

Chapter 8

"Periodic Properties of the Elements"

Q12: What is the n value for Fe?

A. 5

B. 4

C. 3

D. 2

n value = the last  $e^-$  filled

Mendeleev

- Order elements by atomic mass
- Saw a repeating pattern of properties
- Periodic Law** – When the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically
- Put elements with similar properties in the same column

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Mendeleev's Predictions

Gallium (meta-aluminum)			Germanium (neo-silicon)		
	Mendeleev's predicted properties	Actual properties		Mendeleev's predicted properties	Actual properties
Atomic mass	About 60 amu	69.72 amu	Atomic mass	About 23 amu	27.67 amu
Boiling point	Low	20.2 °C	Boiling point	High	31.8 °C
Density	5.9 g/cm <sup>3</sup>	5.9 g/cm <sup>3</sup>	Density	5.3 g/cm <sup>3</sup>	5.35 g/cm <sup>3</sup>
Formula of oxide	$Al_2O_3$	$Ga_2O_3$	Formula of oxide	$NO_2$	$GeO_2$
Formula of chloride	$AlCl_3$	$GaCl_3$	Formula of chloride	$NaCl$	$GeCl_4$
Formula of fluoride	$AlF_3$		Formula of fluoride		

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## What vs. Why

- Mendeleev's Periodic Law allows us to predict what the properties of an element will be based on its position on the table
- it doesn't explain why the pattern exists
- Quantum Mechanics is a theory that explains why the periodic trends in the properties exist

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## Electron Spin: the 4th number

- Experiments by Stern and Gerlach showed a beam of silver atoms is split in two by a magnetic field
- The experiment reveals that the electrons spin on their axis as they spin, they generate a magnetic field

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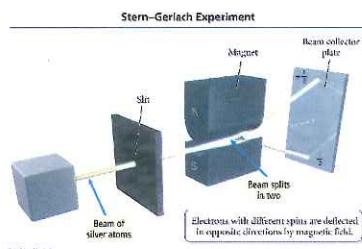


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## Electron Spin Experiment




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if asked e<sup>-</sup> configuration in Theory  
then do not consider the exceptions

if asked actual then do consider the  
exception

### Spin Quantum Number, $m_s$

- Spin quantum number describes how the electron spins on its axis
  - clockwise or counterclockwise
  - spin up or spin down
- Spins must cancel in an orbital
  - paired when they cancel 1 $\downarrow$
- $m_s$  can have values of  $\pm\frac{1}{2}$

Know for multiple choice

### Pauli Exclusion Principle

- No two electrons in an atom may have the same set of 4 quantum numbers
- Therefore no orbital may have more than 2 electrons, and they must have with opposite spins
  - s sublevel has 1 orbital, therefore it can hold 2 electrons
  - p sublevel has 3 orbitals, therefore it can hold 6 electrons
  - d sublevel has 5 orbitals, therefore it can hold 10 electrons
  - f sublevel has 7 orbitals, therefore it can hold 14 electrons

### Allowed Quantum Numbers

$$n = 10$$

$$l = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9$$

$$m_l = \begin{matrix} \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 1, 3, 5, 7, 9, 11, 13, 15, 17, 19 \end{matrix}$$

$$\# \text{ of } \downarrow = 2, 6, 10, 14, 18, 22, 26, 30, 34, 38$$

possible

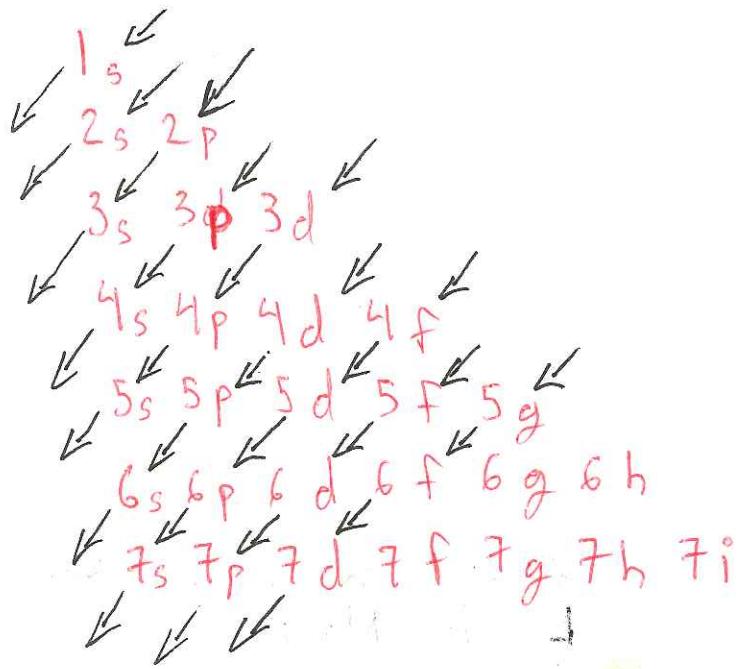
Quiz: What is the value  
of  $n$ ?

A. 0

B. 1

C. 2

D. 3



## Electron Configuration

- The **ground state** of the electron is the lowest energy orbital it can occupy
- The distribution of electrons into the various orbitals in an atom in its ground state is called its **electron configuration**  $1s^2 2s^2 2p^1$ 
  - Orbital Diagrams: Show electrons as arrows
  - Electron Configuration: show electrons as a superscript number  $1s^2 2s^2 2p^1$
  - Condensed Notation: show the electron configuration with a noble gas being used in place of the inner core electrons  $[He] 2s^2$

## Order of Subshell Filling in Ground State Electron Configurations

1s
2s      2p
3s      3p      3d
4s      4p      4d      4f
5s      5p      5d      5f
6s      6p      6d
7s

**Know this:**

Cu, Ag, Au

Theory Predicts:  $s^2 d^9$

Actual:  $s^1 d^{10}$

## Filling the Orbitals with Electrons

- Energy shells fill from lowest energy to high
- Subshells fill from lowest energy to high
  - $s \rightarrow p \rightarrow d \rightarrow f$
  - Aufbau Principle
- Orbitals that are in the same subshell have the same energy
- No more than 2 electrons per orbital
  - Pauli Exclusion Principle
- When filling orbitals that have the same energy, place one electron in each before completing pairs
  - Hund's Rule

**Know this:**

Cr, Mo

Theory Predicts:  $s^2 d^4$

Actual:  $s^1 d^5$



## Examples

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## Valence Electrons

- The electrons in all the subshells with the highest principal energy shell are called the **valence electrons**
- Electrons in lower energy shells are called **core electrons**

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## Electron Configuration & the Periodic Table

- The Group number corresponds to the number of valence electrons
- The length of each "block" is the maximum number of electrons the sublevel can hold
- The Period number corresponds to the principal energy level of the valence electrons



block P can fit 6 e<sup>-</sup>

Valence shell = row

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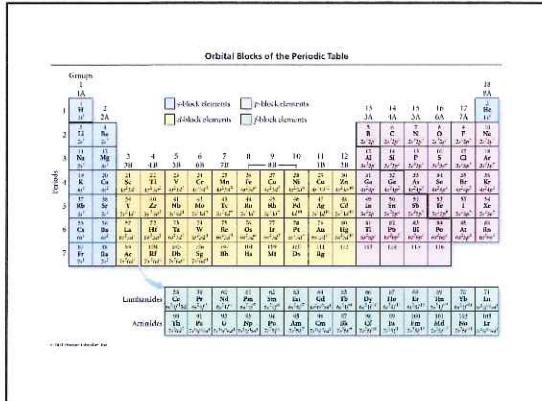


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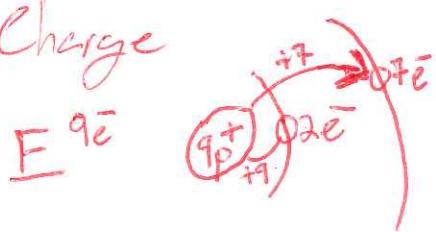
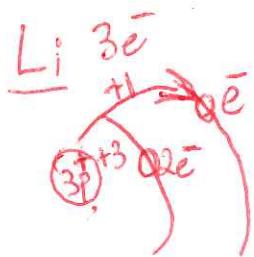
## Properties & Electron Configuration

- Elements in the same column have similar chemical and physical properties because they have the same number of valence electrons in the same kinds of orbitals**

## Electron Configuration & Ion Charge

- We have seen that many metals and nonmetals form one ion, and that the charge on that ion is predictable based on its position on the Periodic Table
  - Group 1A = +1, Group 2A = +2, Group 7A = -1, Group 6A = -2, etc.
- These atoms form ions that will result in an electron configuration that is the same as the nearest noble gas

Effective Nuclear Charge



### Electron Configuration of Anions in their Ground State

- Anions are formed when atoms gain enough electrons to have 8 valence electrons
  - filling the s and p sublevels of the valence shell

Quiz: Sodium Ion is larger than Sodium metal  
 $\text{Na}^+ > \text{Na}$ ?



False

### Electron Configuration of Cations in their Ground State

- Cations are formed when an atom loses all its valence electrons
  - resulting in a new lower energy level valence shell
  - however the process is always endothermic

### Effective Nuclear Charge

- In a multi-electron system, electrons are simultaneously attracted to the nucleus and repelled by each other
- Outer electrons are **shielded** from full strength of nucleus
  - screening effect
- **Effective nuclear charge** is net positive charge that is attracting a particular electron

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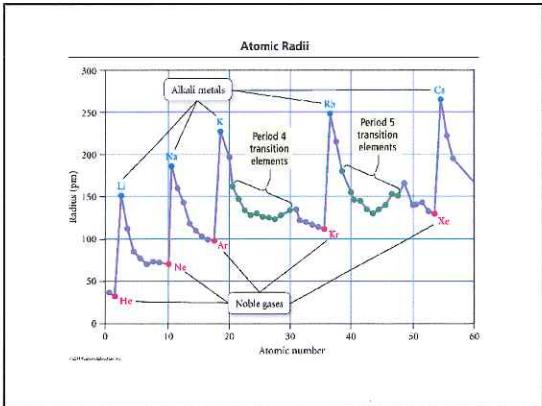


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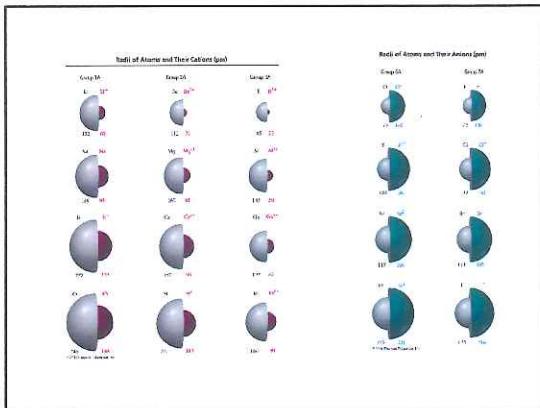
### Magnetic Properties of Transition Metal Atoms & Ions

- Electron configurations that result in unpaired electrons mean that the atom or ion will have a net magnetic field – this is called **paramagnetism**
  - will be attracted to a magnetic field
- Electron configurations that result in all paired electrons mean that the atom or ion will have no magnetic field – this is called **diamagnetism**
  - slightly repelled by a magnetic field

### Trends in Ionic Radius

- Ions in same group have same charge
- Ion size increases down the group
  - higher valence shell, larger
- Cations smaller than neutral atom;
- Anions bigger than neutral atom
- Cations smaller than anions






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### Ionization energy

- Minimum energy needed to remove an electron from an atom
  - gas state
  - endothermic process
  - valence electron easiest to remove

The bigger the atom  
the easier it is to  
give up an  $e^-$  since  
those valence  $e^-$  are  
ready to go

Quiz: Which of the  
following elements  
would have the easiest  
time ionizing?

### General Trends in 1<sup>st</sup> Ionization Energy

- Larger the effective nuclear charge on the electron, the more energy it takes to remove it
- the farther the most probable distance the electron is from the nucleus, the less energy it takes to remove it
- 1st IE **decreases** down the group
  - valence electron farther from nucleus
- 1st IE generally **increases** across the period
  - effective nuclear charge increases

- ✓ A. K      B. Mg  
C. Al      D. Si



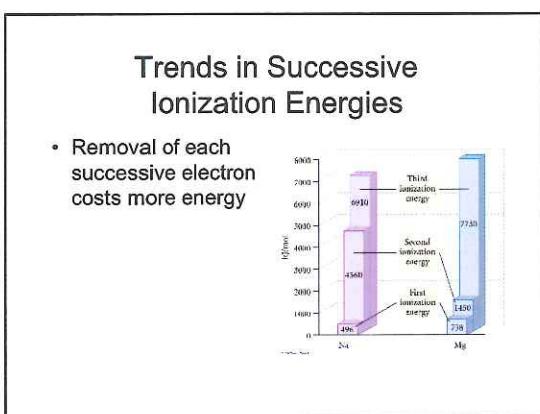
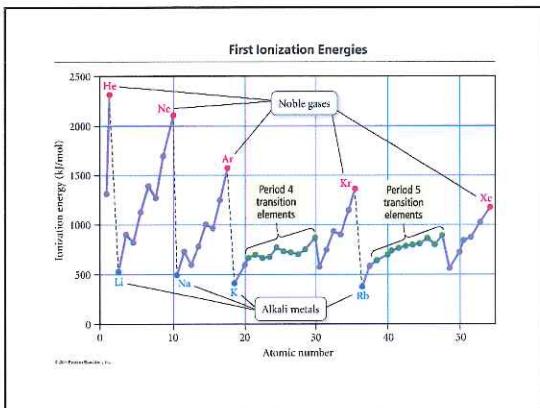


TABLE 8.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)						
Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>
Na	496	4550				
Mg	738	1450	7730			
Al	578	1820	2750	11,500		
Si	786	1380	3250	4380	10,100	
P	1012	1900	2910	4950	6770	22,200
S	1080	2250	3360	4500	7010	8800
Cl	1251	2300	3220	5180	6540	9460
Ar	1521	2070	3930	5770	7240	8780

Core electrons

Core e<sup>-</sup> take a whole lot more energy to remove



## Trends in Electron Affinity

- Energy released when a neutral atom gains an electron
- Defined as exothermic (-), but may actually be endothermic (+)
- More energy released (more -); the larger the EA
- Generally increases across period

Electron wanting

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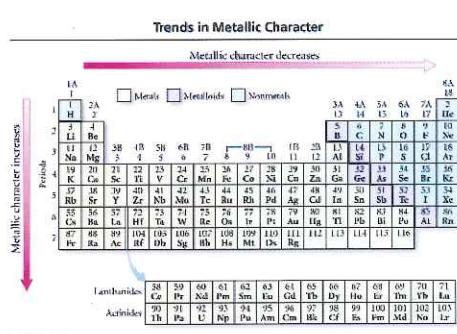
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## Metallic Character

- Metals
  - malleable & ductile
  - shiny, lusterous, reflect light
  - conduct heat and electricity
  - most oxides basic and ionic
  - form cations in solution
  - lose electrons in reactions - oxidized
- Nonmetals
  - brittle in solid state
  - dull
  - electrical and thermal insulators
  - most oxides are acidic and molecular
  - form anions and polyatomic anions
  - gain electrons in reactions - reduced

\*metallic character increases left

\*metallic character increase down





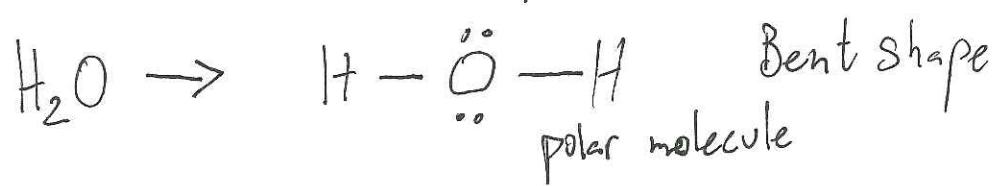
### Trends in the Noble Gases

- Atomic radius increases down the column
- Ionization energy decreases down the column
  - very high IE
- Very unreactive
  - only found uncombined in nature
  - used as "inert" atmosphere when reactions with other gases would be undesirable
- Melting point and boiling point increases down the column
  - all gases at room temperature
  - very low boiling points
- Density increases down the column
  - in general, the increase in mass is greater than the increase in volume

The End

Concepts needed

E<sub>PQ</sub> Tetrahedral



**Chapter 9**

"Chemical Bonding I: Lewis Theory"

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### Bonding

- Explain how and why atoms attach together
- Explain why some combinations of atoms are stable and others are not
- One of the simplest bonding theories is called **Lewis Theory**, it emphasizes valence electrons to explain bonding
- Using Lewis Theory, we can draw models – called **Lewis structures** (Electron Dot Structures)

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**Bonding**

A chemical bond forms when the potential energy of the bonded atoms is less than the potential energy of the separate atoms

- Have to consider following interactions:
  - nucleus-to-nucleus repulsion
  - electron-to-electron repulsion
  - nucleus-to-electron attraction

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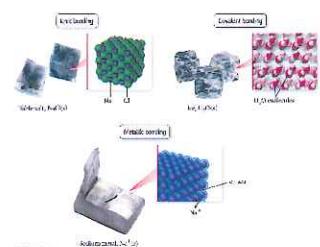
### Types of Bonds

Types of Atoms	Type of Bond	Bond Characteristic
metals to nonmetals	Ionic	electrons transferred
nonmetals to nonmetals	Covalent	electrons shared
metal to metal	Metallic	electrons pooled

Polyatomic ions

have metals doing  
covalent bonds with  
non-metal

### Types of Bonds



### Ionic Bonding

- When metals bond to nonmetals, some electrons from the metal atoms are transferred to the nonmetal atoms
- An ionic compound is held together by an electrostatic interaction

held together by an  
electrostatic interaction

if you see a polyatomic  
ion it is automatically  
an ionic bond



## Covalent Bonding

- Nonmetals have relatively high ionization energies, so it is difficult to remove electrons from them
- When nonmetals bond together, it is better in terms of potential energy for the atoms to share valence electrons
- Shared electrons hold the atoms together by attracting nuclei of both atoms

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## Lewis Symbols of Atoms

- AKA electron dot symbols
  - Uses the symbol of element to represent nucleus and inner electrons
  - Uses dots around the symbol to represent valence electrons
- ~~• C but should be C:~~



Dot placement is very crucial

"S" shell on the right side of the element &  
"P" shell around

## Review: Octet Rule

- When atoms bond, they tend to gain, lose, or share electrons to result in 8 valence electrons
- $ns^2np^6$
- There are many exceptions

Quiz: How many valence e<sup>-</sup> does Oxygen have?

A: 4

✓ B: 6

C: 8

D: 10



## Energetics of Ionic Bond Formation

- The ionization energy of the metal is endothermic
- The electron affinity of the nonmetal is exothermic
- The ionization energy of the metal is larger than the electron affinity of the nonmetal, therefore the formation of the ionic compound should be endothermic but the heat of formation of most ionic compounds is exothermic and generally large; Why?

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## Ionic Bonds

- Electrostatic attraction is nondirectional!
  - no direct anion-cation pair
- Ions are arranged in a pattern called a **crystal lattice**
  - every cation surrounded by anions; and every anion surrounded by cations
  - maximizes attractions between + and - ions

Heat is produced because a large amount of energy is used on attraction & when it reaches a stable state it can release a lot of energy or Heat

## Covalent Bonding: Bonding and Lone Pair Electrons

- Covalent bonding results when atoms share pairs of electrons to achieve an "octet"
- Electrons that are shared by atoms are called **bonding pairs** → BP
- Electrons that are not shared by atoms but belong to a particular atom are called **lone pairs**

BE - bonding  $\bar{e}$

BP - bonding pair

LP - lone pairs

LE - lone  $\bar{e}$



## Covalent Bonding Predictions from Lewis Theory

- Lewis theory allows us to predict the formulas of molecules
- Lewis theory predicts that some combinations should be stable, while others should not
- Lewis theory predicts in covalent bonding that the attractions between atoms are **directional**

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## Bond Polarity

- Covalent bonding between unlike atoms results in **unequal sharing of the electrons**
  - one atom pulls the electrons in the bond closer to its side
- The result is a **polar covalent bond**
  - the end with the larger electron density gets a partial negative charge
  - the end that is electron deficient gets a partial positive charge

*Partial = Not exactly +1 charge or -1*

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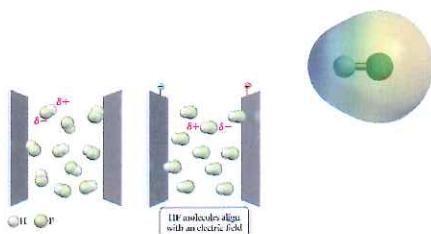


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## Example: HF




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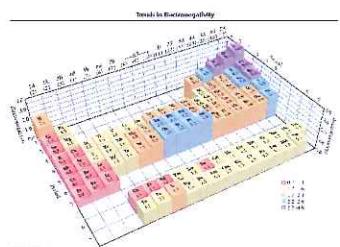


### Electronegativity

- Measure of the pull an atom has on bonding electrons
  - Increases across period (left to right)
  - Decreases down group (top to bottom)
- The larger the difference in electronegativity, the more polar the bond

Pg 373 has a very important table

### Electronegativity



On homework use this charge table

Ex: HF

$$H = 2.1 \quad F = 4.0$$

$$= 2.1 - 4.0$$

$$= \boxed{1.9}$$

### Electronegativity

- If the difference is 0, the bond is **pure covalent**
- If the difference is 0.1 to 0.4, the bond is **nonpolar covalent**
- If the difference is between 0.5 to 1.9, the bond is **polar covalent**
- If the difference is larger than or equal to 2.0, the bond is **ionic**

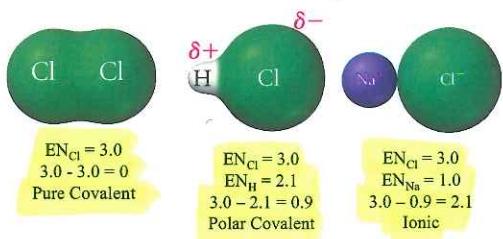
You can only have values up to one decimal place so 0.49 does not exist

Quiz: For a polar covalent bond the difference in electronegativity is greater than:

✓ 0.4

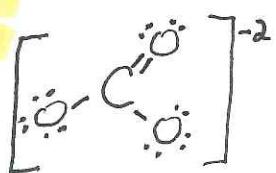


## Bond Polarity



## Writing Lewis Structures of Molecules or Polyatomic Ions

- Count valence electrons
  - sum the valence electrons for each atom
  - add 1 electron for each - charge
  - subtract 1 electron for each + charge



$$\begin{array}{r} 24 \\ -6 \\ \hline 18 \end{array}$$

## Writing Lewis Structures of Molecules or Polyatomic Ions

- H always terminal
- make least electronegative atom central





### Writing Lewis Structures of Molecules or Polyatomic Ions

Attach central atom to the surrounding atoms with pairs of electrons and subtract from the total

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### Writing Lewis Structures of Molecules or Polyatomic Ions

Complete octets, outside-in

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### Writing Lewis Structures of Molecules or Polyatomic Ions

If all octets complete, give extra electrons to central atom.

- elements with *d* orbitals can have more than 8 electrons
  - Period 3 and below



$$\begin{array}{r} 40 \\ -10 \\ \hline 30 \end{array}$$

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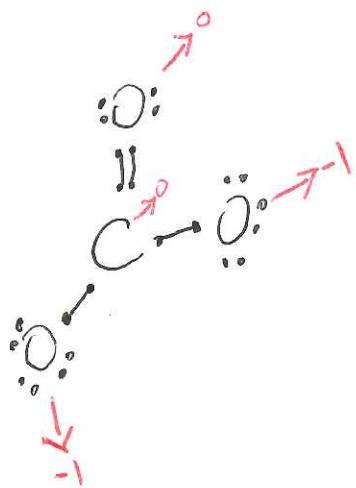
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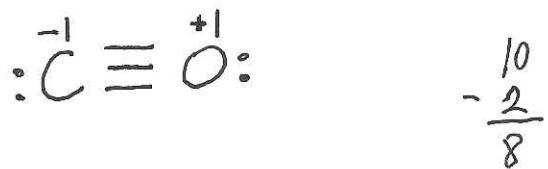


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Overall charge of  
this molecule is  
 $-\frac{2}{3}$

\* The  $-2e^-$  divided  
by all the possible  
terminal atoms that  
can house these  $e^-$



### Writing Lewis Structures of Molecules or Polyatomic Ions

If central atom does not have octet, bring in electrons from outside atoms to share

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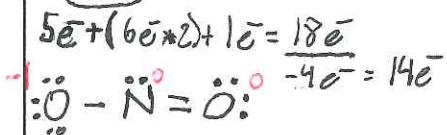


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### Practice - Lewis Structures



A bond  $\neq <$  half.

That double bond can shift between oxygens

So overall charge on O can be  $-\frac{1}{2}$

### Formal Charge

- during bonding, atoms may wind up with more or less electrons in order to fulfill octets - this results in atoms having a **formal charge**

Quiz: Which set gives the correct charge?



\* since N brought  $5e^-$  but has  $6e^-$



### Writing Lewis Formulas of Molecules (cont'd)

- Assign formal charges to the atoms
- May need to minimize charges
- Examples:
  - $\text{SO}_4^{2-}$

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### Resonance

- When there is more than one Lewis structure for a molecule that differ **only** in the position of the electrons, they are called **resonance structures**
- The actual molecule is a combination of the resonance forms – a **resonance hybrid**
  - it does **not** resonate between the two forms, though we often draw it that way

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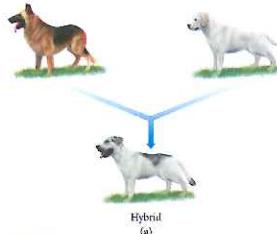
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### Resonance: Hybrid



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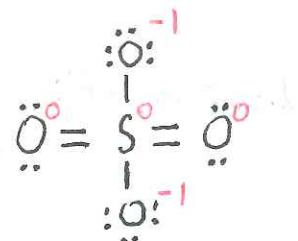
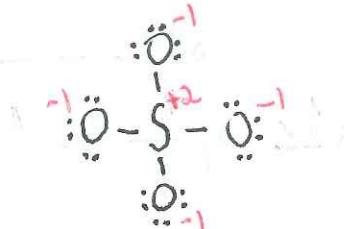
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$$SO_4^{2-} = 32e^-$$



10/10/10

### Resonance Rules

- Resonance structures must have the same connectivity
- Resonance structures must have the same number of electrons
- Second row elements have a maximum of 8 electrons
- Formal charges must total same
- Better structures have fewer formal charges
- Better structures have smaller formal charges
- Better structures have - formal charge on more electronegative atom

\* You ideally want to get the central atom at a charge of 0

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## Chapter 6

### Bond Energies

- Chemical reactions involve breaking bonds in reactant molecules and making new bond to create the products
- The  $\Delta H^\circ_{\text{reaction}}$  can be calculated by comparing the cost of breaking old bonds to the profit from making new bonds
- The amount of energy it takes to break one mole of a bond in a compound is called the **bond energy**

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## CH 6

### Using Bond Energies to Estimate $\Delta H^\circ_{\text{rxn}}$

- The actual bond energy depends on the surrounding atoms and other factors
- We often use **average bond energies** to estimate the  $\Delta H_{\text{rxn}}$
- Bond breaking is endothermic,  $\Delta H = +$
- Bond making is exothermic,  $\Delta H = -$

$$\Delta H_{\text{rxn}} = \sum (\Delta H(\text{bonds broken})) + \sum (\Delta H(\text{bonds formed}))$$

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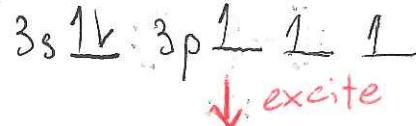
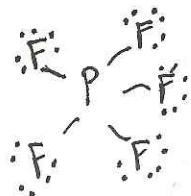
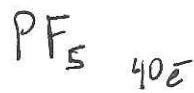


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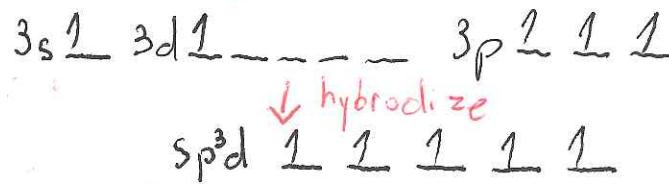


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An example with a D shell  
Show the hybridization of:



excite

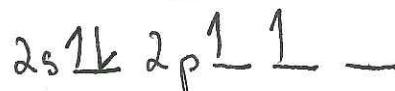
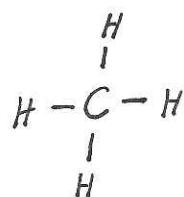


hydrogenize



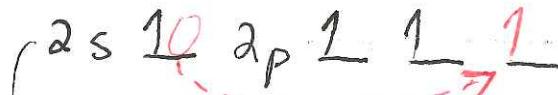
On Exam

## Metallic Bond



can only share  $2\bar{e}$  if you look at this setup. Now what?

use energy to move  $\bar{e}$  from first orbital



Now we can form 4 bonds

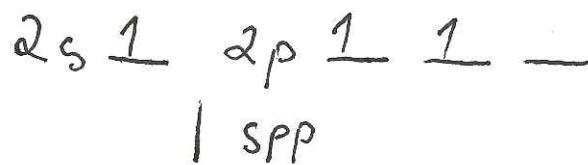
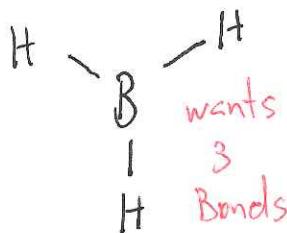


This is hybridization state

## Another Example



excite



spp



This is the hybridization state

## CH 6 Example



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## Metallic Bonds

- Low ionization energy of metals allows them to lose electrons easily
- The simplest theory of metallic bonding involves the metal atoms releasing their valence electrons to be shared by all atoms/ions in the metal
  - an organization of metal cation islands in a sea of electrons
  - electrons delocalized throughout the metal structure
- Bonding results from attraction of cation for the delocalized electrons

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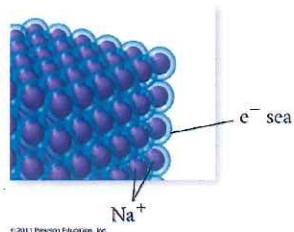
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## Metallic Bonds



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The End

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## Chapter 10

"Chemical  
Bonding II"



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## Structure Determines Properties!

- Properties of molecular substances depend on the structure of the molecule
- The structure includes many factors, including:
  - the skeletal arrangement of the atoms
  - the kind of bonding between the atoms
  - the shape of the molecule
- Bonding theory allow you to predict the shapes of molecules

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## Molecular Geometry

- Molecules are 3-dimensional objects
- The geometric figures also have characteristic angles that we call **bond angles**

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## VSEPR Theory

- Electron groups around the central atom will be most stable when they are as far apart as possible – we call this **valence shell electron pair repulsion** theory
- The resulting geometric arrangement will allow us to predict the shapes and bond angles in the molecule

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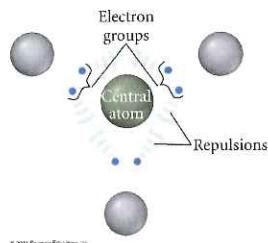
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## VSEPR Theory



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## Molecular Geometries

- There are 5 basic arrangements of electron groups around a central atom
  - based on a maximum of 6 bonding electron groups
- Each of these 5 basic arrangements results in 5 different basic molecular shapes

5 EPG's or 5  
e paired geometrys

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On Exam

## Molecular Shape

+ EPG

### Linear Geometry

- When there are 2 electron groups around the central atom, it will result in the molecule taking a **linear geometry**
- The bond angle is  $180^\circ$

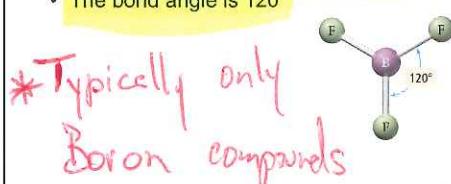


### Linear Geometry



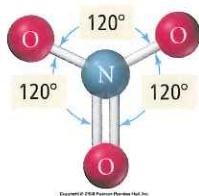
### Trigonal Geometry

- When there are 3 electron groups around the central atom, it will result in the molecule taking a **trigonal planar geometry**
- The bond angle is  $120^\circ$





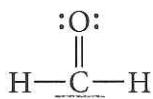
### Trigonal Geometry



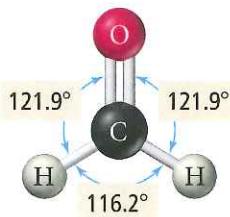
Other than Boron, A compound with a double bond like this is also Trig Planar

### \* Concept on Exam

#### Not Quite Perfect Geometry



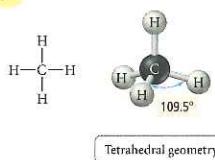
Because the bonds are not identical, the observed angles are slightly different from ideal.



The double bond between the C & O force the Hydrogen further out making an uneven angle

### Tetrahedral Geometry

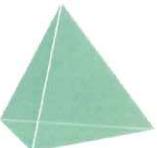
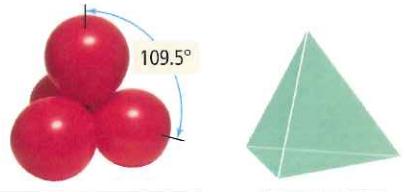
- When there are 4 electron groups around the central atom, it will result in the molecule taking a **tetrahedral geometry**
- The bond angle is  $109.5^\circ$



Tetrahedral geometry



## Tetrahedral Geometry



Tetrahedron

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## Trigonal Bipyramidal Geometry

- When there are 5 electron groups around the central atom, it results in the molecule taking a **trigonal bipyramidal geometry**
- The positions above and below the central atom are called the **axial** positions where the bond angle is  $90^\circ$
- The positions in the same base plane as the central atom are called the **equatorial** positions where the bond angle is  $120^\circ$

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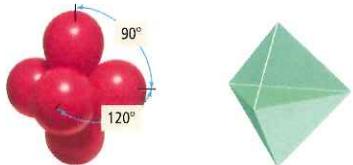
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## Trigonal Bipyramidal Geometry



Trigonal bipyramidal

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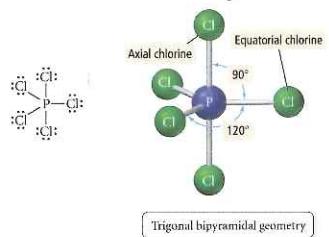
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## Trigonal Bipyramidal Geometry

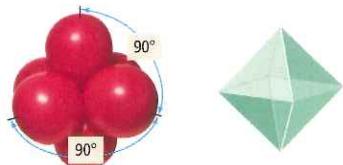


Trigonal bipyramidal geometry

## Octahedral Geometry

- When there are 6 electron groups around the central atom, it will result in the molecule taking an **octahedral geometry**
- All positions are equivalent
- The bond angle is 90°

## Octahedral Geometry



Octahedral geometry

Octahedron

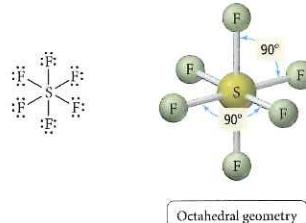
Octahedral because  
it has 8 Planes

Quiz:  $\text{PF}_5$  would have  
an electron pair geometry  
of:

- A - Linear      D - Trig Bipl  
B - Trig Plan  
C - Tetrahed      E - Octahed



## Octahedral Geometry



On Exam

## The Effect of Lone Pairs

- lone pair groups "occupy more space" on the central atom
  - because their electron density is exclusively on the central atom rather than shared like bonding electron groups
- relative sizes of repulsive force interactions is:  
Lone Pair - Lone Pair > Lone Pair - Bonding Pair > Bonding Pair - Bonding Pair
- This effects the bond angles, making them smaller than expected

Know This

Strongest = Lone pair - Lone pair

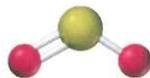
Medium = Lone Pair - Bond Pair

Weakest = Bond P - Bond P

Epg - Trig Planar

## Derivative of Trigonal Geometry

- When there are 3 electron groups around the central atom, and 1 of them is a lone pair, the resulting shape of the molecule is called a **trigonal planar - bent shape**
- The bond angle is  $< 120^\circ$



Molecular Shape

Bent

Trig Bent - if you remove  
a Bonding Pair from  
Trigonal Planar



if asked specifically for EPG of something like this Trigonal Pyramidal it is Tetrahedral

Trigonal Planar = Molecular Geometry

EPG = Tetrahedral

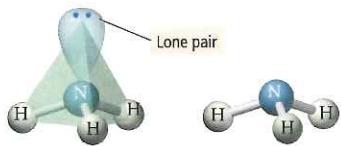
### Derivatives of Tetrahedral Geometry

- When there are 4 electron groups around the central atom, and 1 is a lone pair, the result is called a **pyramidal shape**
- When there are 4 electron groups around the central atom, and 2 are lone pairs, the result is called a **tetrahedral-bent shape**
- Both shapes, the bond angle is  $< 109.5^\circ$

Pg 408 helps a lot  
with the names

\* She wants this as  
Trigonal Pyramidal

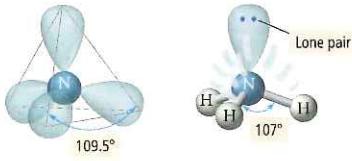
### Pyramidal Shape



Electron geometry:  
tetrahedral

Molecular geometry:  
trigonal pyramidal

### Bond Angle Distortion from Lone Pairs

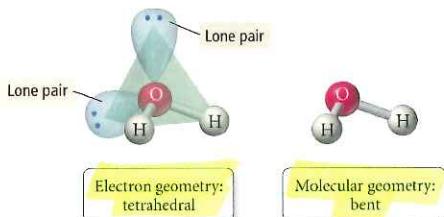


Ideal tetrahedral geometry

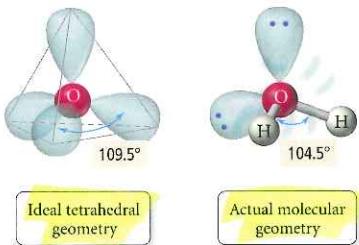
Actual molecular geometry



## Tetrahedral-Bent Shape



## Bond Angle Distortion from Lone Pairs



\*NEW

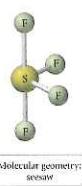
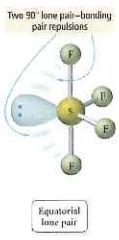
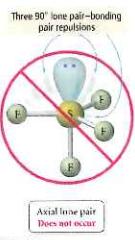
### Derivatives of the Trigonal Bipyramidal Geometry

- When there are 5 electron groups around the central atom, and 1 is a lone pair, the result is called **see-saw shape**
- When there are 5 electron groups around the central atom, and 2 are lone pairs, the result is called **T-shaped**
- When there are 5 electron groups around the central atom, and 3 are lone pairs, the result is called a **linear shape**

Always equatorial atoms removed!



### Replacing Atoms with Lone Pairs in the Trigonal Bipyramidal System



Never remove  
The Axial Pairs

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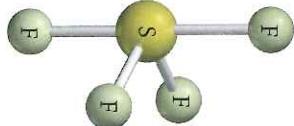
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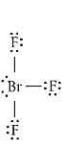
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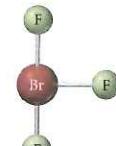
### See-Saw Shape



### T-Shape



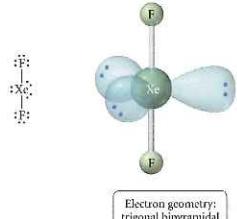
Electron geometry:  
trigonal bipyramidal



Molecular geometry:  
T-shaped



## Linear Shape



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## Derivatives of the Octahedral Geometry

- When there are 6 electron groups around the central atom, and 1 is a lone pair, the result is called a **square pyramid shape**
- When there are 6 electron groups around the central atom, and 2 are lone pairs, the result is called a **square planar shape**

Remove whichever atom  
then remove the one  
on the opposite side

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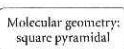
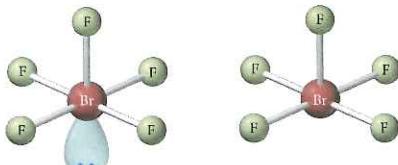
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## Square Pyramidal Shape



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Quiz:  $\text{PCl}_3$  what is the  
Molecular shape?

✓ Trigonal Pyramidal

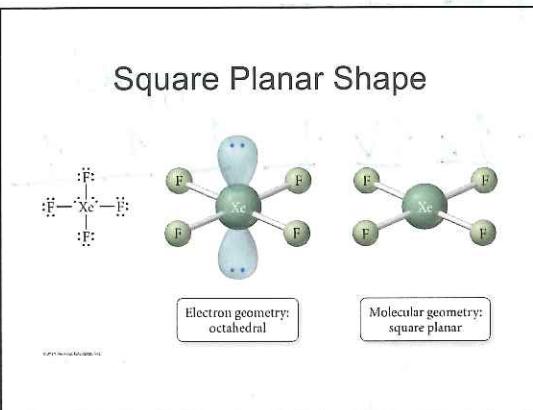
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### Example

- Predict the Molecular Geometry and Bond Angles in  $\text{SiF}_5^-$

### Representing 3-D Shapes on a 2-D Surface

- One of the problems with drawing molecules is trying to show their dimensionality
- By convention, the central atom is put in the plane of the paper
- Put as many other atoms as possible in the same plane and indicate with a **straight line**
- For atoms in front of the plane, use a **solid wedge**
- For atoms behind the plane, use a **hashed wedge**

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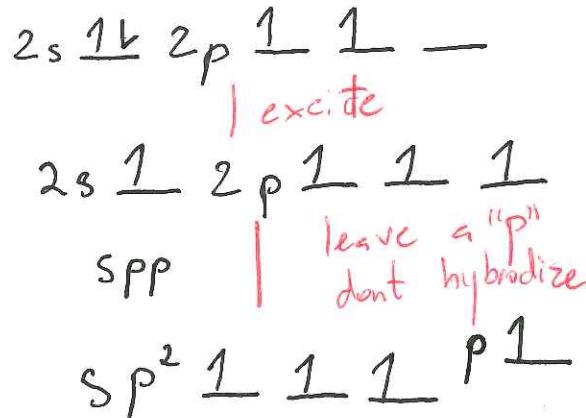
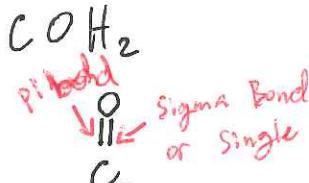
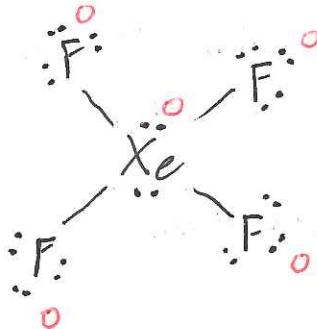
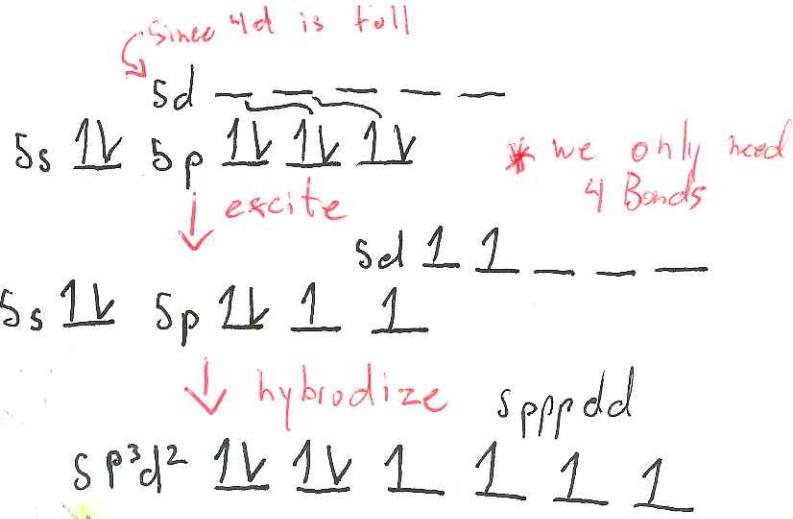


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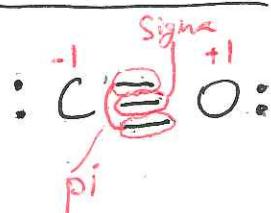


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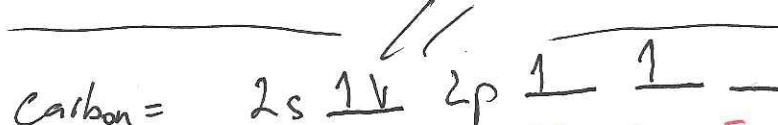
Exam



when you see a pi  
leave a "p"



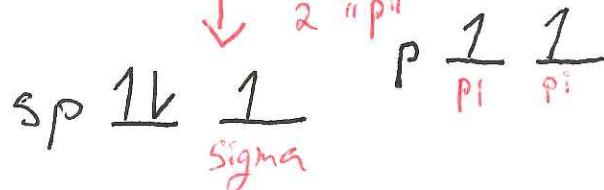
Sigma cannot rotate



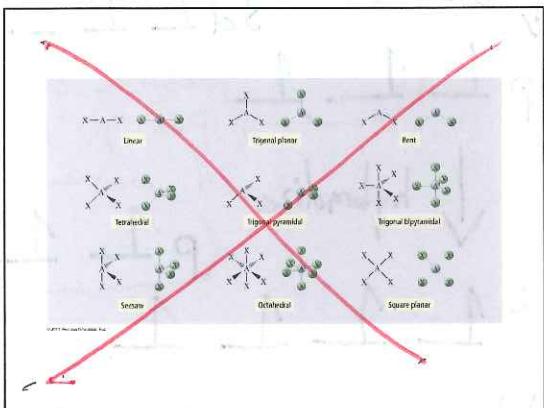
$\downarrow$  add extra  $e^-$   
for the -1



$\downarrow$  2 pi so leave  
2 "p"



Sigma bond = Extremely strong



As long as there is no double bonds

Octahedral =  $SP^3D^2$

Tetrahedral =  $SP^3$

Trigonal Bipyramidal  $\approx SP^3D$

Quiz:

What is the hybridization of  $XeF_2$ ?

A -  $SP$       B -  $SP^2$

C -  $SP^3$       D -  $SP^3D$

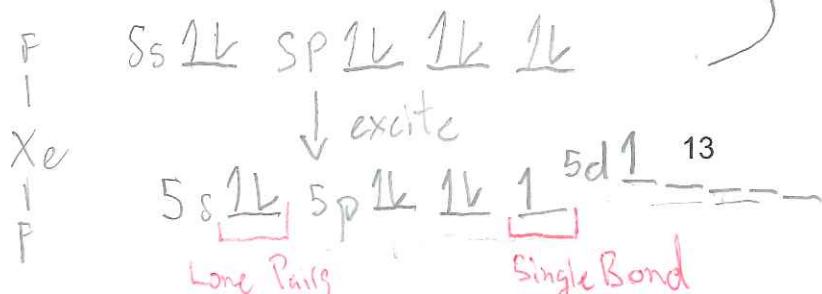
E -  $SP^3D^2$

### Polarity of Molecules

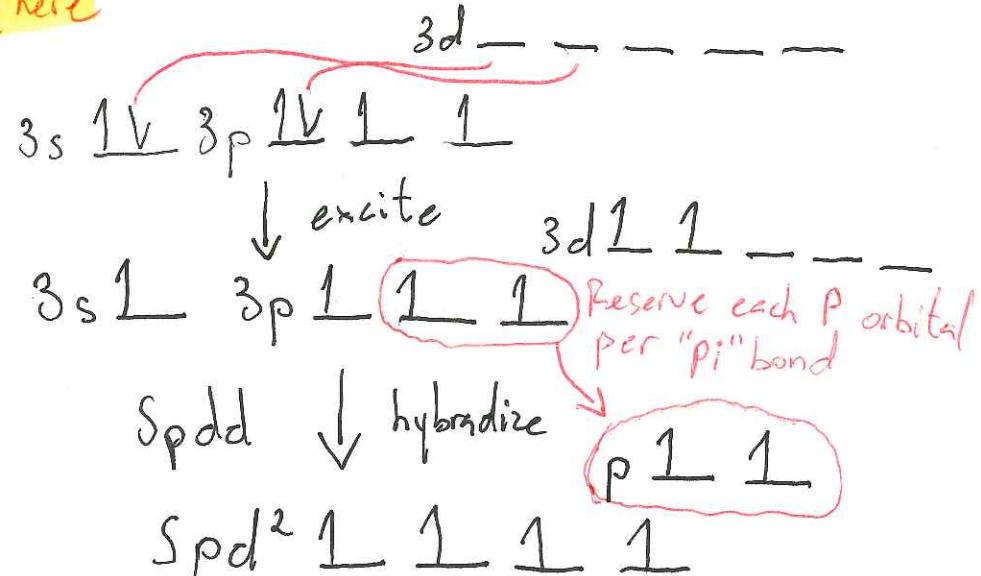
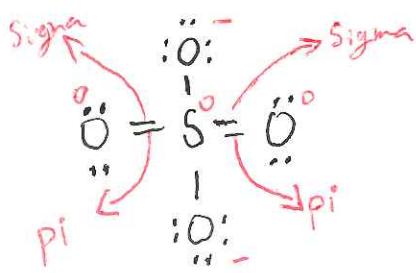
- In order for a molecule to be polar it must have polar bonds have an unsymmetrical shape
- Polarity affects the intermolecular forces of attraction
- Nonbonding pairs affect molecular polarity, strong pull in its direction

TABLE 10.5 Common Cases of Adding Dipole Moments to Determine whether a Molecule is Polar	
 Linear Molecule The dipole moment of two identical polar bonds in opposite directions will cancel. The molecule is nonpolar.	 Bent Molecule The dipole moment of two polar bonds with an angle of less than 180° between them will not cancel. The resultant dipole moment vector is non-zero. The molecule is polar.
 Trigonal planar Molecule The dipole moment of three identical polar bonds at 120° from each other will cancel. The molecule is nonpolar.	 Tetrahedral Molecule The dipole moment of four identical polar bonds in a tetrahedral arrangement (109.5° from each other) will not cancel. The resultant dipole moment vector is non-zero. The molecule is polar.
 Trigonal bipyramidal Molecule The dipole moment of five polar bonds in a trigonal bipyramidal arrangement (109.5° from each other) will not cancel. The resultant dipole moment vector is non-zero. The molecule is polar.	 Square pyramidal Molecule The dipole moment of five polar bonds in a square pyramidal arrangement (109.5° from each other) will not cancel. The resultant dipole moment vector is non-zero. The molecule is polar.

Symmetrical Planes cancel their polarities

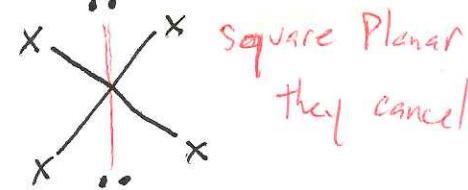
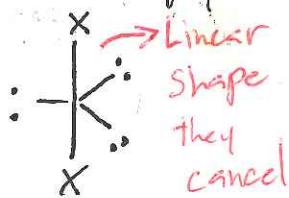


Shortcut doesn't work here

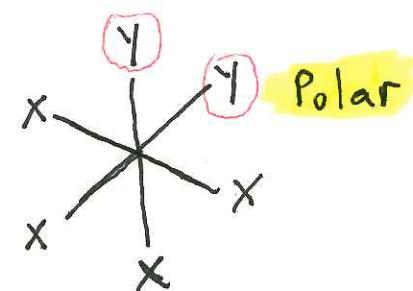
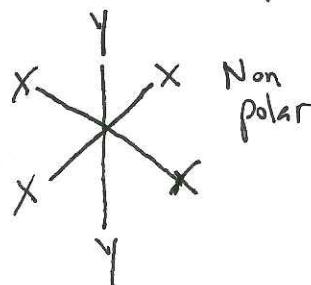


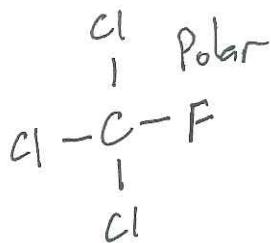
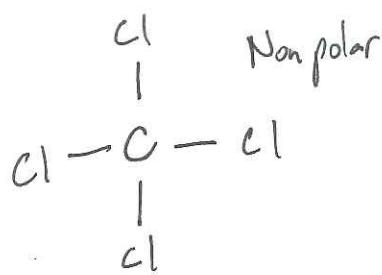
Non polar shapes if all surrounding groups are equal

- Linear
- Trigonal Planar
- Tetrahedral
- Trigonal Bipyramidal
- Octahedral



### Exceptions:





### Molecule Polarity

No net dipole moment

The O-C bond is polar. The bonding electrons are pulled equally toward both O ends of the molecule. The net result is a nonpolar molecule.

have to be the same group to cancel out

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### Molecule Polarity

Net dipole moment

The H-O bond is polar. The both sets of bonding electrons are pulled toward the O end of the molecule. The net result is a polar molecule.

Bent cannot cancel out because of their shape

\*Know: Polyatomic Ions are always Polar

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### Molecule Polarity

The H-N bond is polar. All the sets of bonding electrons are pulled toward the N end of the molecule. The net result is a polar molecule.

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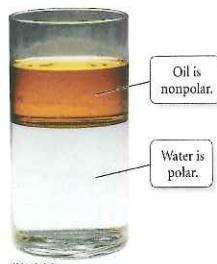
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### Molecular Polarity Affects Solubility in Water



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### Problems with Lewis Theory

- Lewis theory gives good first approximations of the bond angles in molecules, but usually cannot be used to get the actual angle
- Lewis theory cannot write one correct structure for many molecules where resonance is important
- Lewis theory often does not predict the correct magnetic behavior of molecules

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### Valence Bond Theory

- Linus Pauling and others applied the principles of quantum mechanics to molecules
- They reasoned that bonds between atoms would arise when the orbitals on those atoms interacted to make a bond
- The kind of interaction depends on whether the orbitals align along the axis between the nuclei, or outside the axis

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## Orbital Interaction

- As two atoms approached, the partially filled or empty valence atomic orbitals on the atoms would interact to form **molecular orbitals**
- The molecular orbitals would be more stable than the separate atomic orbitals because they would contain paired electrons shared by both atoms

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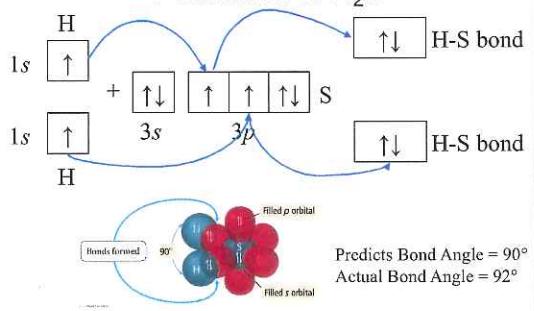
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## Orbital Diagram for the Formation of H<sub>2</sub>S



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## Valence Bond Theory - Hybridization

- One of the issues that arose was that the number of partially filled or empty atomic orbital did not predict the number of bonds or orientation of bonds
  - C =  $2s^2 2p_x^1 2p_y^1 2p_z^0$  would predict 2 or 3 bonds that are 90° apart, rather than 4 bonds that are 109.5° apart
- To adjust for these inconsistencies, it was postulated that the valence atomic orbitals could **hybridize** before bonding took place
  - one hybridization of C is to mix all the 2s and 2p orbitals to get 4 orbitals that point at the corners of a tetrahedron

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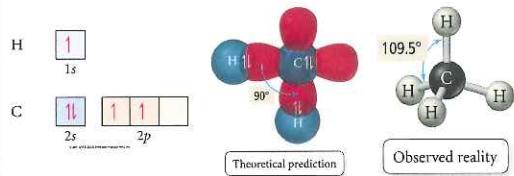
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## Unhybridized C Orbitals Predict the Wrong Bonding & Geometry



## Valence Bond Theory Main Concepts

1. The valence electrons in an atom reside in the quantum mechanical atomic orbitals or hybrid orbitals
2. A chemical bond results when these atomic orbitals overlap and there is a total of 2 electrons in the new molecular orbital  
the electrons must be spin paired
3. The shape of the molecule is determined by the geometry of the overlapping orbitals

## Hybridization

- Some atoms **hybridize** their orbitals to maximize bonding
  - hybridizing is mixing different types of orbitals to make a new set of degenerate orbitals
  - $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$
  - more bonds = more full orbitals = more stability
- Better explain observed shapes of molecules
- Same type of atom can have different hybridization depending on the compound
  - C =  $sp$ ,  $sp^2$ ,  $sp^3$



## Hybrid Orbitals

- H cannot hybridize!!
- The number of standard atomic orbitals combined = the number of hybrid orbitals formed
- The number and type of standard atomic orbitals combined determines the shape of the hybrid orbitals
- The particular kind of hybridization that occurs is the one that yields the lowest overall energy for the molecule

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## Orbital Diagrams with Hybridization

- Place electrons into hybrid and unhybridized valence orbitals as if all the orbitals have equal energy
- When bonding,  $\sigma$  bonds form between hybrid orbitals and  $\pi$  bonds form between unhybridized orbitals that are parallel

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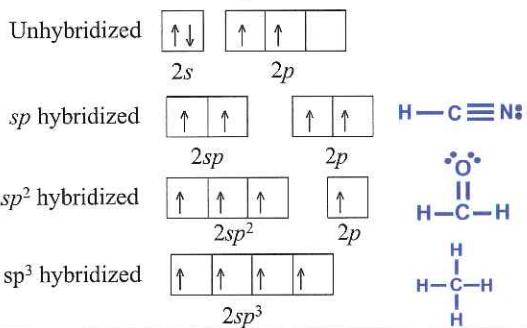
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## Carbon Hybridizations



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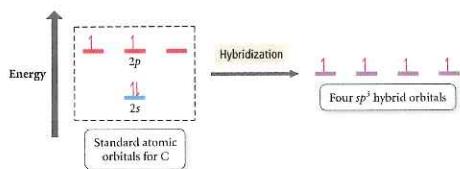
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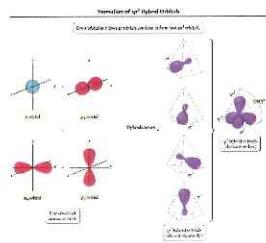
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## $sp^3$ Hybridization of C



## $sp^3$ Hybridization of C



## Example

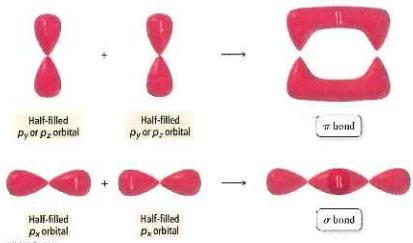
- Draw the Orbital Diagram for the  $sp^3$  Hybridization of Cl and N



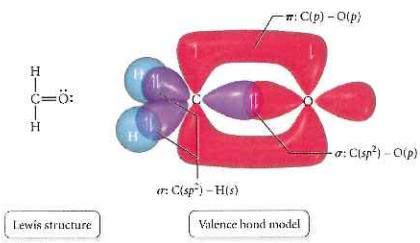
## Types of Bonds

- A **sigma ( $\sigma$ ) bond** results when the bonding atomic orbitals point along the axis connecting the two bonding nuclei (either standard atomic orbitals or hybrids)
- A **pi ( $\pi$ ) bond** results when the bonding atomic orbitals are parallel to each other and perpendicular to the axis connecting the two bonding nuclei (between unhybridized parallel  $p$  orbitals)
- The interaction between parallel orbitals is not as strong as between orbitals that point at each other; therefore  **$\sigma$  bonds are stronger than  $\pi$  bonds**

## Types of Bonds



## Types of Bonds

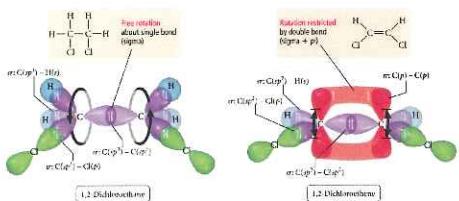




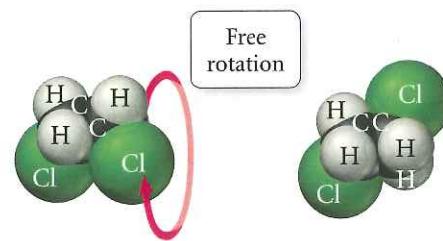
## Bond Rotation

- Orbitals that form the  $\sigma$  bond point along the internuclear axis, rotation around that bond does not require breaking the interaction between the orbitals
- In contrast orbitals that form the  $\pi$  bond interact above and below the internuclear axis, so rotation around the axis requires the breaking of the interaction between the orbitals

## Bond Rotation

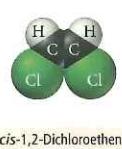


## Bond Rotation





## Bond Rotation



cis-1,2-Dichloroethene



trans-1,2-Dichloroethene

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## $sp^2$

- An atom with 3 areas of electrons
  - trigonal planar system
    - C = trigonal planar
    - N = trigonal bent
    - O = "linear"
  - 120° bond angles
  - flat
- An atom uses hybrid orbitals for  $\sigma$  bonds and lone pairs, may use nonhybridized  $p$  orbital for  $\pi$  bond

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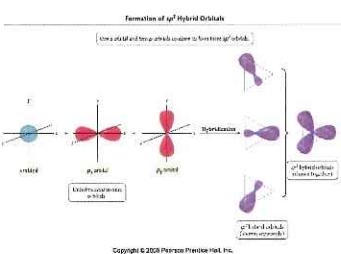
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## $sp^2$



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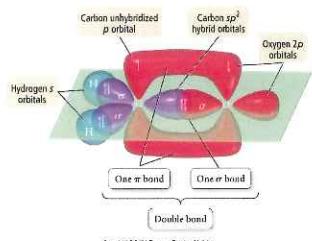
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*sp*<sup>2</sup>



### *sp*<sup>2</sup> Hybridized Atoms Orbital Diagrams

Unhybridized atom		C	<i>sp</i> <sup>2</sup> hybridized atom		
2s	2p		3 $\sigma$	2 $sp^2$	2p
$\uparrow\downarrow$	$\uparrow\uparrow$			$\uparrow\uparrow\uparrow$	$\uparrow$
2s	2p	N	2 $\sigma$	2 $sp^2$	2p
$\uparrow\downarrow$	$\uparrow\uparrow$		$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$	$\uparrow$

### Example

- Draw the Orbital Diagram for the *sp*<sup>2</sup> Hybridization of B and O.



## sp

- An atom with 2 areas of electrons
  - linear shape
  - $180^\circ$  bond angle
- An atom uses hybrid orbitals for  $\sigma$  bonds or lone pairs, may use nonhybridized  $p$  orbitals for  $\pi$  bonds

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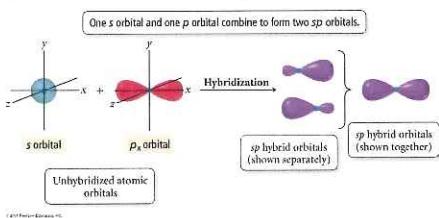
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## sp

Formation of sp Hybrid Orbitals



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## sp



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## $sp^3d$

- An atom with 5 areas of electrons around it
  - trigonal bipyramidal shape
  - See-Saw, T-Shape, Linear
  - $120^\circ$  &  $90^\circ$  bond angles
- Uses empty  $d$  orbitals from valence shell

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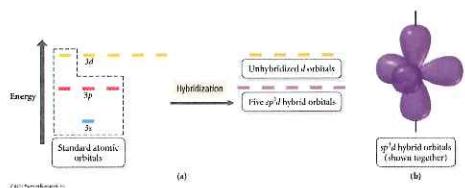
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## $sp^3d$



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## $sp^3d^2$

- An atom with 6 areas of electrons around it
  - octahedral shape
  - Square Pyramidal, Square Planar
  - $90^\circ$  bond angles
- Uses empty  $d$  orbitals from valence shell

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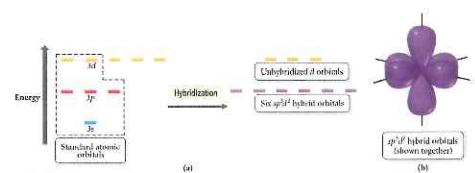
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$sp^3d^2$



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### Example

- Predict the Hybridization of All the Atoms in  $H_3BO_3$

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### Problems with Valence Bond Theory

- VB theory predicts many properties better than Lewis Theory
  - bonding schemes, bond strengths, bond lengths, bond rigidity
- However, there are still many properties of molecules it doesn't predict perfectly
  - Example: magnetic behavior of  $O_2$

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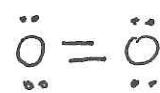
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if all  $\bar{\sigma}$  are paired then molecules should be  
diamagnetic = No attraction to magnets



## Molecular Orbital Theory

- In MO theory, we apply Schrödinger's wave equation to the molecule to calculate a set of **molecular orbitals**
- In this treatment, the electrons belong to the whole molecule – so the orbitals belong to the whole molecule **Like metals**
  - unlike VB Theory where the atomic orbitals still exist in the molecule

## LCAO

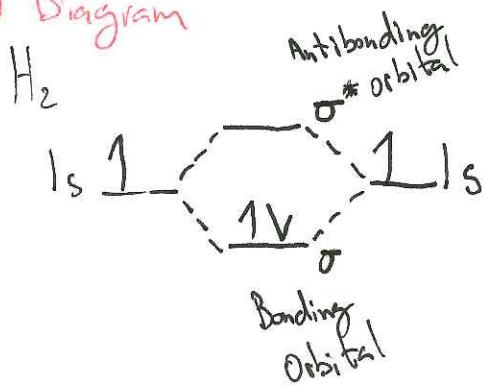
- The simplest guess starts with the atomic orbitals of the atoms adding together to make molecular orbitals – this is called the **Linear Combination of Atomic Orbitals** method
- Because the orbitals are wave functions, the waves can combine either **constructively** or **destructively**

## Molecular Orbitals

- When the wave functions combine **constructively**, the resulting molecular orbital has less energy than the original atomic orbitals – it is called a **Bonding Molecular Orbital**
- When the wave functions combine **destructively**, the resulting molecular orbital has more energy than the original atomic orbitals – it is called a **Antibonding Molecular Orbital**

↳ higher in energy

## MO Diagram



Bonding  $\bar{e}$  — Antibonding  $\bar{e}$   
 # of  $\bar{e}$  in bond

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

0 = No bond  
 1 = Single  
 2 = Double  
 3 = Triple

1. Does Molecule exist?

Yes = 1, 2 or 3

3. What type of bond?

Single

2. What is the bond order?

1

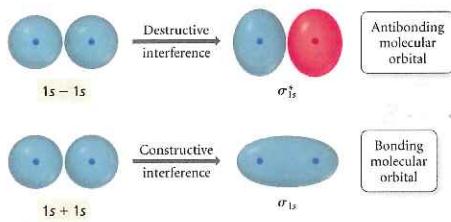
4. Is it Paramagnetic or Diamagnetic?

Diamagnetic

Paramagnetic = Unpaired, Single  $\bar{e}$  (magnetic)

Diamagnetic = All paired  $\bar{e}$  (Non-Magnetic)

### Interaction of 1s Orbitals



Quiz: Elements that respond to a magnetic field are?

- A - Paramagnetic  
B - Diamagnetic

### Molecular Orbital Theory

- Electrons in bonding MOs are stabilizing
  - Lower energy than the atomic orbitals
- Electrons in anti-bonding MOs are destabilizing
  - Higher in energy than atomic orbitals
  - Electron density located outside the internuclear axis
  - Electrons in anti-bonding orbitals cancel stability gained by electrons in bonding orbitals

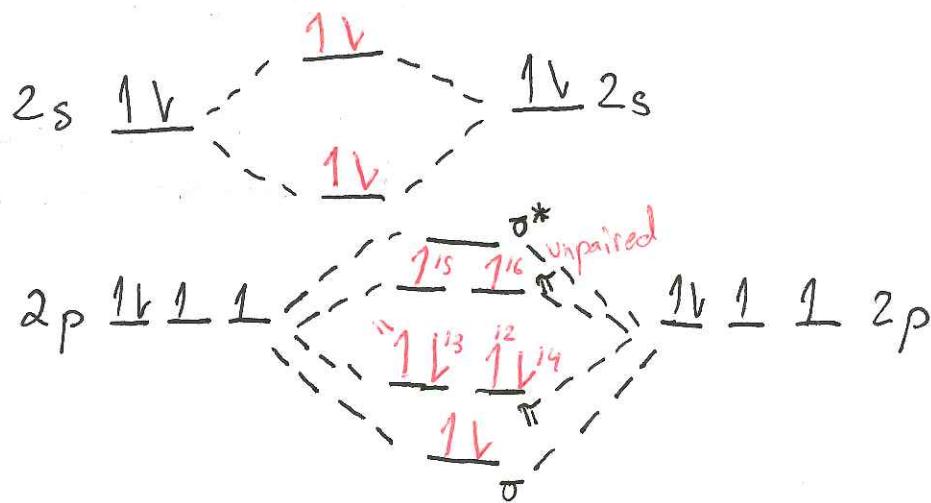
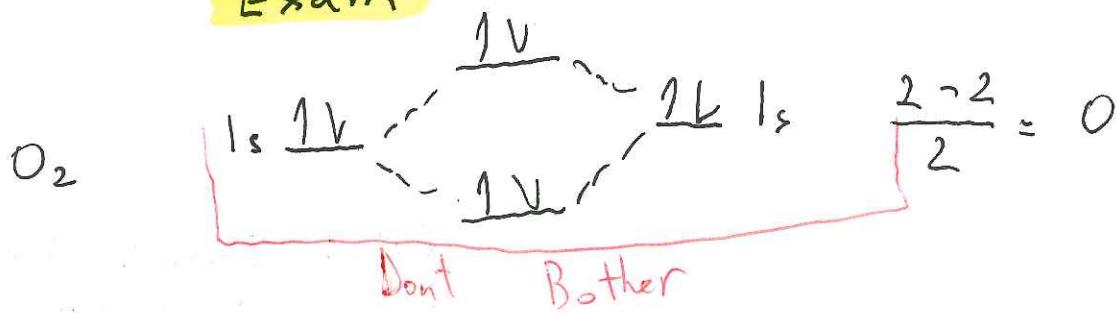
### Molecular Orbital Theory

- Bond Order = difference between number of electrons in bonding and antibonding orbitals divided by 2
  - may be a fraction
  - higher bond order = stronger and shorter bonds
  - if bond order = 0, then bond is unstable compared to individual atoms - no bond will form.
- A substance will be paramagnetic if its MO diagram has unpaired electrons
  - if all electrons paired it is diamagnetic

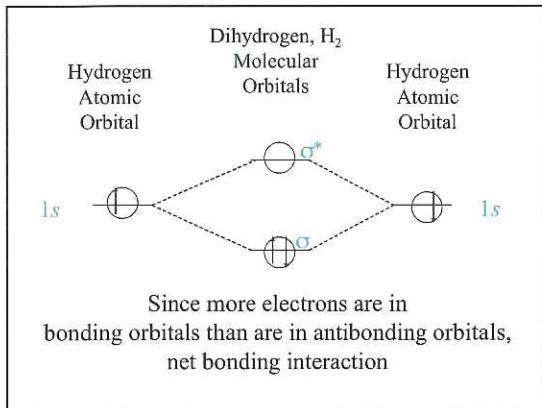
Pg 439  
Right side of  
the page diagram

≈ 59 min Lecture

Exam



$\frac{B-E}{A_E}$  =  $\boxed{2}$  = double Bond




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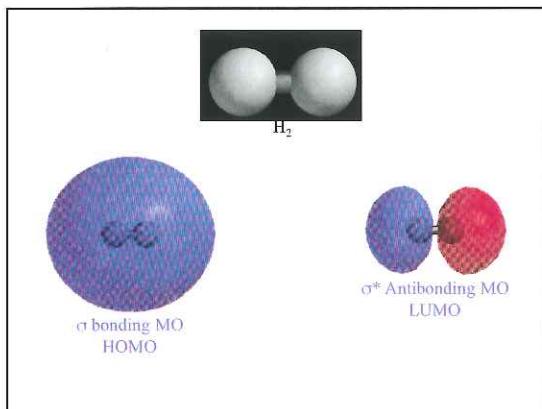
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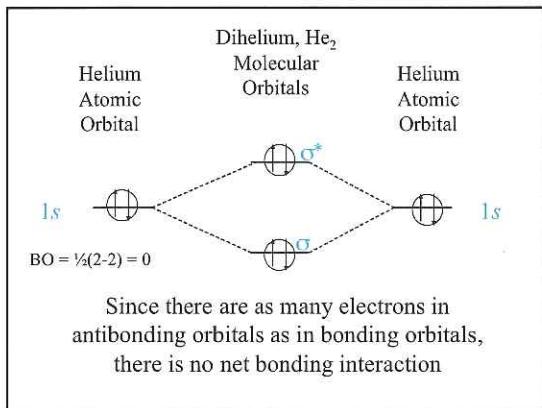
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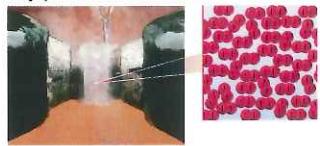


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## O<sub>2</sub>

- Dioxygen is paramagnetic
- Paramagnetic material have unpaired electrons
- Neither Lewis Theory nor Valence Bond Theory predict this result



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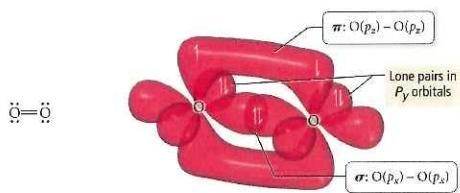
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## O<sub>2</sub> as described by Lewis and VB theory



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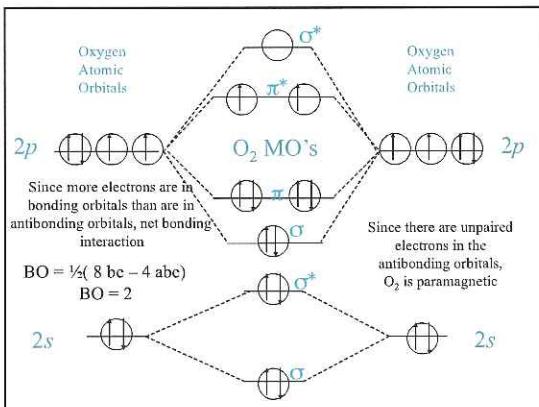
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## Example

- Draw a molecular orbital diagram of N<sub>2</sub> and predict its bond order and magnetic properties

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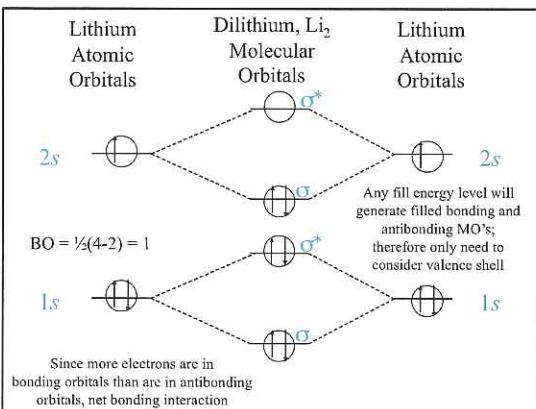
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The End

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Chapter 5

"Gases"

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### Gases Pushing

- Gas molecules are constantly in motion
- As they move and strike a surface, they push on that surface  
– push = force

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### Pressure Imbalance in Ear

If there is a difference in pressure across the eardrum membrane, the membrane will be pushed out – what we commonly call a "popped eardrum."

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## The Pressure of a Gas

- The pressure of a gas depends on several factors
  - number of gas particles in a given volume
  - volume of the container
  - average speed of the gas particles

A diagram showing a cylindrical container filled with a gas. Inside the container, there are several small, colored spheres representing gas particles. The container has a lid with a valve.

increase in Temperature  
means increase in  
Pressure

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## Measuring Air Pressure

- Use a **barometer**
- Column of mercury supported by air pressure
- Force of the air on the surface of the mercury balanced by the pull of gravity on the column of mercury

A diagram of a barometer. It shows a glass tube open at the top and closed at the bottom, containing a column of mercury. The height of the mercury column is labeled as 760 mm (29.92 in). The tube is connected to a larger reservoir of mercury at the bottom. Labels include "Vacuum" at the top, "Glass tube" for the tube itself, "Atmospheric pressure" pointing to the top of the mercury column, and "Mercury" pointing to the reservoir at the bottom.

$$\text{Pressure} = \frac{\text{force}}{\text{Area}}$$


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$$1 \text{ ATM} = 760 \text{ mmHg} = 760 \text{ torr}$$


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## Common Units of Pressure

Unit	Average Air Pressure at Sea Level
pascal (Pa)	101,325
kilopascal (kPa)	101.325
atmosphere (atm)	1 (exactly)
millimeters of mercury (mmHg)	760 (exactly)
inches of mercury (inHg)	29.92
torr (torr)	760 (exactly)
pounds per square inch (psi, lbs./in <sup>2</sup> )	14.7

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