

VSEPR Theory and Molecular Shapes



Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

- The molecular shape is the three-dimensional arrangement of nuclei joined by the bonding groups.
- **VSEPR Theory** allows us to predict the shapes of molecules based on the number of **electron groups** around a **central atom**.
- **Basic principle** : “To minimize repulsions, each group of valence electrons around a central atom is located as far as possible from the others.”



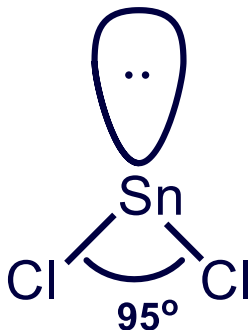
Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

- An “**electron group**” is any number of electrons that occupies a localized region around an atom.
- A single bond, double bond, triple bond, lone pair, or single electron all count as a single group.
- Only electron groups around the central atom affect shape; electrons on atoms other than the central atom do not.



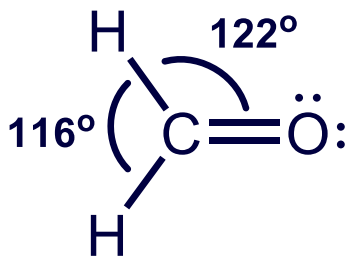
Factors Affecting Bond Angles

- **Lone (or Non-bonding) Pairs**



A lone pair repels bonding pairs more strongly than bonding pairs repel each other. This decreases the angle between the bonding pairs.

- **Double Bonds**



The ideal angle is 120°.

A double bond has greater electron density than a single bond, and repels the single bond electrons more than they repel each other.

Electronic Shape vs Molecular Shape

- The ***electronic shape*** or ***electronic geometry*** is defined by both bonding and nonbonding (lone pairs) electron groups.
- The ***molecular shape*** or ***molecular geometry*** is the three-dimensional arrangement of the **atoms only**. Lone pairs are ignored while determining this shape.
- Molecular shape is classified using the designation:




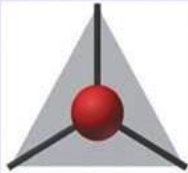


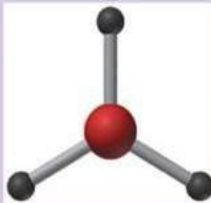
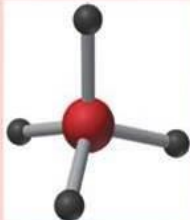


A = central atom

X = surrounding atom

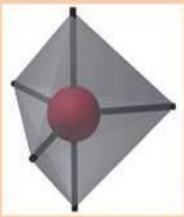
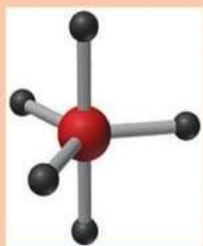
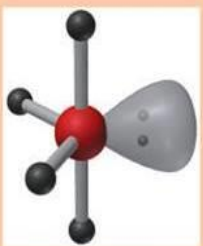

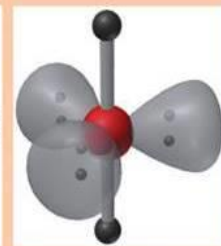
E = nonbonding electrons or lone pair

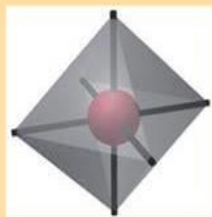
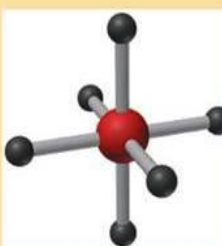
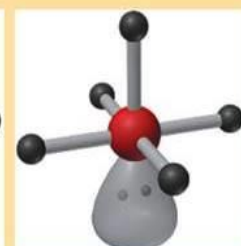
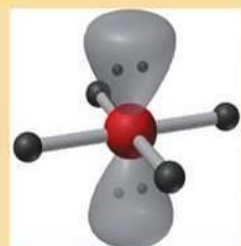
m and ***n*** are integers

Common Molecular Shapes with Two, Three and Four Electron Groups

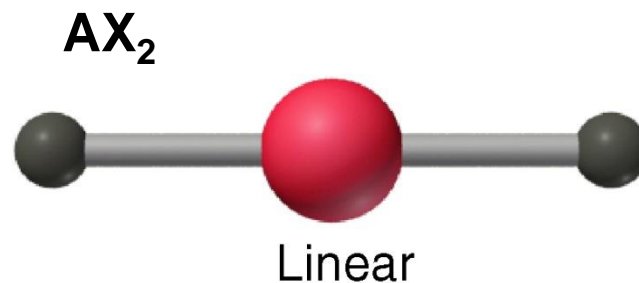
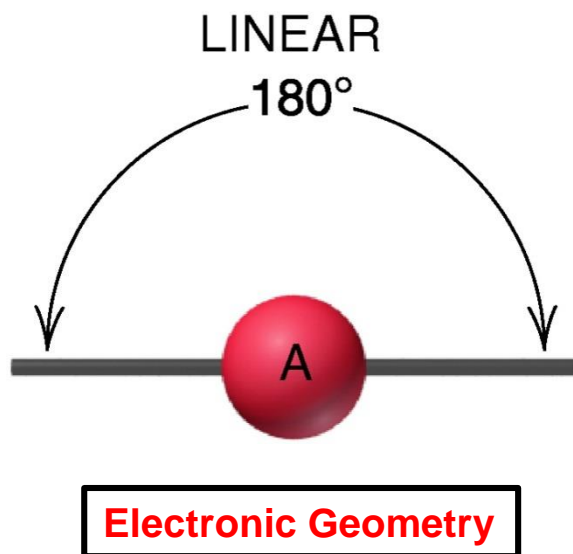
e ⁻ Group arrangement (no. of groups)	 Linear (2)		 Trigonal planar (3)		 Tetrahedral (4)				
Molecular shape (class)	 Linear (AX ₂)		 Trigonal planar (AX ₃)		 Tetrahedral (AX ₄)			 Trigonal pyramidal (AX ₃ E)	 V shaped or bent (AX ₂ E ₂)
No. of bonding groups	2		3		4			3	2
Bond angle	180°		120°		109.5°			<109.5°	<109.5°

Common Molecular Shapes with Five and Six Electron Groups

e ⁻ Group arrangement (no. of groups)	 Trigonal bipyramidal (5)			
Molecular shape (class)	 Trigonal bipyramidal (AX ₅)	 Seesaw (AX ₄ E)	 T shaped (AX ₃ E ₂)	 Linear (AX ₂ E ₃)
No. of bonding groups	5	4	3	2
Bond angle	90° (ax) 120° (eq)	<90° (ax) <120° (eq)	<90° (ax)	180°

e ⁻ Group arrangement (no. of groups)	 Octahedral (6)		
Molecular shape (class)	 Octahedral (AX ₆)	 Square pyramidal (AX ₅ E)	 Square planar (AX ₄ E ₂)
No. of bonding groups	6	5	4
Bond angle	90°	<90°	90°

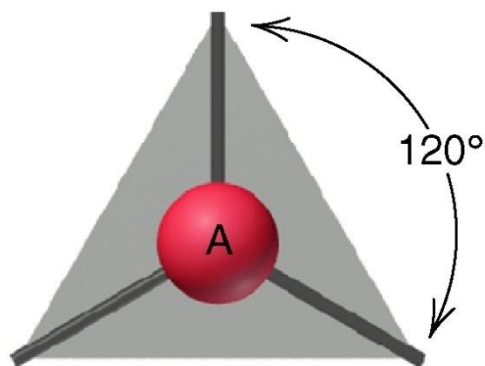
Molecular Shape with Two Electron Groups



Examples:
 CS_2 , HCN, BeF_2 , CO_2

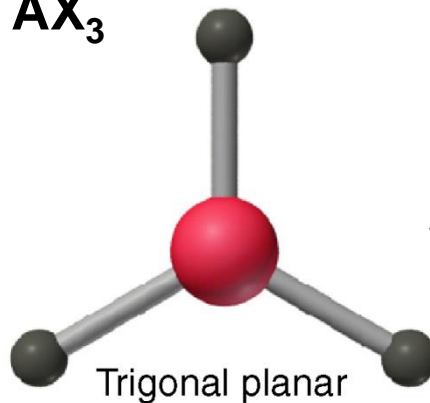
Molecular Shapes with Three Electron Groups

TRIGONAL PLANAR



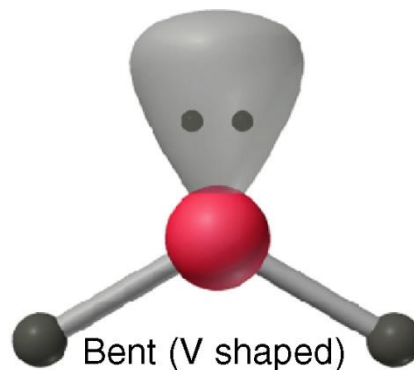
Electronic Geometry

AX_3



Examples:
 SO_3 , BF_3 , NO_3^- , CO_3^{2-}

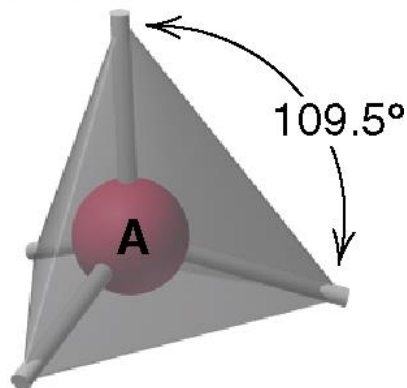
AX_2E



Examples:
 SO_2 , O_3 , $PbCl_2$, $SnBr_2$

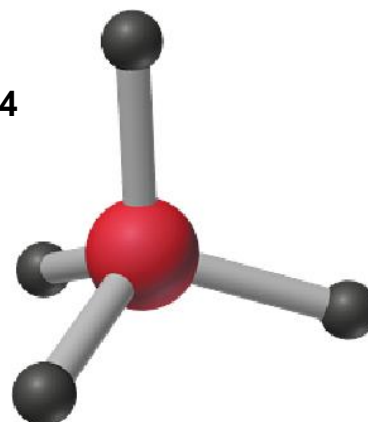
Molecular Shapes with Four Electron Groups

TETRAHEDRAL



Electronic Geometry

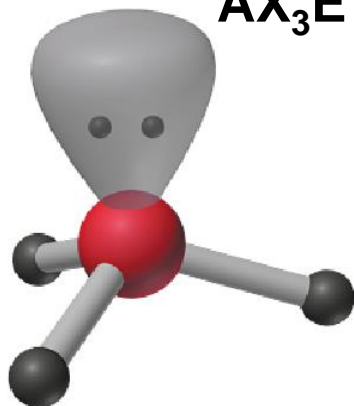
AX_4



Tetrahedral

Examples:
 CH_4 , $SiCl_4$,
 SO_4^{2-} , ClO_4^-

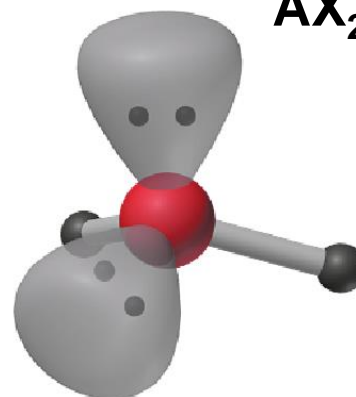
AX_3E



Trigonal pyramidal

Examples:
 NH_3 , PF_3
 ClO_3^- , H_3O^+

AX_2E_2

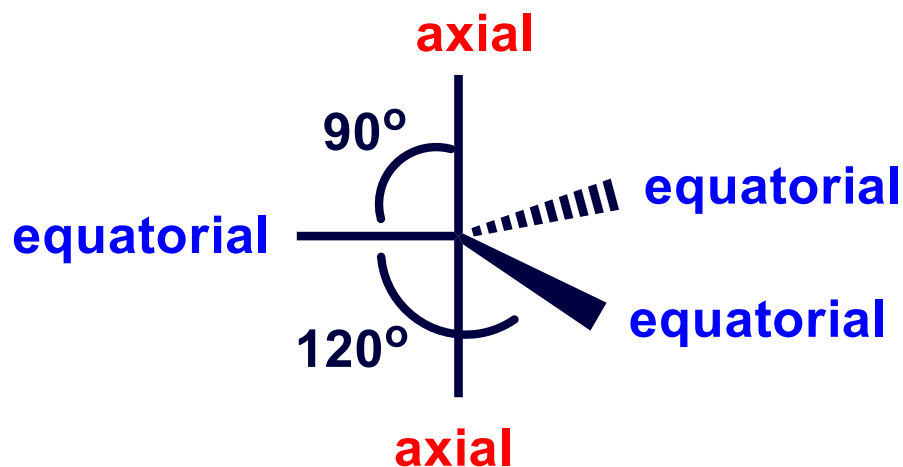


Bent (V shaped)

Examples:
 H_2O , OF_2 , SCl_2

Axial and Equatorial Positions

- A five electron-group system has two different positions for electron groups, and two ideal bond angles.

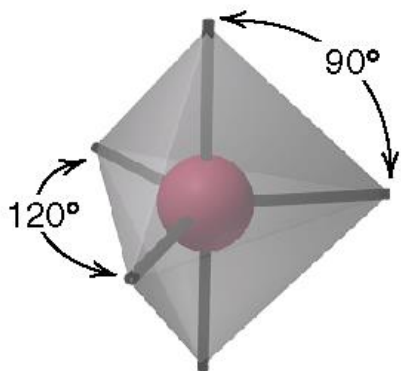


Equatorial-equatorial repulsions are ***weaker*** than axial-equatorial repulsions.

- Where possible, lone pairs in a five electron-group system occupy ***equatorial*** positions to minimize repulsion.

Molecular Shapes with Five Electron Groups

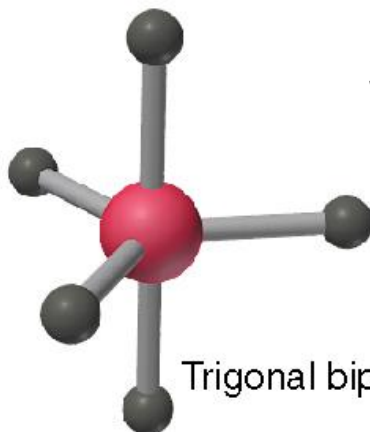
TRIGONAL BIPYRAMIDAL



Electronic Geometry

AX_5

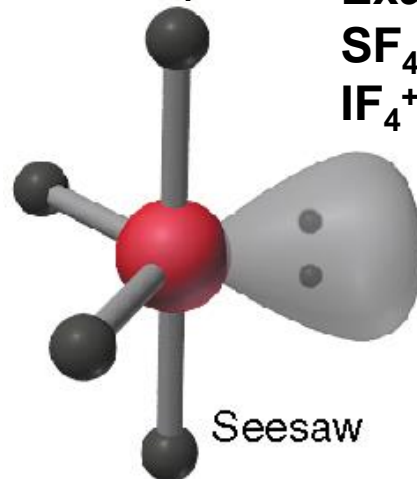
Examples:
 PF_5 , AsF_5 ,
 SOF_4



Trigonal bipyramidal

AX_4E

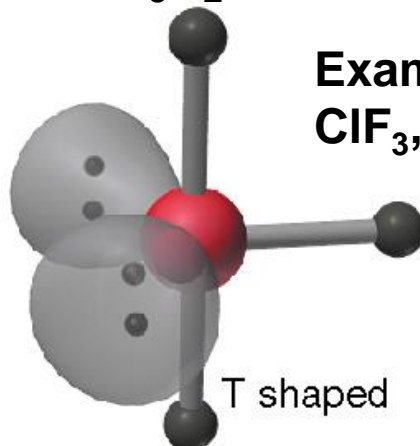
Examples:
 SF_4 , XeO_2F_2
 IF_4^+ , $IO_2F_2^-$



Seesaw

AX_3E_2

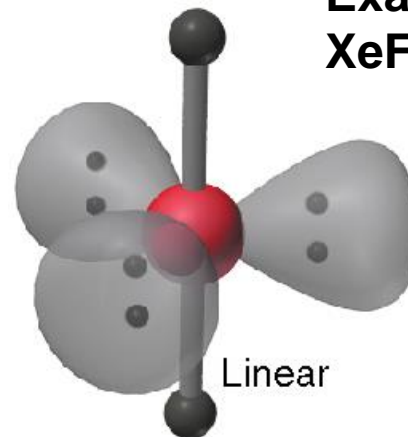
Examples:
 ClF_3 , BrF_3



T shaped

AX_2E_3

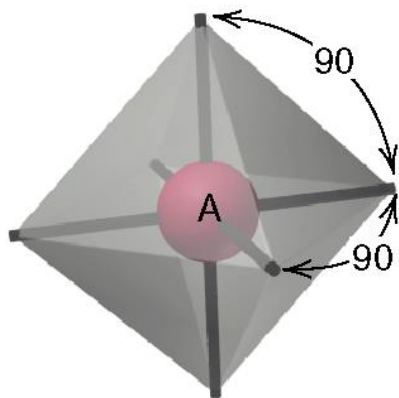
Examples:
 XeF_2 , I_3^- , IF_2^-



Linear

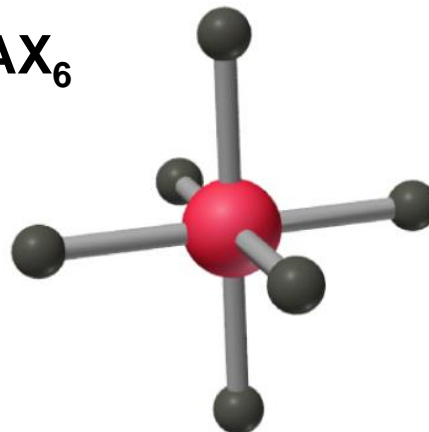
Molecular Shapes with Six Electron Groups

OCTAHEDRAL



Electronic Geometry

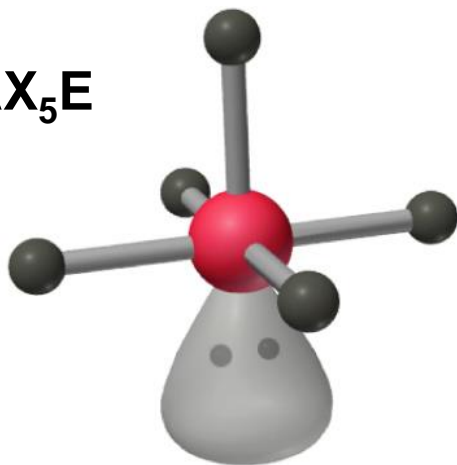
AX_6



Octahedral

Examples:
 SF_6 , IOF_5

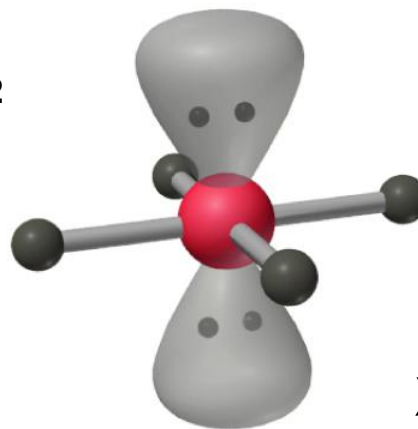
AX_5E



Square pyramidal

Examples:
 BrF_5 , TeF_5^- ,
 $XeOF_4$

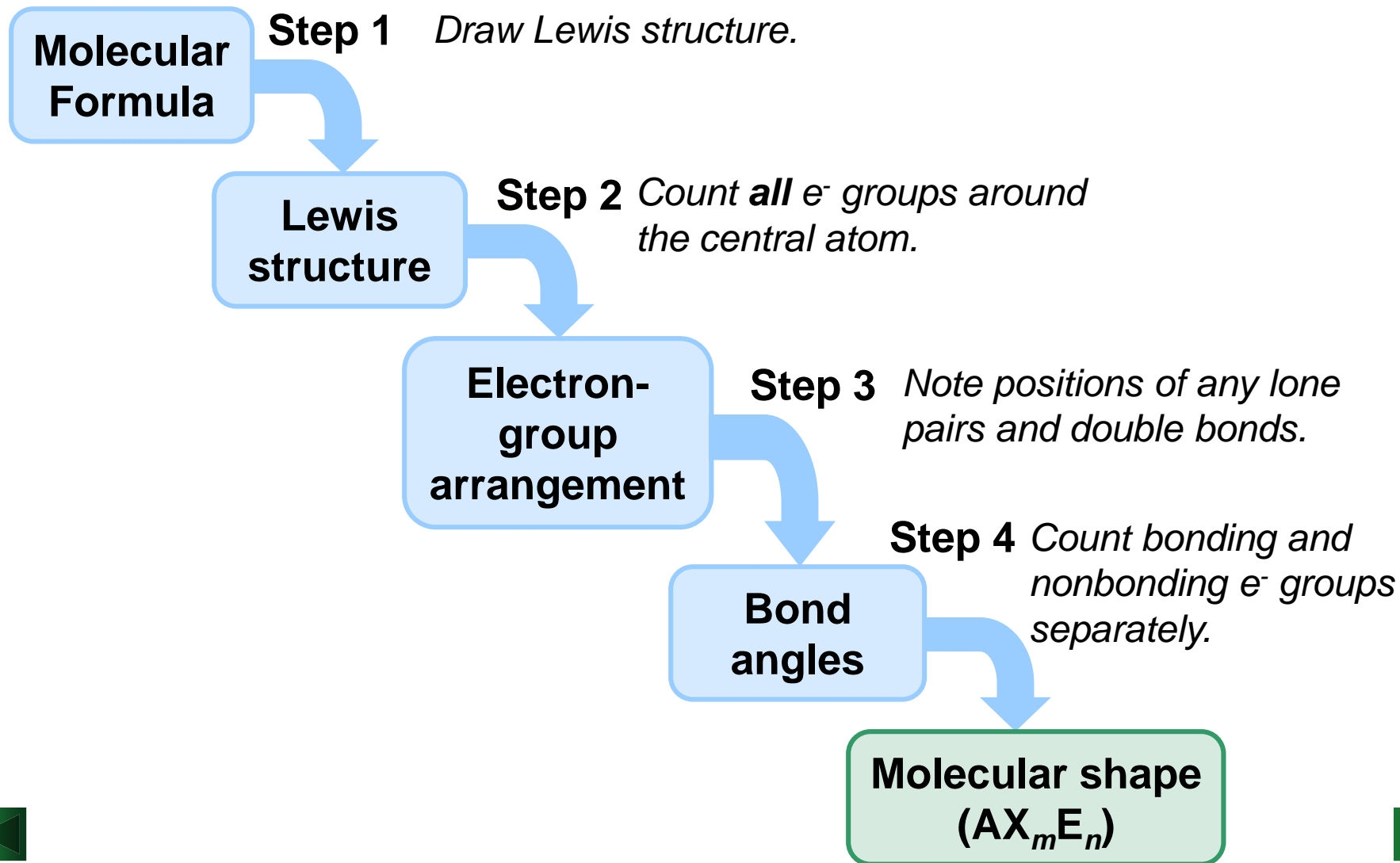
AX_4E_2



Square planar

Examples:
 XeF_4 , ICl_4^-

The Four Steps in Converting a Molecular Formula to a Molecular Shape



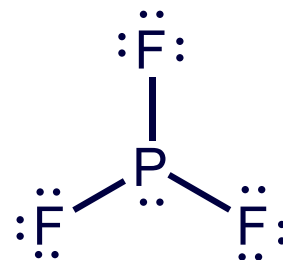
Sample Problem 10.6

Examining Shapes with Two, Three, or Four Electron Groups

PROBLEM: Draw the molecular shape and predict the bond angles (relative to the ideal bond angles) of **(a)** PF_3 and **(b)** COCl_2 .

SOLUTION:

(a) For PF_3 , there are 26 valence electrons.
The Lewis structure is

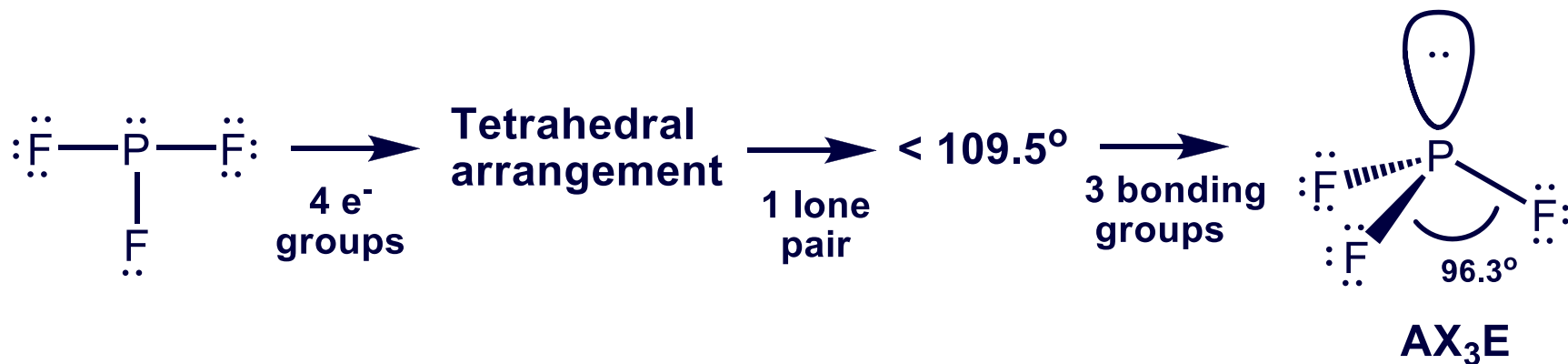


There are four electron groups around P, giving a tetrahedral electron-group arrangement. **The ideal bond angle is therefore 109.5° .**

There is one lone pair and three bonding pairs, so the actual bond angle will be **less than 109.5° .**

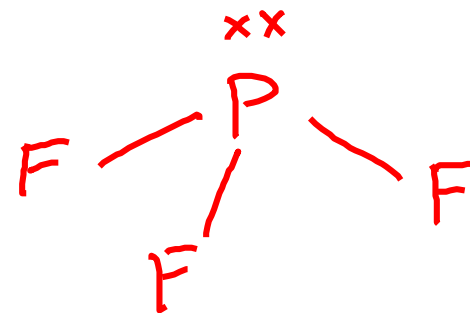
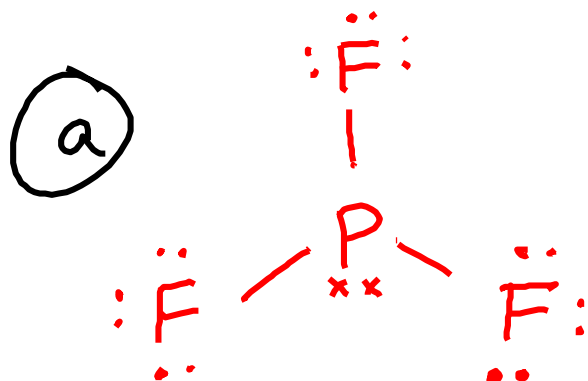
Sample Problem 10.6

(a) The molecular shape for PF_3 is **trigonal pyramidal** (AX_3E).

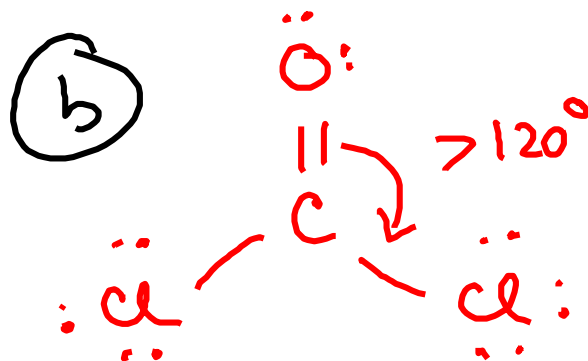


Sample Problem 10.6

Draw the molecular shape and predict the bond angles (relative to the ideal bond angles) of (a) PF_3 (b) COCl_2



E. geometry = Tetrahedral.
M. geometry = Trigonal Pyramidal.



E. geometry = Trigonal Planar
M. geometry = Trigonal Planar

Molecular Shape and Molecular Polarity



Molecular Shape and Molecular Polarity

- Overall **molecular polarity** depends on both **shape** and **bond polarity** (electronegativity difference between the atoms).
- The polarity of a molecule is measured by its ***dipole moment*** (μ), which is given in the unit **Debye (D)**.



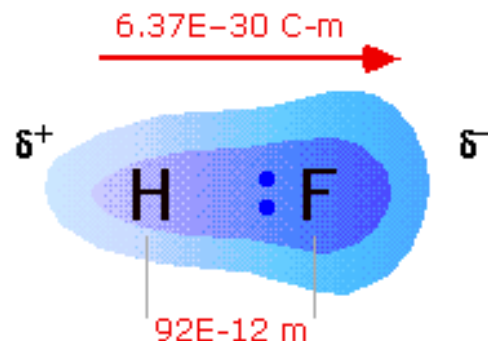
Dipole Moment

A quantitative measure of the polarity of a bond is its dipole moment (μ), which is the product of the charge Q and the distance r between the charges.

$$\mu = Q \times r$$

Q is the charge, r is the distance between charges,

$$1 \text{ D} = 3.34 \times 10^{-30} \text{ C m}$$



Bond Polarity, Bond Angle, and Dipole Moment

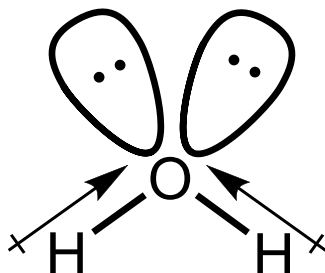
- The presence of polar bonds does not always result in a polar molecule; we must also consider shape and the atoms surrounding the central atom
- A molecule is polar if
 - ✓ it contains one or more ***polar bonds*** and
 - ✓ the individual bond dipoles ***do not cancel***



Bond Polarity, Bond Angle, and Dipole Moment

Example: H₂O

The ΔEN between H (EN = 2.1) and O (EN = 3.5) makes each H-O bond polar.

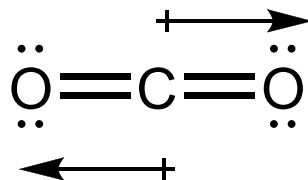


H₂O has a V shaped (bent) geometry and the individual bond polarities do **not** cancel. This molecule has an **overall molecular polarity**. The O is partially negative while the H atoms are partially positive.

Bond Polarity, Bond Angle, and Dipole Moment

Example: CO₂

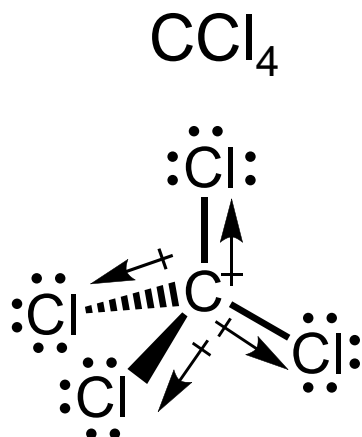
The ΔEN between C (EN = 2.5) and O (EN = 3.5) makes each C=O bond polar.



CO₂ is linear, the bond angle is 180° , and the individual bond polarities therefore cancel. The molecule has ***no net dipole moment*** ($\mu = 0 \text{ D}$).

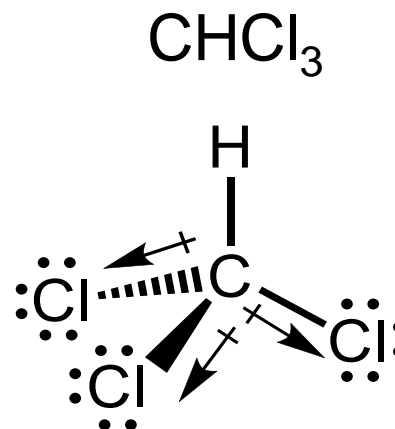
Bond Polarity, Bond Angle, and Dipole Moment

- Molecules with the same shape may have different polarities.



Individual bonds are polar, but the **bond polarities cancel**.

Non-polar Molecule



Individual bonds are polar and **bond polarities do not cancel**.

Polar Molecule

Sample Problem 10.9

Use the molecular shape and EN values to predict whether the molecule is polar:

(a) Ammonia, NH_3

(b) Boron trifluoride, BF_3

(c) Carbonyl sulfide, SCO

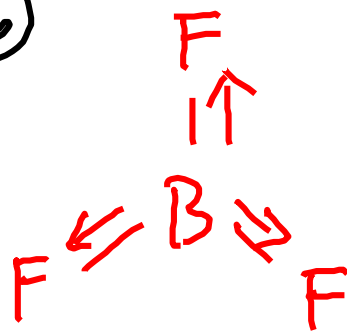
(a)



M.G. = Trigonal pyramidal
E.G. = Tetrahedral

Polar

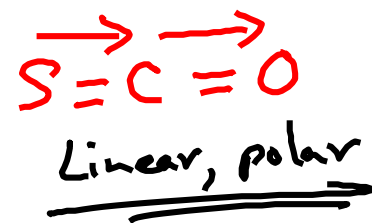
(b)



M.G. = E.G. = Trigonal Planar.

Non-polar

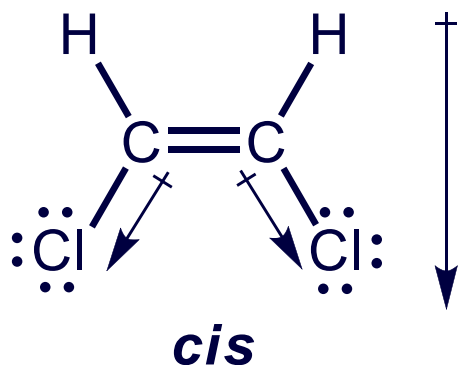
(c)



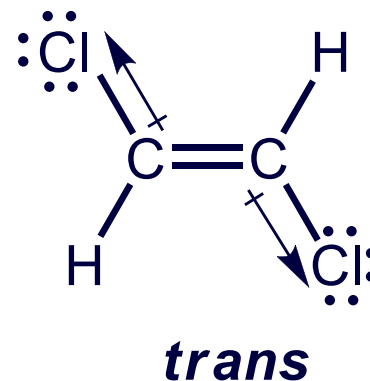
Linear, polar

The Effect of Molecular Polarity on Physical Properties

- The *cis* and *trans* isomers of $C_2H_2Cl_2$



Polar Molecule



Non-polar Molecule

- The *cis* isomer is polar while the *trans* isomer is not.
- The boiling point of the *cis* isomer is 13°C **higher** than that of the *trans* isomer.

Valence Bond (VB) Theory for Main-Group Elements

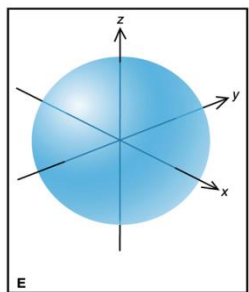


Valence Bond (VB) Theory for Main-Group Elements

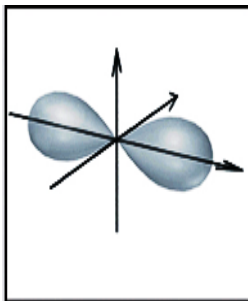
- Both **VB theory** and **VSEPR model** are extensively used for the molecules of *main-group elements*.
- **VB theory** and **VSEPR model** go hand-in-hand — we use the **VB theory** to explain *bonding* and the **VSEPR model** to explain the *observed shapes* of the molecules.
- According to **VB theory**, the *atomic orbitals* first mix together to form *hybrid orbitals*. The process is referred to as *hybridization*.
- The *hybrid orbitals* then overlap with the **orbitals** of the **adjacent atoms** to form *covalent bonds*.

Why do we need *hybrid orbitals* to explain bond-formation??

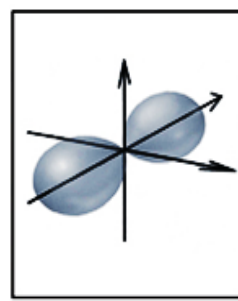
- The **atomic p orbitals** are **perpendicular to each other**, and so they **fail** to describe the ***different shapes*** of molecules.



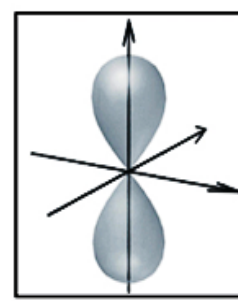
s orbital



p_x orbital



p_y orbital



p_z orbital

- The **mixed atomic orbitals** or **hybrid orbitals** can efficiently describe the various shapes of the molecules ***on most occasions***.

Key Features of Hybrid Orbitals

- The ***number*** of hybrid orbitals formed ***equals*** the number of atomic orbitals mixed.
 - e.g. **four sp^3 hybrid orbitals** are formed by mixing **four** different **atomic orbitals** — **one s** and **three p** orbitals.
- The **number of hybrid orbitals** matches the ***number of electron-groups***.
 - **Single/Double/Triple bonds** and **lone electron pairs** count as **electron-groups**.
- The ***shape*** and ***orientation*** of a hybrid orbital **maximizes overlap** with the other atom in the bond and **minimizes electron-electron repulsion**.



How do I predict the hybridization of the central atom?

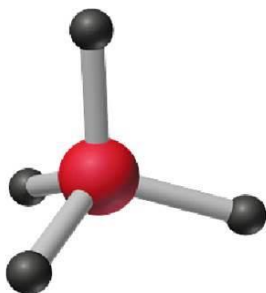
1. Draw the Lewis structure of the molecule.
2. Count the number of lone pairs AND the number of atoms bonded to the central atom

<u># of Lone Pairs +</u> <u># of Bonded Atoms</u>	<u>Hybridization</u>	<u>Examples</u>
2	sp	BeCl ₂
3	sp ²	BF ₃
4	sp ³	CH ₄ , NH ₃ , H ₂ O
5	sp ³ d	PCl ₅
6	sp ³ d ²	SF ₆



Predicting the Hybrid Orbitals

Methane (CH_4)

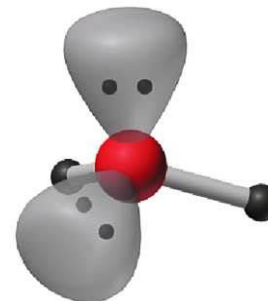


Electronic Shape: **Tetrahedral**

Molecular Shape: **Tetrahedral**

Hybrid Orbitals: **Four sp^3**

Water (H_2O)

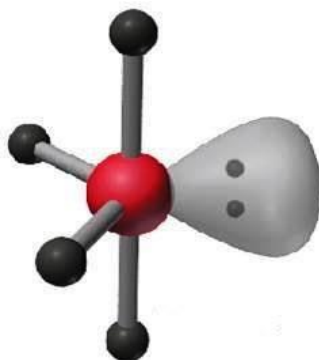


Electronic Shape: **Tetrahedral**

Molecular Shape: **Bent (or V-shaped)**

Hybrid Orbitals: **Four sp^3**

Sulfur tetrafluoride (SF_4)



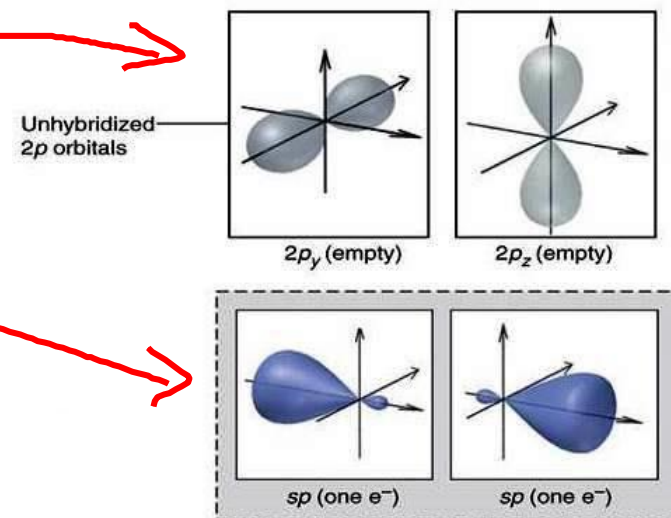
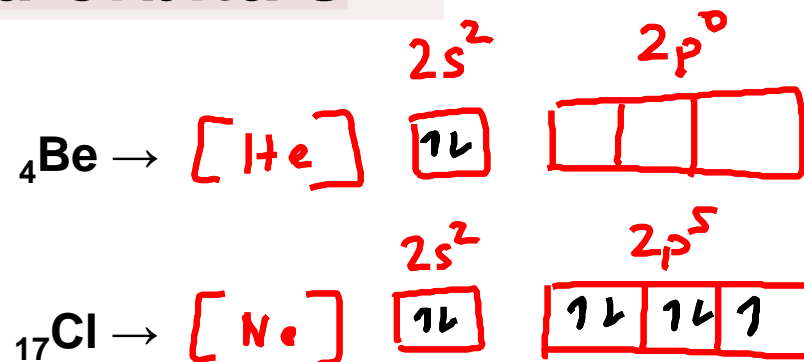
Electronic Shape: **Trigonal bipyramidal**

Molecular Shape: **Seesaw**

Hybrid Orbitals: **Five sp^3d**

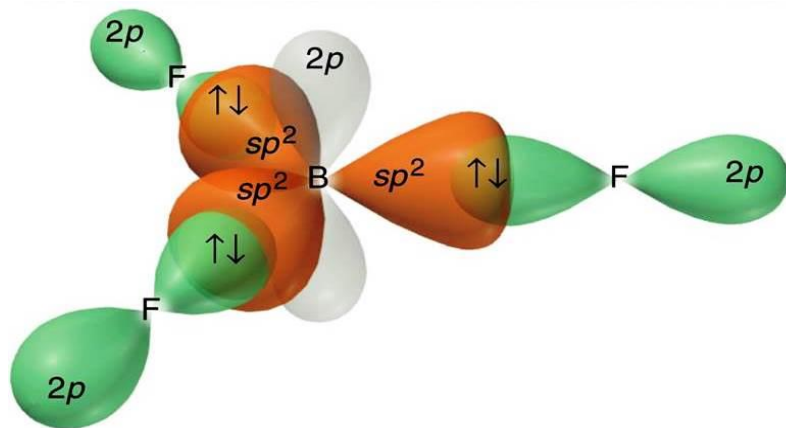
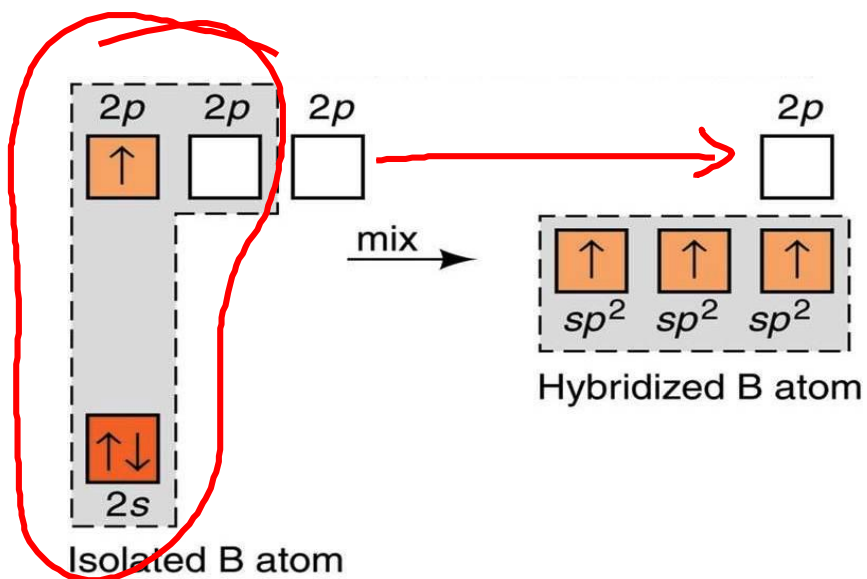
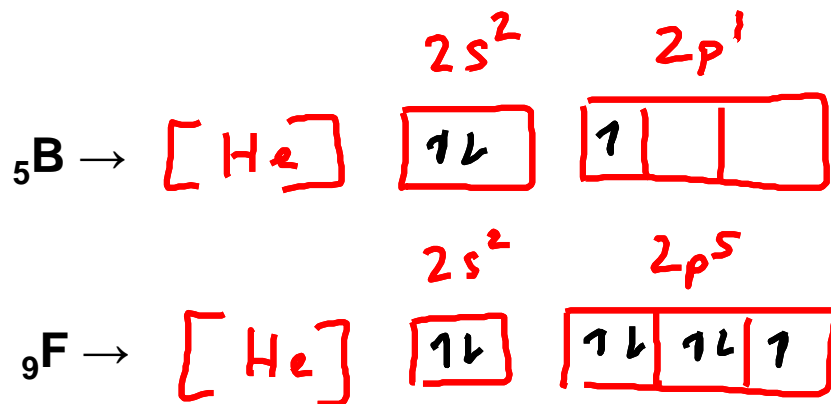
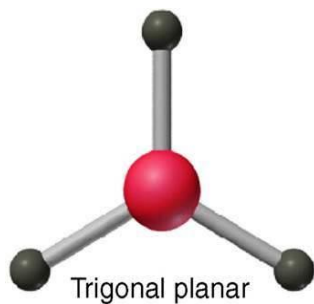
sp hybrid orbitals

▪ Beryllium Chloride (BeCl_2)



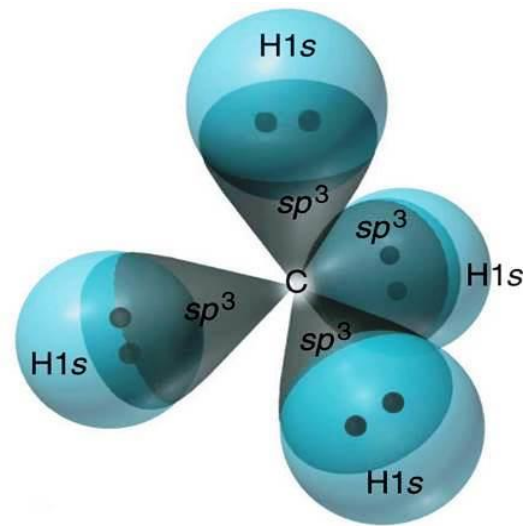
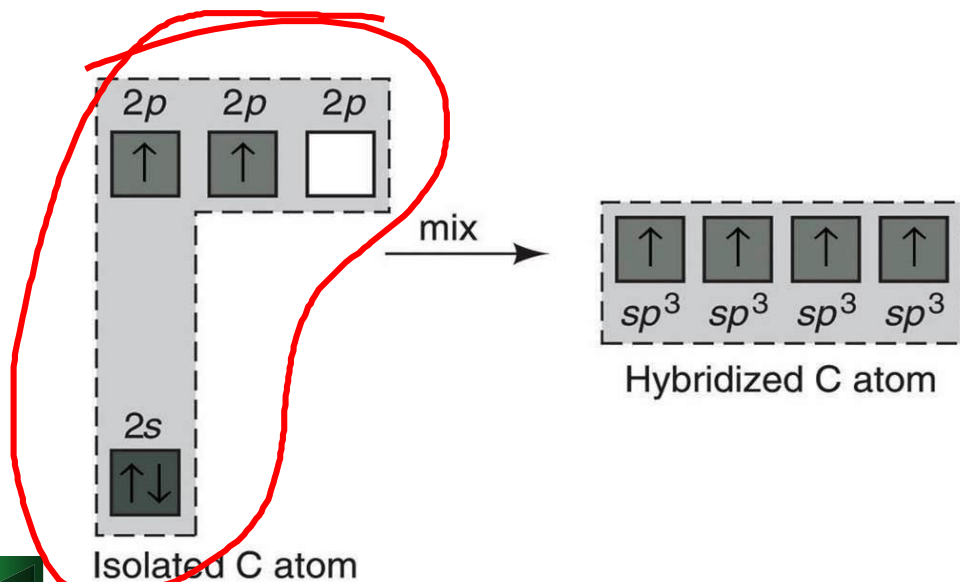
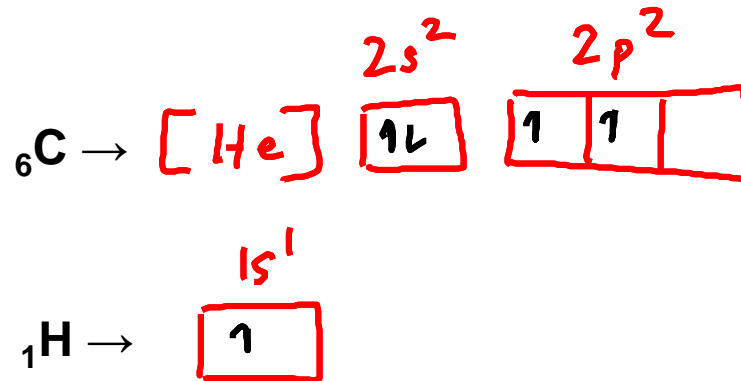
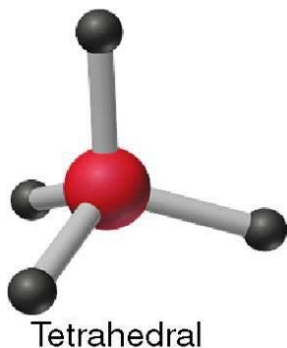
sp^2 hybrid orbitals

- Boron trifluoride (BF_3)



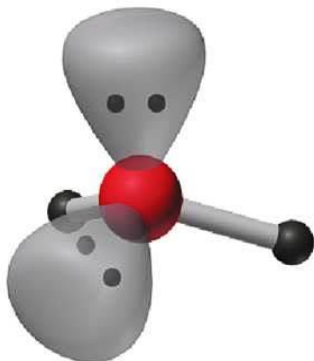
sp^3 hybrid orbitals

▪ Methane (CH_4)

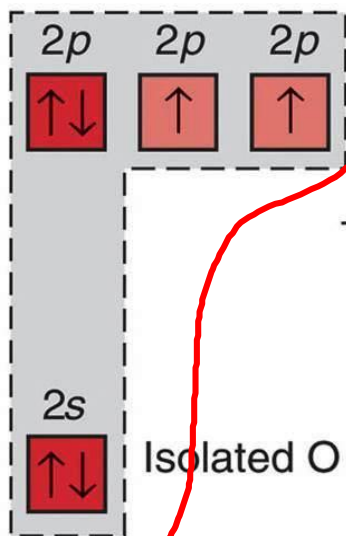
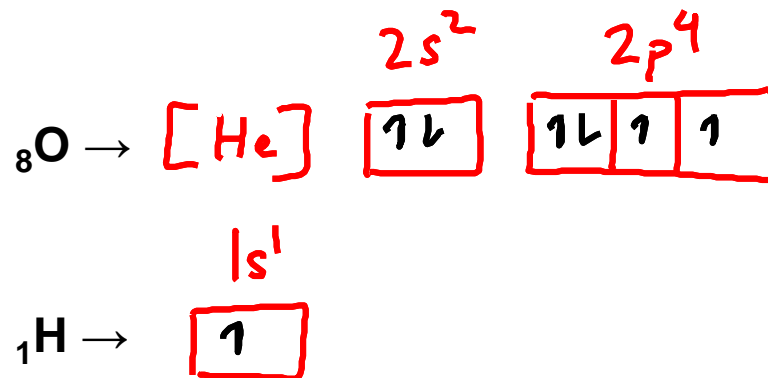


Another Example of sp^3 hybrid orbitals

- Water (H_2O)

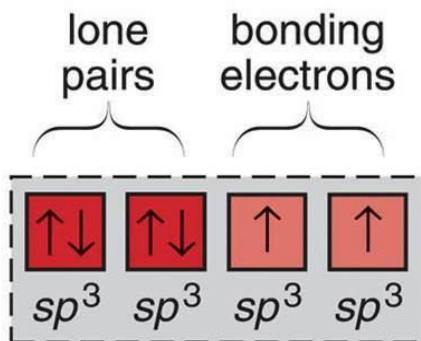


Bent (V shaped)

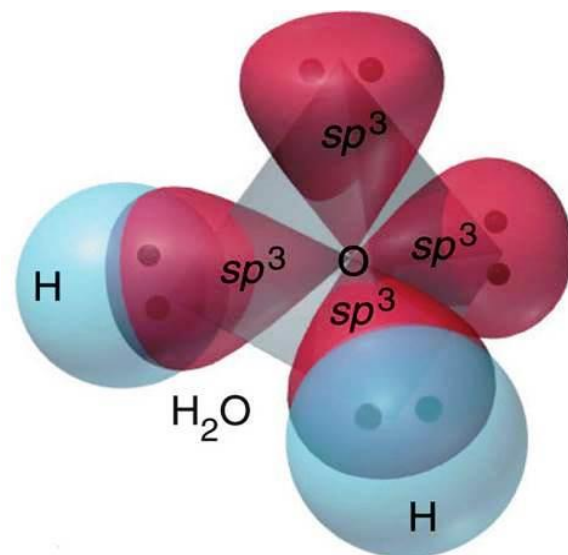


Isolated O atom

mix

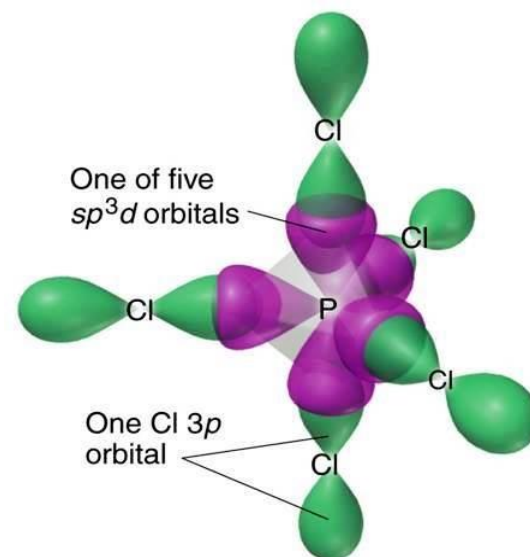
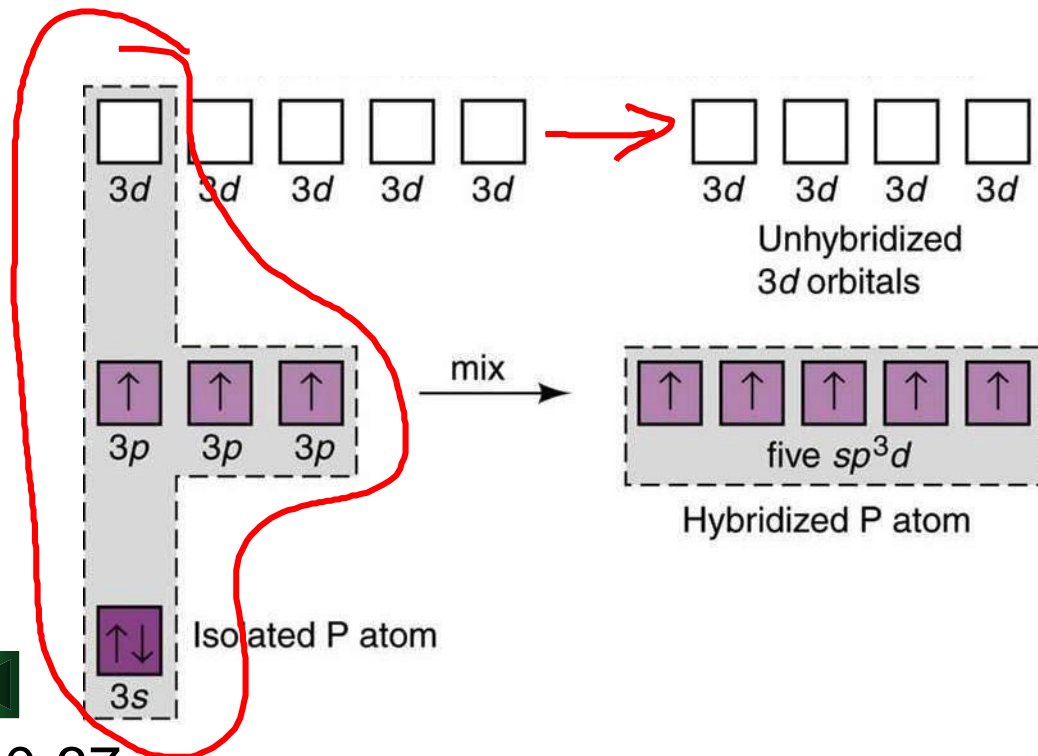
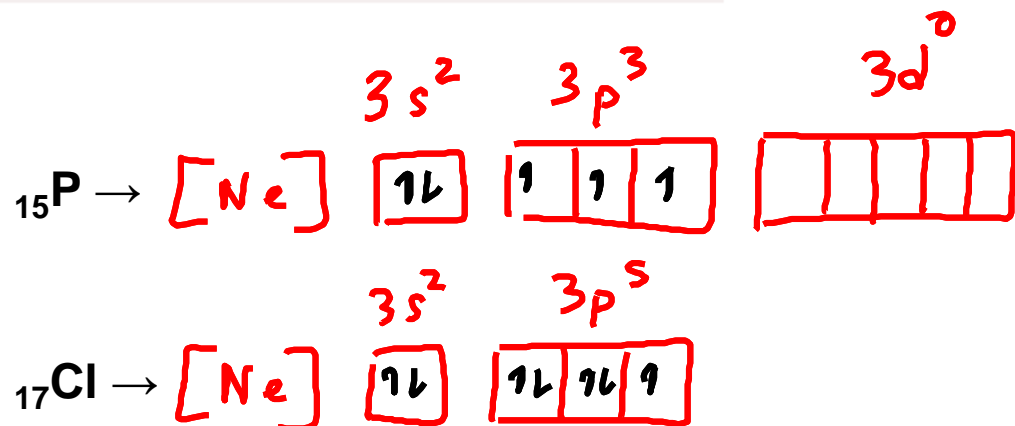
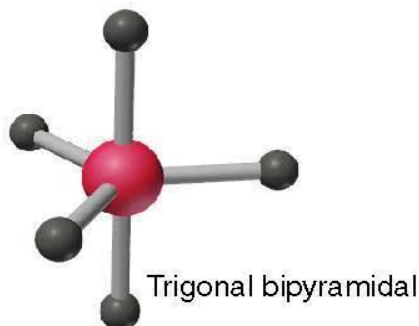


Hybridized O atom



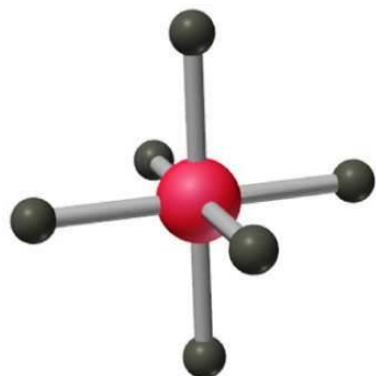
sp^3d hybrid orbitals

- Phosphorus pentachloride (PCl_5)

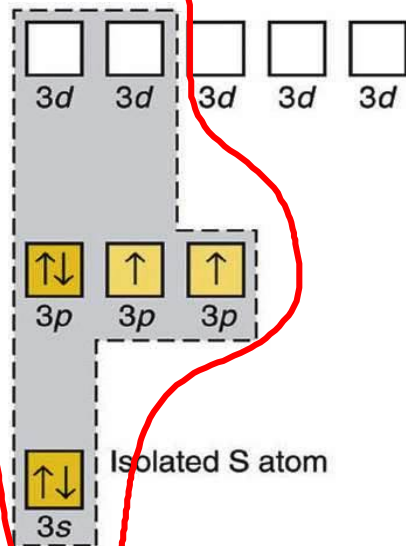
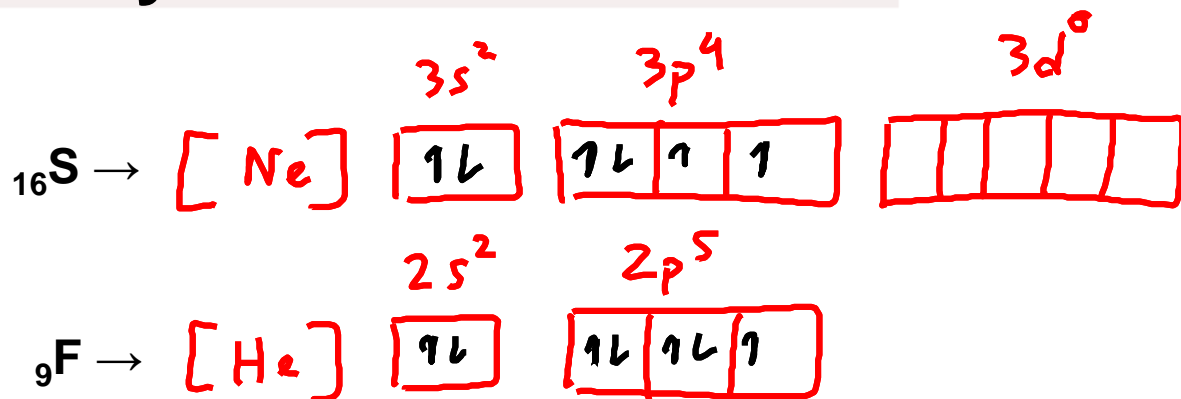


sp^3d^2 hybrid orbitals

▪ Sulfur hexafluoride (SF_6)



Octahedral



mix →



Hybridized S atom

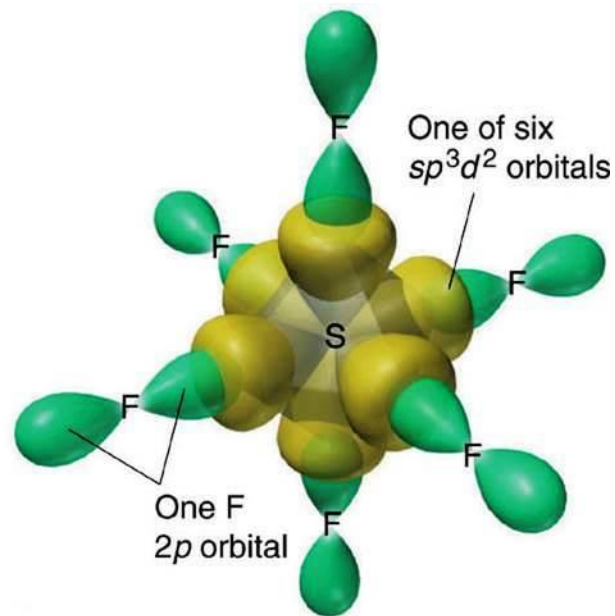


Table 11.1 Composition and Orientation of Hybrid Orbitals

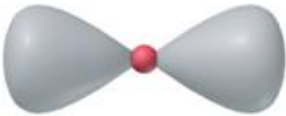
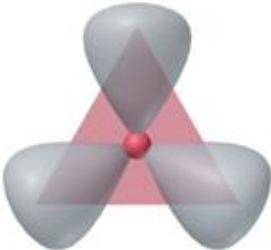
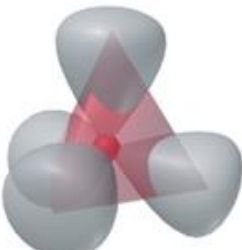
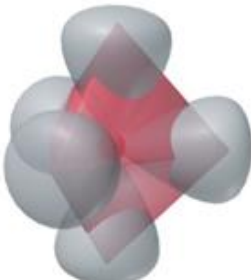

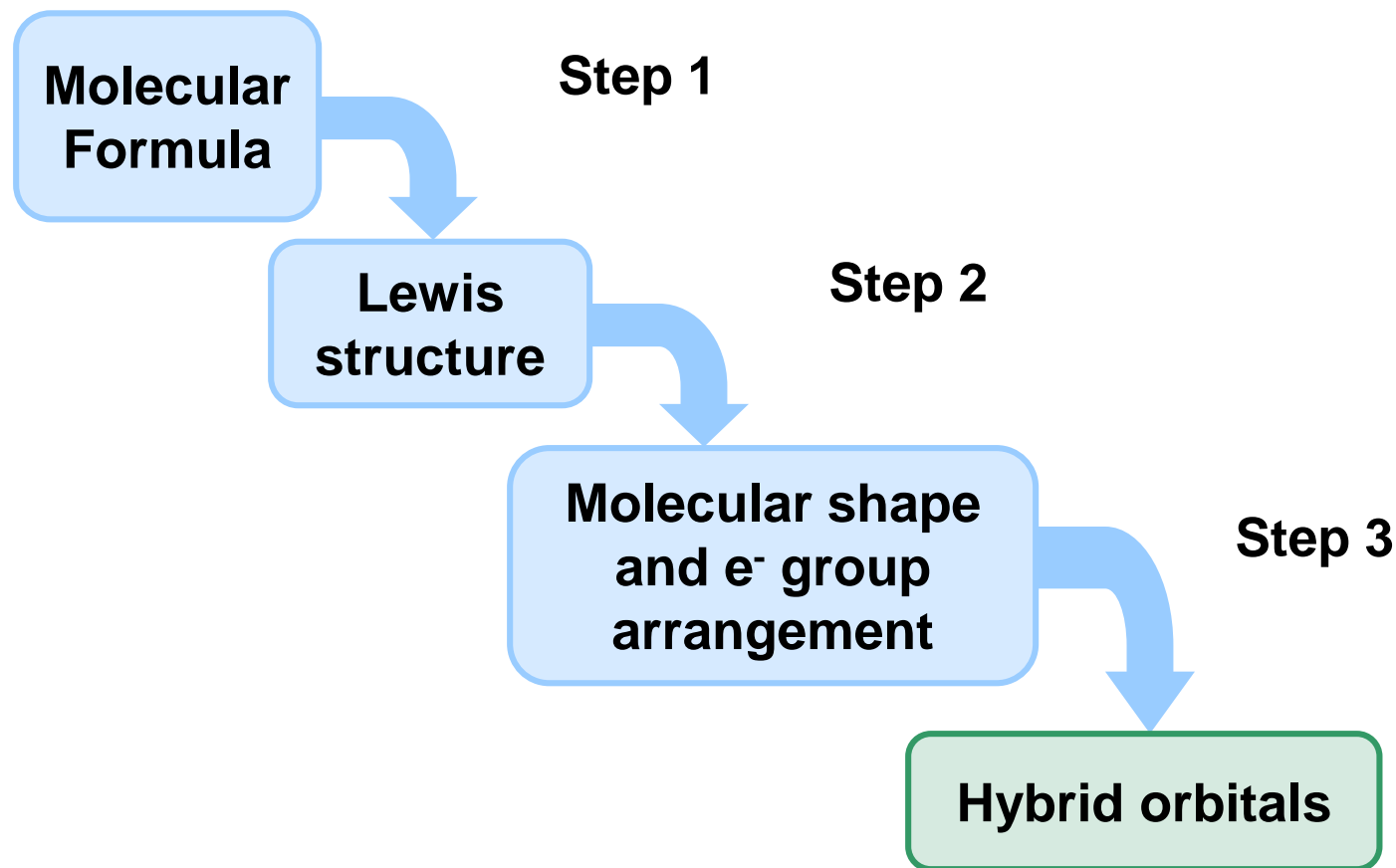
	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one s one p	one s two p	one s three p	one s three p one d	one s three p two d
Hybrid orbitals formed	two sp	three sp^2	four sp^3	five sp^3d	six sp^3d^2
Unhybridized orbitals remaining	two p	one p	none	four d	three d
Orientation					

Figure 11.8 From molecular formula to hybrid orbitals.



Sample Problem 11.1

Postulating Hybrid Orbitals in a Molecule

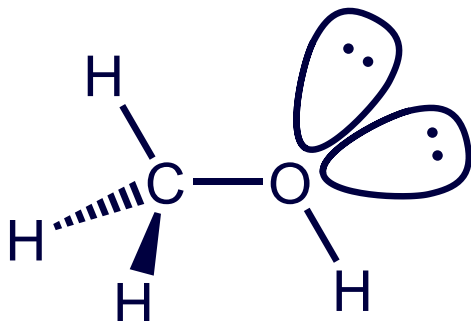
PROBLEM: Use partial orbital diagrams to describe how mixing of the atomic orbitals of the central atom(s) leads to hybrid orbitals in each of the following:

- (a) Methanol, CH_3OH (b) Sulfur tetrafluoride, SF_4

PLAN: We use the molecular formula to draw the Lewis structure and determine the electron-group arrangement around each central atom. We then postulate the type of hybrid orbitals required and write a partial orbital diagram.

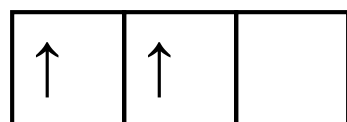
SOLUTION:

(a) CH_3OH

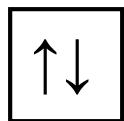


The electron-group arrangement is tetrahedral around both the C and the O atoms.

Sample Problem 11.1

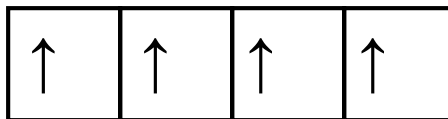


2p



2s

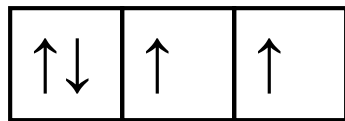
isolated C atom



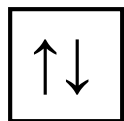
sp^3

hybridized C atom

C has four half-filled sp^3 orbitals.

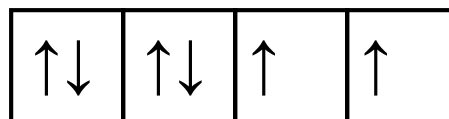


2p



2s

isolated O atom



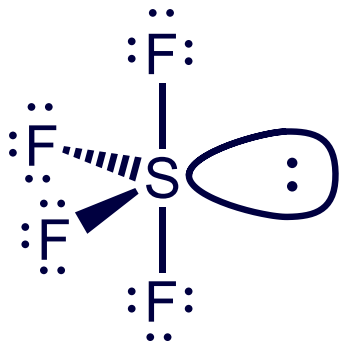
sp^3

hybridized O atom

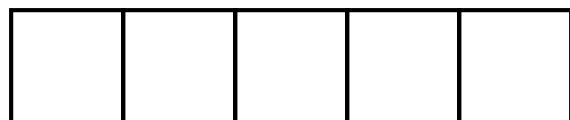
The O atom has two half-filled sp^3 orbitals and two filled with lone pairs.

Sample Problem 11.1

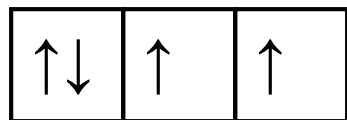
(a) SF_4



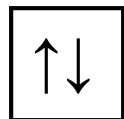
The electron-group arrangement is trigonal bipyramidal, so the central S atom is sp^3d hybridized.



$3d$

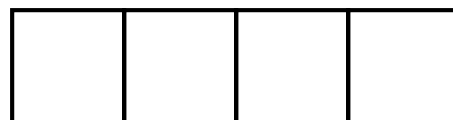


$3p$

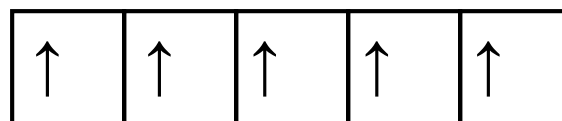


$3s$

isolated S atom



$3d$



sp^3d

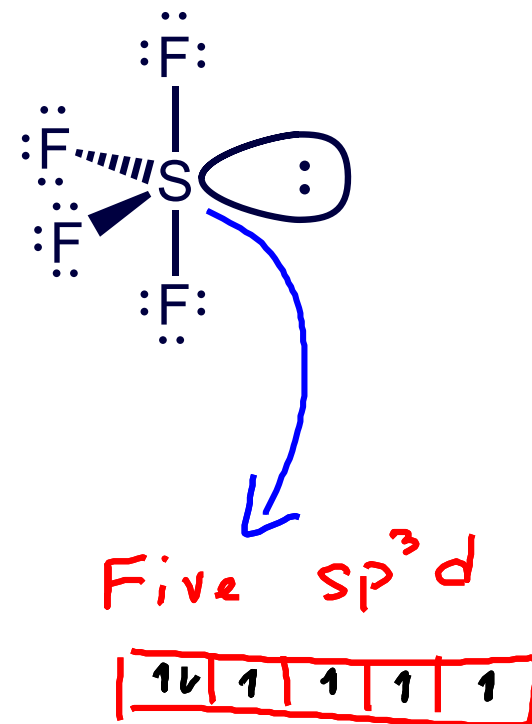
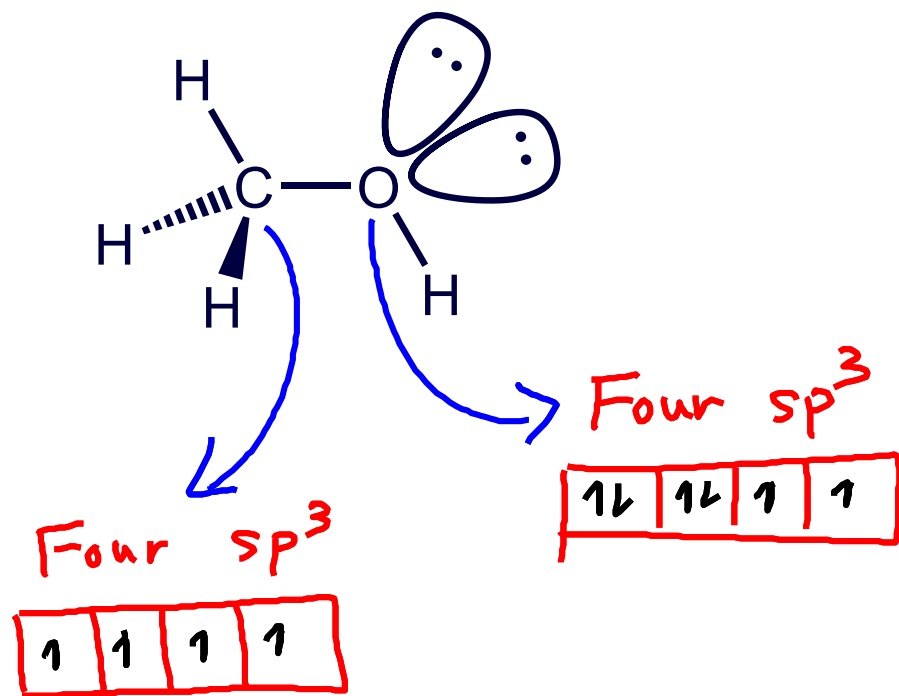
hybridized S atom

Sample Problem 11.1

Write down the hybrid orbitals for the central atom(s) in the following:

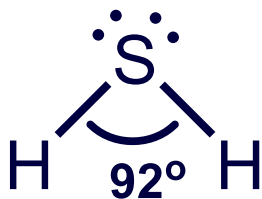
(a) Methanol, CH_3OH

(b) Sulfur tetrafluoride, SF_4



Limitations of the Hybridization Model

- Hybridization is not always consistent with observed molecular shapes. This is particularly true for the bonding of **Period 3** elements.



The bond angle in H₂S is closer to the angle between unhybridized *p* orbitals.

- Often the difficulty in explaining the molecular shapes for **Period 3** elements using the hybridization model is that ***d*-orbitals** do not always hybridize effectively with ***s*** and ***p* orbitals**, which are much lower in energy and more stable.

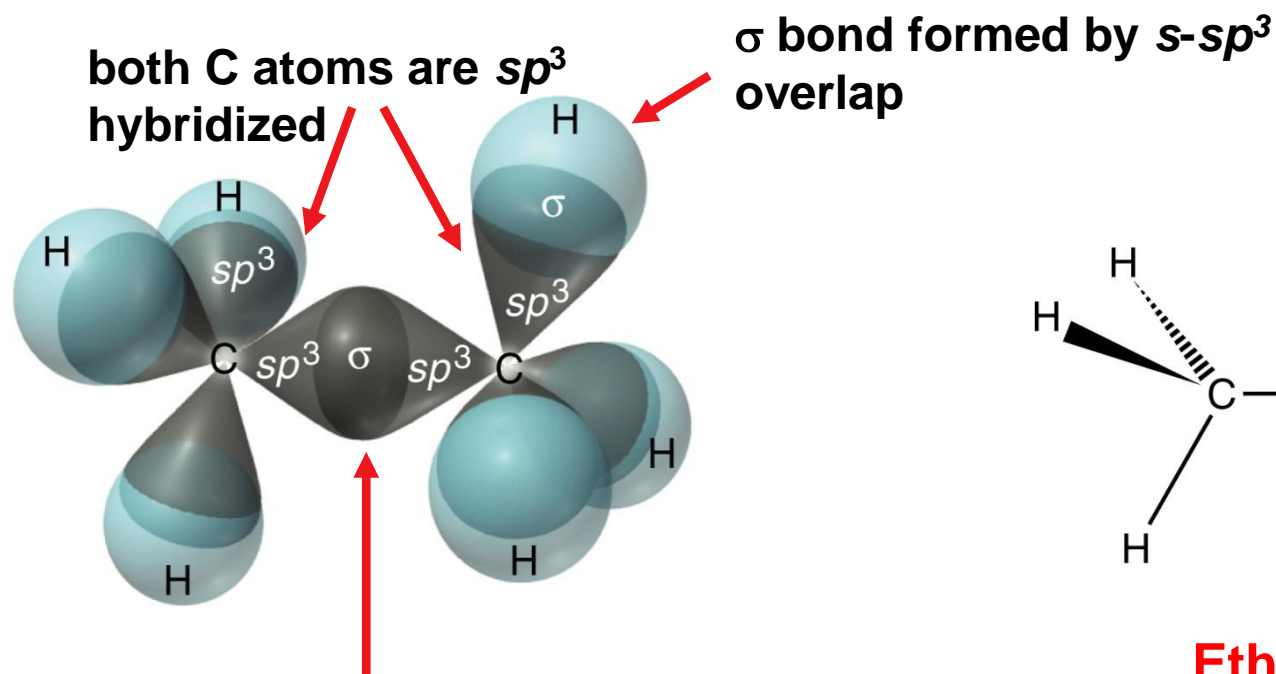
Orbital Overlap

Sigma (σ) and Pi (π) Covalent Bonds

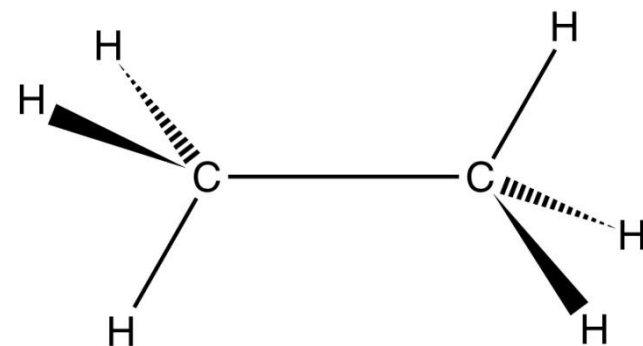


Sigma (σ) Bond

- A **sigma** (σ) bond is formed by **end-to-end** or **head-on** overlap of orbitals.
- All **single bonds** are **σ bonds**.



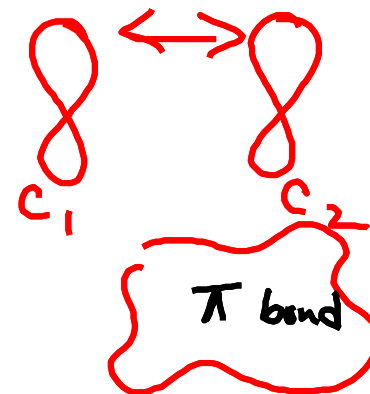
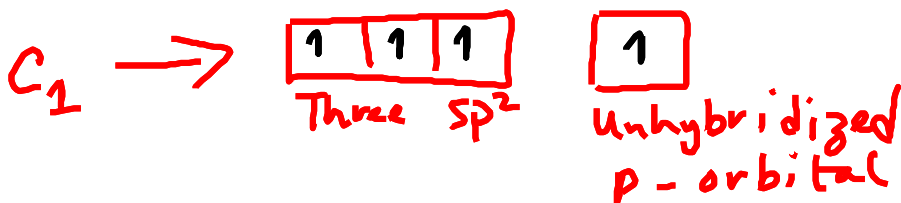
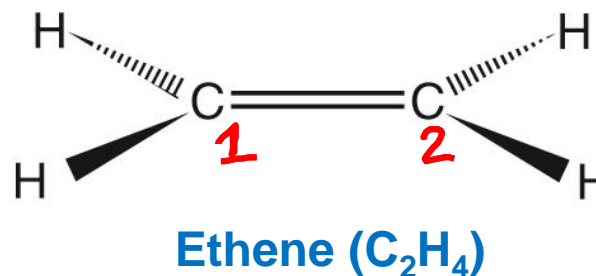
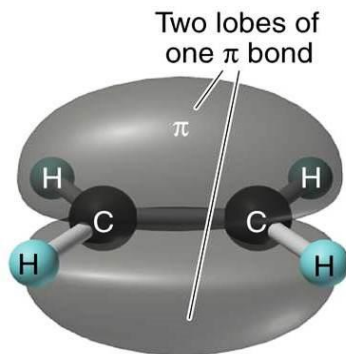
End-to-end sp^3-sp^3 overlap to form a σ bond



Ethane (C_2H_6)

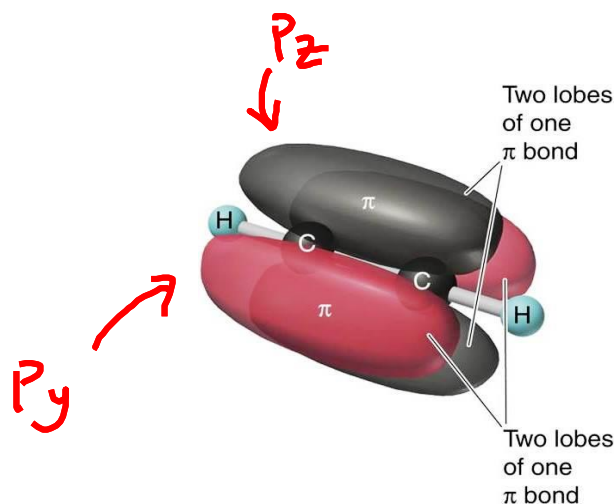
Pi (π) Bond

- A ***pi*** (π) bond is formed by ***sideways*** overlap of **unhybridized *p* orbitals**.
- A π **bond** is weaker than a σ **bond** because sideways overlap is less effective than end-to-end overlap.
- A **double bond** always consists of **one σ bond** and **one π bond**.

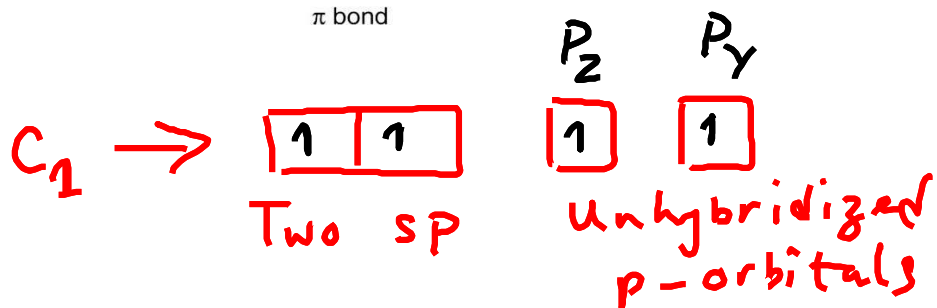


Triple Bond

- A **triple bond** always consists of **one σ bond** and **two π bonds**.

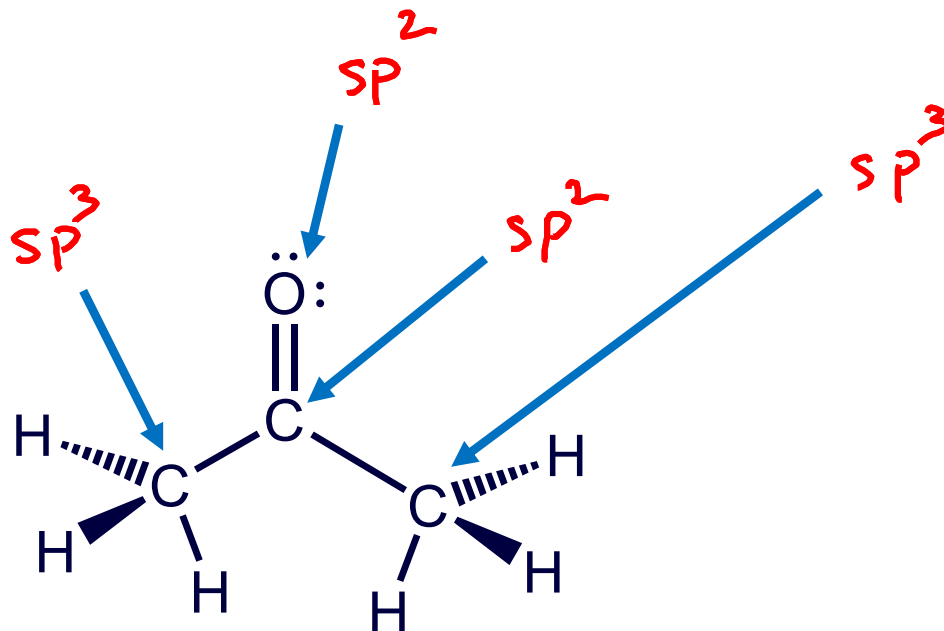


Ethyne (C_2H_2)



Sample Problem 11.2

- a) Describe the types of bonds and orbitals in acetone, $(\text{CH}_3)_2\text{CO}$.
b) How many σ bonds and π bonds are there?

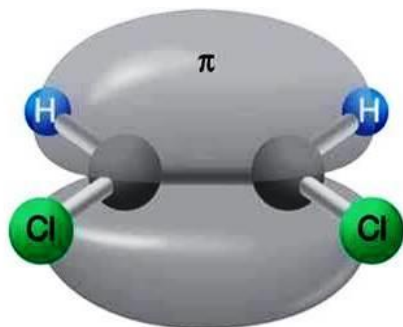


σ bonds = 9

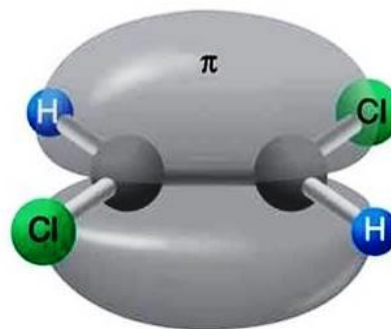
π bonds = 1

Restriction of Rotation around a Pi (π) Bond

- Rotation is restricted around a π **bond** since the overlap gets disrupted.
- Also, **180° rotation** causes the two **overlapping p orbitals** to be **out-of-phase**.
- Structural (*cis-trans*) isomers have different physical and chemical properties.

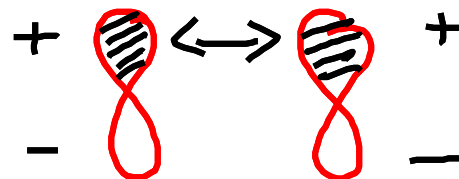


cis-1,2-Dichloroethylene



trans-1,2-Dichloroethylene

In both the *cis* and *trans* isomers, the *p* orbitals overlap in phase. However, rotation would make them go out-of-phase.



Difference in Sigma and Pi bond

Sigma (σ) MO

1. It is formed by **head to head** overlapping of atomic orbitals.
2. The overlap is **along internuclear axis**.
3. As a result of this **strong** bond is formed.
4. This orbital is **symmetrical to rotation** about the line joining the two nuclei.
5. The region of overlap is **greater**.

Pi (π) MO

1. It is formed by the **sidewise** overlapping of p_y or p_x atomic orbitals.
2. The overlap is **perpendicular to internuclear axis**.
3. As a result of this **weak** bond is formed.
4. This orbital is **not symmetrical to rotation** about the line joining the two nuclei.
5. The region of overlap is **lesser**.





Thank you.

Any Questions?

