

# Chapter 8

## Basic Concepts of Chemical Bonding

### Chemical Bonds

forces of attraction which hold atoms or ions together

3 fundamental types of bonding

Ionic - metals & nonmetals

Covalent - nonmetals (semimetals)

Metallic - metals

## B) Lewis Symbols & Octet Rule

Valence  $e^-$  involved in chem. bonding

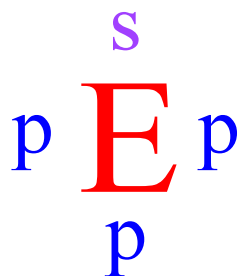
For representative elements:

$e^-$  in highest energy s & p subshells

$$\text{val. } e^- = \text{group \#}$$

### 1) Lewis Symbols

Represent  $e^-$  in the s & p orb. of the valence shell as dots arranged around the symbol of the element.



a) Separate Atoms

Show  $e^-$  as they appear in the orbital diagram



b) For Bonding

Place  $e^-$  around symbol singly before pairing



## 2) “OCTET” Rule

Atoms tend to gain, lose or share  $e^-$  to achieve noble gas configuration.



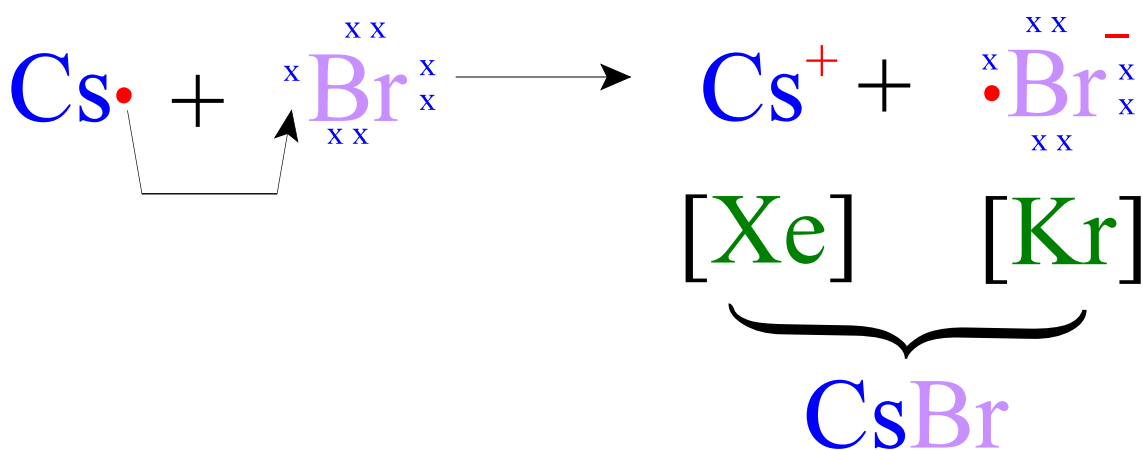
Full s & p subshells

## II) Ionic Bonding

electrostatic attraction between (+) & (-) ions resulting from complete  $e^-$  transfer

- Cations & Anions formed

Show using  $e^-$  dot or Lewis Structures

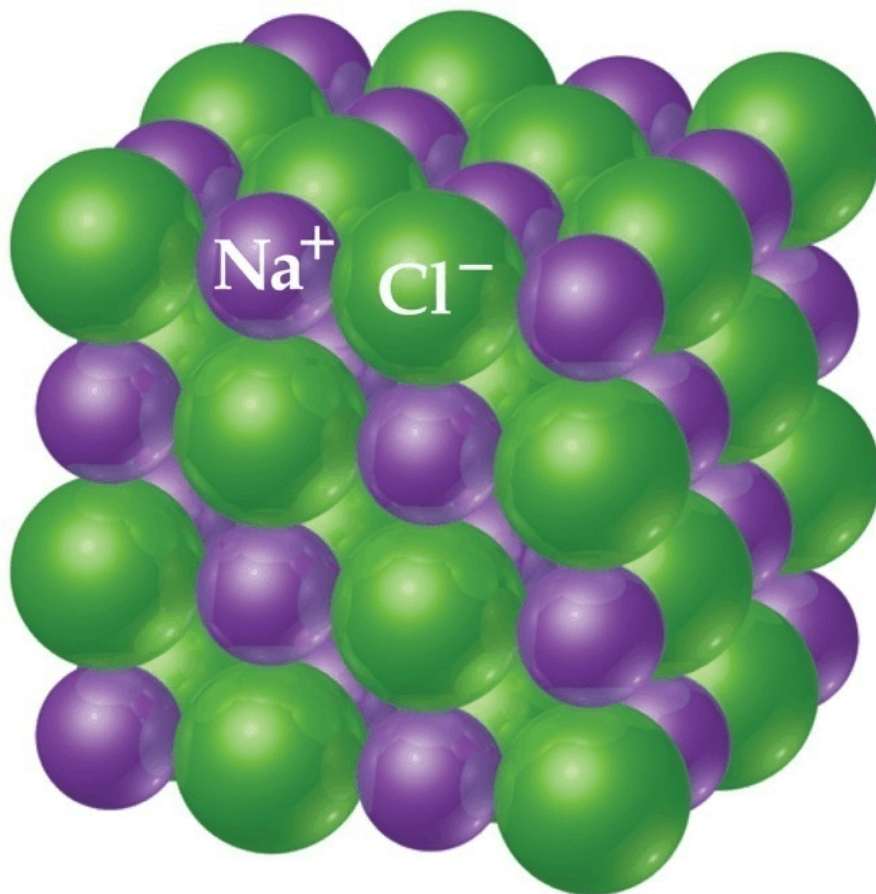


Cs: metal, low I.E.

Br: nonmetal, large neg. EA

## A) Energetics

Ionic compd. is an **array** (lattice or crystal structure) of **(+)** & **(-)** **ions**, packed so **attractive forces** between **ions of opposite charges** are **maximized** & **repulsive forces** between **ions of same charge** are **minimized**.

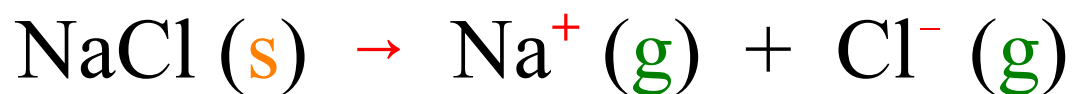


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# 1) Lattice Energy

Measure of the **strength** of **attraction** between (+) & (-) ions

**Energy** required to **separate** 1 mole of **ionic solid** to **gaseous** ions



$$\text{LE} \propto \frac{Q_1 Q_2}{d}$$

$Q_1, Q_2$  : charges on ions

$d$  : distance between ions  
- sum of ionic radii

For a given arrangement of ions:

LE inc. as charges on ions inc.  
& as their radii dec.

i.e. Greater charges and smaller  
ions  $\Rightarrow$  greater LE

a) Charge is more impt. factor



b) Same charges, consider size





			Sum of radii (Å)	LE (kJ/mol)
KF	K <sup>+</sup>	F <sup>-</sup>	2.71	808
CaO	Ca <sup>2+</sup>	O <sup>2-</sup>	2.40	3414
ScN	Sc <sup>3+</sup>	N <sup>3-</sup>	2.44	7547

Ionic bonds are very strong resulting in very high melting points (m.p.) but solids are brittle as they cleave along planes of ions.

## 2) Born-Haber Cycle

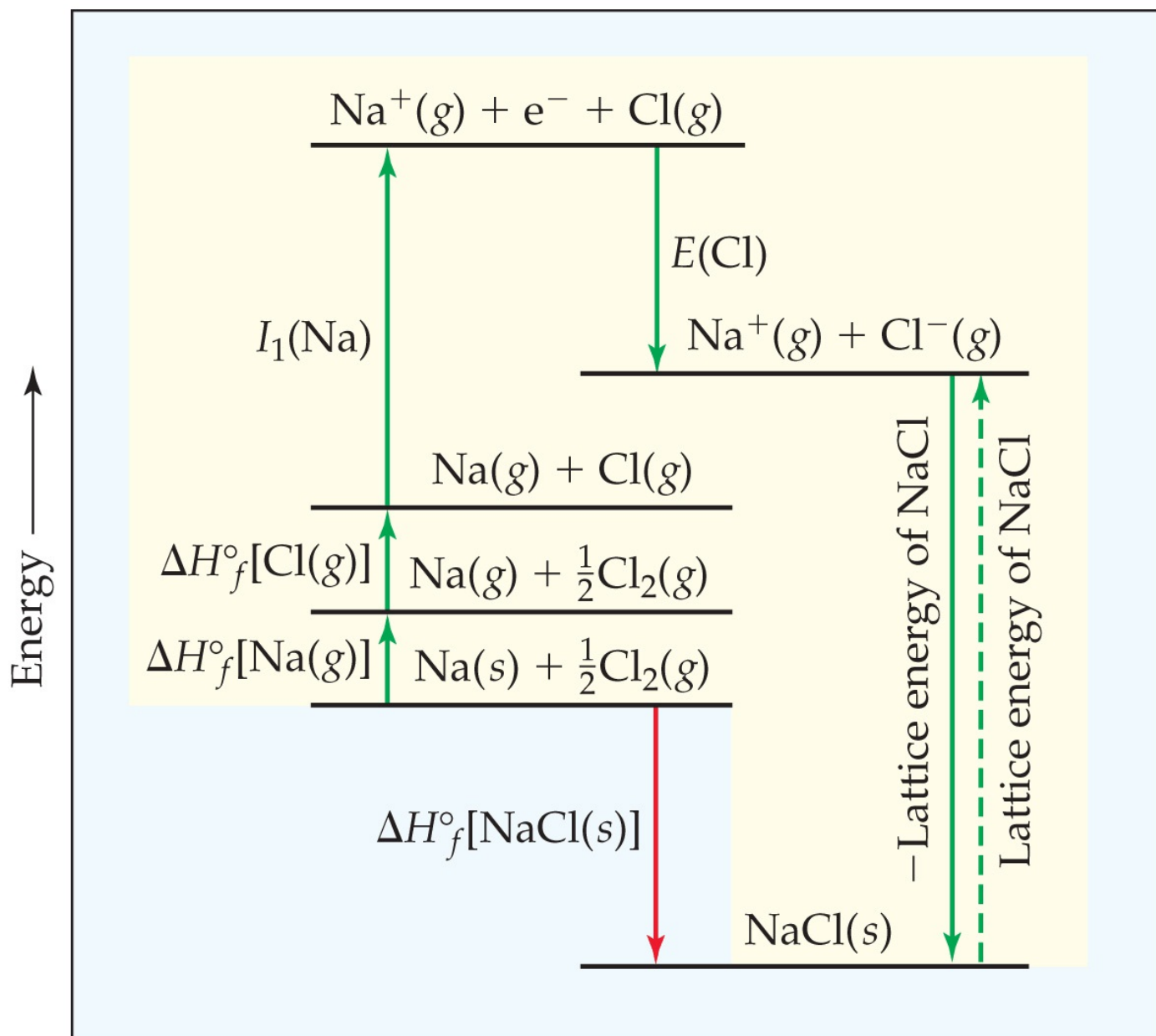


$$\text{LE} = ?$$

### Born-Haber Cycle

- analyze the **formation** rxn. for **ionic solid** as a **series of steps**  
(based on **Hess's Law**)

# Born-Haber Cycle for formation of NaCl(s)

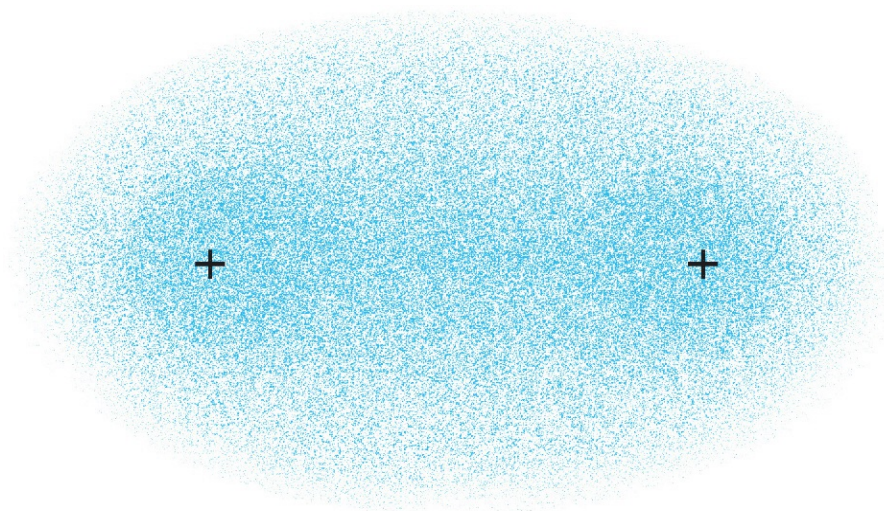
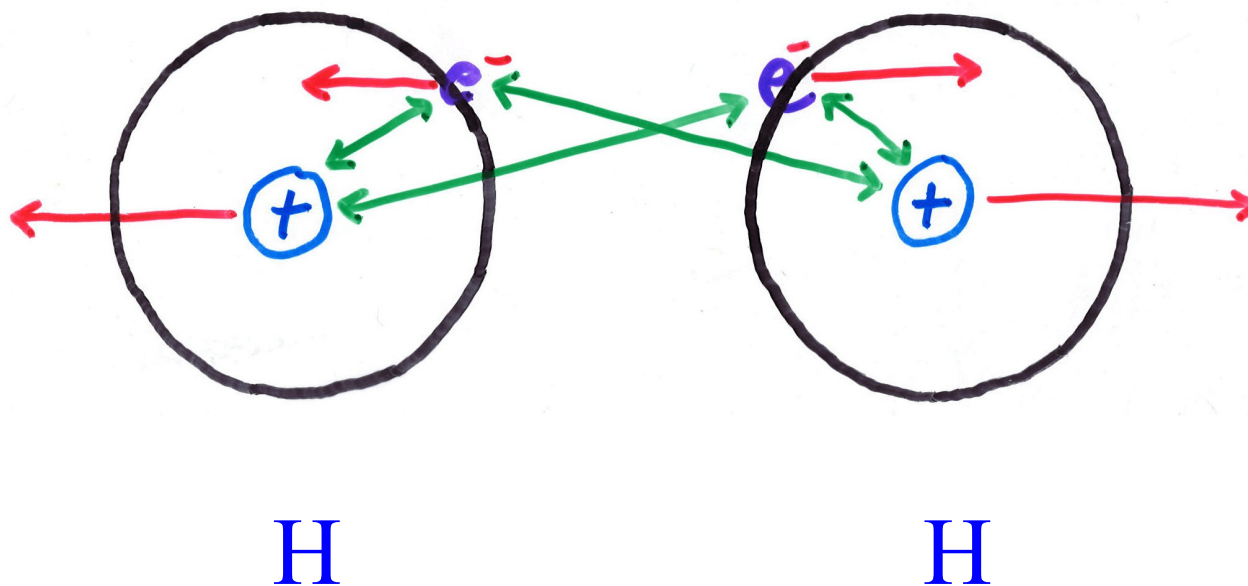


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### III) Covalent Bonds

Not complete  $e^-$  transfer

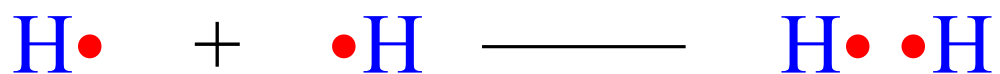
Covalent Bond: pair of  $e^-$  are shared



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## A) Single Bond

2 e<sup>-</sup> shared by 2 atoms



Attraction of e<sup>-</sup> for both nuclei  
that holds molecules together

## Lewis Structure

replace bonding e<sup>-</sup> pair w. line



- single bond

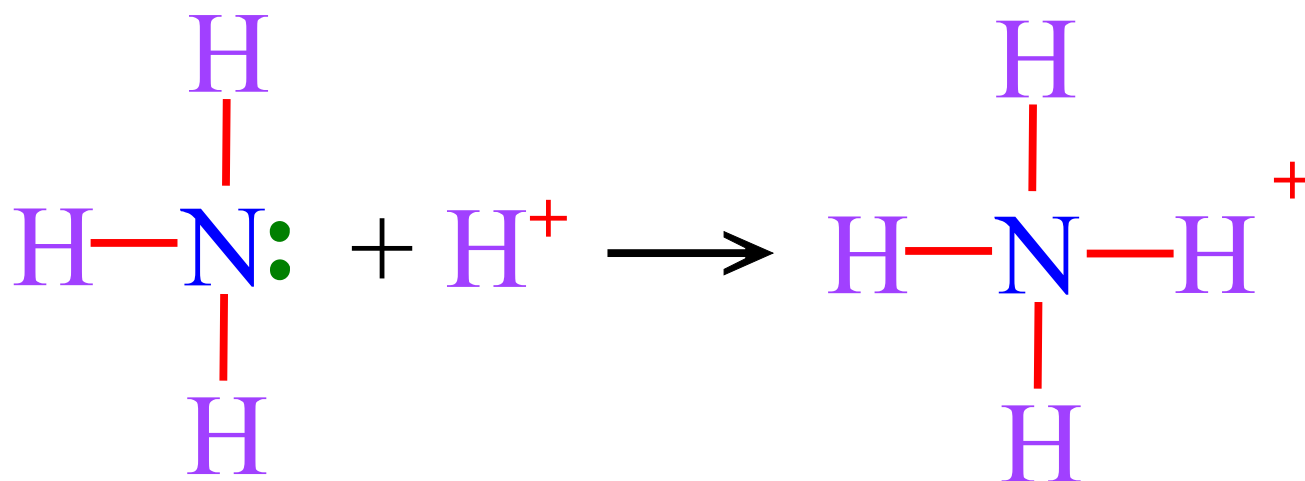
# 1) Coordinate Covalent Bonds

Both  $e^-$  in the shared pair donated by one atom

- atoms w. l.p.e.

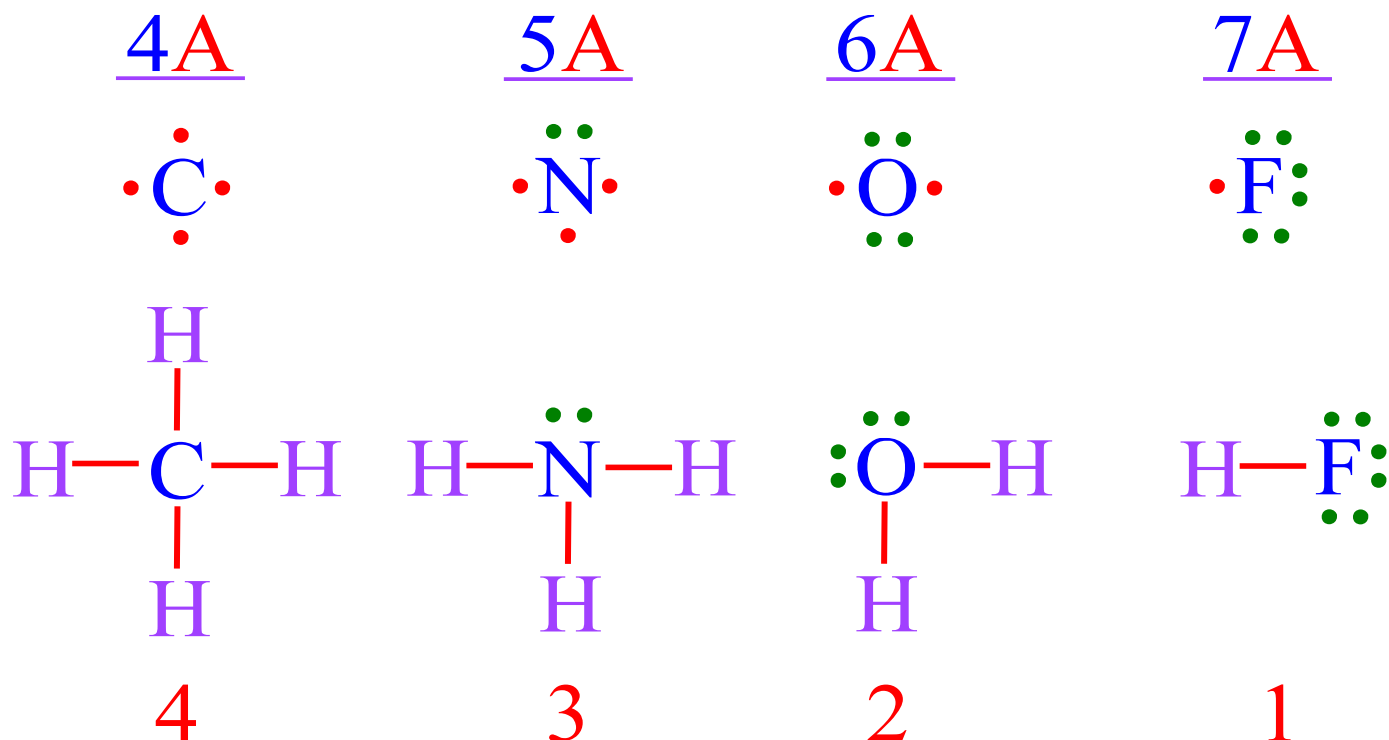
Once formed this bond is indistinguishable from other bonds.

a) Ex.



## B) Group No. & Number of Bonds Formed

Atoms combine to achieve noble gas config.,  $1s^2$  or  $ns^2np^6$ , an OCTET



Unshared  $e^-$  pairs shown as dots :

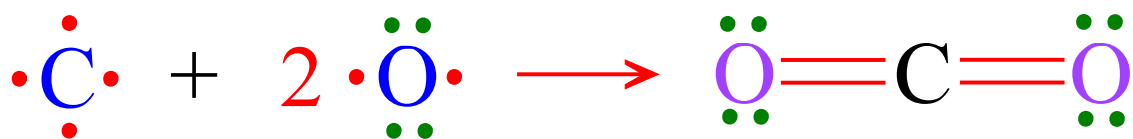
nonbonding or lone pair  $e^-$

## C) Multiple Bonds

Complete **octet** by forming **more** than **one bond** between **same 2 atoms**

### 1) Double Bond

Sharing of **2 pairs** of  $e^-$  (**4  $e^-$** )



### 2) Triple Bond

Sharing of **3 pairs** of  $e^-$  (**6  $e^-$** )





## IV) Bond Polarity & Electronegativity

### A) Bond Polarity

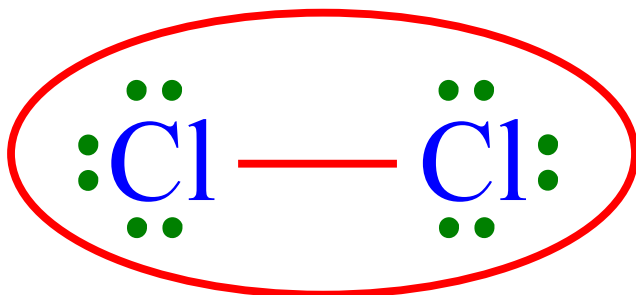
#### 1) Ionic Bond

complete  $e^-$  transfer

$\text{Cs}^+$   $\text{Cl}^-$   $e^-$  from  $\text{Cs}^+$  spends  
most of its time in  
vicinity of  $\text{Cl}^-$ .

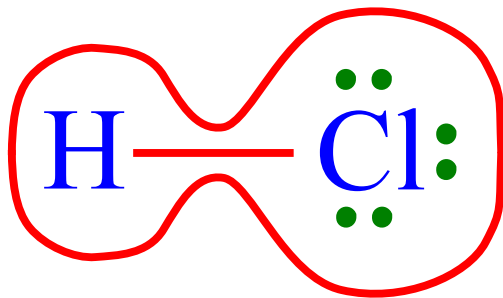
#### 2) Pure Covalent Bond:

$e^-$  pair shared equally  
by 2 identical atoms



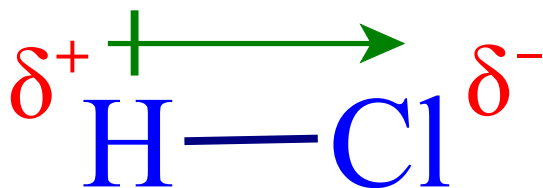
### 3) Polar Covalent Bond:

- $e^-$  pair shared **unequally** between **2 diff. atoms**
- Somewhere **between** ionic & **covalent** bonds

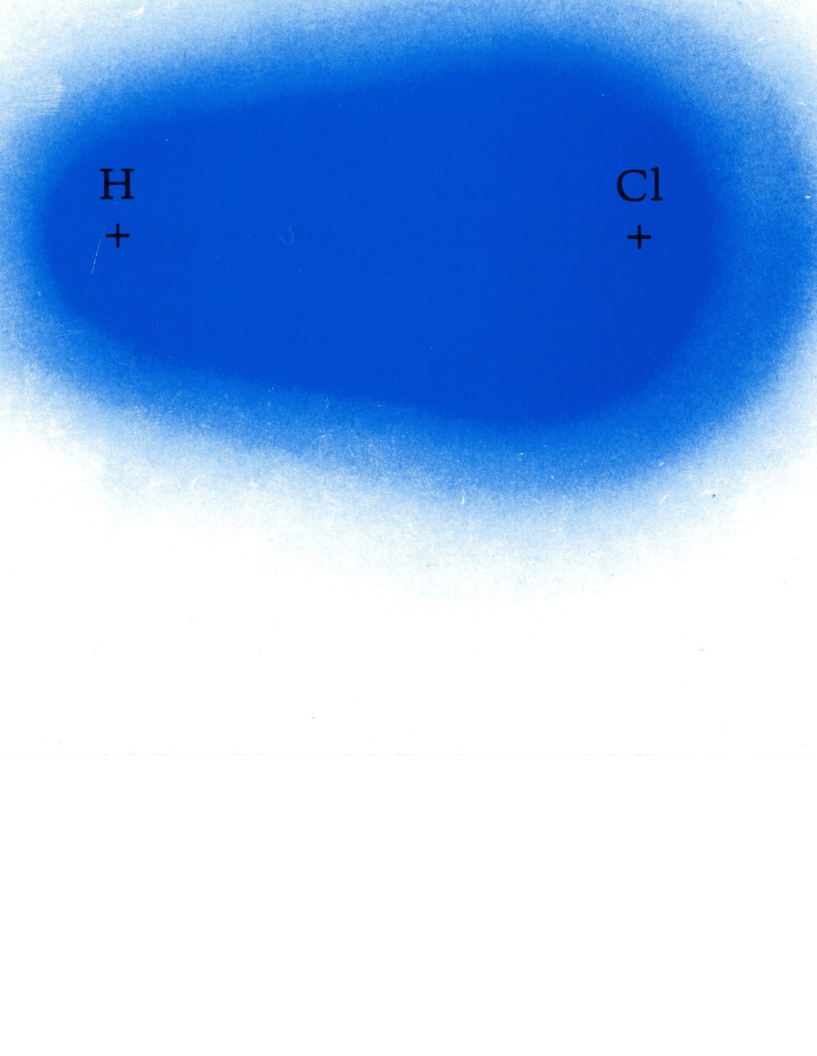


**Dipole** : (+) & (-) charges  
separated by a **distance**

**Extent** of **polarity** **depends** on  
**IE** and **EA** of 2 **atoms** involved



Ebbing, GENERAL CHEMISTRY  
Figure 7.4 Distribution of bonding electrons in HCl



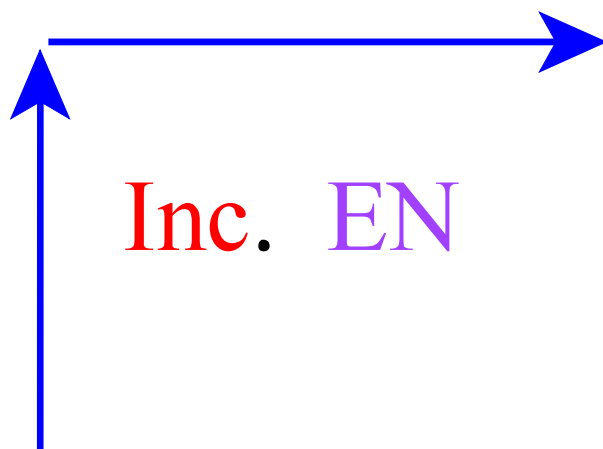
## B) Electronegativity

Reflects the **ability** of an **atom** in a **molecule** to **attract** bonding  $e^-$  to itself.

- depends somewhat on **bonds** **formed** & **rest** of **molecule**

### Relative Scale:

**F** is most **EN** element and has a value of **4.0** (Pauling Scale)



increasing electronegativity  $\longrightarrow$

IA		IIA	IIIA	IVA	VA	VIA	VIIA	
<b>H</b> <b>2.1</b>								
<b>Li</b> <b>1.0</b>	<b>Be</b> <b>1.5</b>	<b>B</b> <b>2.0</b>	<b>C</b> <b>2.5</b>	<b>N</b> <b>3.0</b>	<b>O</b> <b>3.5</b>	<b>F</b> <b>4.0</b>		
<b>Na</b> <b>0.9</b>	<b>Mg</b> <b>1.2</b>	<b>Al</b> <b>1.5</b>	<b>Si</b> <b>1.8</b>	<b>P</b> <b>2.1</b>	<b>S</b> <b>2.5</b>	<b>Cl</b> <b>3.0</b>		
<b>K</b> <b>0.8</b>	<b>Ca</b> <b>1.0</b>	<b>Ga</b> <b>1.6</b>	<b>Ge</b> <b>1.8</b>	<b>As</b> <b>2.0</b>	<b>Se</b> <b>2.4</b>	<b>Br</b> <b>2.8</b>		
<b>Rb</b> <b>0.8</b>	<b>Sr</b> <b>1.0</b>	<b>In</b> <b>1.7</b>	<b>Sn</b> <b>1.8</b>	<b>Sb</b> <b>1.9</b>	<b>Te</b> <b>2.1</b>	<b>I</b> <b>2.5</b>		
<b>Cs</b> <b>0.7</b>	<b>Ba</b> <b>0.9</b>	<b>Tl</b> <b>1.8</b>	<b>Pb</b> <b>1.8</b>	<b>Bi</b> <b>1.9</b>	<b>Po</b> <b>2.0</b>	<b>At</b> <b>2.2</b>		
<b>Fr</b> <b>0.7</b>	<b>Ra</b> <b>0.9</b>							

increasing electronegativity  $\uparrow$

## C) EN & Bond Polarity

Generally, use **diff.** between E.N. to **predict** the **type** of **bond** formed.


$\Delta EN > 2.0$  ionic

$0.5 \leq \Delta EN < 2.0$  polar covalent

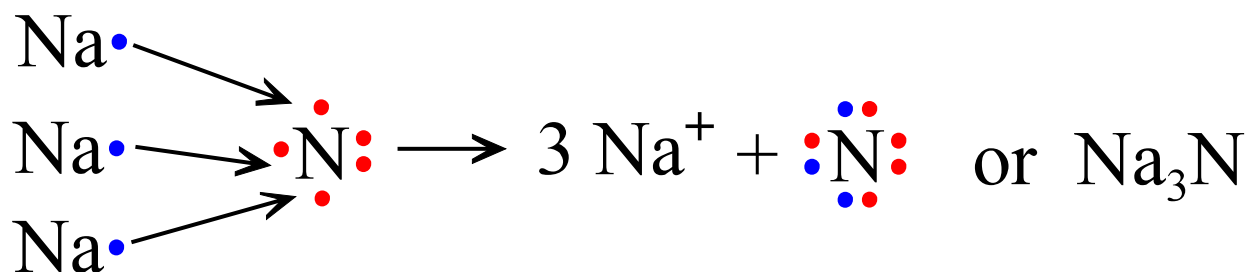
$\Delta EN < 0.5$  nonpolar covalent

$\Delta EN = 0$  pure covalent

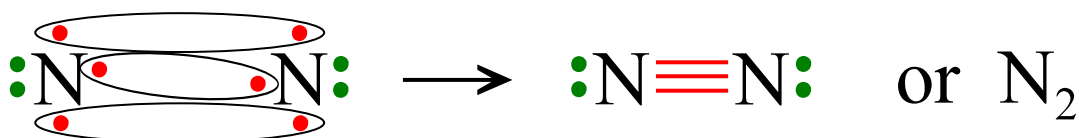
## Nitrogen Can Achieve the Noble Gas Configuration of Neon in Three Ways

Lewis structure of nitrogen atom, Group 5A  three electrons short of neon configuration

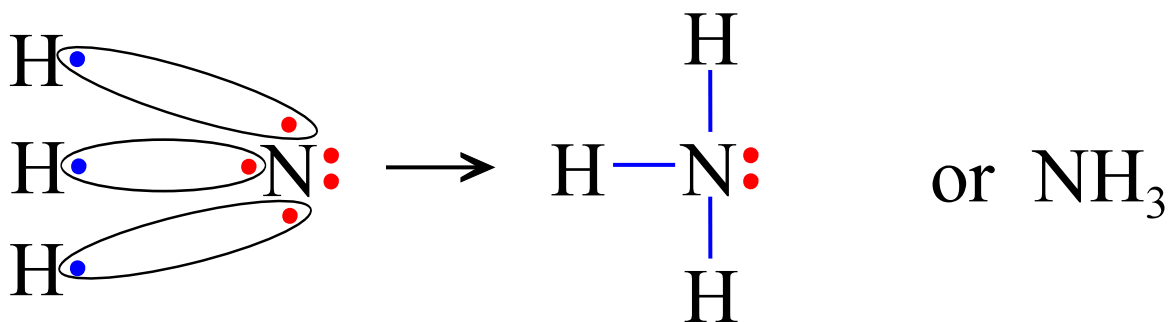
1. electron transfer  $\longrightarrow$  ionic bond



2. equal sharing of electron pairs  $\longrightarrow$  pure covalent bond



3. unequal sharing of electron pairs  $\longrightarrow$  polar-covalent bond



## D) Dipole Moment

A polar molecule has opposite charges separated by a distance,

it has a dipole moment

magnitude of charge  $\times$  distance between charges

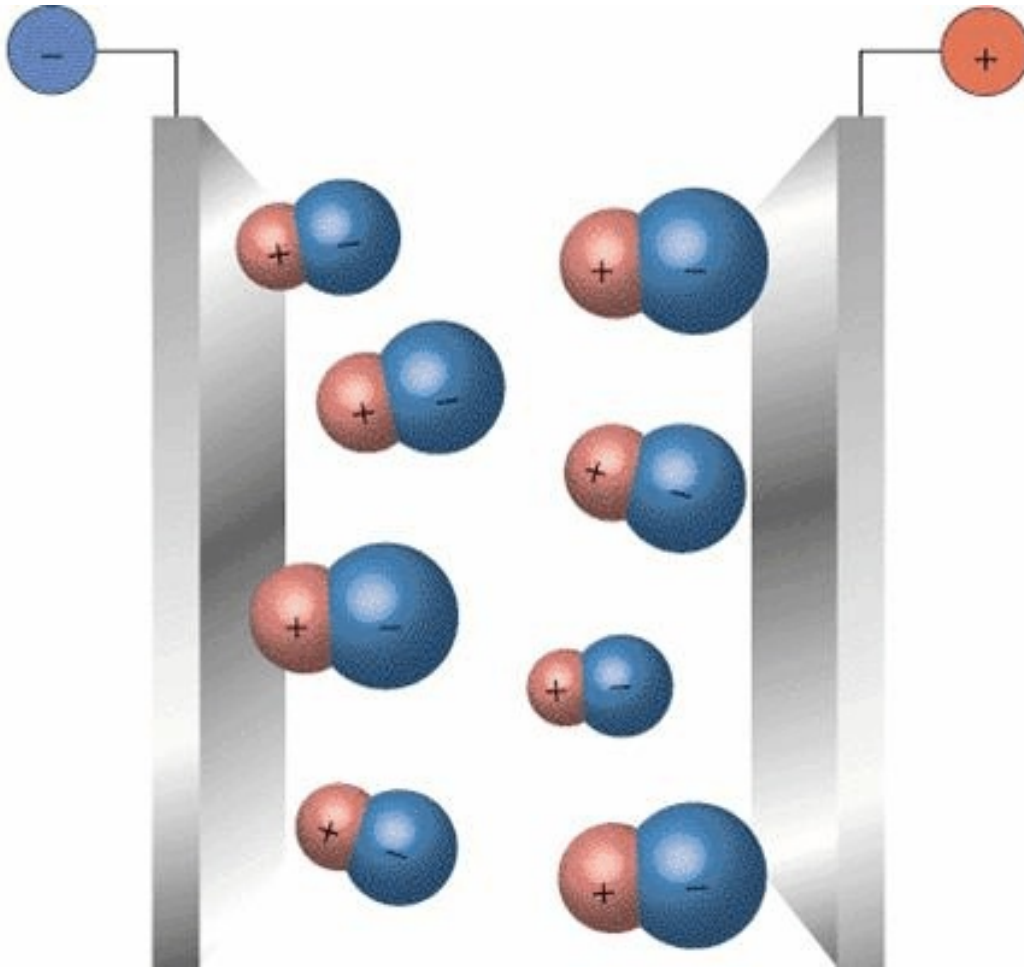
$$\mu = Q \cdot r \quad (\text{Debye, D})$$

$$1 \text{ D} = 3.34 \times 10^{-30} \text{ coulomb-meters}$$

The magnitude of the charge is indicated by the difference in EN & the distance which is the bond length



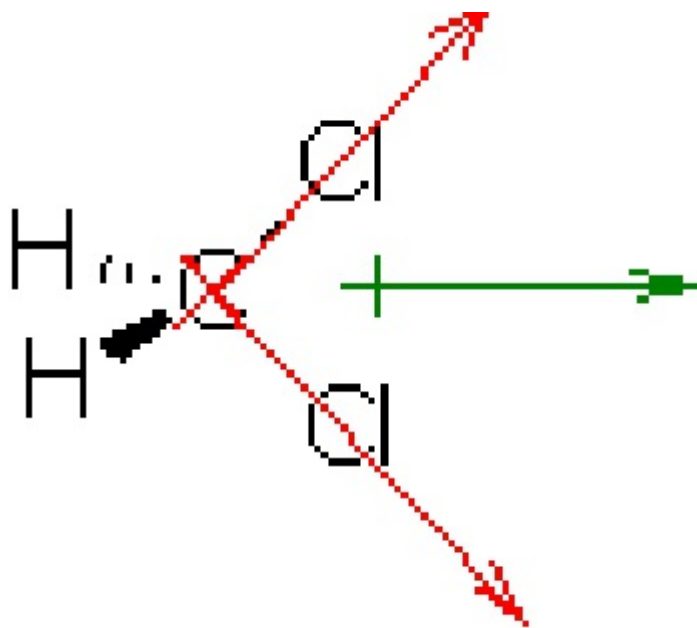
# Polar molecules **interact** w. **electric fields**



Experimentally the **dipole moment** is determined by how the **molecule behaves** in an **electric field**.

The **more polar** the **molecule**, the **larger** the **dipole moment**.

The **molecular dipole moment** is the **vector sum** of the **bond moments**, i.e.



1) Ex: Calculate **dipole moment** and **partial charges** on the atoms for HF. The **bond length** is 0.92 Å.

a) Calc. dipole moment assuming charges of +1 and -1

$$\mu = Q \cdot r$$

$$r = 0.92 \text{ \AA} \times (10^{-10} \text{ m/1 \AA})$$

$$\mu = (1.60 \times 10^{-19} \text{ C})(9.2 \times 10^{-11} \text{ m}) \left( \frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C}\cdot\text{m}} \right)$$

$$\mu = 4.407 \text{ D}$$

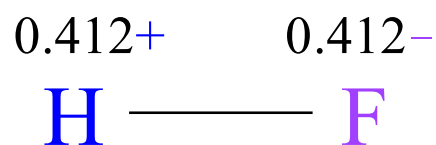
b) Calc. **partial charges** in  $e$

Experimentally,  $\mu = 1.82 \text{ D}$

$$Q = \frac{\mu}{r}$$
$$= \frac{(1.82 \text{ D}) (3.34 \times 10^{-30} \text{ C}\cdot\text{m}/1 \text{ D})}{(0.92 \times 10^{-10} \text{ m})}$$
$$= \underline{6.607} \times 10^{-20} \text{ C}$$

$Q$  in  $e$ :

$$= (6.607 \times 10^{-20} \text{ C}) \times \frac{1 e}{1.60 \times 10^{-19} \text{ C}}$$
$$= \underline{0.412} e$$



**TABLE 8.3 ■ Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides**

<b>Compound</b>	<b>Bond Length (Å)</b>	<b>Electronegativity Difference</b>	<b>Dipole Moment (D)</b>
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

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## V) Lewis Structures, (LS)

Very simple model of chemical bonding and the structure of molecules.

deals with valence shell  $e^-$

- generally think octet rule

Do **not** provide information about the observed geometry (shape) of molecules, explain how or why bonds form, or how the  $e^-$  are shared in bonds.

## A) 2 General Requirements

- 1) All val.  $e^-$  must be shown
- 2) All atoms generally have octet of  $e^-$

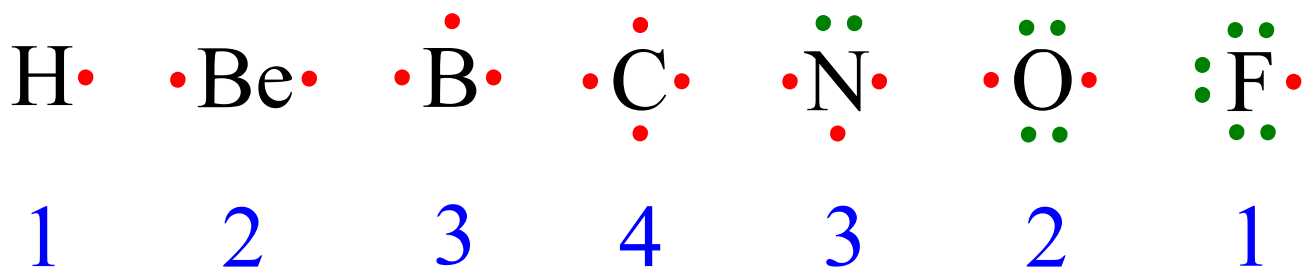
### a) Exceptions

H Li Be B (Al) less than octet

Periods 3-6 greater than octet

## B) Number Bonds Atoms Generally form?

- determined by possible #  
unpaired  $e^-$  in valence shell



## B) Procedure for Drawing Lewis Struc.

### 1) Number val. e<sup>-</sup> Available, A

Determine **total # val. e<sup>-</sup>**

$$\# \text{ val. e}^- = \text{group \#}$$

#### a) adjust for charge

##### 1) subtract for (+) chg.



$$A = 3(1) + 1(6) - 1 = 8 \text{ e}^- \text{ avail.}$$

##### 2) add for (-) chg.



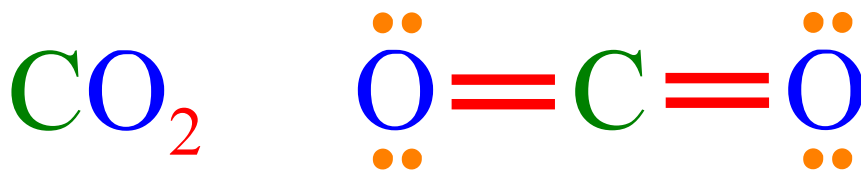
$$A = 1(4) + 3(6) + 2 = 24 \text{ e}^- \text{ avail.}$$



## 2) Draw Skeleton Structure

Connect atoms w. single bond

- a) **least** E.N. element is  
**usually** central element  
( **except** H )



- b) **Multiple** O-atoms **usually**  
**bonded** to **central** atom  
(**not** to **each** other)

3) Complete octets on terminal atoms

4) Place remaining  $e^-$  on central atom

$$\begin{array}{ccc} \# e^- & = & \# e^- \\ \text{remaining} & & \text{available} - \text{used} \end{array}$$

distribute on central atom

- for every  $2 e^-$  short form 1 more bond to central atom

(form multiple bonds)

5) Check Formal Charges

## C) Examples



a) How many e<sup>-</sup> do we have ?

$$\begin{array}{ccccccc} \text{O} & & \text{H} & & +1 \text{ chg} & & \\ 6 \text{ e}^- & + & 3(1 \text{ e}^-) & - & 1 \text{ e}^- & = & 8 \text{ e}^- \end{array}$$

b) Draw skeleton struct. &  
distribute e<sup>-</sup>

c) Complete octet on central atom

## 2) ClO<sub>2</sub><sup>-</sup>

a) How many e<sup>-</sup> do we have ?

$$\begin{array}{ccccccc} \text{Cl} & & \text{O} & & -1 \text{ chg} & & \\ 7 e^- & + & 2(6 e^-) & + & 1 e^- & = & 20 e^- \end{array}$$

b) Draw skeleton struct. &  
distribute e<sup>-</sup>

c) Complete octet on central atom

### 3) Cl<sub>2</sub>CO

a) How many e<sup>-</sup> do we have ?

$$\begin{array}{ccccccc} \text{Cl} & & \text{C} & & \text{O} & & \\ 2(7 \text{ e}^-) & + & 4 \text{ e}^- & + & 6 \text{ e}^- & = & 24 \text{ e}^- \end{array}$$

b) Draw skeleton struct. &  
distribute e<sup>-</sup>

c) Complete octet on central atom

## D) Formal Charges

Decide which **alternative Lewis structures** are **most important**

- 1) **Bonding e<sup>-</sup>** **divided equally** between atoms forming the bond  
- **homolytic bond cleavage**
- 2) **Nonbonding e<sup>-</sup>** assigned **entirely** to atom on which they **reside**

$$\text{FC} = \# \text{ val. e}^- - \left( \frac{1}{2} \# \text{ bond e}^- + \# \text{ n.b.e.} \right)$$

- 3) Should **add** to give **actual charge** on molecule

Note:

do **NOT** represent **real charges**  
(not same as ox. numbers.)

## 4) Rules

a) Choose **LS** with **lowest** magnitudes of **FC**'s

- **lowest sum** of **absolute values** of **FC**'s

b) Choose **LS** w. (-) **FC** on **more EN** atom whenever possible

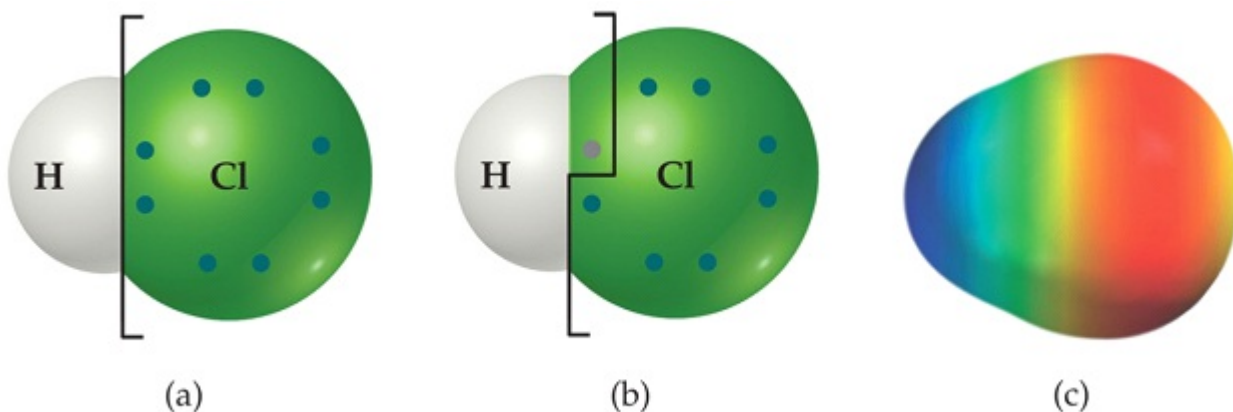
c) **Adjacent Charge Rule**

**LS** w. **FC** of **same sign** on **adjacent atoms** are **NOT** likely

**Note:** Oxidation numbers and FC are **NOT** the same thing.

a) Ox. #'s are calculated by assigning **ALL** electrons in a bond to the more **EN** atom - **heterolytic** bond **cleavage**

b) FC are calculated by assigning the **electrons** in a bond **equally** to both atoms - **homolytic** bond **cleavage**



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4) Ex:  $\text{N}_2\text{O}$ , nitrous oxide

a) Valence  $e^-$

2 N O

b) Skeleton Structure

N N O

c) Complete octets

#  $e^-$  left

Middle N 4  $e^-$  short

N N O N N O

Why **not** the following:

N N O

N O N

N O N

## VI) Resonance Structures

Sometimes can draw **more** than **one** acceptable Lewis Structure

### Resonance Structures

**Differ** **only** in the **placement** of the  $e^-$

**Actual** structure is an “**average**” or “**combination**” of **ALL** the resonance forms

$e^-$  are **delocalized** over **several** atoms

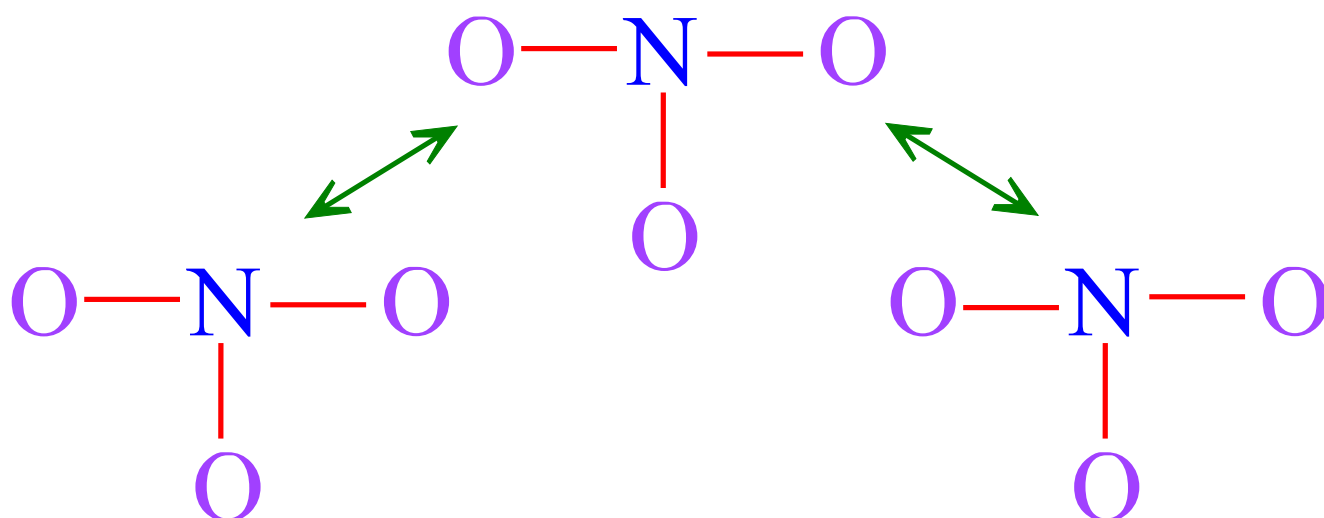
A) NO<sub>3</sub><sup>-</sup>, nitrate ion

a) How many e<sup>-</sup> do we have ?

N      3 O      chg

b) Draw skeleton struct. &  
distribute e<sup>-</sup>

### c) Structure

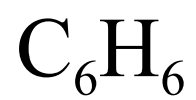


Bonds are somewhere **between**  
**single** & **double** bonds

“**extra**”  $e^-$  **pair** is **Delocalized**

- **spread** out over all  
**3** **bonding** regions

## B) Benzene molecule



## VII) Exceptions to Octet Rule

### A) Odd Number of Electrons - Radicals



1) Ex: NO<sub>2</sub>

a) How many e<sup>-</sup> do we have ?



b) Draw skeleton struct. &  
distribute e<sup>-</sup>



c) Structure

O N O

O N O

O N O

O N O



## B) Central Atom w. Less than Octet

Central atom is  $e^-$  deficient

- Do **NOT** follow **Octet Rule**

Be

B (Al)

$\cdot\text{Be}\cdot$

$\cdot\overset{\cdot}{\text{B}}\cdot$

2

3

bonds

- Do **NOT** form **multiple bonds**

$\text{BeCl}_2$

$\text{BF}_3$

$\text{Cl}-\text{Be}-\text{Cl}$

$\begin{array}{c} \text{F}-\text{B}-\text{F} \\ | \\ \text{F} \end{array}$

## C) Central Atom w. More than Octet

More than 8 e<sup>-</sup> on central atom

“expanded” valence shell

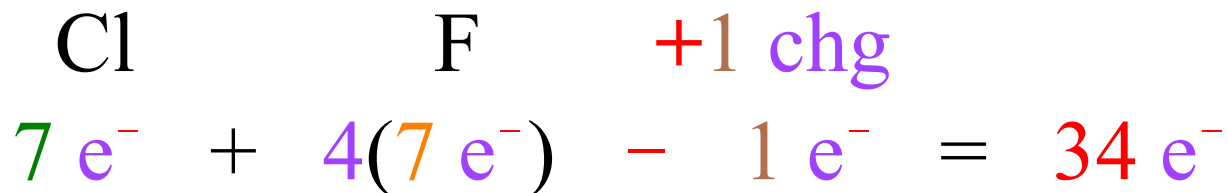
S, P, Cl, Se, As, Br, etc.

occurs **only** for elements  
in **3<sup>rd</sup>** period & **below**

- **larger size** (most impt. factor)
- have **empty d-orbitals**  
in **valence shell**  
(minor factor)

1) Ex:  $\text{ClF}_4^+$

a) How many  $e^-$  do we have ?



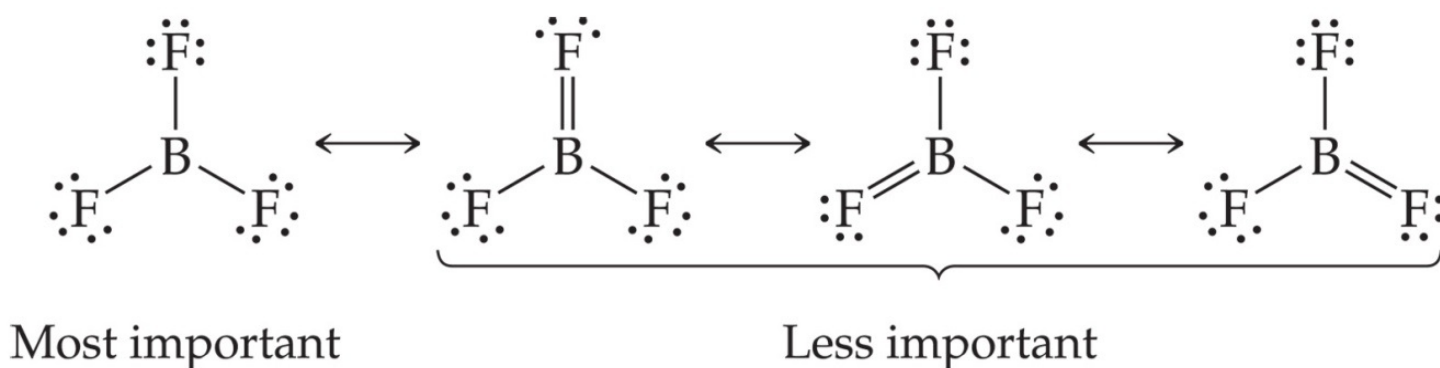
b) Draw **skeleton struct.** &  
**distribute  $e^-$  on outer atoms**

c) Structure

## D) Summary of LS

Good LS should:

- 1) obey **octet rule** if possible
- 2) have **fewest** number of FC's
- 3) have (-) **charges** on **more** EN atoms
- 4) **Not** have **same charge adjacent**



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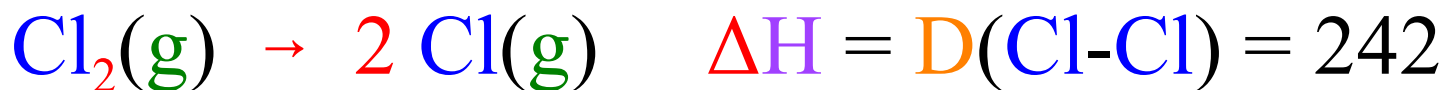
## VIII) Strengths of Covalent Bonds

For ionic compounds LE is an indication of the strength of attraction of the ions.

For covalent bonds the strength is measured as the bond dissociation energy (BDE) or bond enthalpy (BE).

Energy required to dissociate one mole of bonds in the gas phase (kJ/mol)

### A) Homonuclear Molecules



H-H bond is stronger than Cl-Cl bond

H<sub>2</sub>(g) is more stable and less reactive

## B) Polyatomic Molecules

**Average BE** values for a particular bond from several molecules

**TABLE 5.4 Average Bond Enthalpies (kJ/mol)**

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C=C	614	N—O	201	O=O	495	Cl—F	253
C—N	293	N—F	272	O—F	190	Cl—Cl	242
C—O	358	N—Cl	200	O—Cl	203		
C=O	799	N—Br	243	O—I	234	Br—F	237
C—F	485					Br—Cl	218
C—Cl	328	H—H	436			Br—Br	193
C—Br	276	H—F	567				
C—I	240	H—Cl	431			I—Cl	208
		H—Br	366			I—Br	175
		H—I	299			I—I	151

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**NOTE:**



## C) Bond Length & Bond Energy

Diff. between single, double & triple bonds are seen in bond lengths & energies

Bond Length: Distance between nuclei of the 2 atoms bonded

Bond Energy: Energy required to break a mole of a particular bond

	$\text{N}-\text{N}$		$\text{N}=\text{N}$		$\text{N}\equiv\text{N}$
length (nm)	0.145	>	0.123	>	0.109
energy (kJ/mol)	163	<	418	<	941
Bond Order	1		2		3