Chem1028/9

2012

MOLECULAR GEOMETRIES AND BONDING THEORIES

(Please note that you have to attend lectures to complete this set of notes – please use your molecular model kits.)

Mrs Meirim / Room C103

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BONDING AND SHAPES OF MOLECULES

- Molecules form when bonding occurs between atoms.
- In general, molecules are________________
- Bonding and shapes of molecules are important in all chemical reactions, especially in biological systems:
  - Enzymes (lock and key model)
  - Sense of smell and taste
  - Drug design

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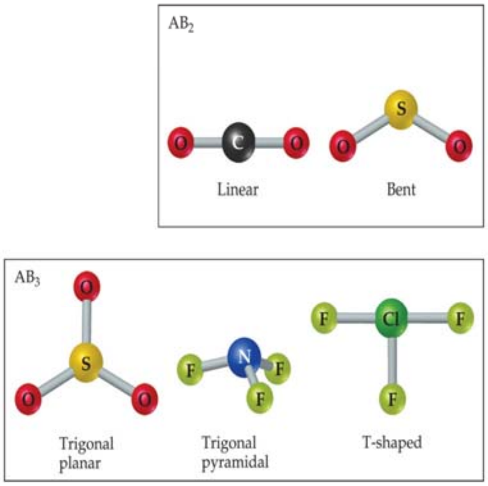
MOLECULAR SHAPES



- The shape of a molecule plays an important role in its_______________.
- By noting the number of __________and nonbonding electron pairs we can easily predict the shape of the molecule.

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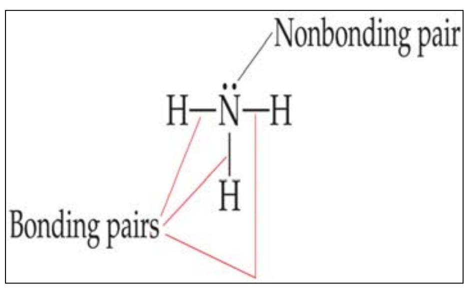
WHAT DETERMINES THE SHAPE OF A MOLECULE?

- Simply put, electron pairs, whether they are bonding or nonbonding, (lone pairs)repel each other.
- By assuming the electron pairs are placed ________ **from each other as possible**, we can predict the shape of the molecule.

(See VSEPR later.)



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ELECTRON DOMAINS

- We can refer to the electron pairs (bonding or nonbonding) as ____________________.
- A ___________________counts as one electron domain, because all the electrons that are shared between those two atoms are on the same side of the central atom.
- Example:
  There are **four electron domains,** i.e. 4 areas of electron-density, **around A.**

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EXAMPLES

How many electron domains are there around the **central** atom of each of these molecules?
NH_3, H_2O and CO_2

Molecule	Lewis Diagram	Electron domains
NH_3		

H_2O	:Ö–H
	   |
	   H	

CO_2		

Note: An **electron-domain** is either a **lone pair** of electrons, a **single bond** or a **multiple bond.**

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PREDICTION OF MOLECULAR SHAPES

We will now consider how molecular shapes can be predicted based largely on:

- Lewis structures and
- the idea of electron-electron repulsions i.e. the valence-shell electron-pair repulsion,__________, model.

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VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

This theory is based on the main idea that:

"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

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ELECTRON-DOMAIN GEOMETRY

- The arrangement of _______________about a central atom of a molecule or ion is called its **electron domain geometry**.
- Electron domain _____________is based on the number of electron domains around the central atom.

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The shape of a molecule can usually be derived from one of five basic geometric structures:

- Linear (eg: _______)
- Trigonal planar (eg: BF_3)
- Tretrahedral (eg: __________)
- Trigonal bipyramidal (eg: PCl_5)
- Octahedral (eg: _____)

(Please use molecular models)

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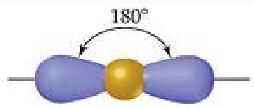
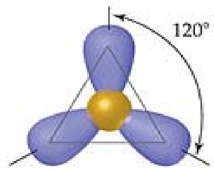
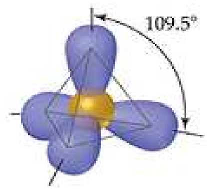
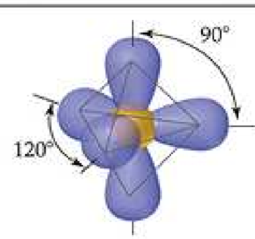
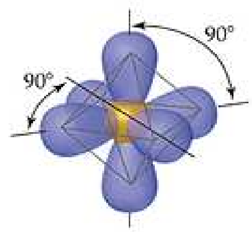
ELECTRON-DOMAIN GEOMETRIES

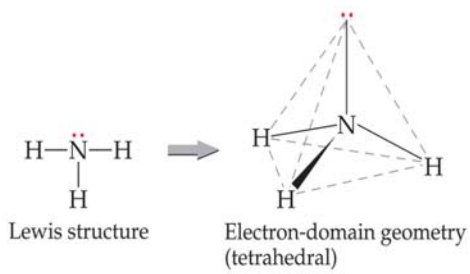
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°

ELECTRON-DOMAIN GEOMETRIES

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

DETERMINING ELECTRON-DOMAIN GEOMETRIES

- One must count the number of electron domains in the **Lewis** structure.
- The electron-domain geometry corresponds to the __________of electron domains.
- Example: NH_3, ________________________:



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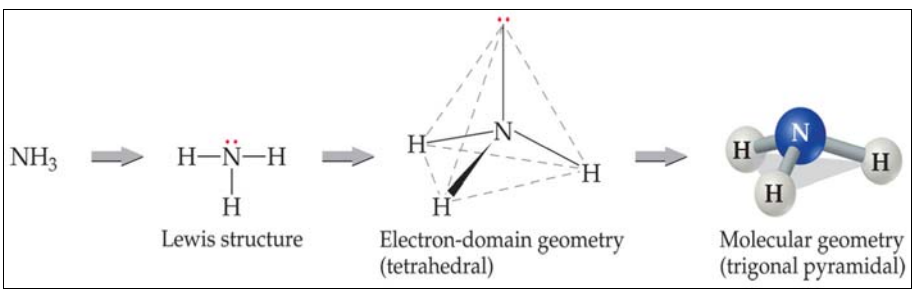
MOLECULAR GEOMETRIES



- The electron-domain geometry is often ***NOT*** the shape of the molecule.
- The **molecular geometry** is defined by the positions of __________________in the molecules, not the nonbonding pairs.

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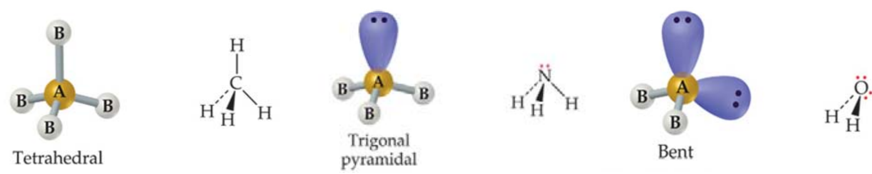
ELECTRON DOMAIN AND MOLECULAR GEOMETRY

- For each **electron domain** geometry, there might be **more than one molecular geometry**.
- All 3 examples have ______electron-domains but each time a bond is replaced by a lone pair a **<u>different</u>** molecular geometry is created.



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LINEAR ELECTRON DOMAIN

- For a linear electron domain, there is only one molecular geometry:_________________

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	Ö=C=Ö

- NOTE: If there are only two atoms in the molecule (eg: CO), the molecule will be linear no matter what the electron domain geometry is.

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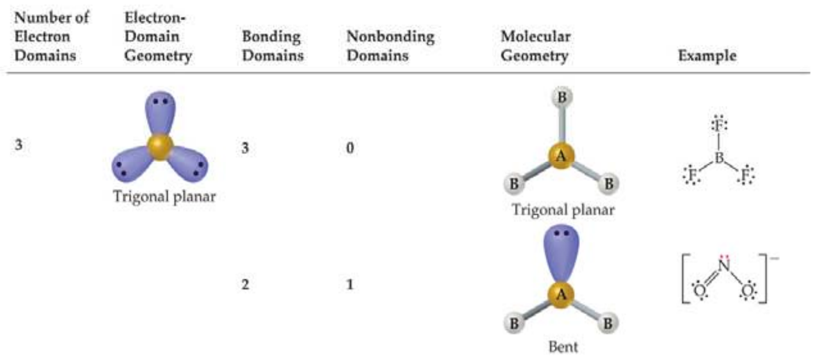
TRIGONAL PLANAR ELECTRON DOMAIN

There are two molecular geometries:

- _______________, if all the electron domains are bonding.
- **Bent,** if one of the domains is a nonbonding pair.



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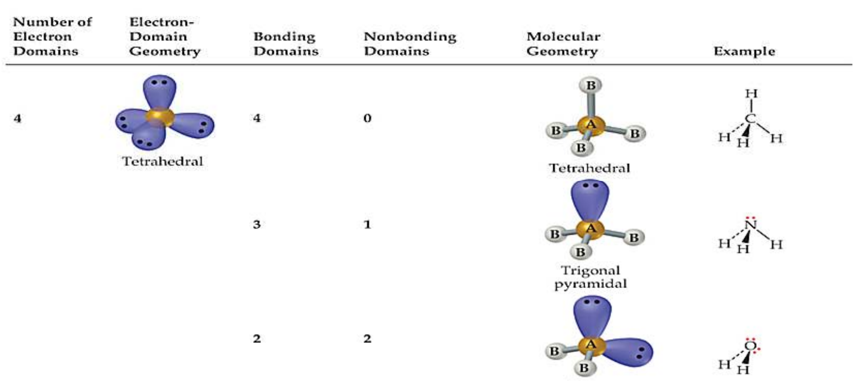
TETRAHEDRAL ELECTRON DOMAIN

There are three molecular geometries:

- **_______________,** if all are bonding pairs.
- **Trigonal pyramidal,** if one is a nonbonding pair.
- **__________,** if there are two nonbonding pairs.



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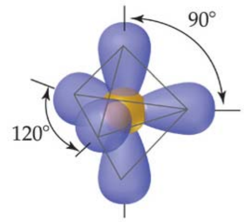
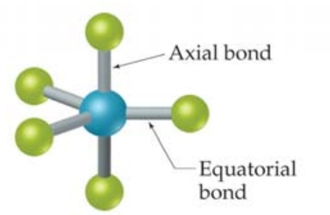
TRIGONAL BIPYRAMIDAL ELECTRON DOMAIN



There are two distinct positions in this geometry:

- Axial
- Equatorial



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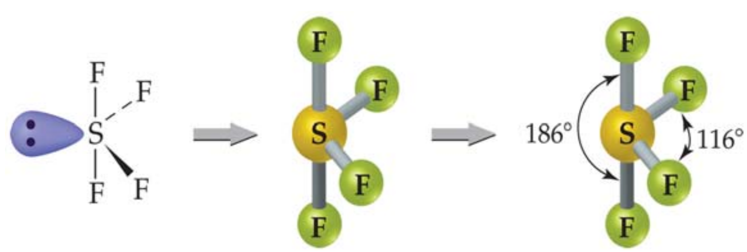
TRIGONAL BIPYRAMIDAL ELECTRON DOMAIN AND NONBONDING ELECTRONS

- If there is one **nonbonding** pair it will occupy an __________ rather than an axial position (____________)



- because an equatorial position is 90° from two other domains whereas an axial position is 90° from three other domains.

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MOLECULAR GEOMETRIES FOR TRIGONAL BIPYRAMIDAL ELECTRON DOMAIN

There are **four** distinct ________**geometries** for this electron domain geometry:

- Trigonal bipyramidal
- Linear
- Seesaw *
- T-shaped *

* Not important for Chem 1028/9

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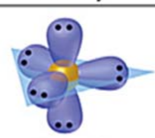
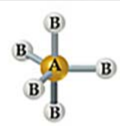
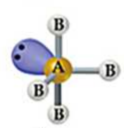
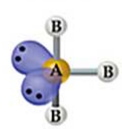
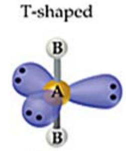
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

Not important for Chem 1028/9

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MOLECULAR GEOMETRIES FOR OCTAHEDRAL ELECTRON DOMAIN

- There are three distinct molecular geometries for this electron domain geometry:
  - ______________
  - Square pyramidal
  - Square planar

- NOTE: All positions are equivalent in the octahedral domain.

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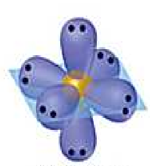
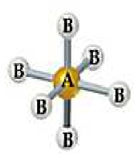
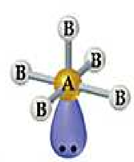
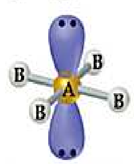
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

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BOND ANGLE

- The bond angle is affected by:
  - the presence of _____________electrons pairs.
  - the presence of ______________bonds.

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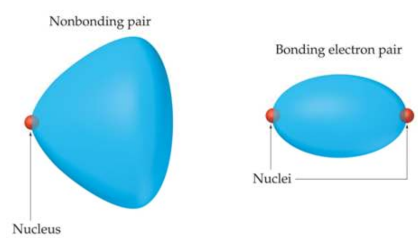
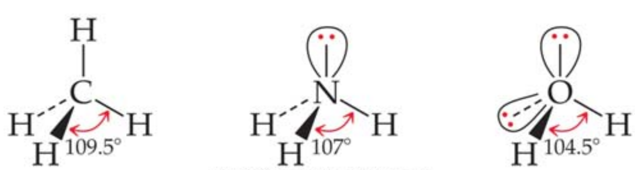
NONBONDING PAIRS AND BOND ANGLE

- Electron domains of nonbonding electron pairs are physically larger than electron domains of bonding pairs.



- Therefore, the repulsions of nonbonding electrons are greater.
- This tends to __________bond angles in a molecule.



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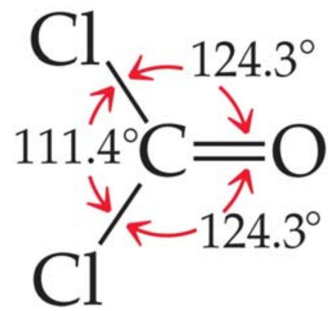
MULTIPLE BONDS AND BOND ANGLES

- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.

- Therefore, they affect bond angles and _____ bond angles result.



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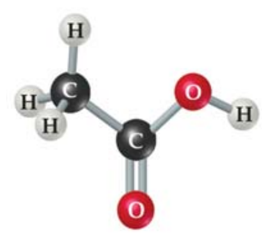
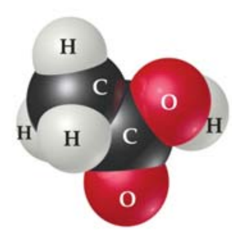
LARGER MOLECULES

In larger molecules, it makes more sense to talk about the geometry <u>about a particular atom</u> rather than the geometry of the molecule as a whole.

This approach makes sense, especially because larger molecules tend to <u>react at a particular site</u> in the molecule.





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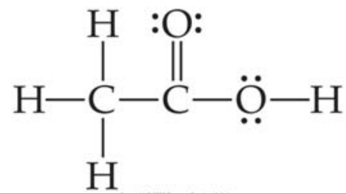
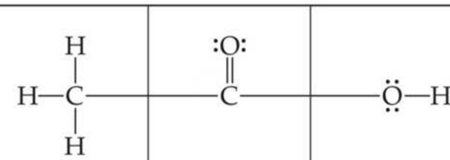
GEOMETRY AROUND ATOMS IN A LARGE MOLECULE

EXAMPLE:





Number of electron domains		3	4
Electron-domain geometry		Trigonal planar	
Predicted bond angles	109.5°	~ 120°	< 109.5°

* Will get deviations in bond angles.

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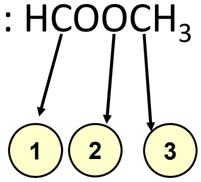
EXAMPLE

Predict the electron domain geometry around the C and O atoms indicated in the following molecule: $HCOOCH_3$



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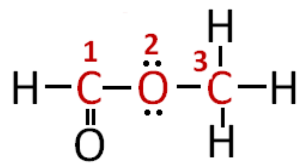
ANSWER



Electron domain geometry:

C-1 –________________________________.

O-2 –________________________________.

C-3 – ________________________________.

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SUMMARY

- **VSEPR Model**
  - Electron domains are regions of electron density.
  - Electron domains are as far apart as possible, to decrease electron-electron repulsion.

- **Molecular Geometry**
  - Arrangement of atoms in space.
  - Molecular geometry is predicted considering the electron domain geometry i.e. the 3D arrangement of the electron domains.

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MOLECULAR SHAPE AND POLARITY

- In Chapter 8 we discussed bond dipoles.
- In a covalent bond electrons are not necessarily ______________________between two atoms.
- But just because a molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.

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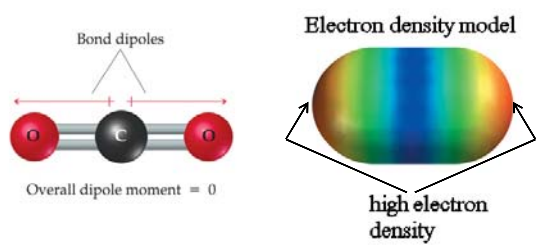
EXAMPLE: CARBON DIOXIDE CO_2



- Electrons are not shared equally between C and O.
- Therefore each C=O bond is polar and has a dipole moment, which are equal in magnitude but exactly oppose each other.
- The ________________ is therefore **zero** and the molecule is **non-polar.**

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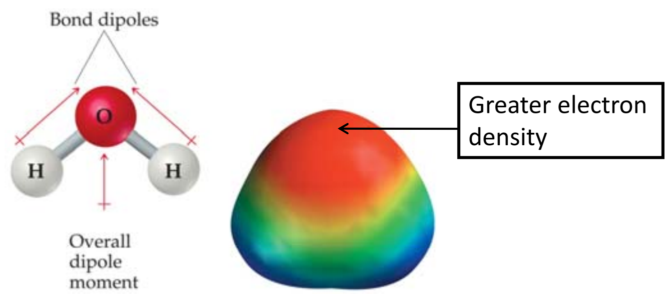
EXAMPLE: WATER, H_2O

- In the water molecule the bond dipoles are equal in magnitude but they do not exactly oppose each other



- Therefore the dipole moments add up to zero and the H_2O molecule is_____________.

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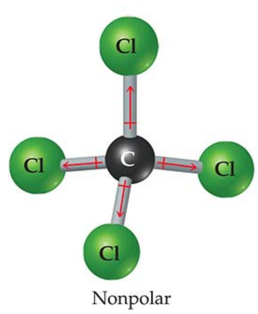
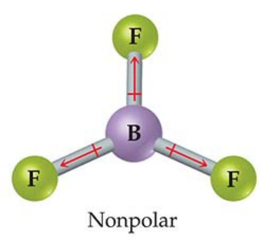
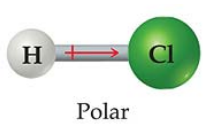
POLARITY DEPENDS ON POLARITY OF BONDS AND SHAPE OF THE MOLECULE

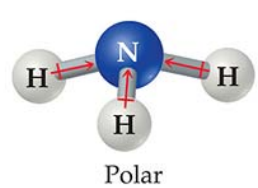
_____________ molecules with polar bonds are non-polar.

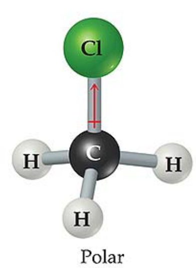
Asymmetrical molecules with polar bonds are polar.











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WHY DO WE CONSIDER POLARITY?

- Polarity of molecules affects the __________ properties of the substance such as melting point, boiling point and solubility.
- For example, non-polar molecules, such as fats, will dissolve in hydrocarbons, which are non-polar.
- Similarly, polar molecules like acids, salts, etc. will dissolve in H_2O, which is polar.
- The general rule is:_________________________

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VALENCE BOND THEORY

- An extension of Lewis's notion of electron pair bonds.
- Covalent bonds are formed when atomic orbitals on neighbouring atoms overlap one another.
- The overlap region is favourable for the two electrons because of their attraction to the two nuclei.
- The greater the overlap, the ___________the bond.

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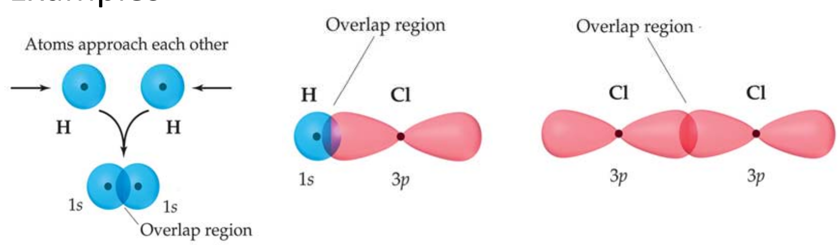
COVALENT BONDING AND ORBITAL OVERLAP

- We think of covalent bonds forming through the _________of electrons by adjacent atoms.
- In such an approach this can only occur when orbitals on the two atoms_____________.
- Examples



H_2 HCl Cl_2

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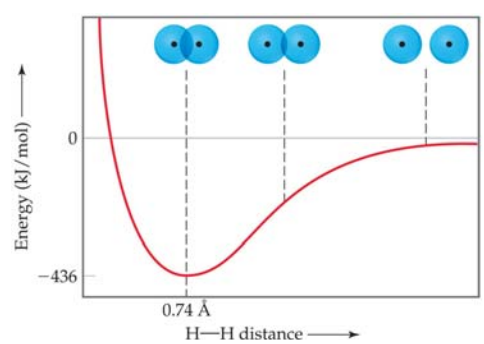
OVERLAP AND BONDING IN H_2

- Increased overlap brings the electrons and _________closer together while simultaneously decreasing electron-electron repulsion. Thus, the energy of the system decreases.



- Energy is at a minimum at _________Å which is the equilibrium bond distance in the H_2 molecule.
- However, if atoms get too close, the internuclear repulsion greatly raises the energy.

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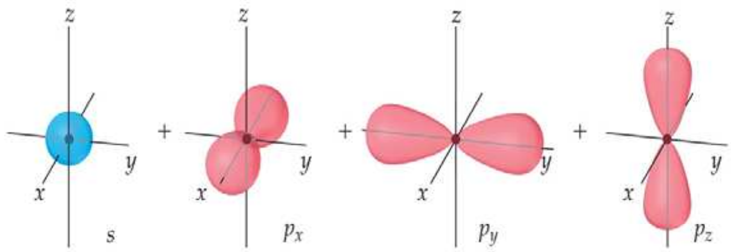
HYBRID ORBITALS

- It's hard to imagine tetrahedral, trigonal bipyramidal, and other geometries arising from the atomic orbitals we recognize.



- To explain these molecular geometries, we assume that atomic orbitals (usually of the central atom) mix to form new orbitals, called___________________.

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HYBRIDIZATION

- Hybridization is a process of mixing different types of atomic orbitals to produce a set of equivalent hybrid orbitals.

- The three common types of hybridization to be considered in this course are:

____

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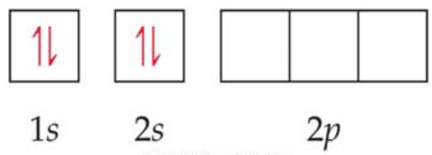
sp HYBRID ORBITALS

Example: **BeF_2**

- Consider **beryllium**:

  In its ground electronic state, $1s^2\ 2s^2$, it would **not** be able to form bonds because it has no singly-occupied orbitals.



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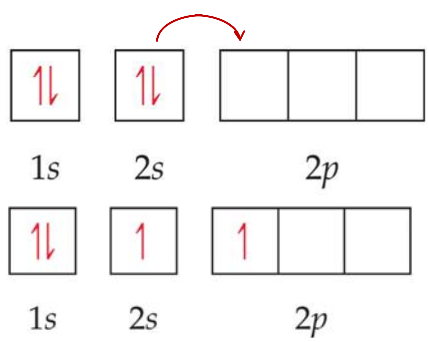
- But if **Be** absorbs the small amount of energy needed to __________ an electron from the 2*s* to the 2*p* orbital, the result is two unpaired electrons.



- Now Be can form two bonds.
- However the two bonds would not be identical because one electron is in 2s and the other in 2p.
- Therefore, this has not explained the BeF_2 structure.

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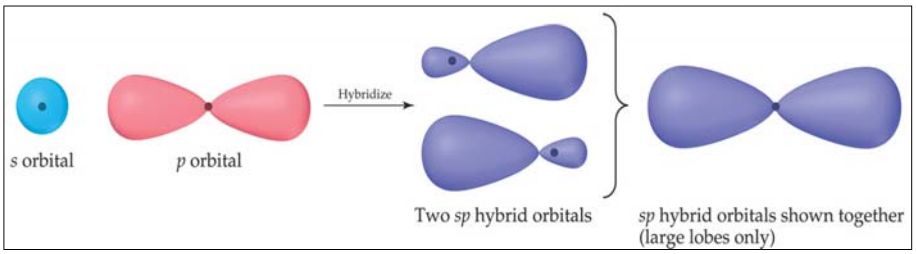
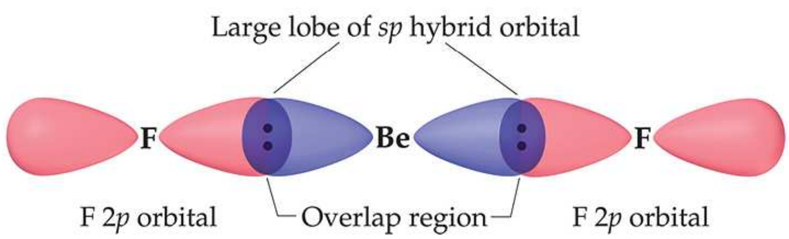
FORMATION OF sp HYBRID ORBITALS

- This problem can be solved by mixing the **s** and **p** atomic orbitals to yield **two** degenerate orbitals that are ________of these two orbitals.(_________________________________)
- These **sp** hybrid orbitals have two lobes (like a p orbital). One of the lobes is larger and more rounded than the other.



sp HYBRID ORBITALS IN THE BeF_2 MOLECULE

- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of beryllium compounds:_____________.



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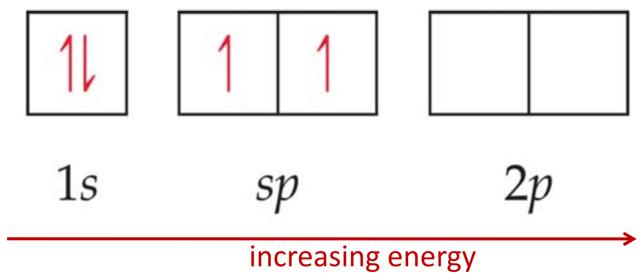
ENERGY OF sp HYBRID ORBITALS

- With hybrid orbitals, the orbital diagram for beryllium would look like this.



- The _____orbitals are higher in energy than the 1*s* orbital but lower than the ___orbitals, ***which are obviously not hybridized*.**

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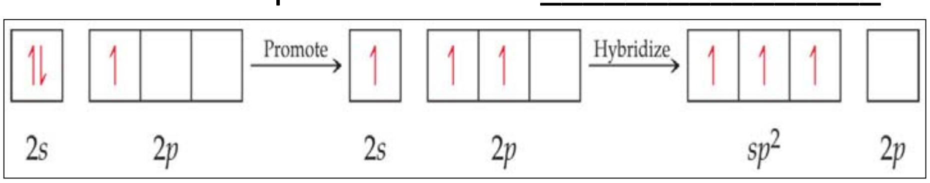
sp^2 HYBRID ORBITALS

Example: BF_3

- Electron configuration of boron is $1s^2\ 2s^2\ 2p^1$ i.e. boron has 3 valence electrons.
- The 2s orbital and two 2p orbitals of B mix to form three sp^2 orbitals.
- One of the p orbitals is left__________________



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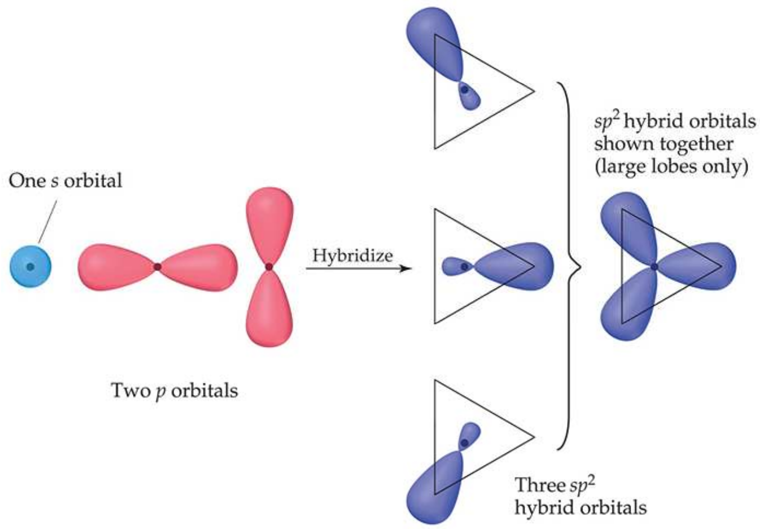
FORMATION OF sp^2 HYBRID ORBITALS

Three degenerate sp^2 orbitals are formed.



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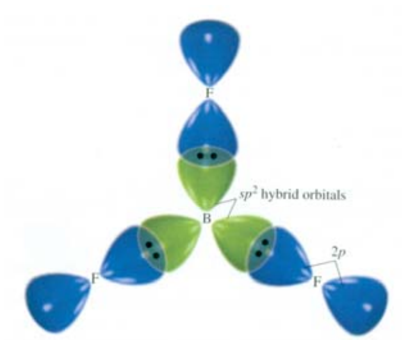
THE BF_3 MOLECULE

- The three degenerate _____orbitals align themselves __________from each other.
- Therefore the molecular geometry of the BF_3 molecule is **trigonal planar.**

- Fluorine :__________.
- A σ bond is formed between one 2p orbital of each fluorine and each of the *sp*[2] orbitals.



Unshared pairs of electrons on F atoms are not shown.

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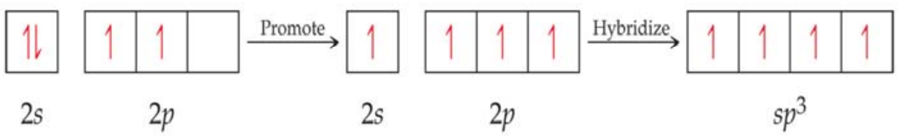
sp^3 HYBRID ORBITALS

Examples: CH_4 and CF_4

With carbon, which has the electron configuration $1s^2\ 2s^2\ 2p^2$, we get four_____ hybridized orbitals.



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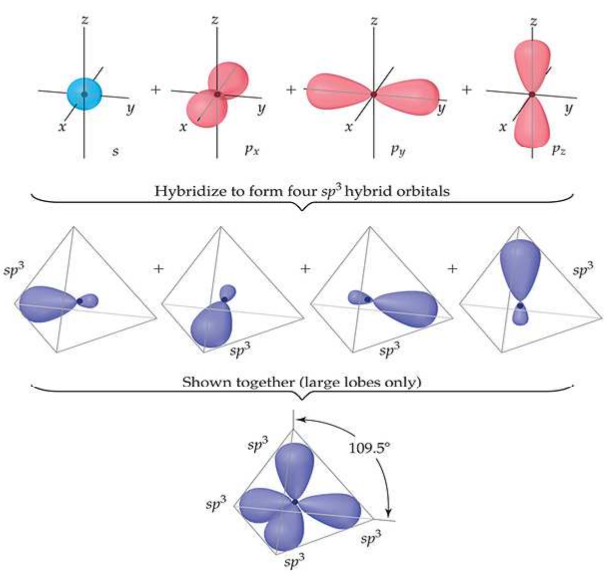
FORMATION OF sp^3 HYBRID ORBITALS

Four degenerate *sp^3* orbitals.



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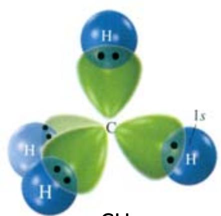
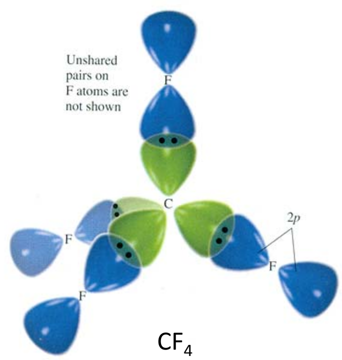
CH_4 AND CF_4 MOLECULES

- The four degenerate *sp^3* orbitals align themselves 109.5° from each other.
- Therefore the molecular geometry of both CH_4 and CF_4 molecules is______________



CH_4



CF_4

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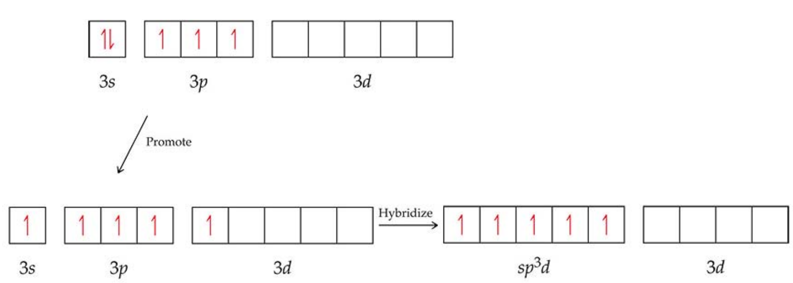
HYBRIDIZATION USING *d* ORBITALS

(Just to note, not important for Chem 1028/9.)

For geometries involving <u>expanded octets</u> on the central atom, we must use *d* orbitals in our hybrids.



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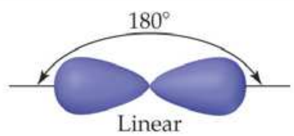
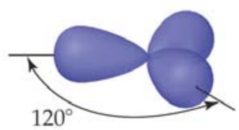
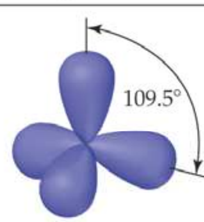
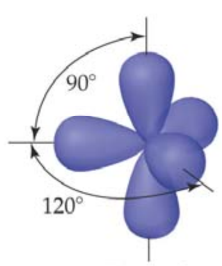
HYBRID ORBITAL SUMMARY

Once you know the **electron-domain geometry**, you know the hybridization state of the atom.

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+
s,p,p,p,d	Five sp^3d	 Trigonal bipyramidal	PF_5, SF_4, BrF_3

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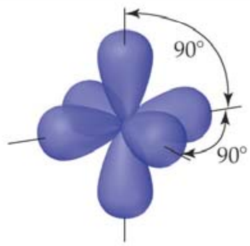
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p,p,p,d,d	Six sp^3d^2	 Octahedral	SF_6, ClF_5, XeF_4, PF_6^-

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SUMMARY

Electron domains around central atom	Number of hybrid orbitals	Hybridization around central atom	Electron domain geometry
2	2		**Linear** (BeF_2,CO_2,HCN) angle ~180°
3	3		**Trigonal planar** (BF_3,H_2CO,Cl_2CO) angle ~120°
4	4		**Tetrahedral** (CH_4,NH_3,CCl_4) angle ~ 109,5°

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EXAMPLE

Determine the hybridization experienced by the central atom of each of the following molecules. Determine both the <u>electron domain geometry and the molecular geometry</u> of the molecules/ions.

NH_3, NH_4^+, Cl_2CO, HCN, BF_3, CH_4

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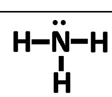
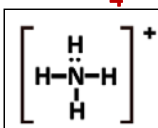
ANSWER

- **NH_3**

Lewis Symbol	Electron domains around central atom	Number of hybrid orbitals	Hybridiza-tion around central atom	Electron domain geometry	Molecular geometry
				tetrahedral	trigonal pyramidal

- **NH_4^+**

	4		sp^3		tetrahedral

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ANSWER

- Cl_2CO

Lewis Symbol	Electron domains around central atom	Number of hybrid orbitals	Hybridiza-tion around central atom	Electron domain geometry	Molecular geometry
	3	3	sp^2	trigonal planar	

- HCN

	2	2		linear	linear

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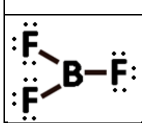
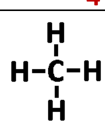
- BF_3

Lewis Symbol	Electron domains around central atom	Number of hybrid orbitals	Hybridiza-tion around central atom	Electron domain geometry	Molecular geometry
				**trigonal planar**	**trigonal planar**

- CH_4

	**4**	**4**		**tetrahedral**	**tetrahedral**

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ORBITAL OVERLAP IN COVALENT BONDS

There are two ways orbitals can overlap to form bonds between atoms:

- head-to-head and
- side-to-side overlap.

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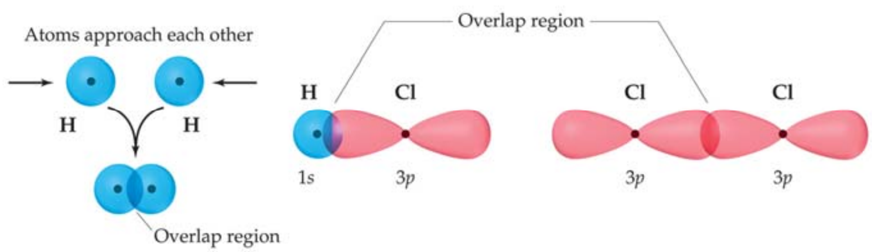
SIGMA (σ) BONDS



Sigma bonds are characterized by:

- _______________overlap (or end-on overlap).
- Electron density concentrated along a line connecting the nuclei i.e. the internuclear axis.

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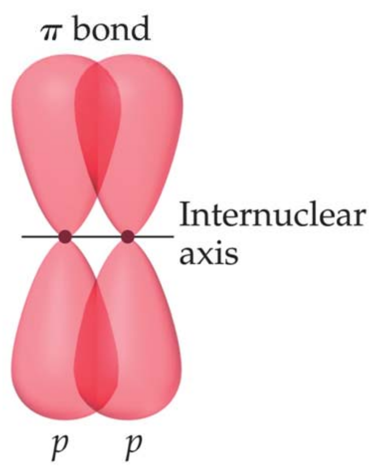
PI (π) BONDS

Pi bonds are characterized by:

- __________ overlap.
- Electron density above and below the internuclear axis.



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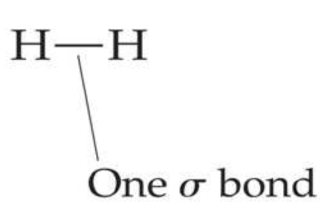
SINGLE BONDS

- Single bonds are always **σ bonds.**
- Because σ overlap is greater, a stronger and more energy lowering bond results.



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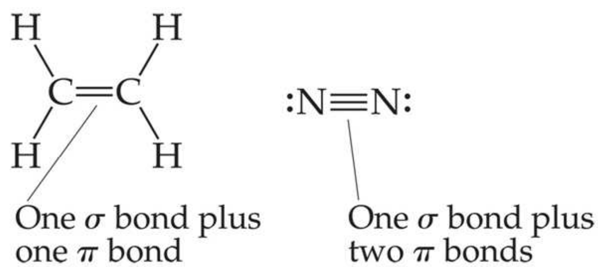
MULTIPLE BONDS

In a multiple bond one of the bonds is a **σ bond** and the rest are ____**bonds**.



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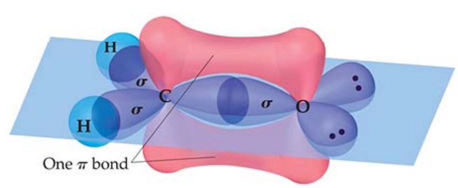
DOUBLE BONDS

Consider a molecule of formaldehyde:

- An ***sp*² orbital** on carbon overlaps **head-to-head** with the corresponding orbital on the oxygen, to form a **σ bond.**
- The **unhybridized *p* orbitals** overlap, side-to-side, to form a ____________.



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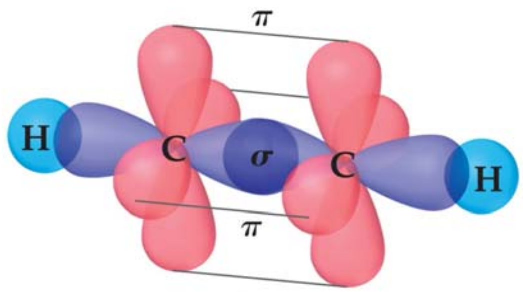
TRIPLE BONDS

In triple bonds, as in acetylene, ethyne, (C_2H_2):

- **Two *sp* orbitals** overlap in σ fashion to form a **σ bond** between the carbons.
- **Two pairs of unhybridized**

  ***p* orbitals** overlap in π fashion to form the **two π bonds.**



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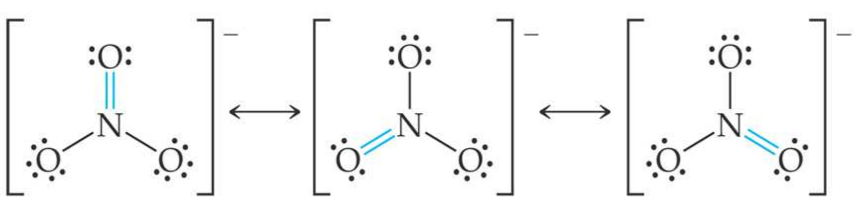
RESONANCE

We have already seen that when writing Lewis structures for species like the nitrate ion, we draw resonance structures to reflect more accurately the structure of the molecule or ion.



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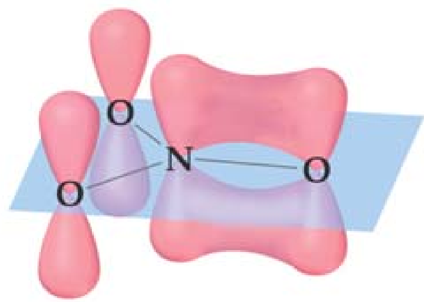
DELOCALIZED ELECTRONS AND RESONANCE

- In reality, each of the four atoms in the nitrate ion has a ____orbital.



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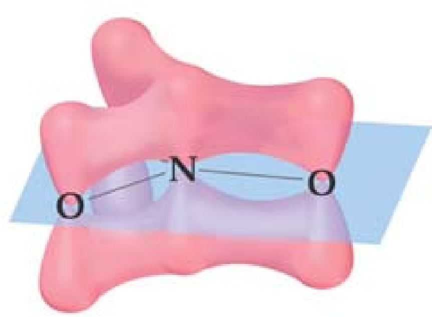
- The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen.
- This means the π electrons __________ localized between the nitrogen and one of the oxygens, but rather are __________ throughout the ion.



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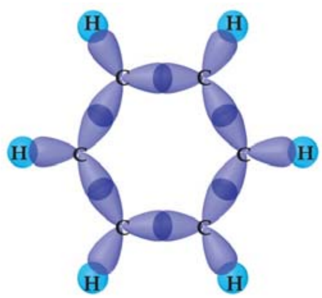
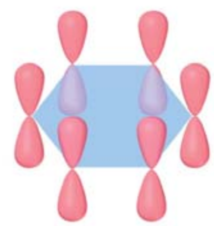
RESONANCE IN BENZENE

The organic molecule benzene, C_6H_6, has six σ bonds and a *p* orbital on each carbon atom.





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- In reality the _____________in benzene are not localized, but **delocalized**.
- The even distribution of the π electrons in benzene makes the molecule unusually________

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EXAMPLE

1) Describe how the bonds in ethene, C_2H_4, are formed in terms of overlaps of appropriate hybridized and unhybridized orbitals. Use the VSEPR model to decide on the electron domain and molecular geometry of the molecule.
2) Do the same for ethyne, C_2H_2

(draw the molecules and the orbitals involved)

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ANSWER

1) **Ethene, C_2H_4 : $H_2C{=}CH_2$**

- The 2s orbital and two 2p orbitals of each carbon form three sp^2 hybrid orbitals.
- These each form three σ bonds:
  - two by the overlap with the 1s orbital of the hydrogen atoms and
  - the third by the overlap of the sp^2 orbitals of each carbon.
- The single unhybridized 2p orbitals on each carbon atom overlap with each other side-to-side to form a π bond.

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- Electron domain geometry – 3 electron domains, therefore_________________.
- No nonbonding electrons therefore molecular geometry is also__________________.

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2) **Ethyne, C_2H_2 : HC ≡ CH**

- The 2s orbital and one 2p orbital of each carbon atom form two sp hybrid orbitals.
- These each form two σ bonds:
  - one by the overlap between the 1s orbital of a hydrogen atom and
  - the second by the overlap of the sp orbitals of each carbon.
- There are two unhybridized 2p orbitals on each carbon. These unhybridized 2p orbitals on each carbon atom overlap with each other side-to-side to form two π bonds.

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- Electron domain geometry – 2 electron domains, therefore__________

- No ___________electrons therefore molecular geometry is also_________

MODELS OF COVALENT BONDING - Summary

- **Lewis structures**

  Covalent bonding - atoms share electrons.

- **VSEPR theory**
  - Predicts shapes of molecules, but does not explain why bonds exist between atoms.
  - Limitations: Does not relate shape of molecules to atomic orbitals.

- **Valence-bond theory**
  - Valence atomic orbitals share a region in space i.e. they overlap.
  - Limitations: Explains bonding in simple diatomic molecules only.

- **Hybridization**
  - Explains bonding and shapes of polyatomic molecules.
  - Atomic orbitals of an atom mix to produce hybrid orbitals. Better overlap therefore stronger bonding.
  - Limitations: Does not explain magnetic properties of substances.

- **Molecular Orbital theory**

(Not important for Chem 1028/1029)

END OF CHAPTER

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