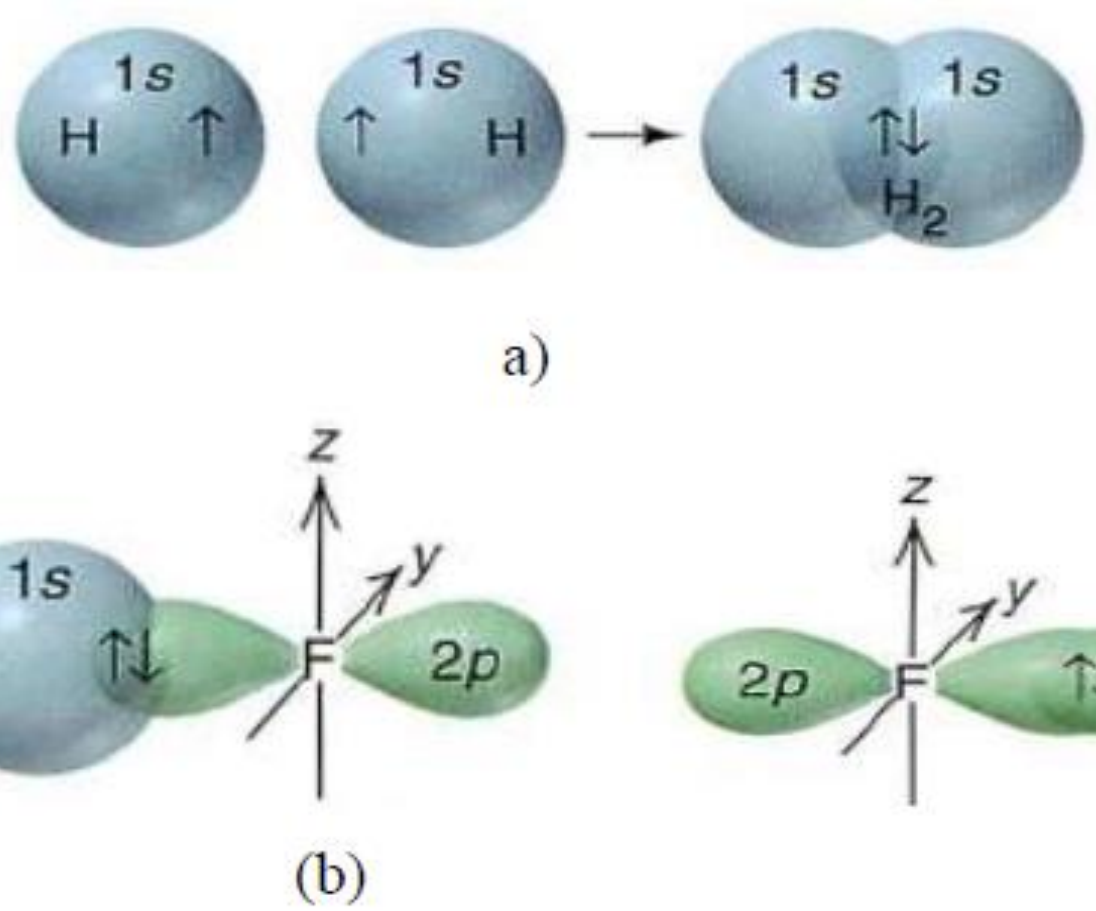
σ_{s-s} bond:



σ_{p-p} bond:



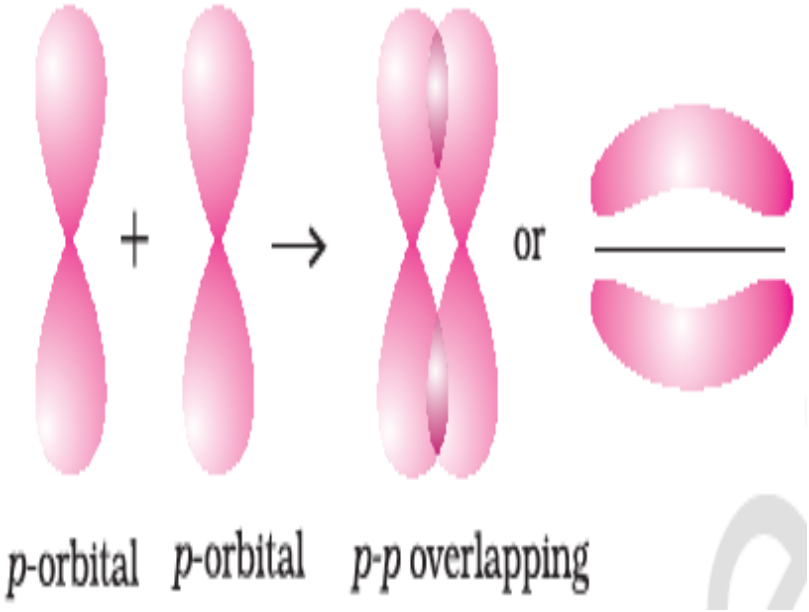
σ_{s-p} bond:



(a) $\sigma_{s\text{-}s}$ overlapping on the formation of H_2 molecule (b) $\sigma_{s\text{-}p}$ overlapping on the formation of HF molecule and (c) $\sigma_{p\text{-}p}$ overlapping on the formation of F_2 molecule

(ii) Pi (π)-Bond:

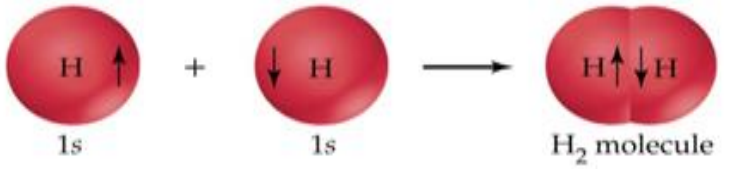
- The covalent bond formed by **sidewise overlapping** of atomic orbitals is called π- bond.
- In this bond, the electron density is present above & below the **inter nuclear axis.**
- It is relatively a weaker bond since the electrons are not strongly attracted by the nuclei of bonding atoms.
- Forms double and triple bonds by sharing electron pair(s) in the space above and below the σ bond.
- Uses the unhybridized *p* orbitals.



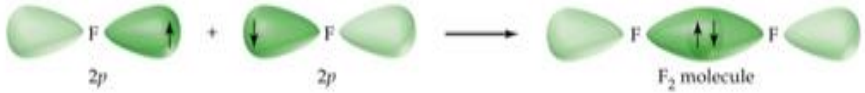
The Restriction of the VBT

Note:

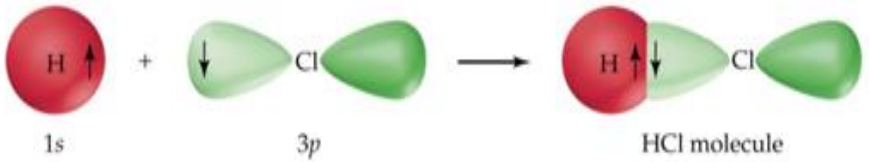
- The 's' orbitals can only form σ-bonds, whereas the p, d & f orbitals can form both σ and π-bonds.
- The valence bond method predicts molecule shapes from the shapes and orientation of the atomic orbitals and their overlap regions when two atoms approach.



Fluorine:



– **HCl?? Again, no problem--even though it's s and p orbital…**



But these are simple molecules

- What about non-linear molecules?

The VBT

- The old version of valence bond theory is limited to diatomic molecules only.
- Forexample, the covalent bond in H_2, O_2, Cl_2, N_2, HCl, *etc*. molecule can be explained by theorbital overlapping of the two atoms.
- It could not explain the structures and bond angles of molecules with more than three atoms.

  E.g. It could not explain the structures and bond angles of H_2O, NH_3 etc.
- In order to explain the structures and bond angles of molecules, Linus Pauling modified thevalence bond theory using **hybridization concept**.

Hybridization and Molecular Shapes

- In most cases the orbitals that overlap are **reconfigured orbitals**, called **hybrid orbitals**, having different shapes & orientations than **pure orbitals.**
- Generally It is define as:
  - ✓ ***the intermixing of two or more pure atomic orbitals of an atom with almost same energy to give same number of identical & degenerate new type of orbitals.***
- Mathematical concept based on quantum mechanics, the wave functions, Ψ of **valence-shell** of atomic orbitals of same atom are combined to give new wave functions corresponding to **hybrid orbitals**
- The number of hybrid orbitals formed is equal to the number of pure atomic orbitals undergoing hybridization.
  - ✓ E.g. If three atomic orbitals intermix with each other, the number of hybrid orbitals formed will be equal to 3.

Important conditions for hybridisation

1. The orbitals present in the valence shell of the atom are hybridised.
2. The orbitals undergoing hybridization should have almost equal energy.
3. Promotion of electron is not essential condition prior to hybridisation.
4. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridization

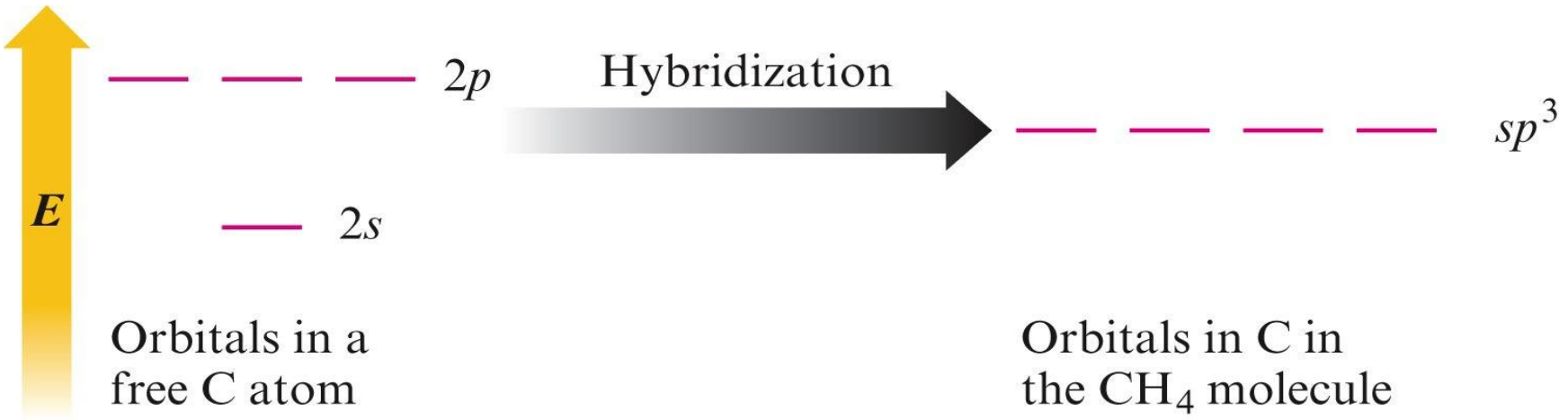
Types of Hybridisation

- There are various types of hybridization involving s, p and d orbitals

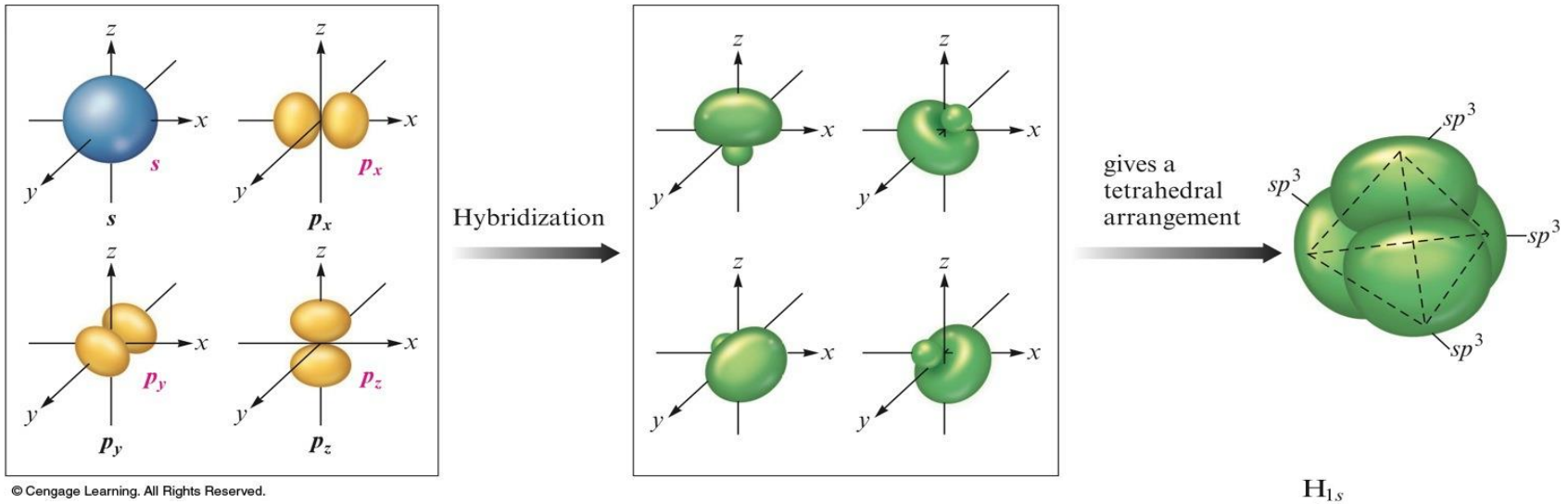
1. sp^3 Hybridization (4 hybrid orbitals)

- Combination of one *s* and three *p* orbitals.
- Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, the localized electron model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes sp^3 hybridized.
- The four orbitals are identical in shape.

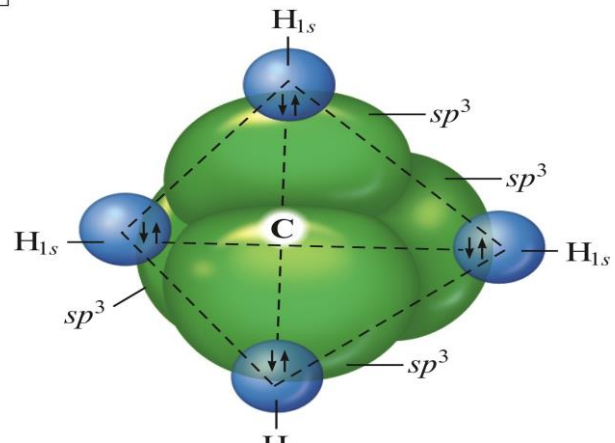
An Energy-Level Diagram Showing the Formation of Four sp^3 Orbitals



The Formation of sp^3 Hybrid Orbitals



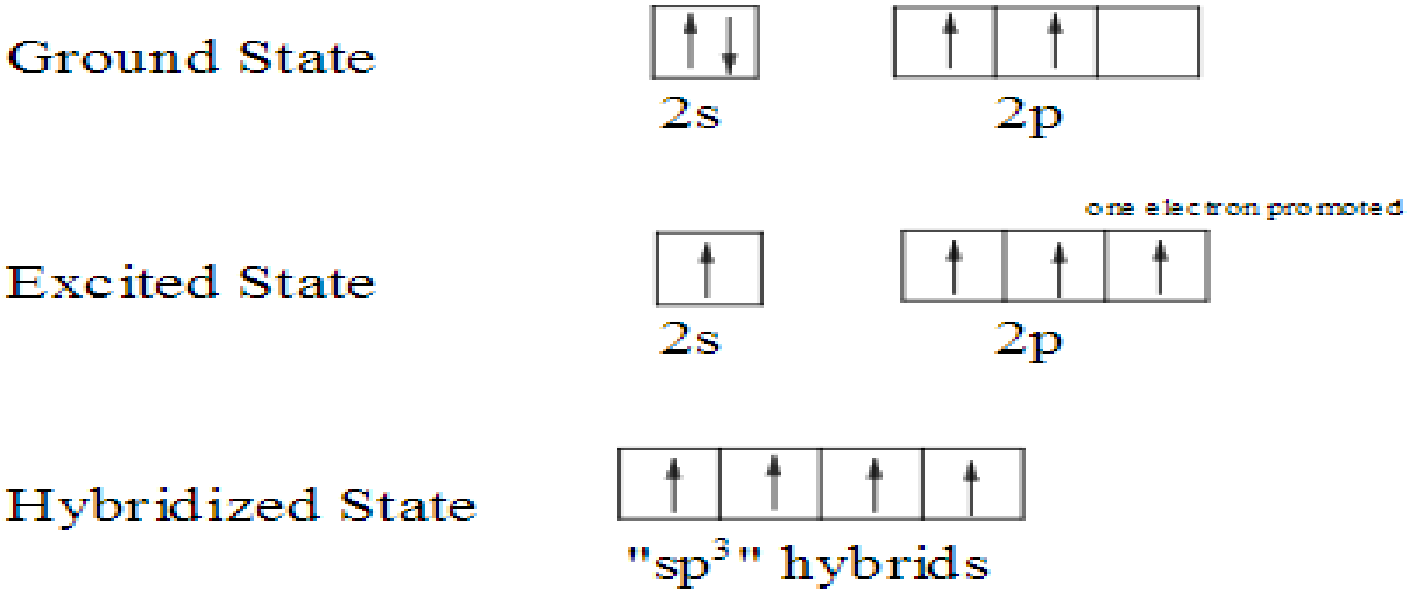
Tetrahedral Set of Four sp^3 Orbitals



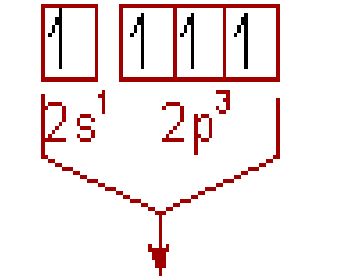
EXAMPLE!

Methane CH_4, Ethane, C_2H_6

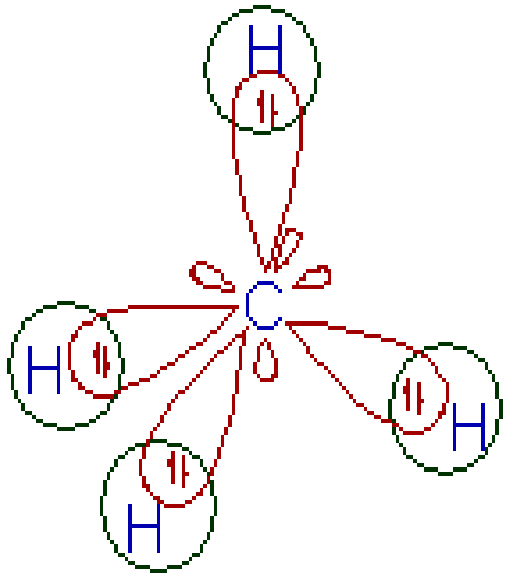
- The ground state of C reveals a pair of electrons in the 2s and two single electrons in the 2p.
- This is not consistent with the need for four single electrons required to form the four bonds with the hydrogens
- so again, electrons are promoted into the p subshell just prior to bonding.

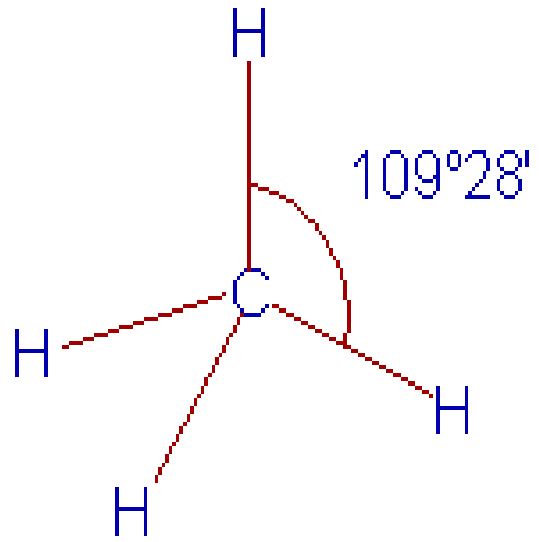


- These four orbitals arrange themselves in a tetrahedral geometry in order to minimize repulsion effects.



sp³ hybridization
(4 σ-bonds)



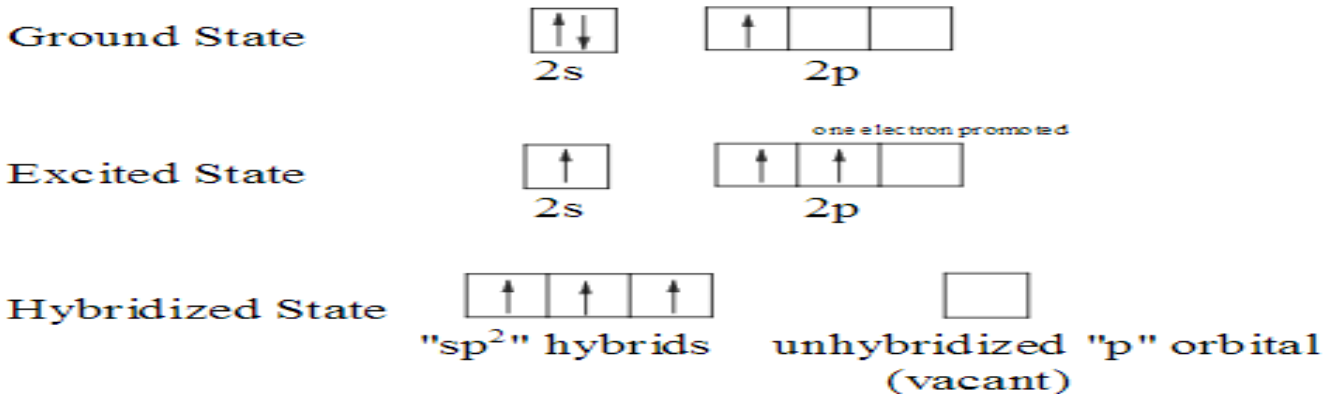


Tetrahedral structure of methane

- **The sp^3 hybrid orbitals have 25% 's' character and 75% 'p' character.**

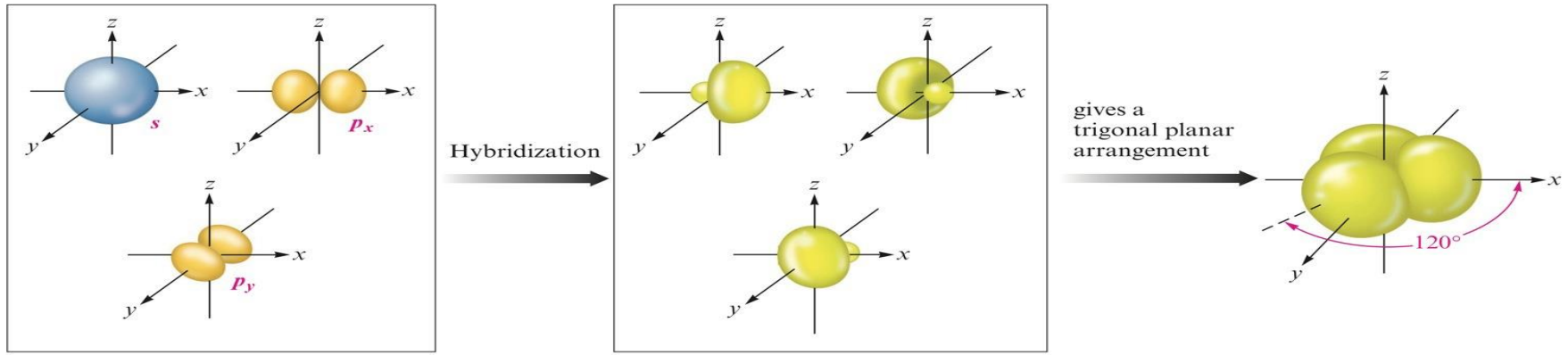
2. sp^2 Hybridization

- Combination of one *s* and two *p* orbitals.
- Gives a trigonal planar arrangement of atomic orbitals.
- One *p* orbital is not used.
  - ✓ Oriented perpendicular to the plane of the sp^2 orbitals.
  - ✓ the mixing of one s and two p orbitals of the central atom to give three hybrid orbitals that point toward the vertices of equilateral triangle , their axes at 120 angle apart are used
- would arrange themselves as far apart as possible forming a **trigonal planar** electron arrangement.
- **The sp^2 hybrid orbitals have 33.3% 's' character and 66.6% 'p' character**.



An Orbital Energy-Level Diagram for sp^2 Hybridization

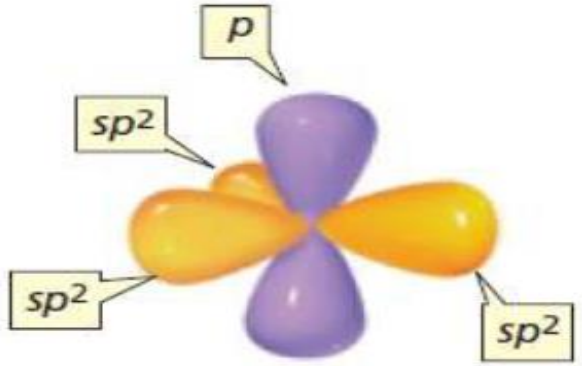
The Hybridization of the s, p_x, and p_y Atomic Orbitals

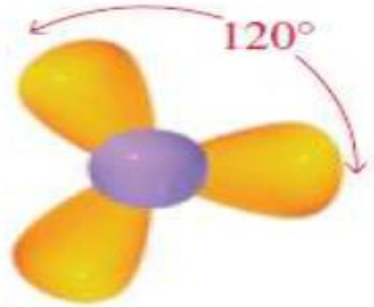


EXAMPLE!

Boron Trifloride **BF_3**

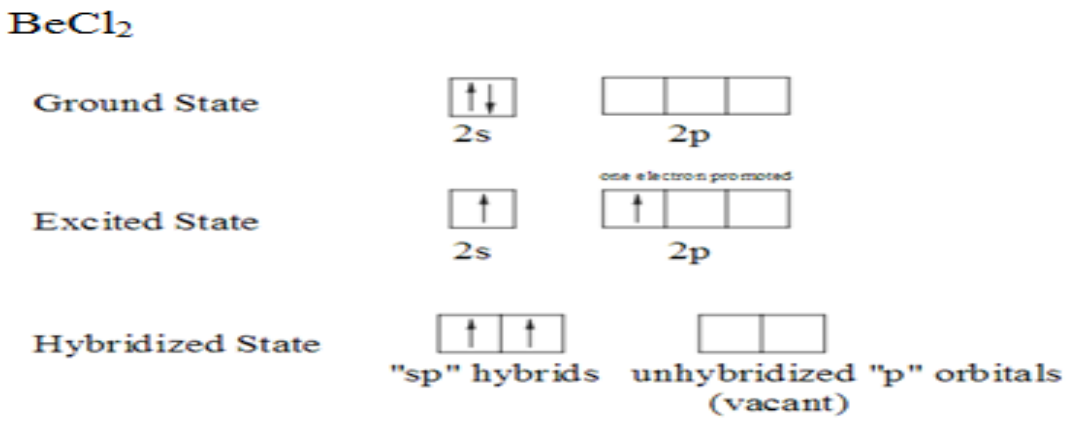
- VB theory proposes that the central B atom in the molecule is sp_2 hybridized.
- Each sp_2 orbital overlaps the 2p orbital of an F atom, and the six valence electrons- three from B and one from each of the three F atoms-form three bonding pairs.
- Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital
- The figure below shows the three-sp_2 orbitals in the **trigonal plane**, with the third 2p orbital unhybridized and perpendicular to this plane.



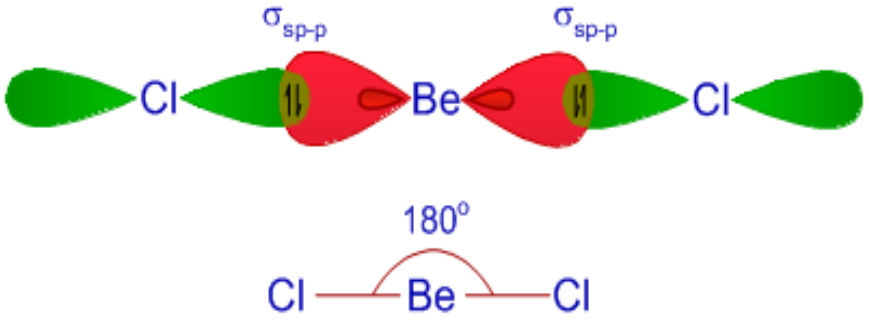


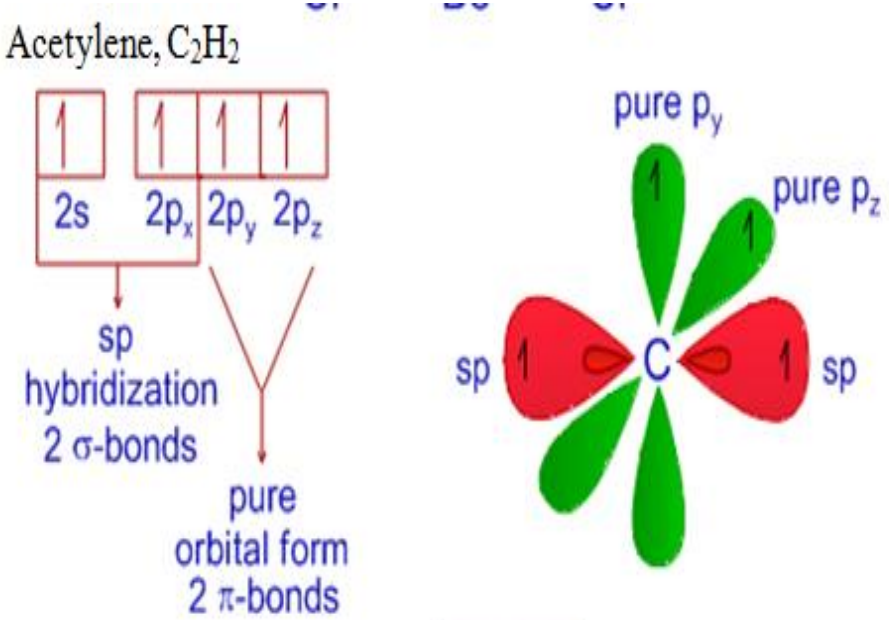
3. *sp* Hybridization

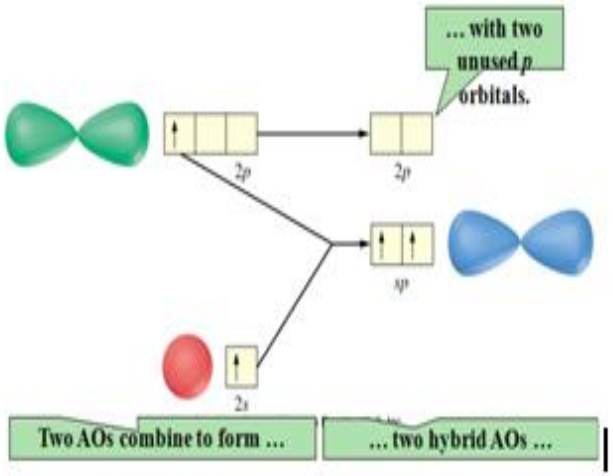
- Combination of one *s* and one *p* orbital.
- Gives a linear arrangement of atomic orbitals.
- Two *p* orbitals are not used.
  - ✓ Needed to form the π bonds.
- These sp-hybrid orbitals are arranged linearly at by making 180^{o} of angle.
- They possess 50% 's' and 50% 'p' character.



- Note that any left-over "p" orbitals are referred to as "unhybridized orbitals".
- These unhybridized orbitals are used to form any double or triple (Pi) bonds in a molecule and since this structure shows no multiple bonding, these unhybridized orbitals are vacant.
- **It should be noted that the "sp" hybrid orbitals will arrange themselves in a linear geometry.**



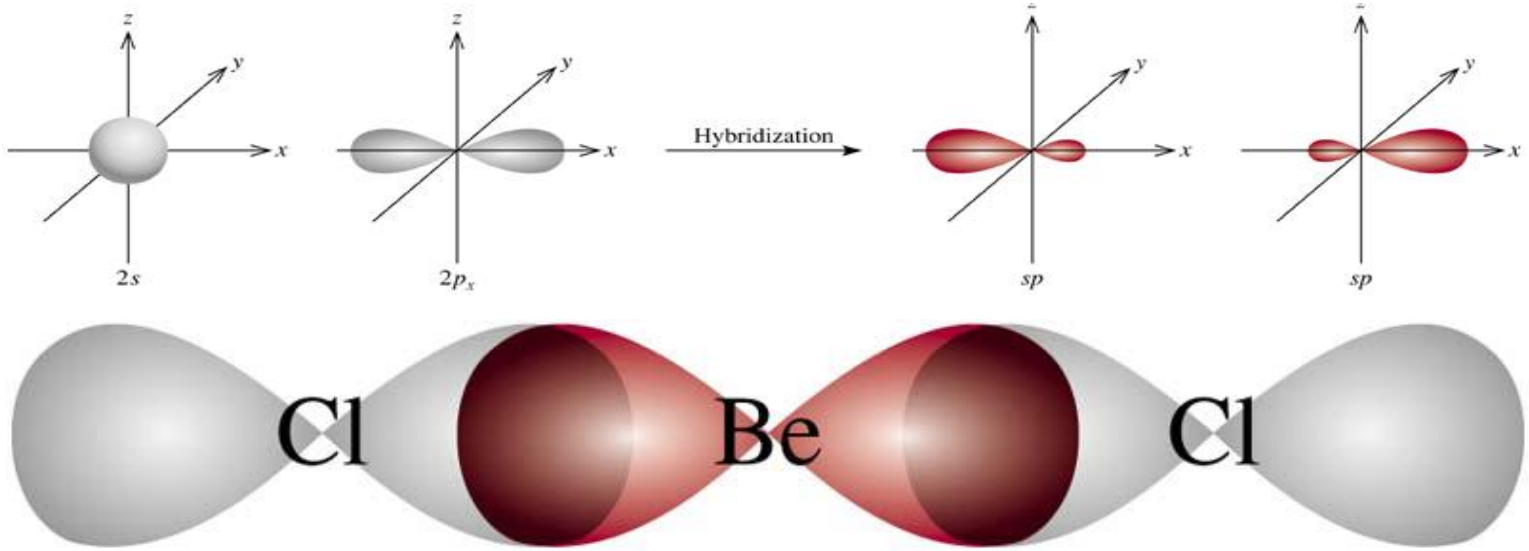




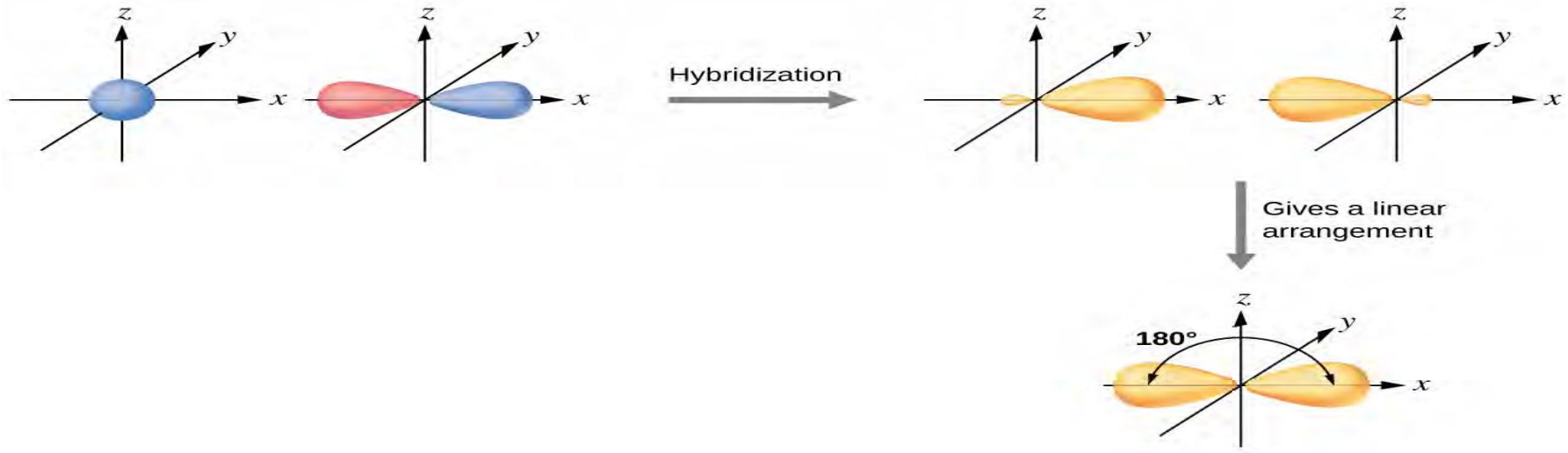
EXAMPLE!

CO_2, $BeCl_2$ etc

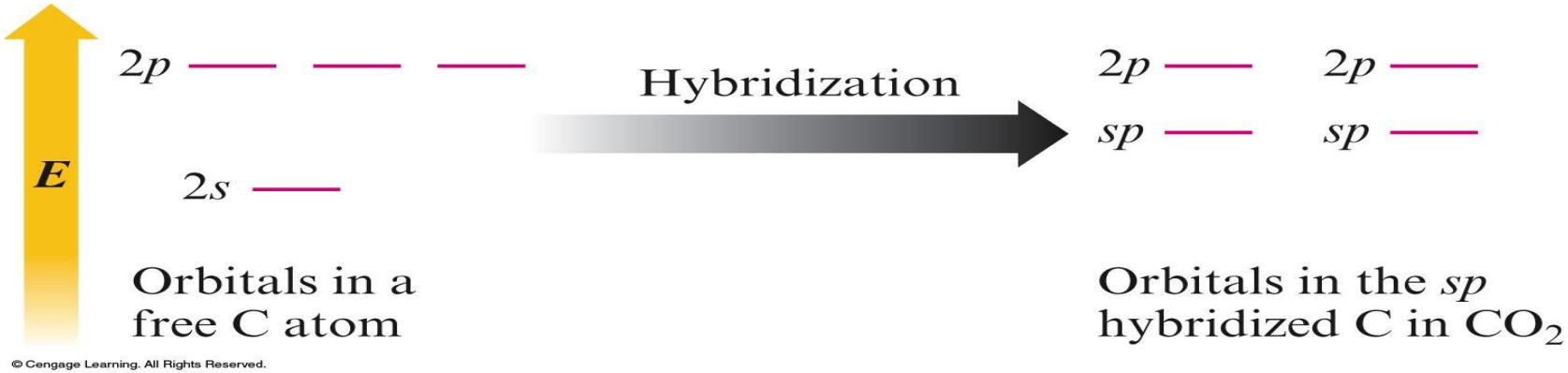
- When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals.
- The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons.
- Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.



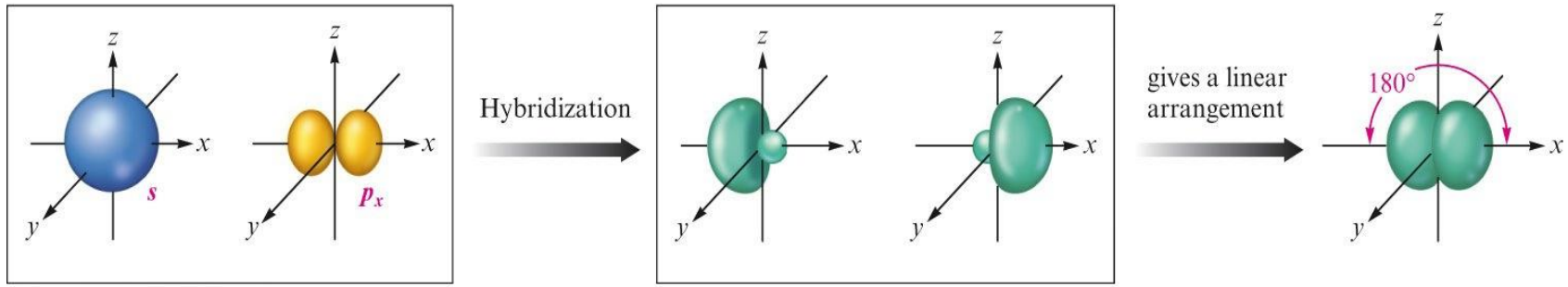
- Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (purple).
- Each hybrid orbital is oriented primarily in just one direction.
- Note: each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains



The Orbital Energy-Level Diagram for the Formation of *sp* Hybrid Orbitals on Carbon



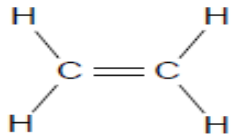
When One *s* Orbital and One *p* Orbital are Hybridized, a Set of Two *sp* Orbitals Oriented at 180 Degrees Results



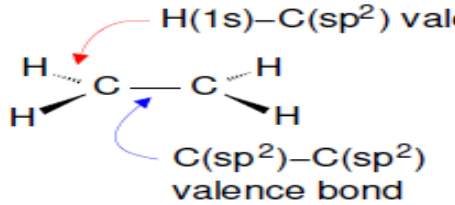
Multiple Bonds

Hybridization in molecules containing double and triple bonds

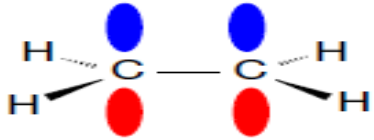
1. **Ethene** C_2H_4



- Trigonal planar carbons $\Longrightarrow$ sp^2 hybridization
- sp^2 hybrids used to make σ bonds to H atoms (with their 1s orbitals) and between the C atoms:

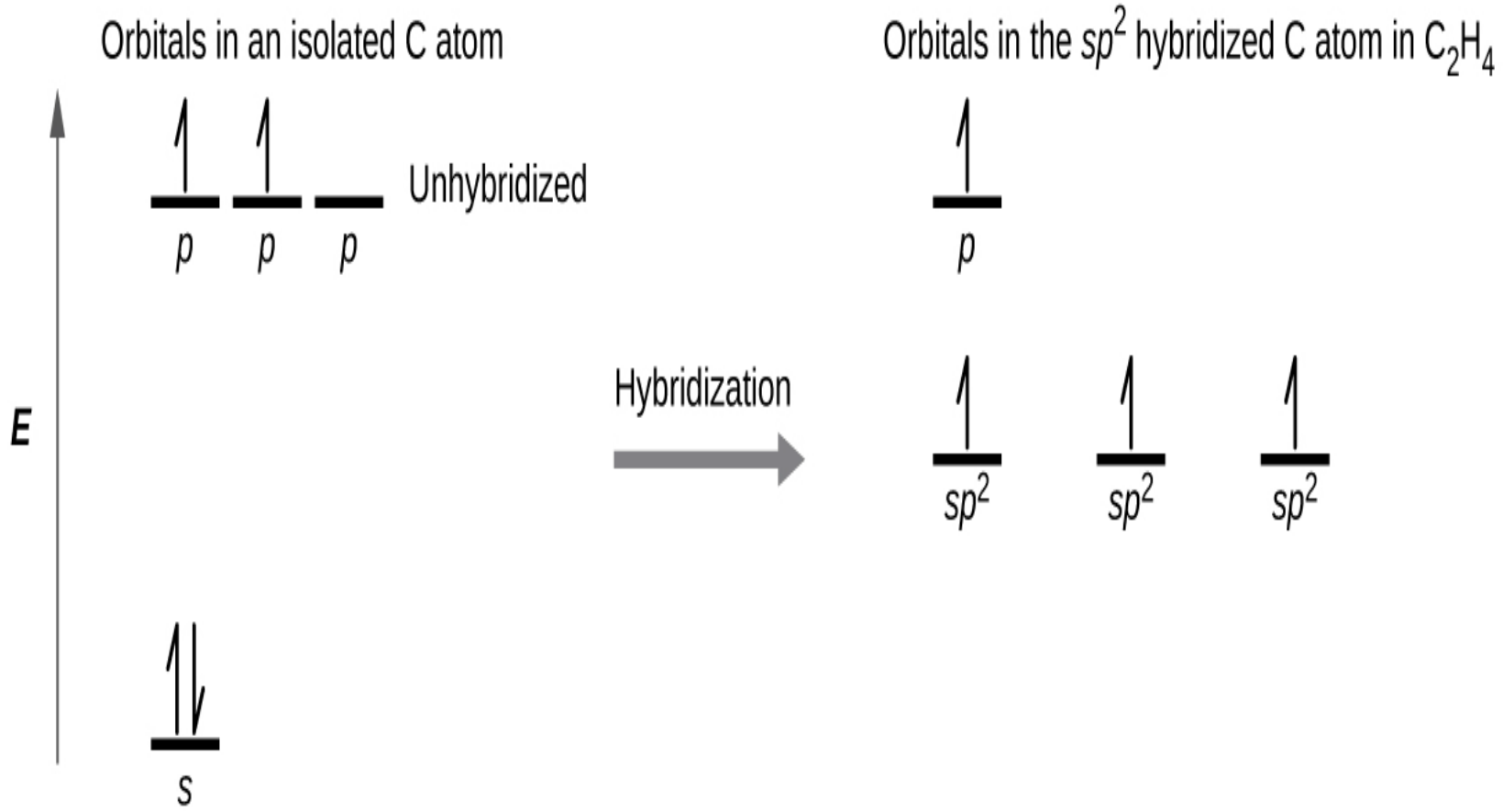


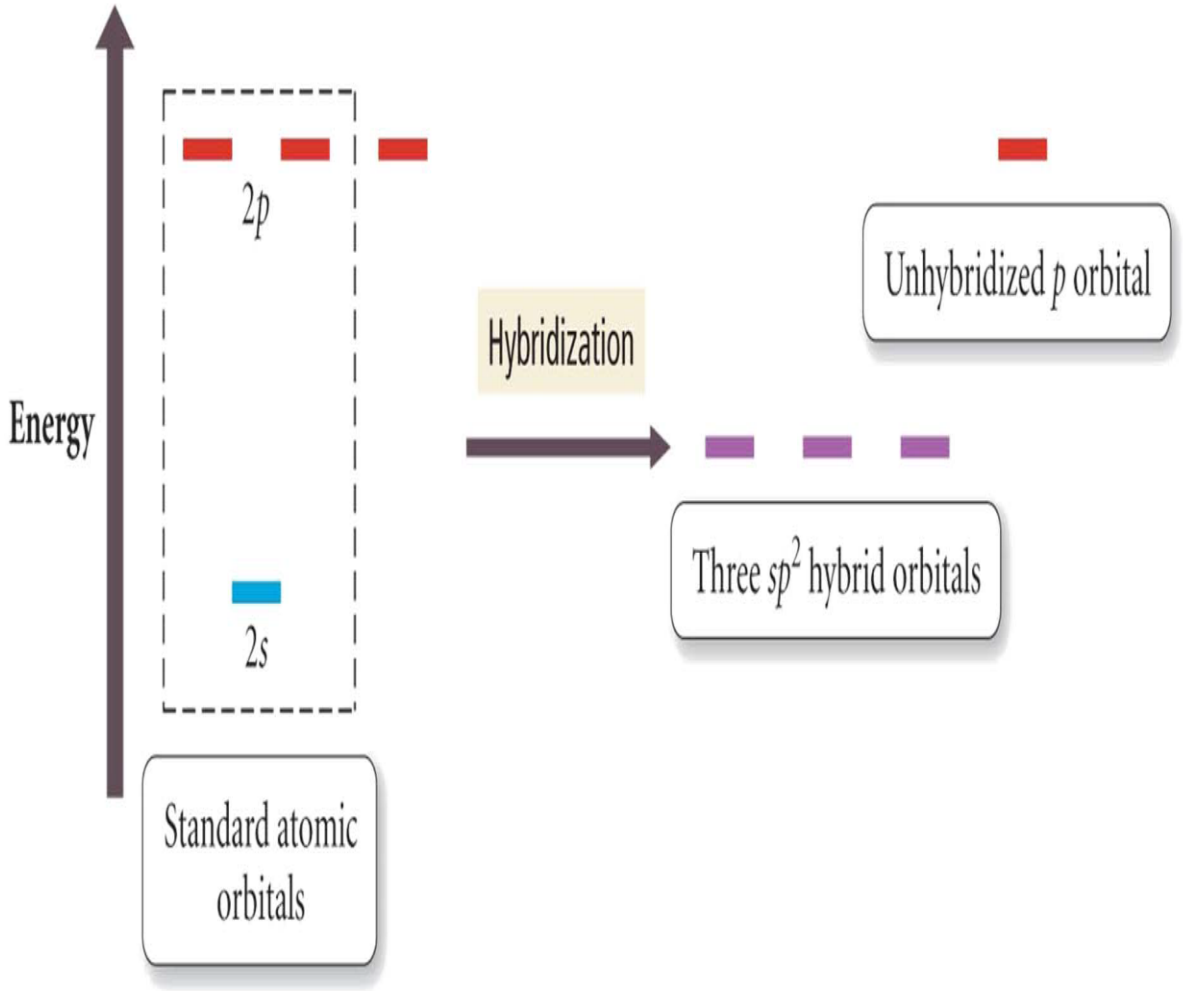
- This leaves one unused p orbital on each carbon atom:

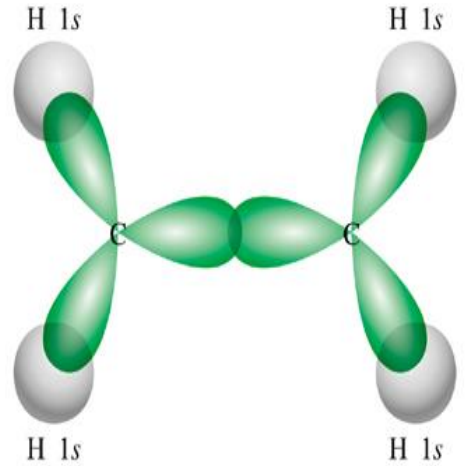


- The overlap of these p orbitals forms a π valence bond.
- VB description of the π bond: C(2p)-C(2p).

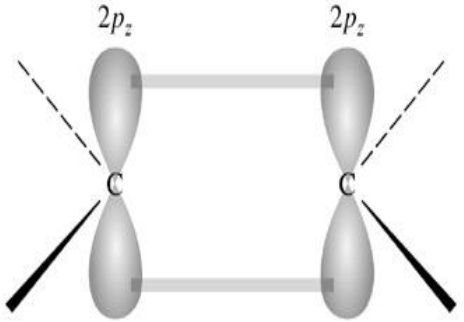
- In ethene, each carbon atom is *sp*2 hybridized, and the *sp*2 orbitals and the *p* orbital are singly occupied.
- The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.







(a)



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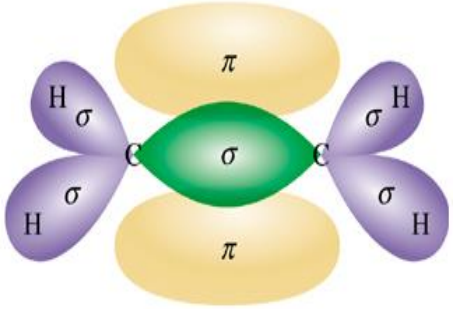
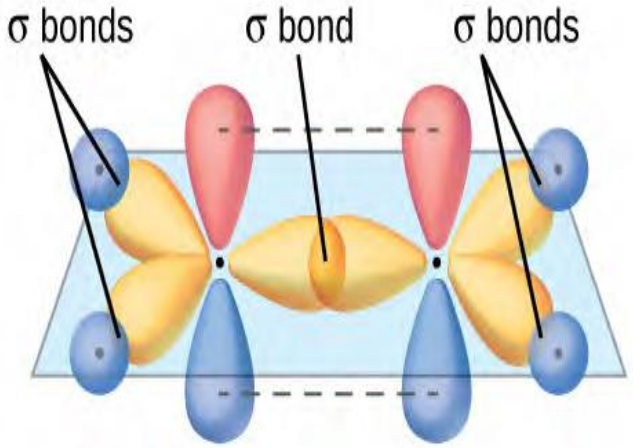
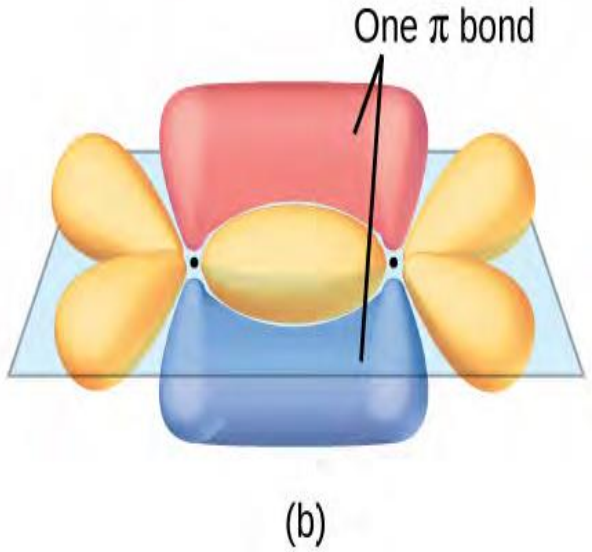


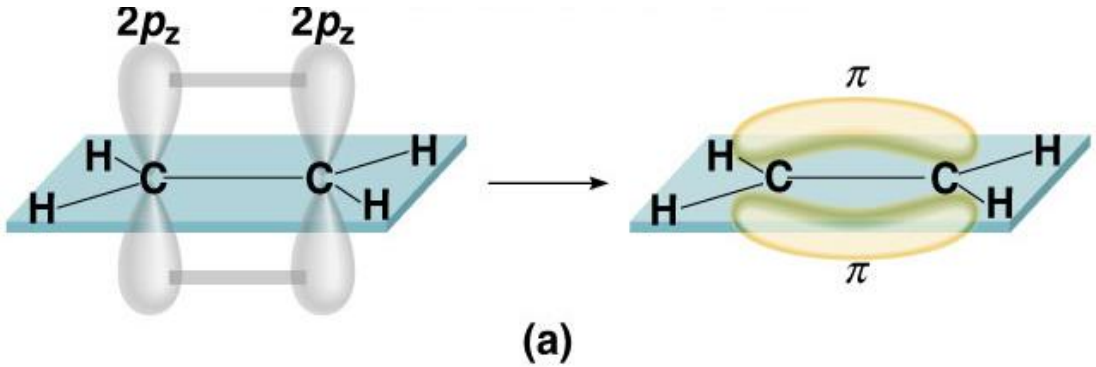
(c)

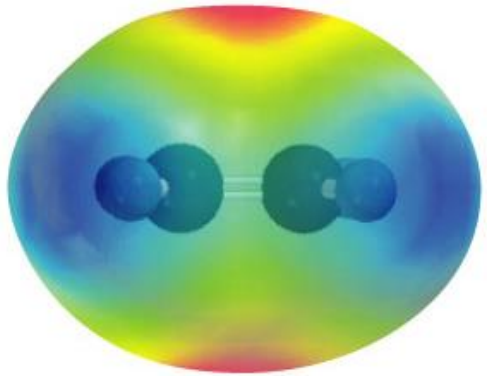
In the ethene molecule, C2H4, there are

- five σ bonds shown in purple. One C–C σ bond results from overlap of *sp*2 hybrid orbitals on the carbon atom with one *sp*2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the *sp*2 orbitals with *s* orbitals on the hydrogen atoms.
- (The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms, which are shown in red. The two lobes of the π bond are above and below the plane of the σ system.



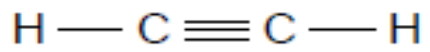




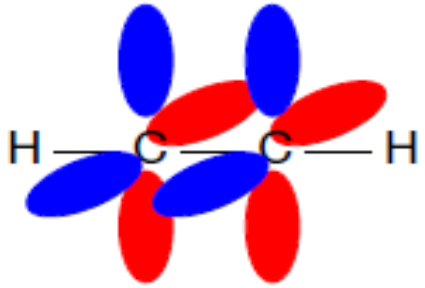


Multiple Bonds

Ethyne C_2H_2

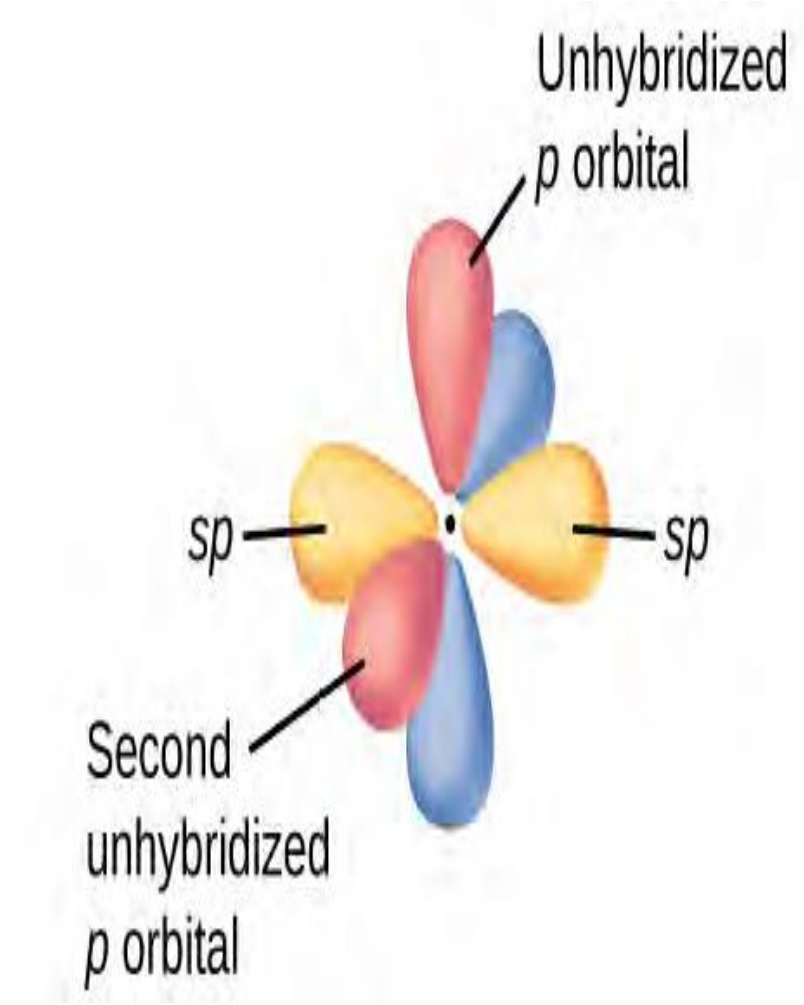


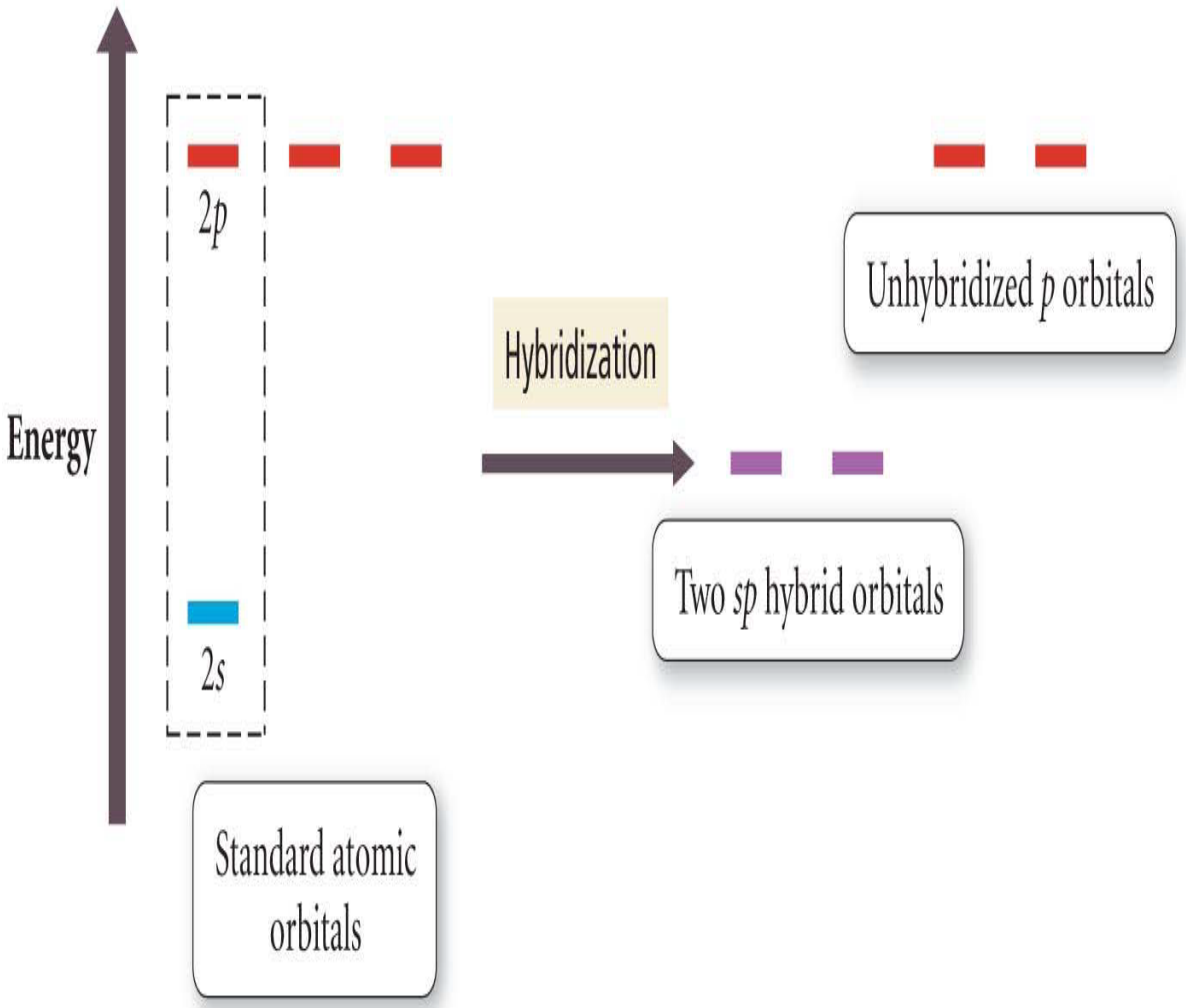
- Linear geometry around each carbon $\Longrightarrow$ sp hybridization
- Each carbon atom has two p orbitals left over:

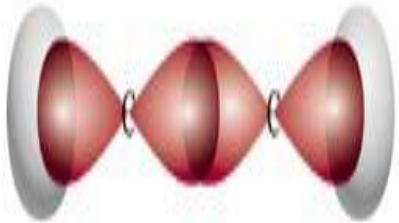


- These p orbitals combine into two π bonds.

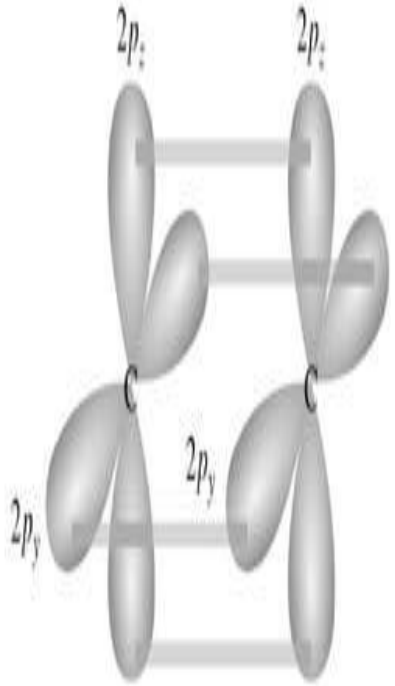
- In molecules with *sp* hybrid orbitals, two unhybridized *p* orbitals remain on the atom.
- We find this situation in acetylene, H−C≡C−H, which is a linear molecule.
- The *sp* hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms.
- The remaining *sp* orbitals form σ bonds with hydrogen atoms.
- The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds.
- The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.







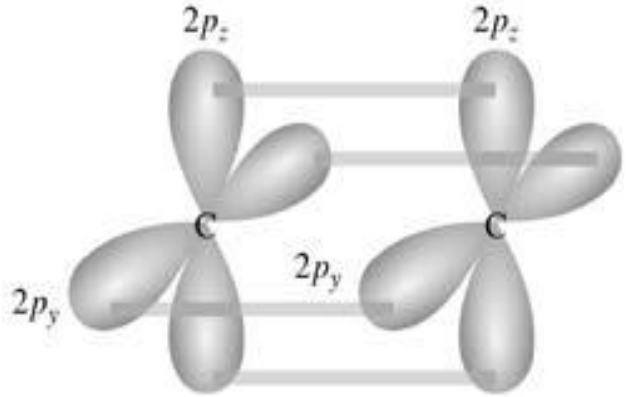
(a)



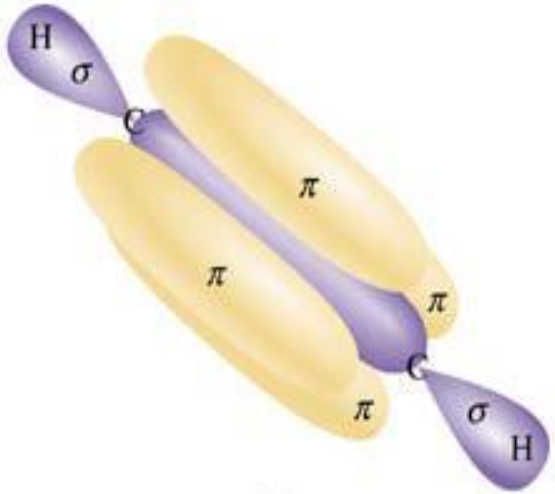
(b)

(c)

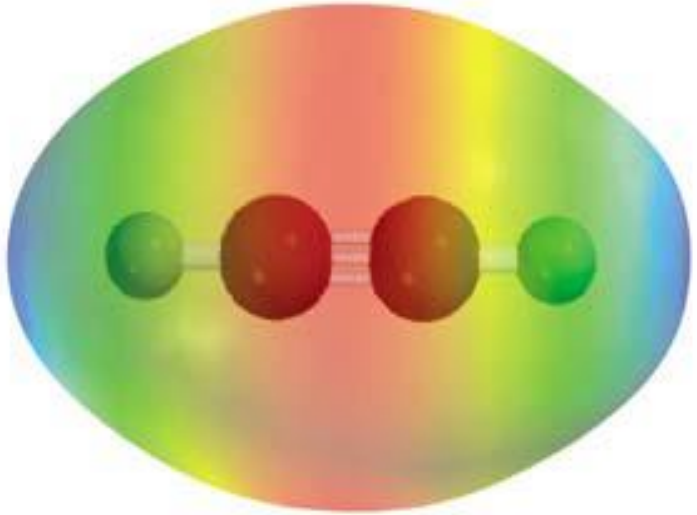
(a)



(b)

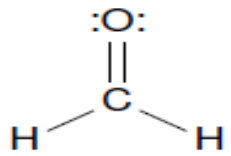


(c)

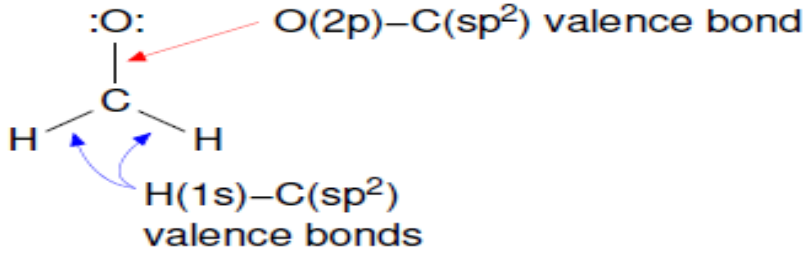


(d)

Formaldehyde

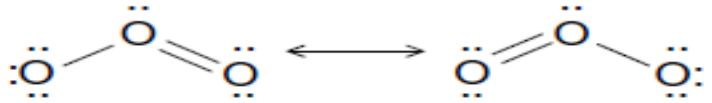


- Trigonal planar geometry at the carbon atom $\Longrightarrow$ sp^2 hybridization
- The O atom can form a σ bond using a p orbital.

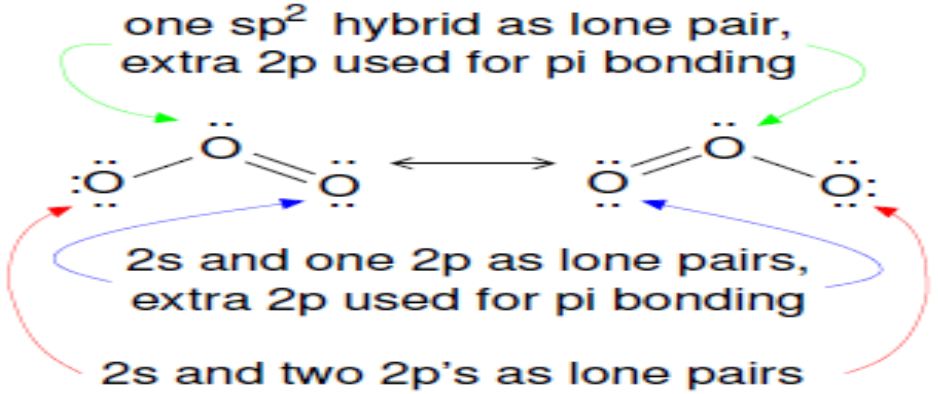


- Why use the O(2p) rather than the O(2s) for bonding?
  - The general assumption in VB theory is that lone pairs go into the lowest-energy AO.
- The carbon atom has one p orbital left over which can combine with the corresponding orbital on O to form the π bond.

Ozone



- The sigma framework of ozone is easy:
  - The central O is sp^2 hybridized.
  - One of the sp^2 hybrids contains a lone pair.
  - The other two form σ bonds with one p orbital on each of the terminal O atoms.
- Construct VB wavefunctions corresponding to both of these structures and average these wavefunctions together:



EXAMPLE!

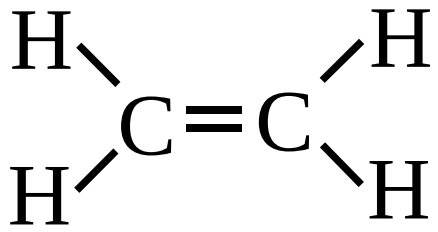
Draw the Lewis structure for C_2H_4 (ethylene)?

What is the shape of an ethylene molecule?

trigonal planar around each carbon atom

What are the approximate bond angles around the carbon atoms?

120°



CONCEPT CHECK!

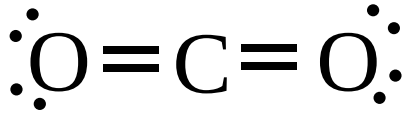
Why can't sp^3 hybridization account for the ethylene molecule?

EXAMPLE!

Draw the Lewis structure for CO_2.

What is the shape of a carbon dioxide molecule?

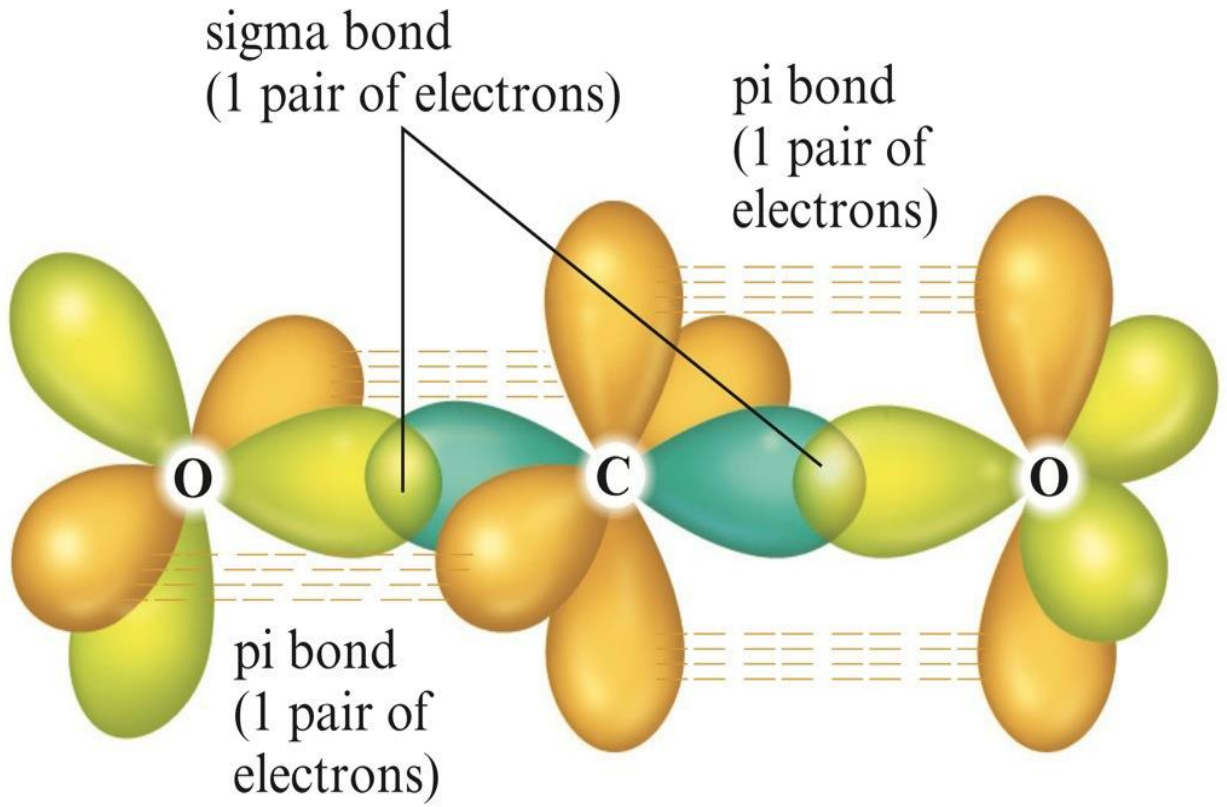
linear



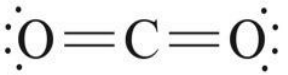
What are the bond angles?

180°

The Orbitals for CO_2



a



b

EXERCISE!

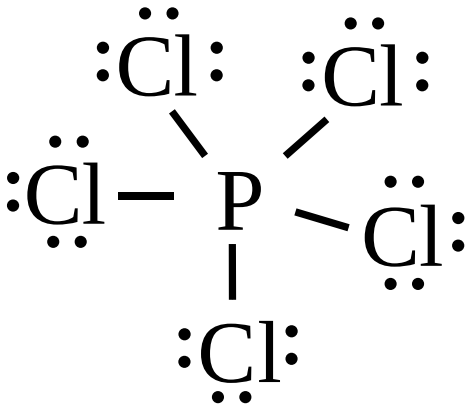
Draw the Lewis structure for PCl_5.

What is the shape of a phosphorus pentachloride molecule?

trigonal bipyramidal

What are the bond angles?

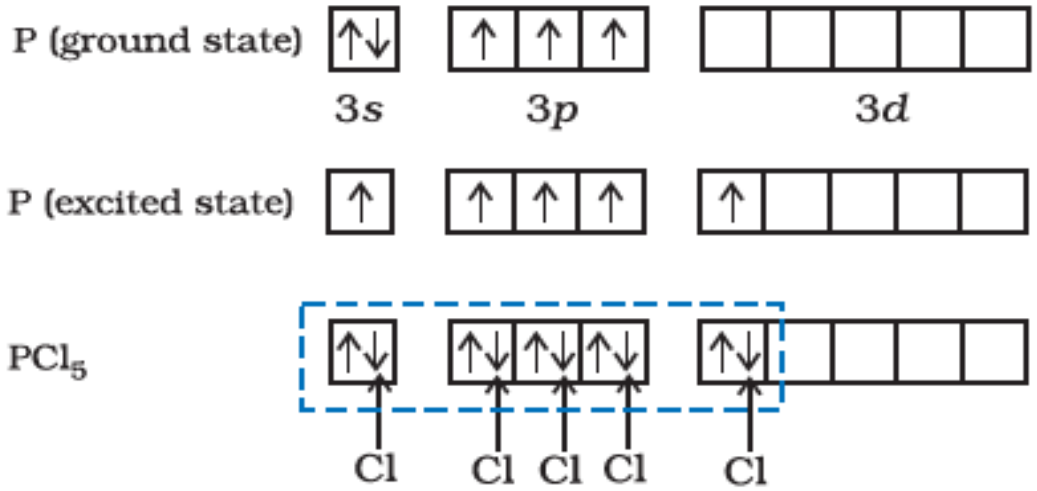
90^o and 120^o

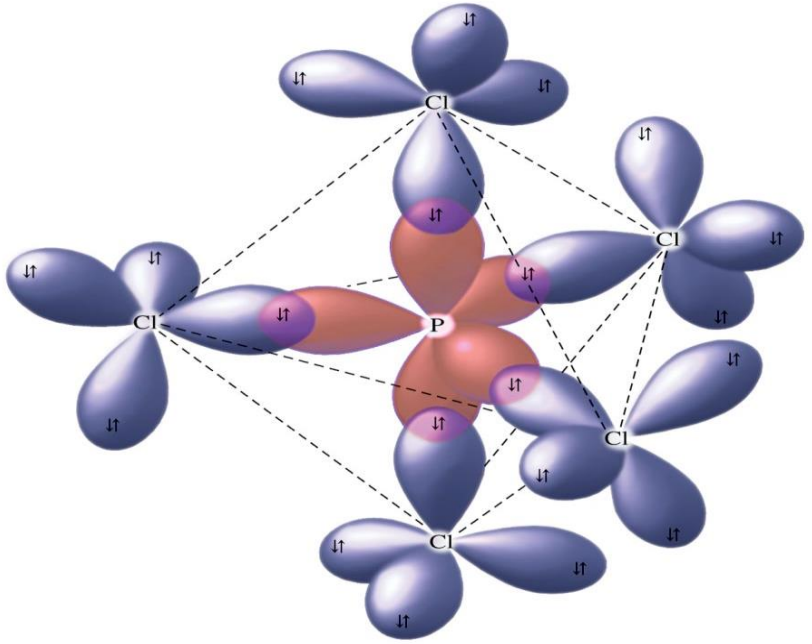


4. dsp^3 Hybridization

- Combination of one *d*, one *s*, and three *p* orbitals.
- Gives a trigonal bipyramidal arrangement of five equivalent hybrid orbitals.

Example: The Orbitals Used to Form the Bonds





EXAMPLE!

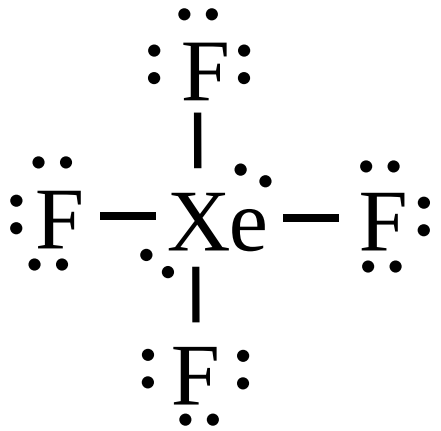
Draw the Lewis structure for XeF_4.

- What is the shape of a xenon tetrafluoride molecule?

  octahedral

- What are the bond angles?

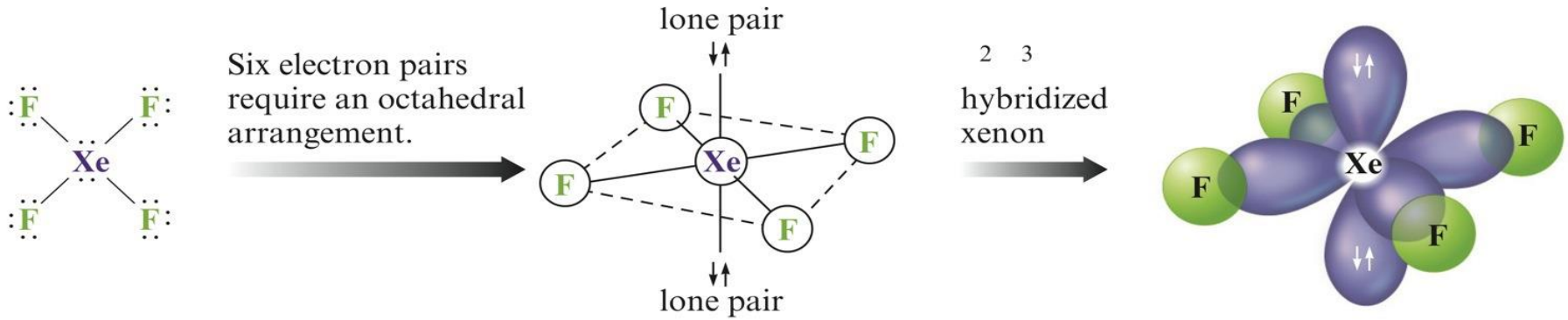
  90^o and 180^o



d^2sp^3 Hybridization

- Combination of two *d*, one *s*, and three *p* orbitals.
- Gives an octahedral arrangement of six equivalent hybrid orbitals.

How is the Xenon Atom in XeF_4 Hybridized?



Lewis structure

Octahedral arrangement of six electron pairs

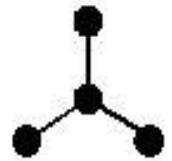
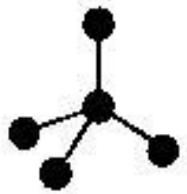
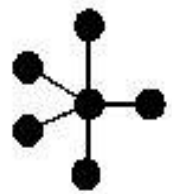
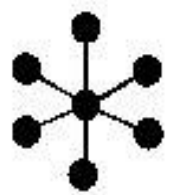
Xenon uses six ^{2} ^{3} hybrid atomic orbitals to bond to the four fluorine atoms and to hold the two lone pairs.

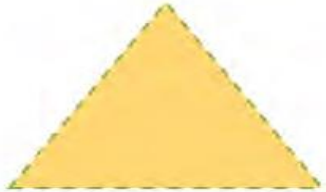
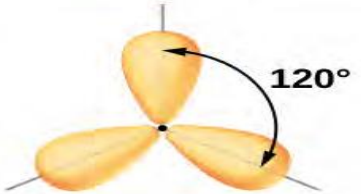
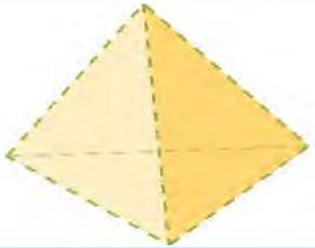
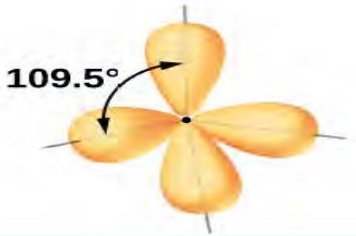
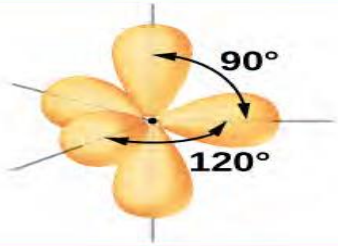
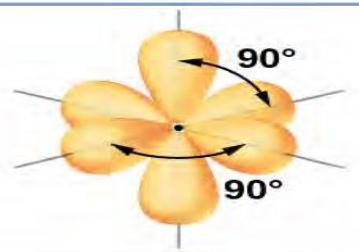
Shortcomings of VB theory

- A lot of things that fall out naturally in MO theory are hard in VB theory:
  - Explanation of photoelectron spectra
  - Explanation of paramagnetism of O2
- In its simplest form, VB theory only tells us what we already know based on Lewis diagrams and VSEPR. It only becomes a predictive theory in its most advanced forms.

The following table summarizes the five types of hybridization addressed in this exercise.

Number of required hybrid orbitals	Electron Pair Arrangement	Type of Hybridization	Atomic Orbitals used to create Hybrids
2	Linear	sp	one s, one p
3	Trigonal planar	sp^2	one s, two p's
4	Tetrahedral	sp^3	one s, three p's
5	Trigonal bipyramidal	sp^3d	one s, three p's, one d
6	Octahedral	sp^3d^2	one s, three p's, two d's

# electron groups	Bond angle	Base geometry	# lone pairs	Shape		Hybridization
2	180°	Linear	0	Linear		sp
3	120°	Trigonal planar	0	Trigonal planar		sp^2
			1	Bent		
4	109.5°	Tetrahedral	0	Tetrahedral		sp^3
			1	Trigonal pyramidal		
			2	bent		
5	90°/120°	Trigonal bipyramidal	0	Trigonal bipyramidal		sp^3d
			1	See-saw		
			2	t-shaped		
			3	Linear		
6	90°	Octahedral	0	Octahedral		sp^3d^2
			1	Square pyramidal		
			2	Square planar		

Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

CONCEPT CHECK!

Why atomic orbitals in a given atom undergo hybridization?

- ✓ The hybrid orbitals are oriented in space so as to minimize repulsions between them.

- This explains why the atomic orbitals undergo hybridization **before bond formation.**
- The reason for hybridization is to minimize the repulsions between the bonds that are going to be formed by the **atoms by using hybrid orbitals.**
- Remember that the:
  - ✓ hybridization is the process that occurs before bond formation.
  - ✓ The shape of the molecule is determined by the type of hybridization, number of bonds formed by them and the number of lone pairs.

Exercise!

Draw the Lewis structure for HCN.

Which hybrid orbitals are used?

Draw HCN:

- Showing all bonds between atoms.
- Labeling each bond as σ or π.

Determine the bond angle and expected hybridization of the central atom for each of the following molecules:

NH_3 SO_2 KrF_2 CO_2 ICl_5

NH_3 – 109.5°, sp^3

SO_2 – 120°, sp^2

KrF_2 – 90°, 120°, dsp^3

CO_2 – 180°, sp

ICl_5 – 90°, 180°, d^2sp^3

Using the Localized Electron Model

- Draw the Lewis structure(s).
- Determine the arrangement of electron pairs using the VSEPR model.
- Specify the hybrid orbitals needed to accommodate the electron pairs.

Molecular Orbital Theory

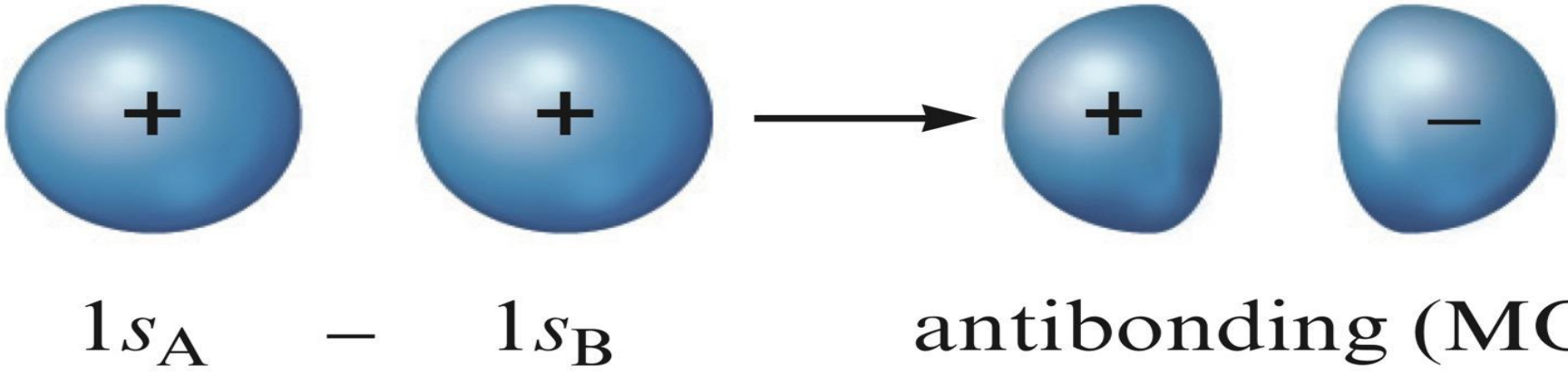
Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the:

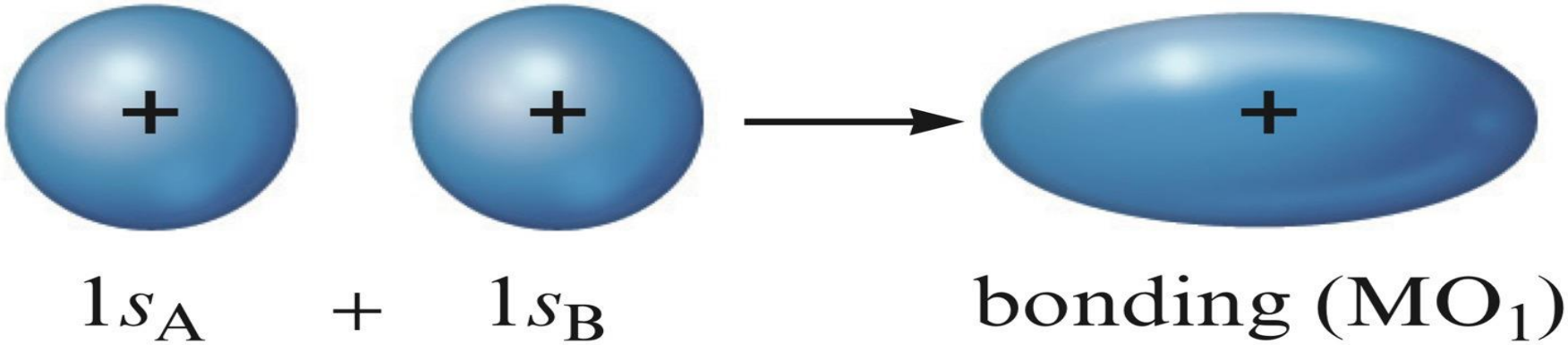
- paramagnetism of the oxygen molecule.
- Explaination the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures.
- Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons.
- Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms.
- MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators

The Molecular Orbital Theory

- Regards a molecule as a collection of nuclei and electrons, where the electrons are assumed to occupy orbitals much as they do in atoms, but having the orbitals extend over the entire molecule.
- The electrons are assumed to be delocalized rather than always located between a given pair of atoms.
- The electron probability of both molecular orbitals is centered along the line passing through the two nuclei.
  - ✓ Sigma (σ) molecular orbitals (MOs)
- In the molecule only the molecular orbitals are available for occupation by electrons.

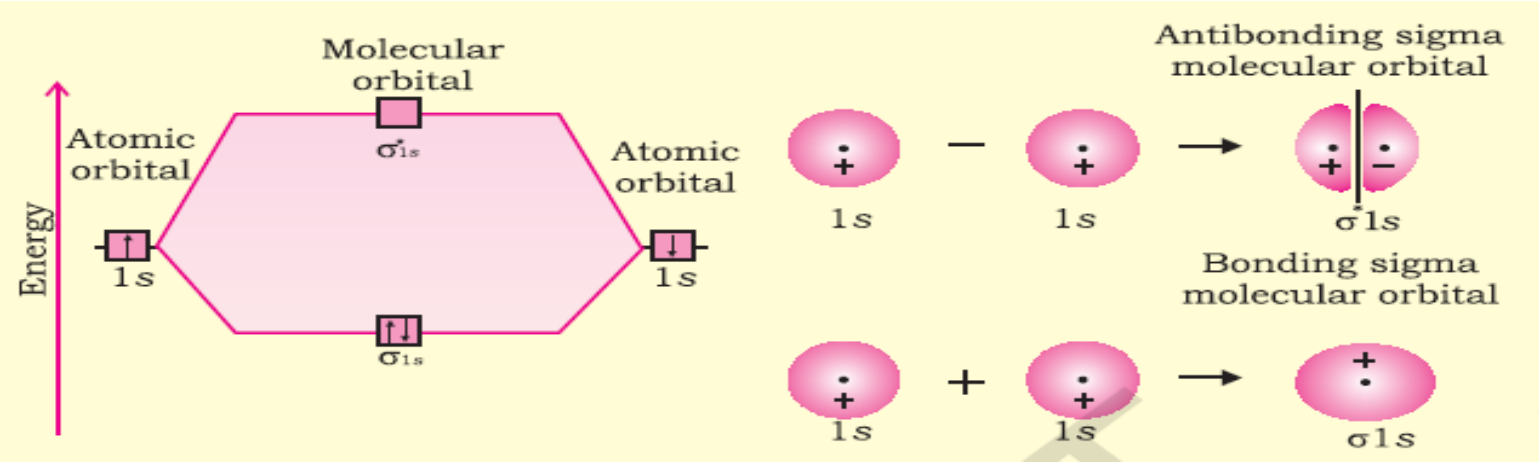
Combination of Hydrogen 1*s* Atomic Orbitals to form MOs





Energy Level Diagram for Molecular Orbitals

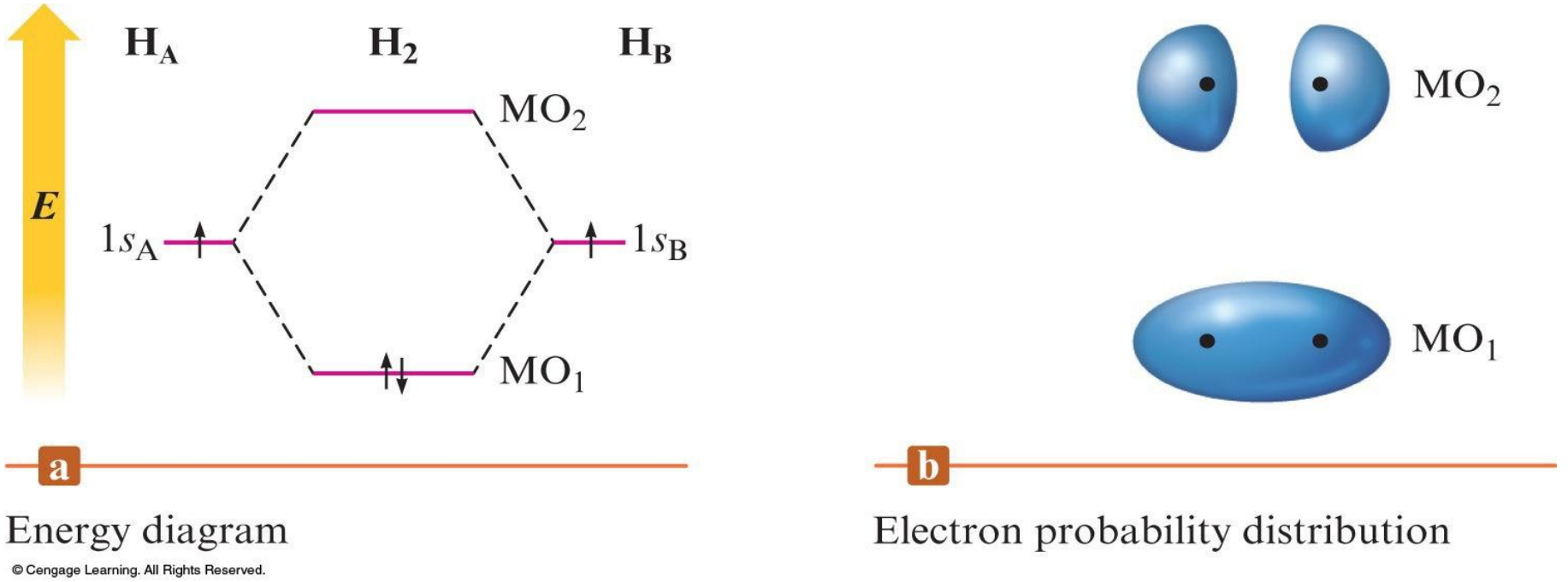
- We have seen that 1*s* atomic orbitals on two atoms form two molecular orbitals designated as σ1*s* and σ*1*s*.



- In the same manner, the 2*s* and 2*p* atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals
  - Antibonding MOS σ*2s* σ*2pz* π*2px* π*2py*
  - Bonding MOs σ2*s* σ2*pz* π2*px* π2*py*

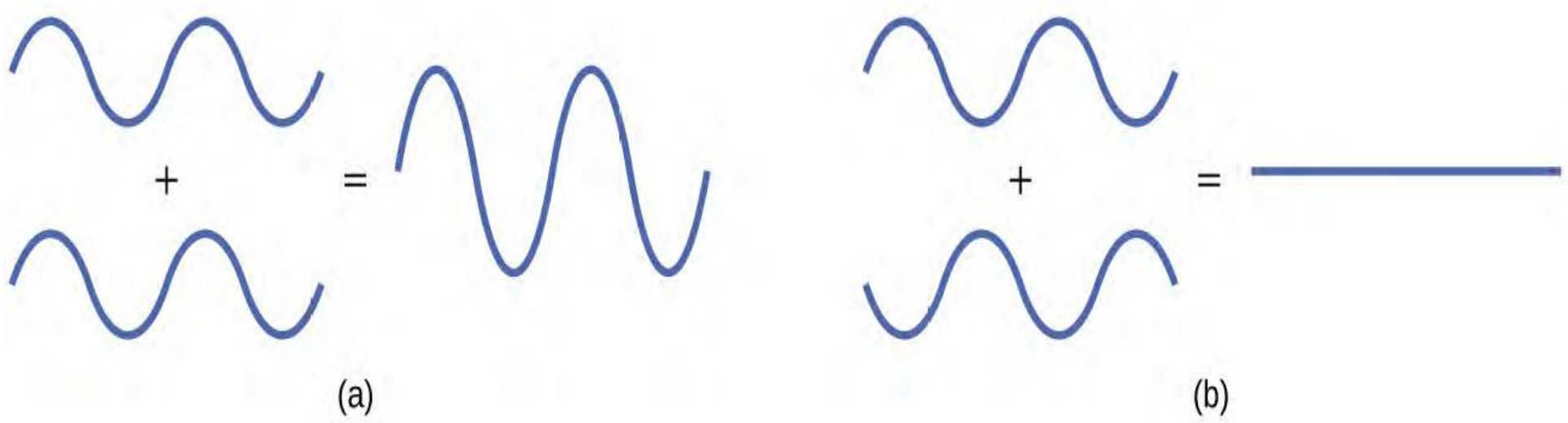
- MO_1 is lower in energy than the *s* orbitals of free atoms, while MO_2 is higher in energy than the *s* orbitals.
  - Bonding molecular orbital – lower in energy
  - Antibonding molecular orbital – higher in energy

MO Energy-Level Diagram for the H_2 Molecule



- The molecular orbital model produces electron distributions and energies that agree with our basic ideas of bonding.
- The labels on molecular orbitals indicate their symmetry (shape), the parent atomic orbitals, and whether they are bonding or antibonding.
- Molecular electron configurations can be written in much the same way as atomic electron configurations.
- Each molecular orbital can hold 2 electrons with opposite spins.
- The number of orbitals are conserved.

- (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.



Types of MO

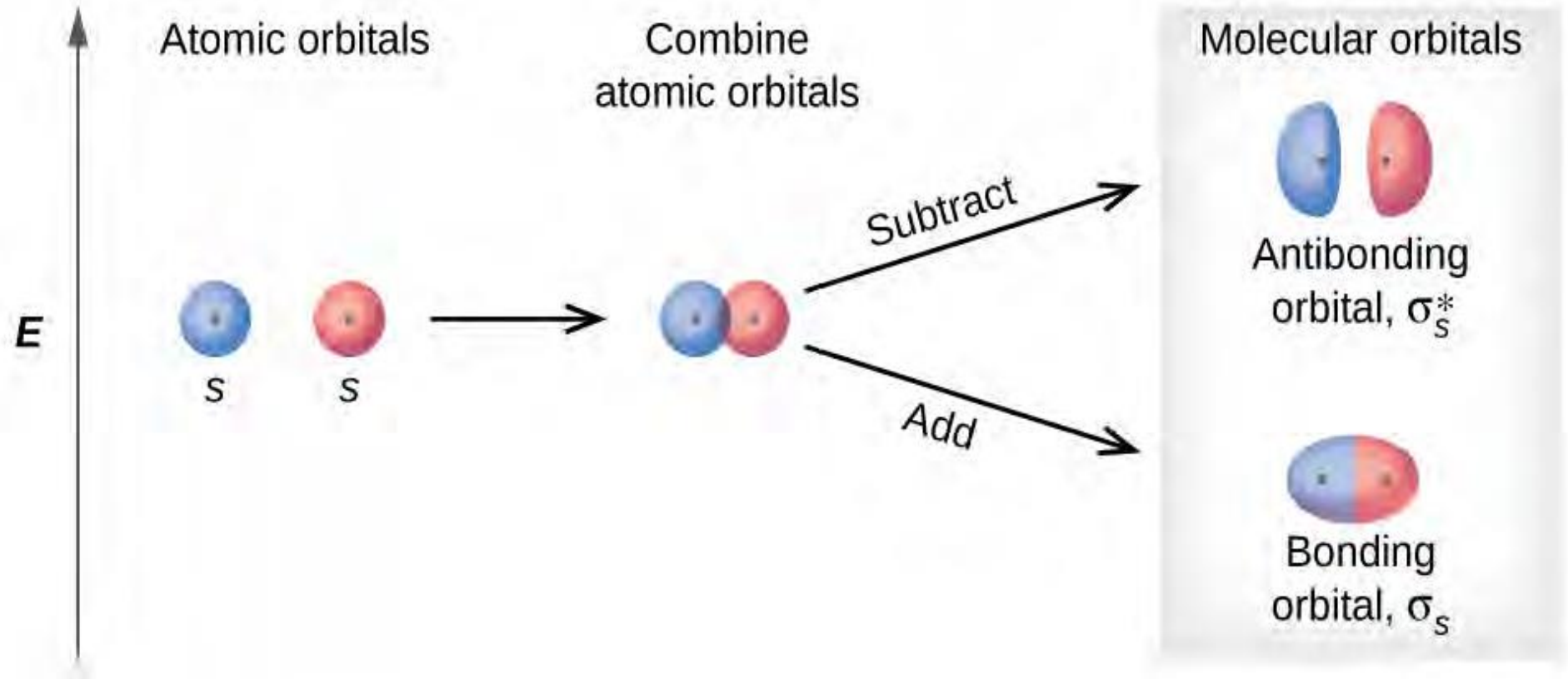
- There are two types of molecular orbitals that can form from the overlap of two atomic s orbitals on adjacent atoms.

  The in-phase combination produces a lower energy **σs molecular orbital** (read as "sigma-s") in which most of the electron density is directly between the nuclei.

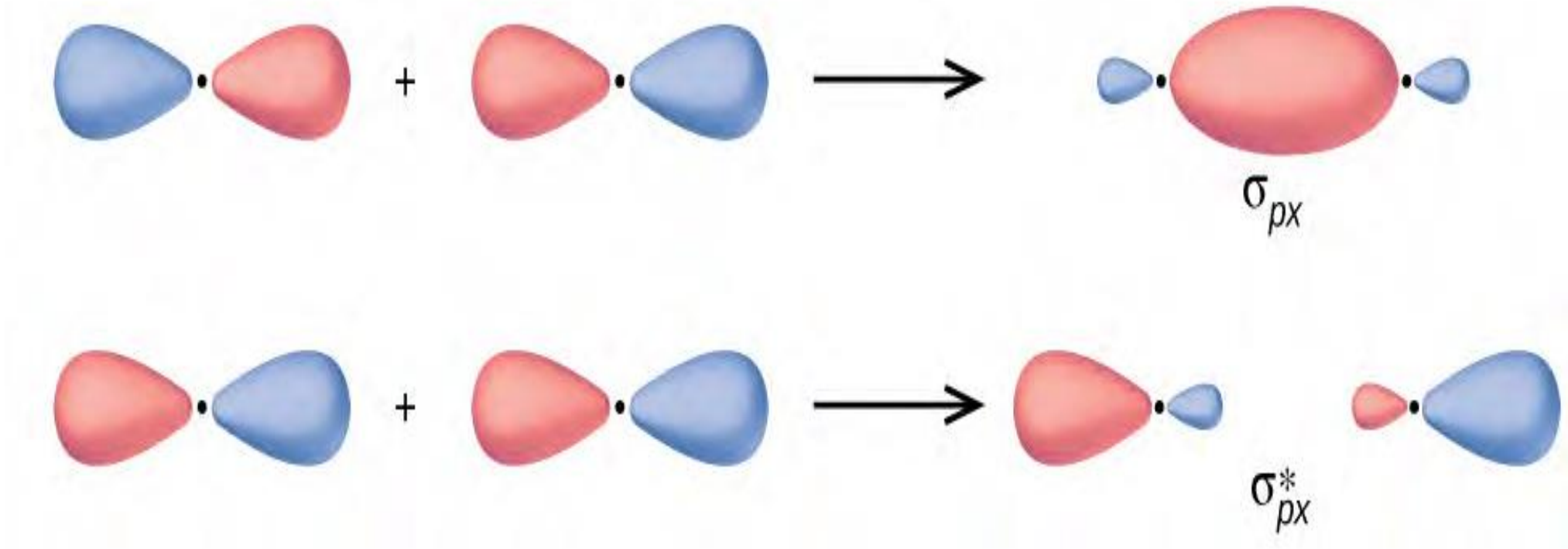
  The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy **molecular orbital** (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei.

  The asterisk signifies that the orbital is an antibonding orbital.

- Electrons in a σs orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals **bonding orbitals**.
- Electrons in the σs * orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called **antibonding orbitals**.
- Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

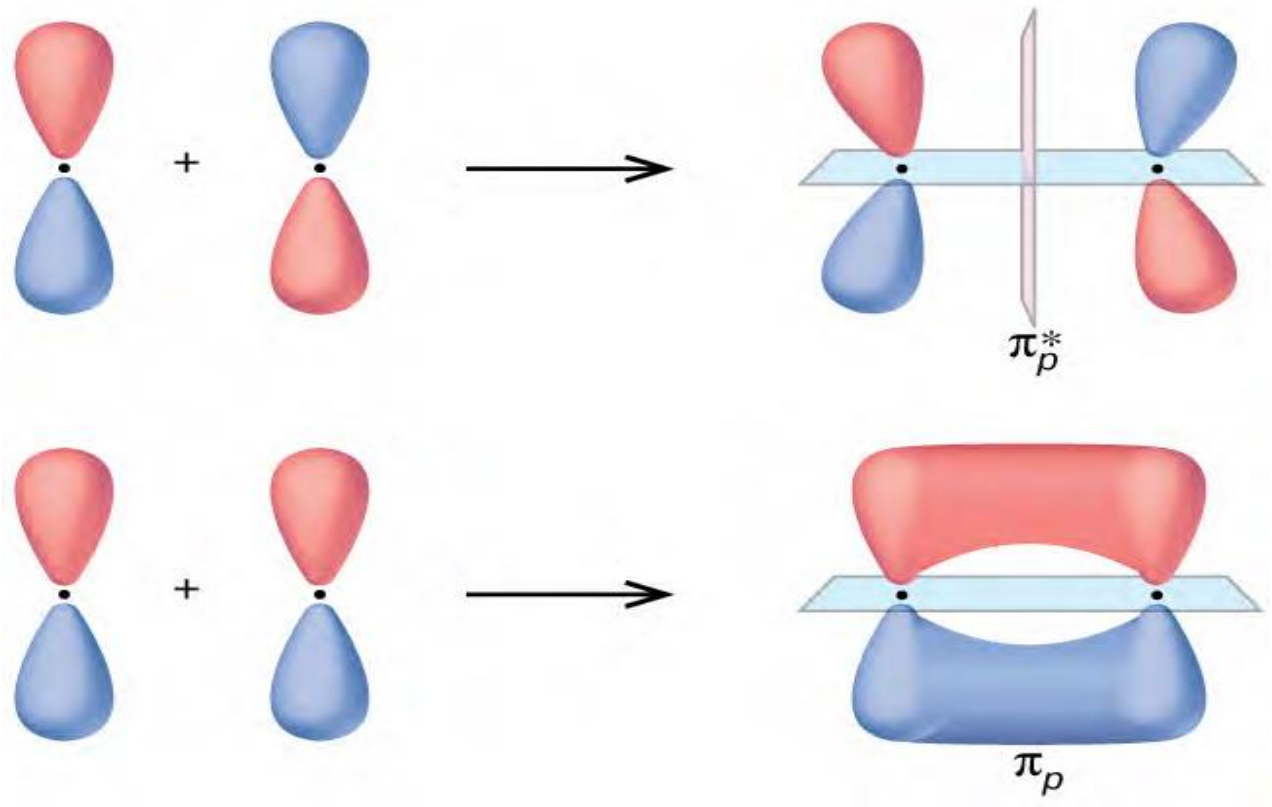

E
Atomic orbitals
s
s
Combine
atomic orbitals
Subtract
Add
Molecular orbitals
Antibonding
orbital, σ_s^*
Bonding
orbital, σ_s

- In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors.
  - When orbital lobes of the same phase overlap, constructive wave interference increases the electron density.
  - When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes.
- When *p* orbitals overlap end to end, they create σ and σ* orbitals.
- If two atoms are located along the x-axis in a Cartesian coordinate system, the two *px* orbitals overlap end to end and form σ*px* (bonding) and σ**px*
- (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital


+
σ_{px}
+
σ^*_{px}

- The side-by-side overlap of two *p* orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibondingmolecular orbital**.
- In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node.
- In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons.
- Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital.
- For the out-of-phase combination, there are two nodal planes created, one along theinternuclear axis and a perpendicular one between the nuclei.

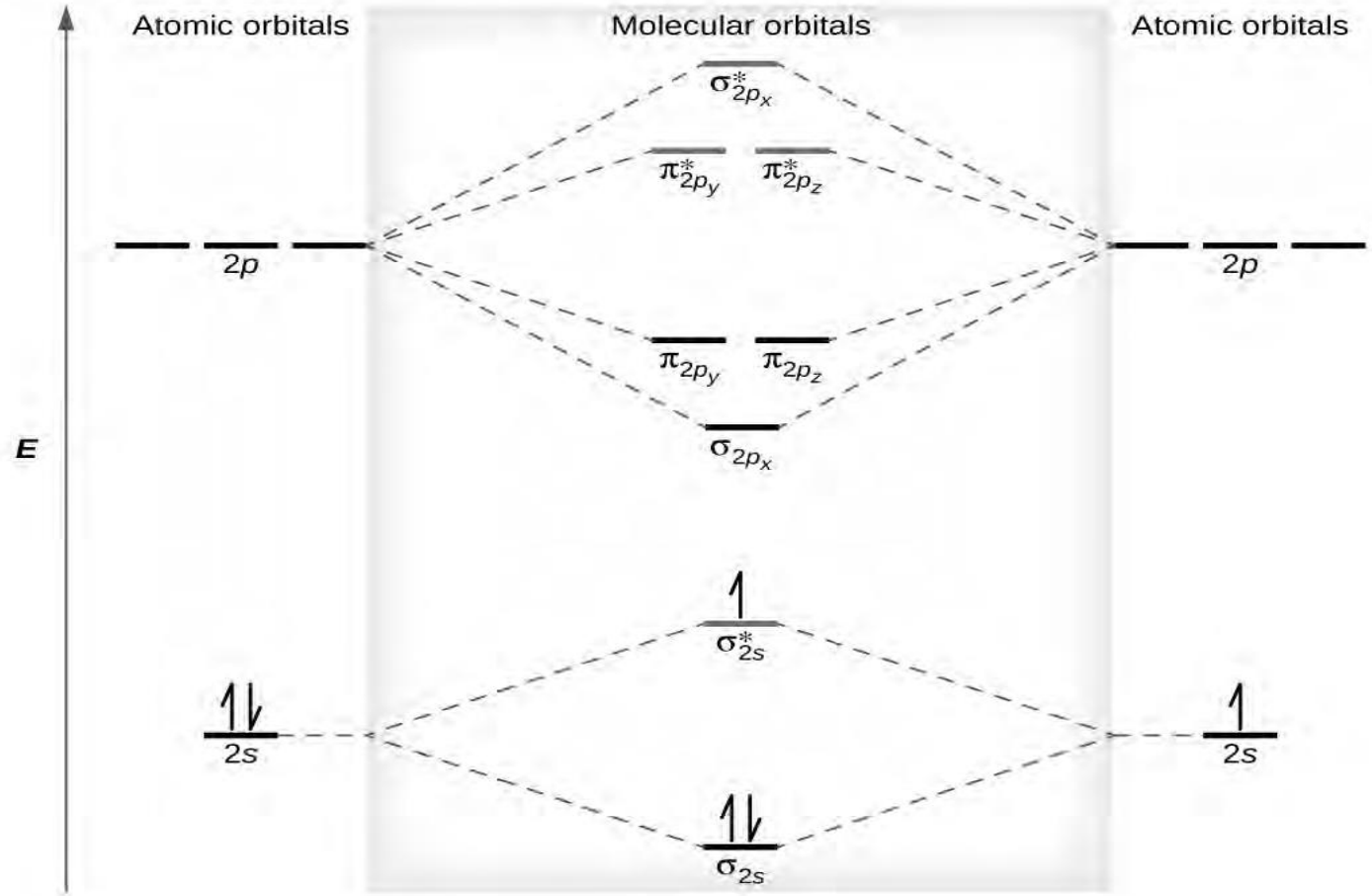
The MO Energy Diagram for Molecules with Multiple Bonds



The MO Energy Diagram for Molecules with Multiple Bonds

- We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins.
- Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital.
- Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be2+) would have the molecular electron configuration (σ1s)2 (σ*1s)2 (σ2s)2 (σ*2s)1. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

The MO Energy Diagram for Molecules with Multiple Bonds

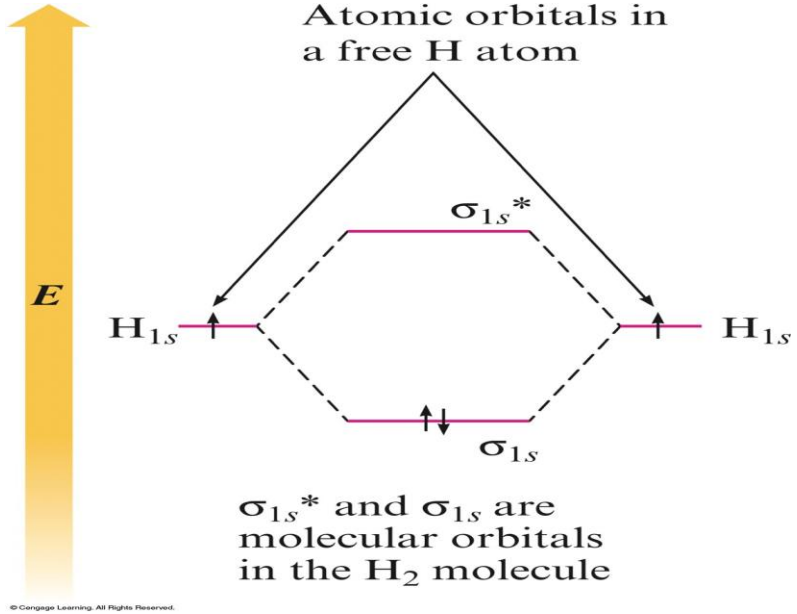


Bond Order

Larger bond order means greater bond strength.

$$\text{Bond order} = \frac{\#\text{ of bonding } e^- \; - \; \#\text{ of antibonding } e^-}{2}$$

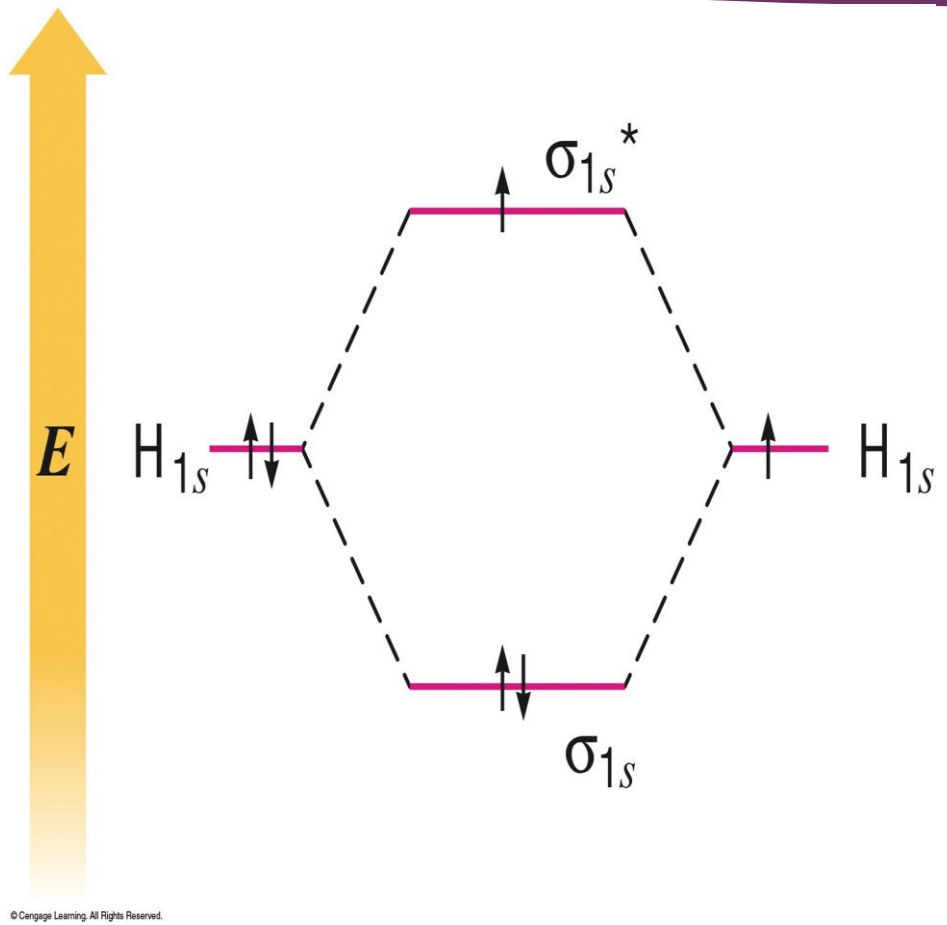
Example: H_2



$$\text{Bond order} = \frac{2 \; - \; 0}{2} = 1$$

- we define bond order as the number of bonding pairs of electrons between two atoms.
- Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same.
- The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

Example: H_2^-



$$\text{Bond order} = \frac{2 - 1}{2} = \frac{1}{2}$$

Bond-length

- The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length.
- The bond length decreases as bond order increases.

Homonuclear Diatomic Molecules

- Composed of 2 identical atoms.
- Only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule.

Paramagnetism

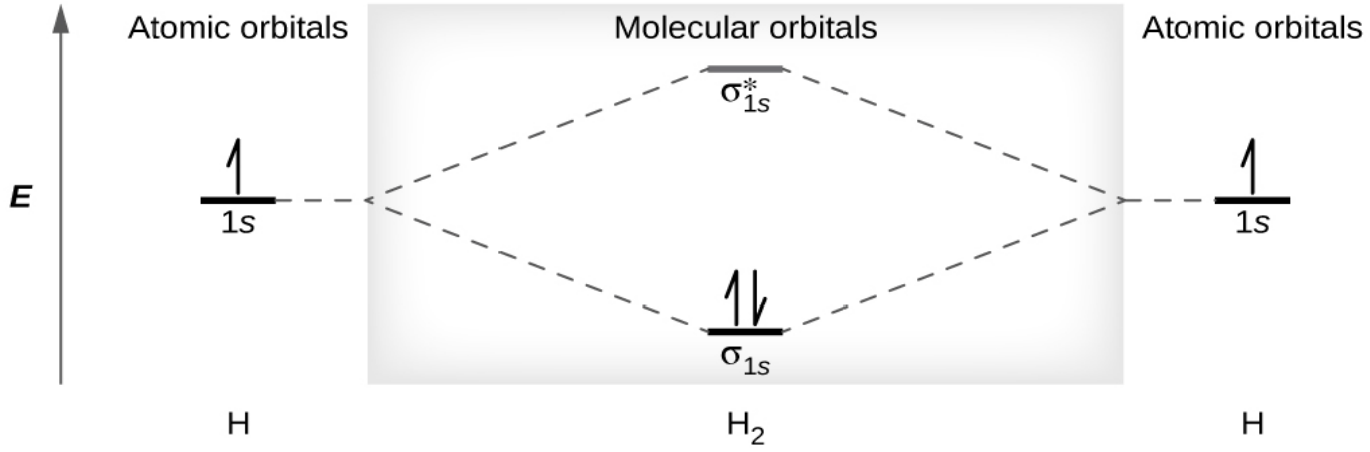
- Paramagnetism – substance is attracted into the inducing magnetic field.
  - ✓ The MO Contains Unpaired electrons (O_2)
- Diamagnetism – substance is repelled from the inducing magnetic field.
  - ✓ The MO Paired electrons (N_2)

Molecular Orbital Summary of Second Row Diatomic Molecules

	B_2	C_2	N_2	O_2	F_2
	σ_{2p}^* π_{2p}^* σ_{2p} π_{2p} σ_{2s}^* σ_{2s}			σ_{2p}^* π_{2p}^* π_{2p} σ_{2p} σ_{2s}^* σ_{2s}	
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

Bonding in Diatomic Molecules

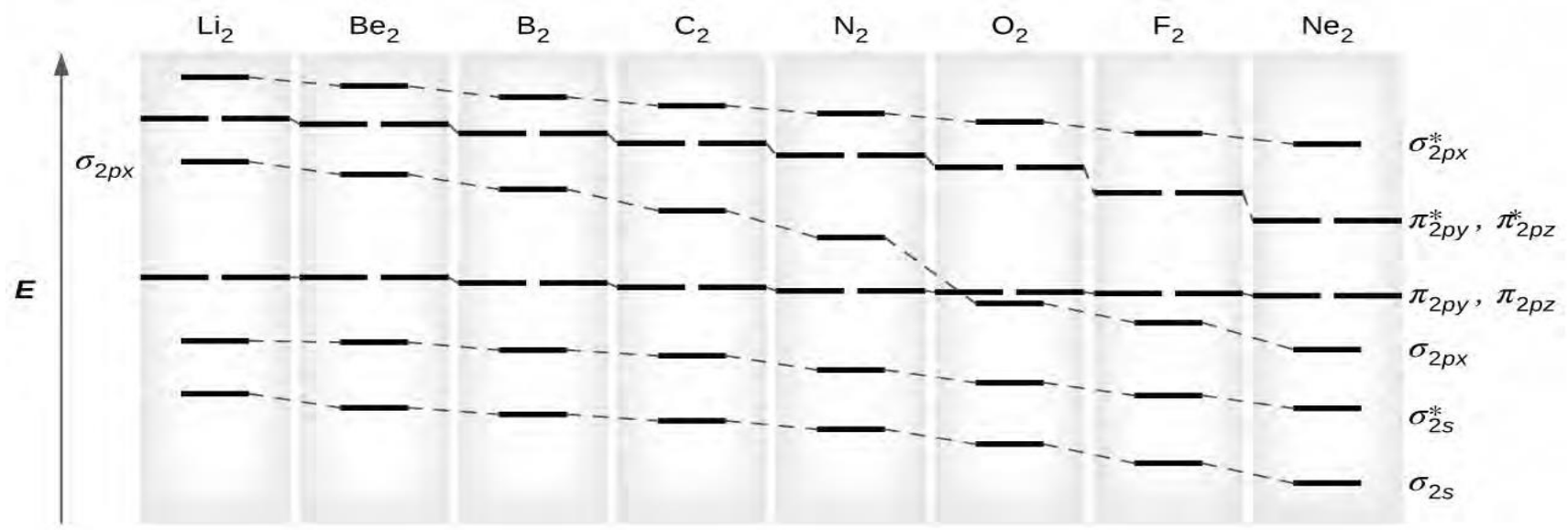
- A dihydrogen molecule (H_2) forms from two hydrogen atoms.
- When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital.
- A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms.
- The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1*s* atomic orbitals.
- A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$.



The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons

The Diatomic Molecules of the Second Period

- 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.



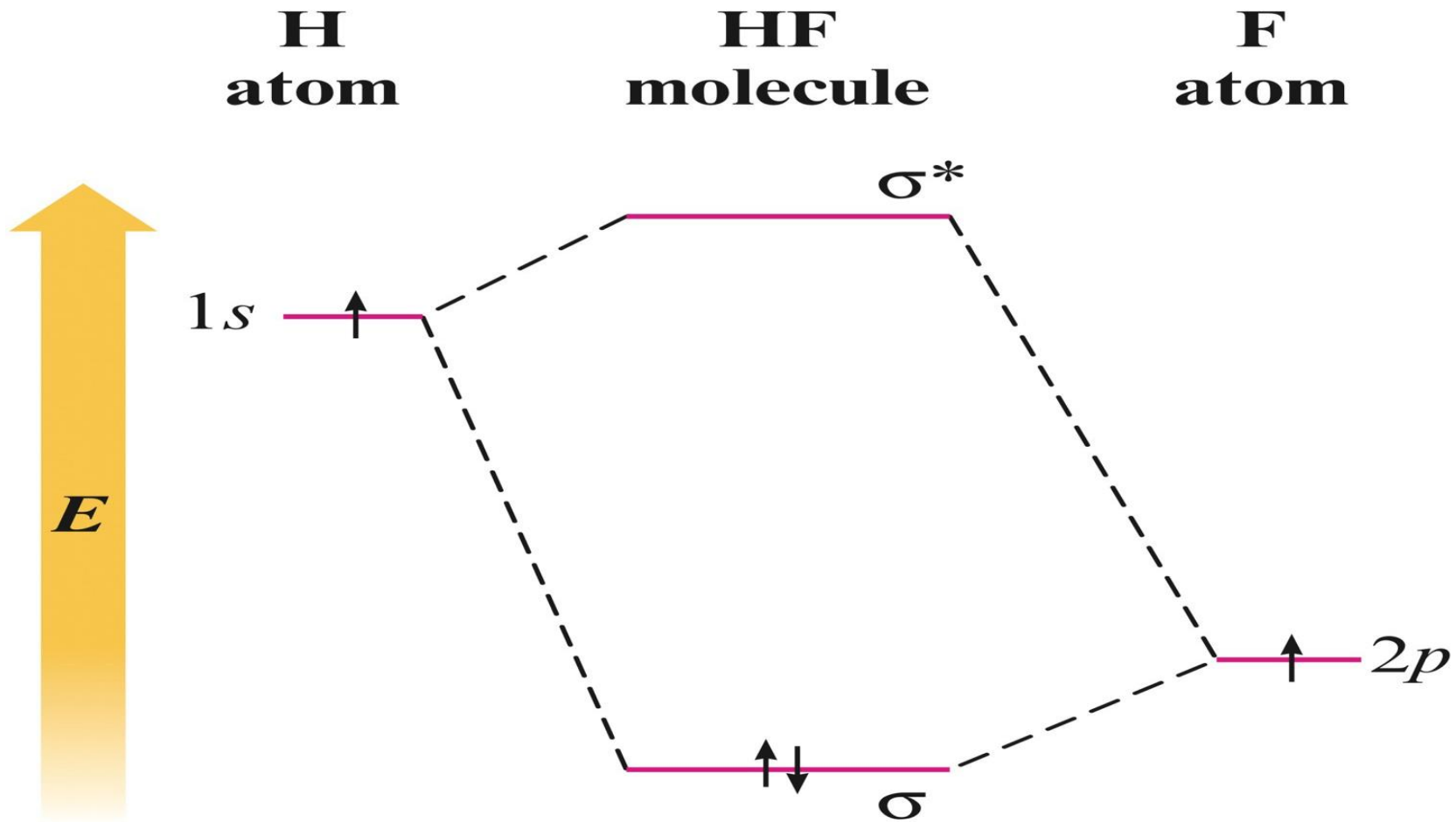
Heteronuclear Diatomic Molecules

- Composed of 2 different atoms.

For Example the Heteronuclear Diatomic Molecule: HF

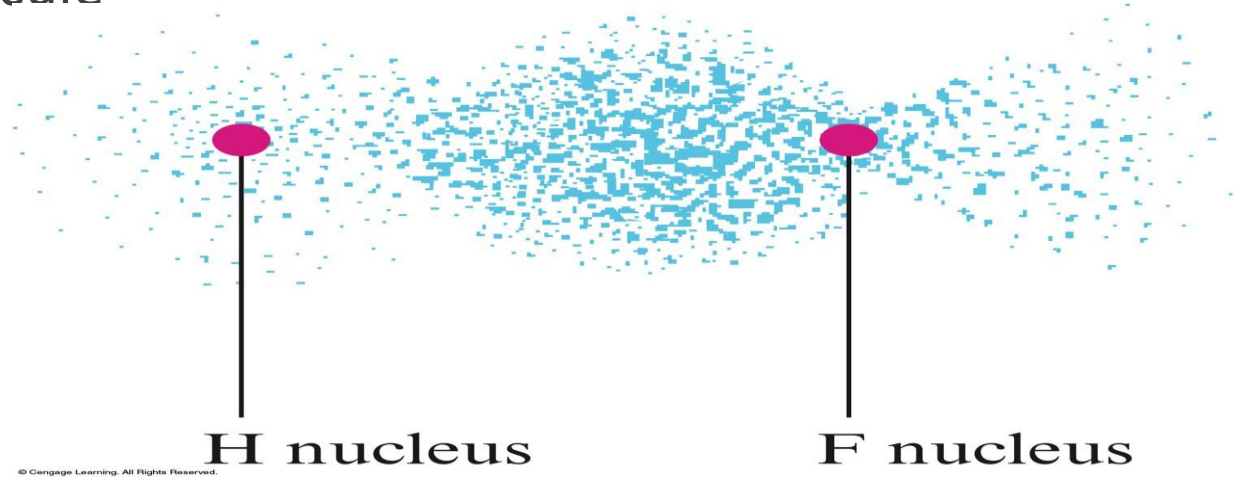
- The 2*p* orbital of fluorine is at a lower energy than the 1*s* orbital of hydrogen because fluorine binds its valence electrons more tightly.
  - ✓ Electrons prefer to be closer to the fluorine atom.
- Thus the 2*p* electron on a free fluorine atom is at a lower energy than the 1*s* electron on a free hydrogen atom.

Orbital Energy-Level Diagram for the HF Molecule



Heteronuclear Diatomic Molecule: HF

- The diagram predicts that the HF molecule should be stable because both electrons are lowered in energy relative to their energy in the free hydrogen and fluorine atoms, which is the driving force for bond formation.
- The Electron Probability Distribution in the Bonding Molecular Orbital of the HF Molecule



Heteronuclear Diatomic Molecule: HF

- The σ molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine.
- The electron pair is not shared equally.
- This causes the fluorine atom to have a slight excess of negative charge and leaves the hydrogen atom partially positive.
- This is exactly the bond polarity observed for HF.

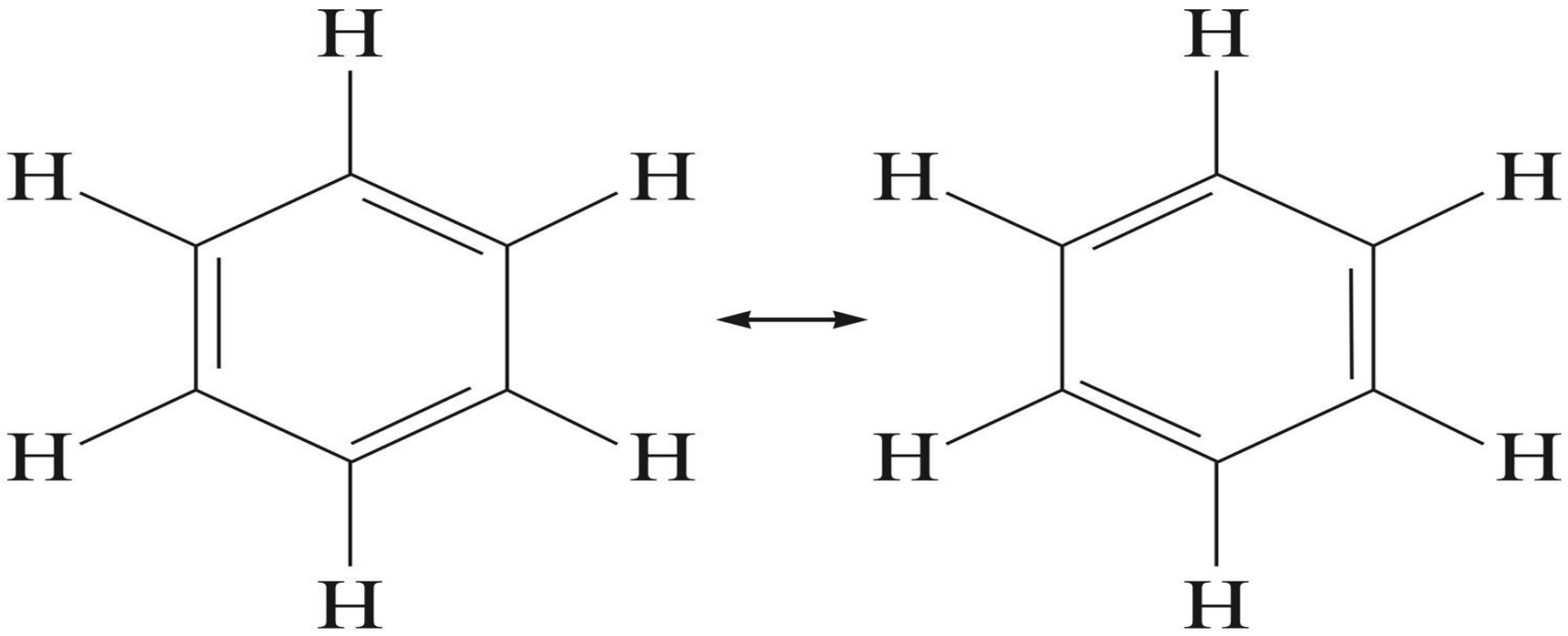
Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*...) and hybrid orbitals (*sp*, sp^2, sp^3...)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

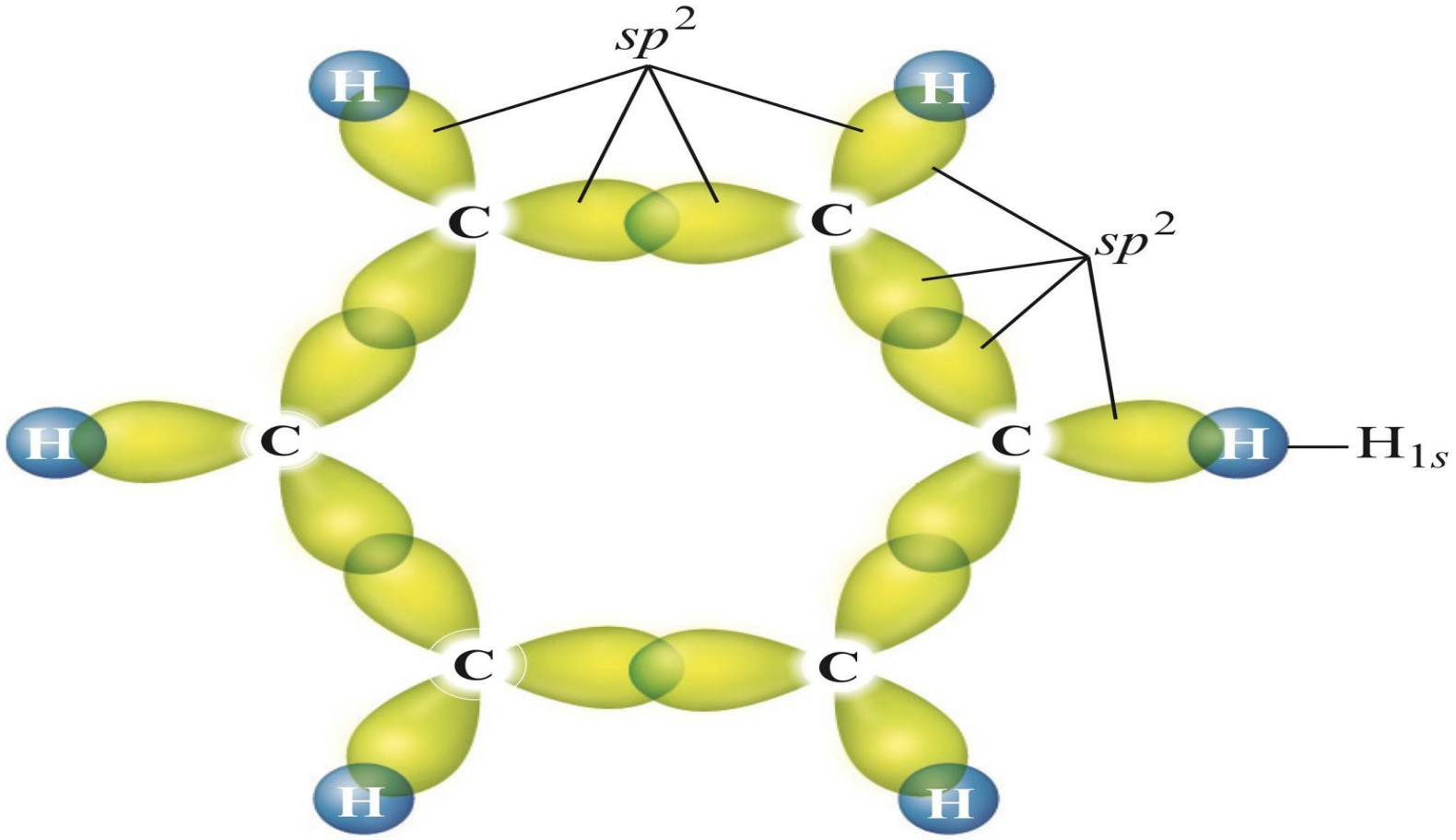
Delocalization

- Describes molecules that require resonance.
- In molecules that require resonance, it is the π bonding that is most clearly delocalized, the σ bonds are localized.
- *p* orbitals perpendicular to the plane of the molecule are used to form π molecular orbitals.
- The electrons in the π molecular orbitals are delocalized above and below the plane of the molecule.

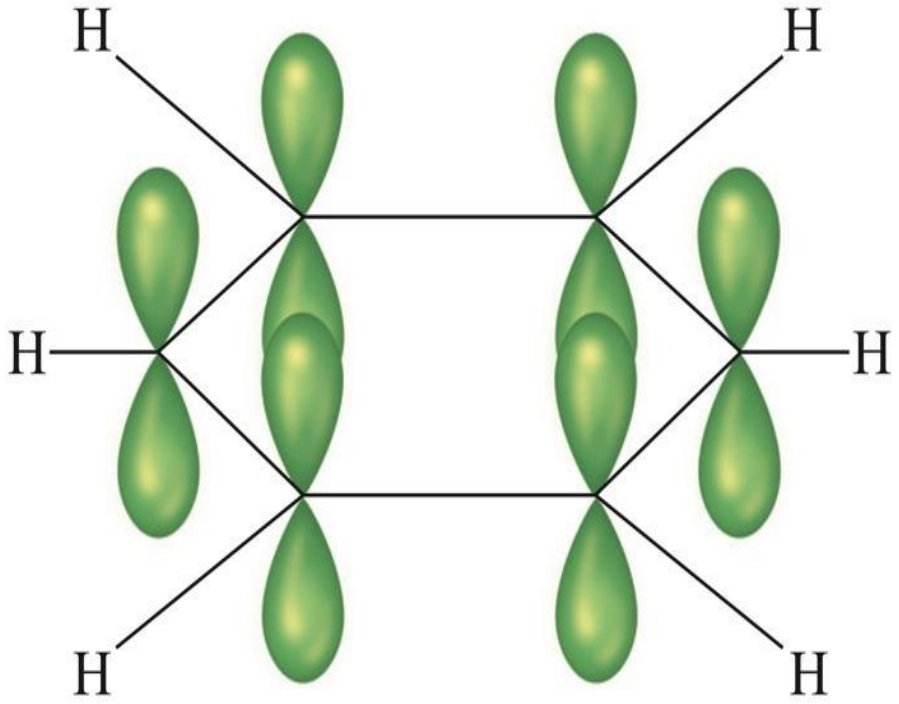
Resonance in Benzene



The Sigma System for Benzene



The Pi System for Benzene



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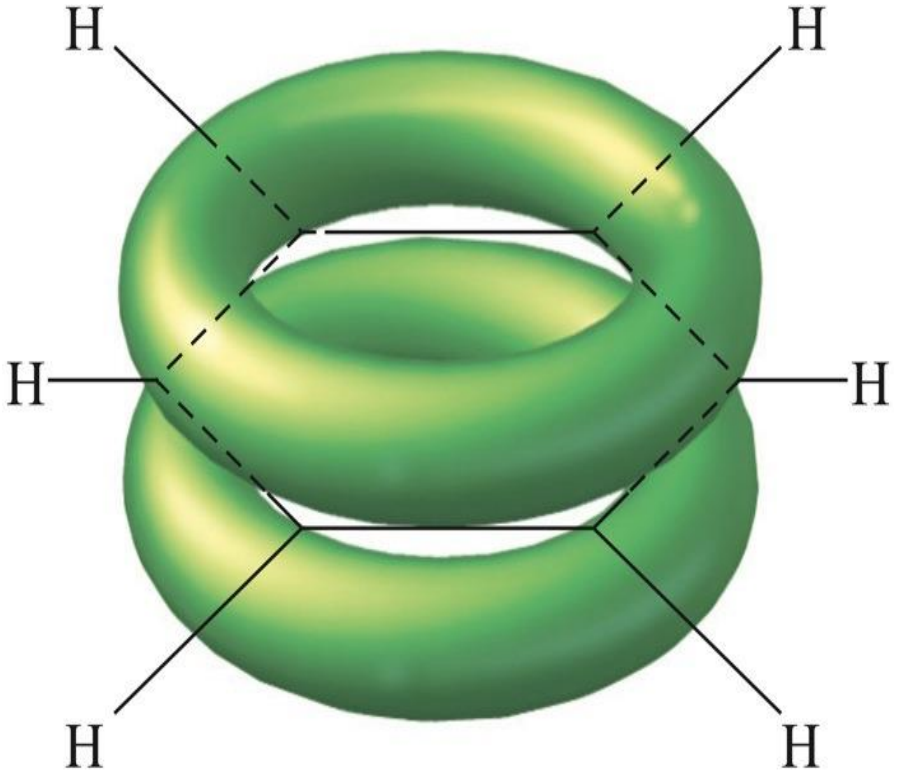

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