Molecules Module – Lecture 1:
Lewis theory and bonding

Learning Objective	Openstax 2e Chapter
Lewis Theory	7.3
Covalent Bonding	7.2
Polar Covalent Bonds	7.2
Electronegativity	7.2

Suggested Practice Problems

Chapter 7 Exercises – Questions: 13, 15, 17, 21

Answers can be found in the Chapter 7 Answer Key

Periodic Table of the Elements

Ground State Electron Configurations

6

C

core $1s^2$ $2s^2p^2$ valence

1A	2A	3B	4B	5B	6B	7B				1B	2B				6A	7A	8A
1 H $1s^1$																	2 He $1s^2$
3 Li $1s^22s^1$	4 Be $1s^22s^2$														8 O	9 F $1s^22s^2p^5$	10 Ne $1s^22s^2p^6$
11 Na $[Ne]3s^1$	12 Mg $[Ne]3s^2$														S	17 Cl $[Ne]3s^2p^5$	18 Ar $[Ne]3s^2p^6$
19 K $[Ar]4s^1$	20 Ca $[Ar]4s^2$	21 Sc $[Ar]3d^14s^2$	22 Ti $[Ar]3d^24s^2$	23 V $[Ar]3d^34s^2$	24 Cr $[Ar]3d^54s^1$	25 Mn $[Ar]3d^54s^2$	26 Fe $[Ar]3d^64s^2$	27 Co $[Ar]3d^74s^2$	28 Ni $[Ar]3d^84s^2$	29 Cu $[Ar]3d^{10}4s^1$	Zn $[Ar]3d^{10}4s^2$	Ga $[Ar]3d^{10}4s^2p^1$	Ge $[Ar]3d^{10}4s^2p^2$	As $[Ar]3d^{10}4s^2p^3$	34 Se $[Ar]3d^{10}4s^2p^4$	35 Br $[Ar]3d^{10}4s^2p^5$	36 Kr $[Ar]3d^{10}4s^2p^6$
37 Rb $[Kr]5s^1$	38 Sr $[Kr]5s^2$	39 Y $[Kr]4d^15s^2$	40 Zr $[Kr]4d^25s^2$	41 Nb $[Kr]4d^45s^1$	42 Mo $[Kr]4d^55s^1$	43 Tc $[Kr]4d^55s^2$	44 Ru $[Kr]4d^75s^1$	45 Rh $[Kr]4d^85s^1$	46 Pd $[Kr]4d^{10}$	47 Ag $[Kr]4d^{10}5s^1$	48 Cd $[Kr]4d^{10}5s^2$	49 In $[Kr]4d^{10}5s^2p^1$	50 Sn $[Kr]4d^{10}5s^2p^2$	51 Sb $[Kr]4d^{10}5s^2p^3$	52 Te $[Kr]4d^{10}5s^2p^4$	53 I $[Kr]4d^{10}5s^2p^5$	54 Xe $[Kr]4d^{10}5s^2p^6$
55 Cs $[Xe]6s^1$	56 Ba $[Xe]6s^2$	57-71 Lanthanides	72 Hf $[Xe]4f^{14}5d^26s^2$	73 Ta $[Xe]4f^{14}5d^36s^2$	74 W $[Xe]4f^{14}5d^46s^2$	75 Re $[Xe]4f^{14}5d^56s^2$	76 Os $[Xe]4f^{14}5d^66s^2$	77 Ir $[Xe]4f^{14}5d^76s^2$	78 Pt $[Xe]4f^{14}5d^96s^1$	79 Au $[Xe]4f^{14}5d^{10}6s^1$	80 Hg $[Xe]4f^{14}5d^{10}6s^2$	81 Tl $[Xe]4f^{14}5d^{10}6s^2p^1$	82 Pb $[Xe]4f^{14}5d^{10}6s^2p^2$	83 Bi $[Xe]4f^{14}5d^{10}6s^2p^3$	84 Po $[Xe]4f^{14}5d^{10}6s^2p^4$	85 At $[Xe]4f^{14}5d^{10}6s^2p^5$	86 Rn $[Xe]4f^{14}5d^{10}6s^2p^6$
87 Fr $[Rn]7s^1$	88 Ra $[Rn]7s^2$	89-103 Actinides	104 Rf $[Rn]5f^{14}6d^27s^{2*}$	105 Db $[Rn]5f^{14}6d^37s^{2*}$	106 Sg $[Rn]5f^{14}6d^47s^{2*}$	107 Bh $[Rn]5f^{14}6d^57s^{2*}$	108 Hs $[Rn]5f^{14}6d^67s^{2*}$	109 Mt $[Rn]5f^{14}6d^77s^{2*}$	110 Ds $[Rn]5f^{14}6d^97s^{1*}$	111 Rg $[Rn]5f^{14}6d^{10}7s^{1*}$	112 Cn $[Rn]5f^{14}6d^{10}7s^{2*}$	113 Uut $[Rn]5f^{14}6d^{10}7s^27p^{1*}$	114 Fl $[Rn]5f^{14}6d^{10}7s^27p^{2*}$	115 Uup $[Rn]5f^{14}6d^{10}7s^27p^{3*}$	116 Lv $[Rn]5f^{14}6d^{10}7s^27p^{4*}$	117 Uus $[Rn]5f^{14}6d^{10}7s^27p^{5*}$	118 Uuo $[Rn]5f^{14}6d^{10}7s^27p^{6*}$

Lanthanides	57 La $[Xe]5d^16s^2$	58 Ce $[Xe]4f^15d^16s^2$	59 Pr $[Xe]4f^36s^2$	60 Nd $[Xe]4f^46s^2$	61 Pm $[Xe]4f^56s^2$	62 Sm $[Xe]4f^66s^2$	63 Eu $[Xe]4f^76s^2$	64 Gd $[Xe]4f^75d^16s^2$	65 Tb $[Xe]4f^96s^2$	66 Dy $[Xe]4f^{10}6s^2$	67 Ho $[Xe]4f^{11}6s^2$	68 Er $[Xe]4f^{12}6s^2$	69 Tm $[Xe]4f^{13}6s^2$	70 Yb $[Xe]4f^{14}6s^2$	71 Lu $[Xe]4f^{14}5d^16s^2$
Actinides	89 Ac $[Rn]6d^17s^2$	90 Th $[Rn]6d^27s^2$	91 Pa $[Rn]5f^26d^17s^2$	92 U $[Rn]5f^36d^17s^2$	93 Np $[Rn]5f^46d^17s^2$	94 Pu $[Rn]5f^67s^2$	95 Am $[Rn]5f^77s^2$	96 Cm $[Rn]5f^76d^17s^2$	97 Bk $[Rn]5f^97s^2$	98 Cf $[Rn]5f^{10}7s^2$	99 Es $[Rn]5f^{11}7s^2$	100 Fm $[Rn]5f^{12}7s^2$	101 Md $[Rn]5f^{13}7s^2$	102 No $[Rn]5f^{14}7s^2$	103 Lr $[Rn]5f^{14}6d^17s^2$

* values are based on theory and are not verified

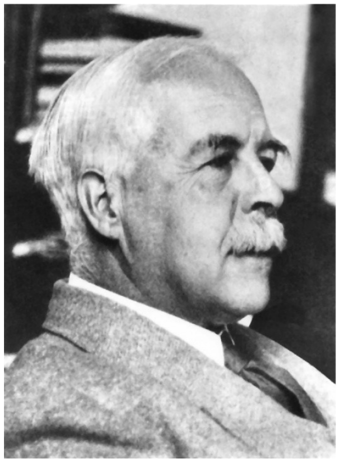
1s 2s 2p 3s 3p 3d

Hund's Rule

Lewis Theory: An Overview

One of the simplest methods of representing chemical bonding.

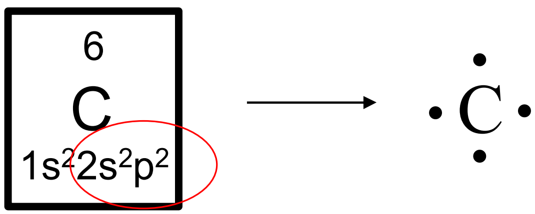
1. Valence electrons (V.E.), the electrons in the outermost shell, play a fundamental role in chemical bonding.
2. Complete electron transfer from one atom to another atom leads to an **ionic bond**.
3. Sharing of electrons between two atoms leads to a **covalent bond**.
4. Electrons are transferred or shared to give each atom a noble gas electron configuration - the **octet** rule (i.e., there are eight electrons in the valence shell of each atom, except hydrogen atoms with two electrons).
   - Rigidly followed in top two rows of periodic table.



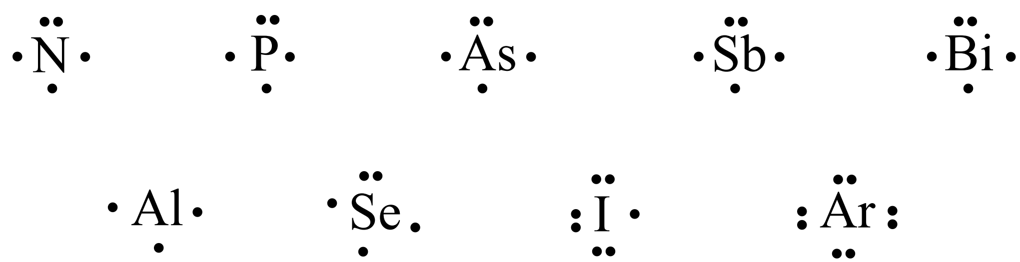
Gilbert N. Lewis
(1875-1946)

Lewis Symbols

1. The chemical symbol for the element represents the <u>nucleus</u> and the <u>core electrons</u>.
2. Dots around the symbol represent <u>valence electrons</u>. Place single dots on the sides of the symbol, up to a maximum four, then pair up dots.



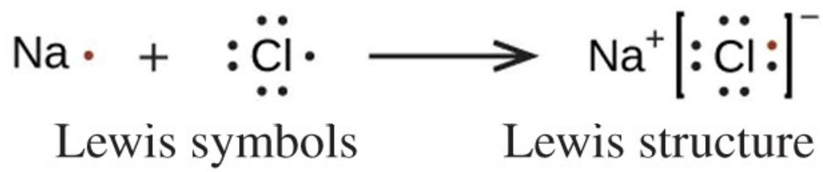
For C, there are 4 valence electrons (V.E.)



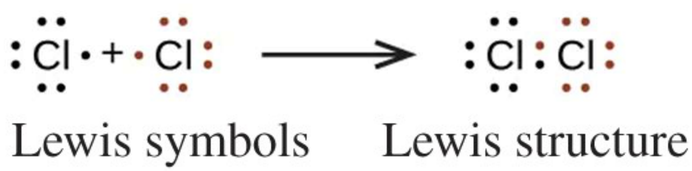
Lewis Structures

A combination of Lewis symbols that represent either transfer or sharing of electrons in a chemical bond.

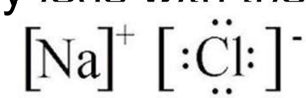
Ionic bonding (transfer of electrons):



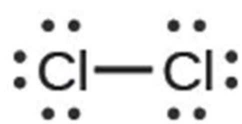
Covalent bonding (sharing of electrons):



- Ionic compounds are drawn as the Lewis structures of the individual ions. Square brackets are used to identify ions with the charge given as a superscript.



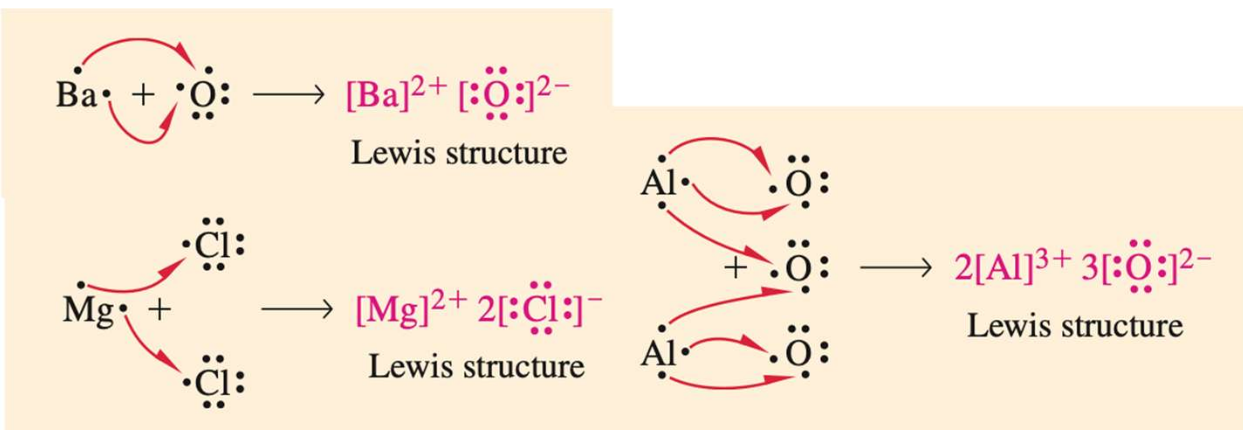
- Covalent compounds are drawn with the shared electrons represented as a line, indicating that the shared electrons are in a “covalent bond”.



Lewis Structures for Multivalent Ionic Compounds

- Formula unit of an ionic compound is the simplest electrically neutral collection of cations and anions from which the chemical formula of the compound can be established.
    1. The Lewis symbols of metal ions have no dots when all valence electrons are lost
    2. The ionic charges of both anions and cations are shown.

- Lewis structures of binary ionic compounds:



Note: The "half" arrow symbol depicts movement of a single electron.

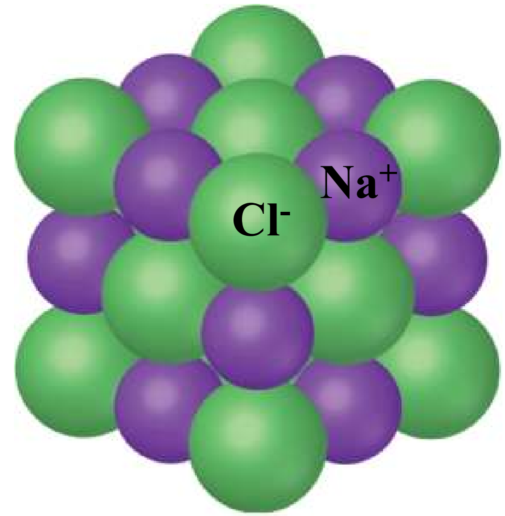
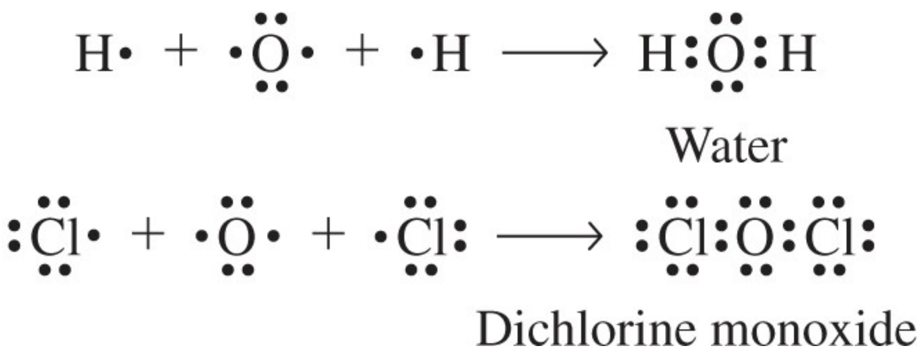


Figure 1: Portion of an <u>ionic crystal</u>

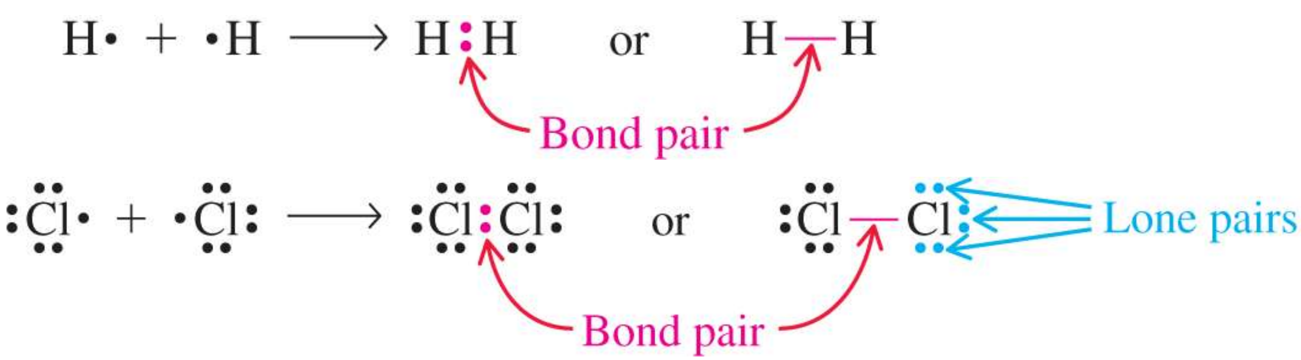
No bond is 100% ionic. All chemical bonds have some covalent character.

Covalent Bonding: An Introduction



Note: electrons in a bonding pair count in the octet of both atoms sharing them (yes, they get counted twice!). These Cl and O atoms all have satisfied octets because of the shared bonding electrons.

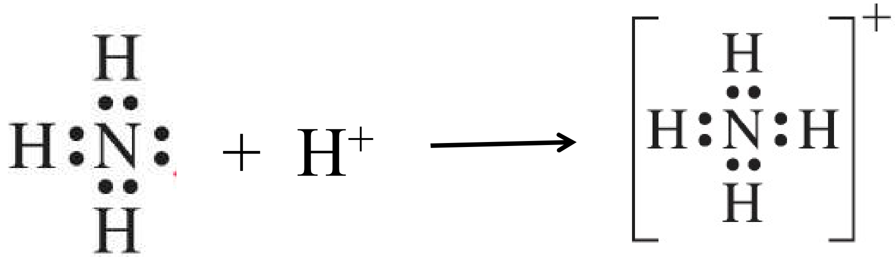
Usually, different symbols are used for describing “bond pair” and “lone pair” electrons. “Lines” are used for bonds but still represent two shared electrons.



Coordinate Covalent Bonds

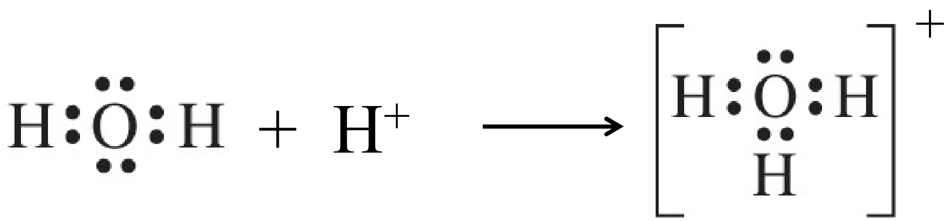
A covalent bond in which a single atom contributes both of the electrons to a shared pair.

Ammonia



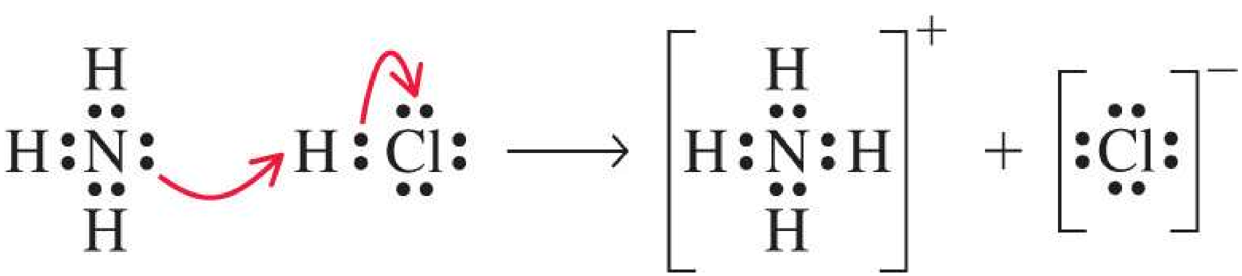
Ammonium ion

Water



Hydronium ion

The "bond pair" electrons come from one atom, but the coordinate covalent bond is indistinguishable from a regular covalent bond.

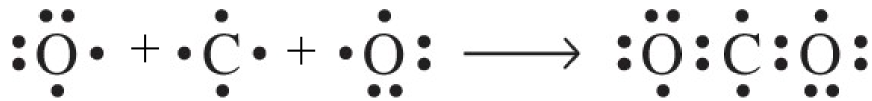


Note: The "full" arrow symbol depicts movement of electron pair.

Multiple Covalent Bonds

When more than one pair of electrons must be shared if an atom is to attain an octet.

CO_2

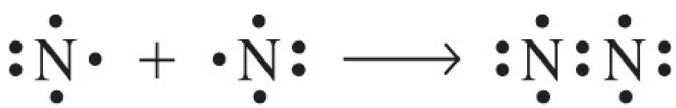


(*Octet not satisfied*)

Two double bonds

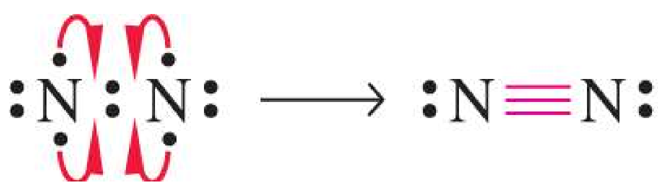
(4 “bond pair” electrons between C and each O)

N_2



(*Incorrect*)

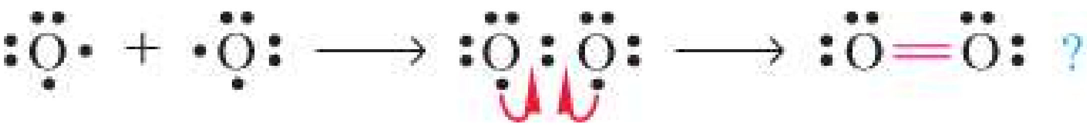
(*Octet not satisfied*)



A triple bond

(6 “bond pair” electrons between 2 N)

What about O_2?



- O_2 is paramagnetic (must have unpaired electrons), but the Lewis structure fails to account for it!

- Keep in mind that that merely being able to write a plausible Lewis structure does not prove that it is the correct electronic structure. Proof can come only through confirming experimental evidence.

Figure 2: Paramagnetism of Oxygen. Liquid oxygen is attracted between the poles of a magnet.

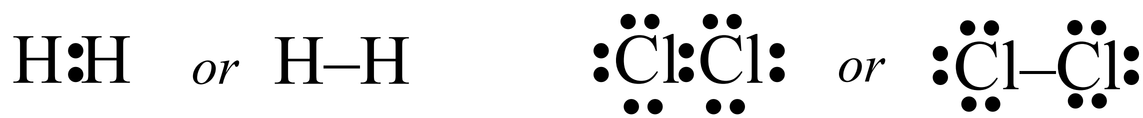
Polar Covalent Bonds

Most chemical bonds fall between the 2 extremes of 100% ionic and 100% covalent.

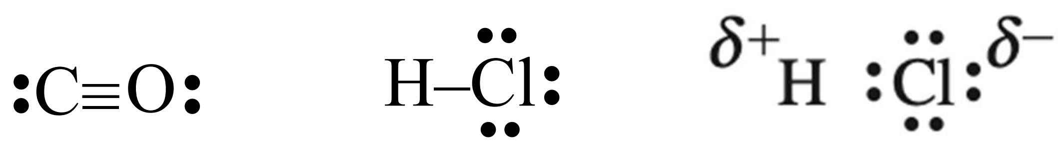
A covalent bond in which the electrons are <u>not shared equally</u> between two atoms is called a **polar covalent bond**.

In such a bond, electrons are displaced toward the more nonmetallic element resulting in partial charges on each atom.

Non-polar Covalent Bonds:

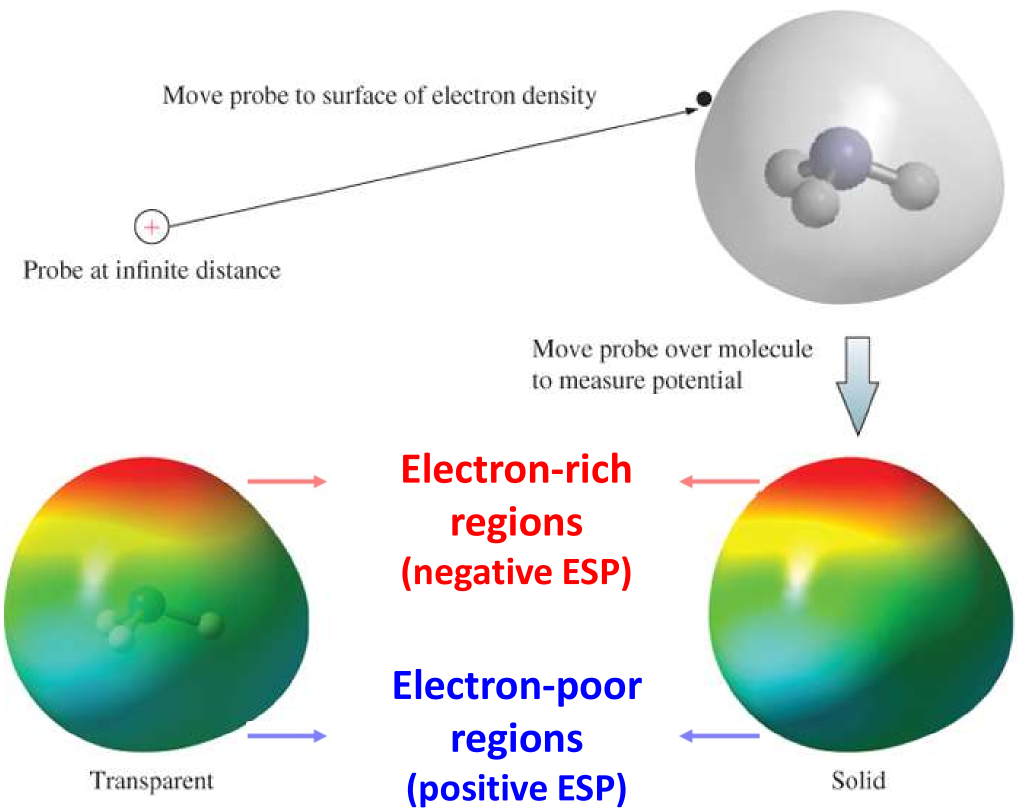


Polar covalent bonds:



Electrostatic Potential (ESP) Maps

A way to visualize the charge distribution within a molecule.



Electron density surface containing 95% of the charge density

Figure 3: Determination of the ESP map for ammonia

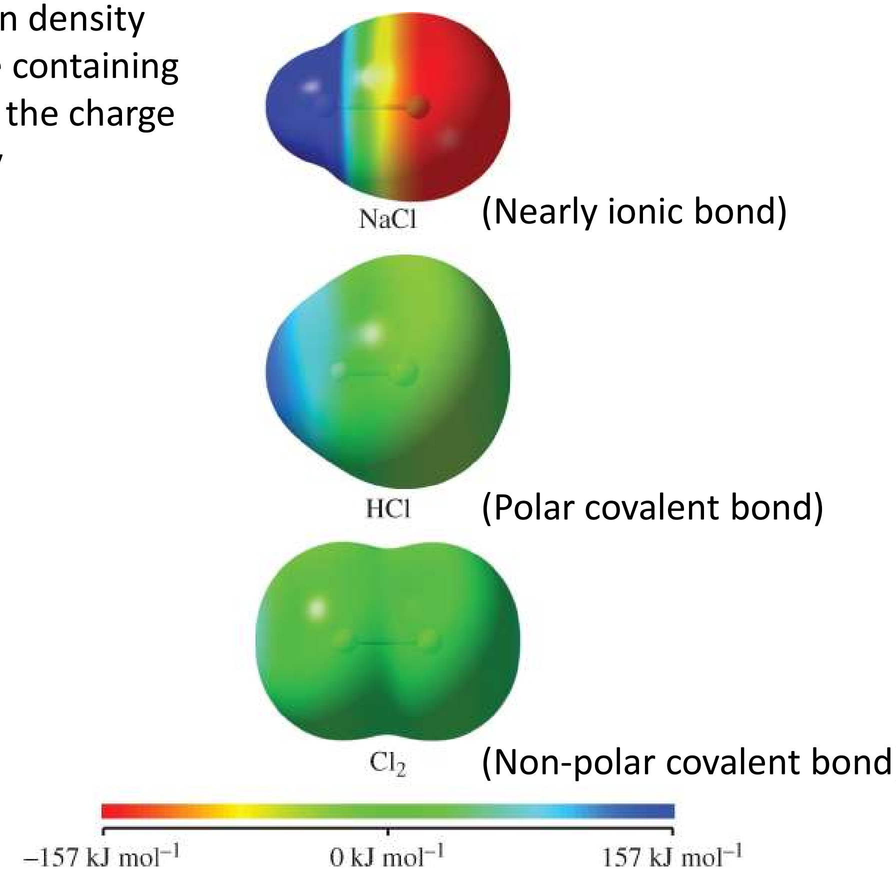


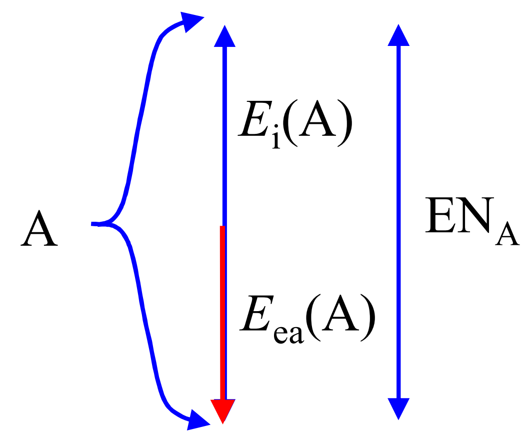
Figure 4: ESP map for NaCl, HCl, and Cl_2

Electronegativity (EN)

What determines the polarity of a covalent bond?

EN describes an atom's ability to compete for electron (or electron charge density) with other atoms to which it's bonded.

$$\mathrm{EN_A} \propto E_i(\mathrm{A}) - E_{ea}(\mathrm{A})$$



- $E_i(\mathrm{A}) > 0$ is the ionization energy of atoms A
  $\mathrm{A} \rightarrow \mathrm{A}^+ + \mathrm{e}^-$
- $E_{ea}(\mathrm{A}) < 0$ is the electron affinity of atoms A
  $\mathrm{A} + \mathrm{e}^- \rightarrow \mathrm{A}^-$

Variation of Bond Polarity with Electronegativity

When atoms A and B form a covalent bond, the polarity of this bond is determined by the absolute value of the difference between EN_A and EN_B, i.e.,

$$\Delta EN = |\ EN_A - EN_B\ |$$

0.9 0.7 0.4 = ΔEN

Greatest ionic character
Greatest range of colors

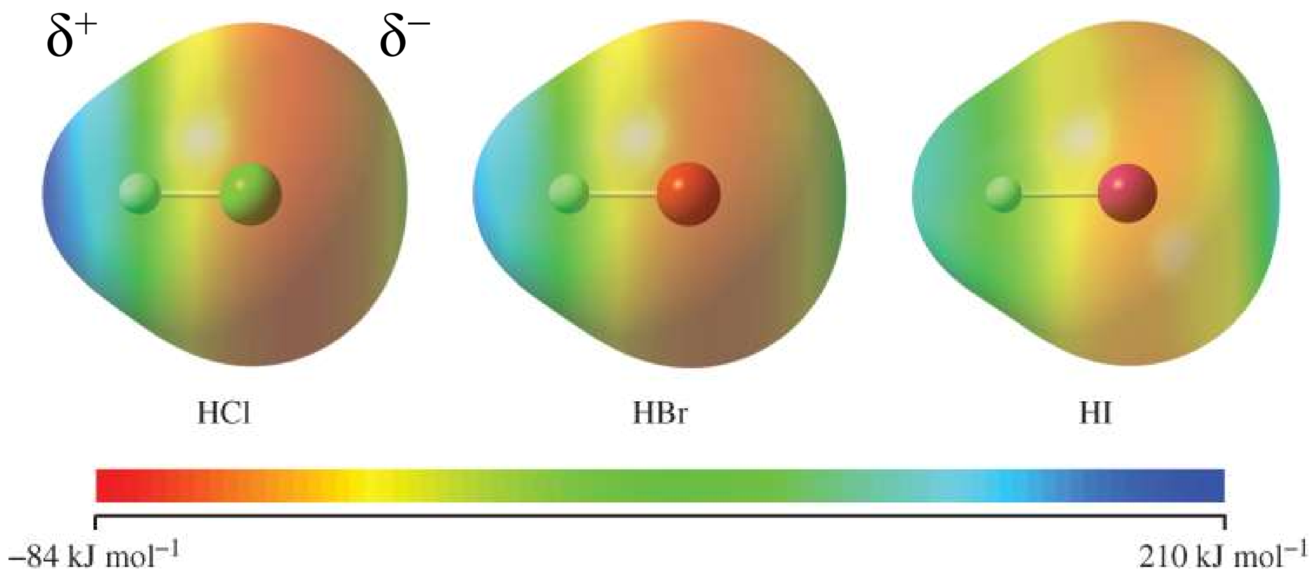


Figure 5. Electrostatic potential maps demonstrating differences in ionic character.

In general:

- The lower the EN, the more metallic the element is, and the higher the EN, the more nonmetallic it is.
- Electronegativities decrease from top to bottom in a group and increase from left to right in a period of elements
  -same pattern as ionization energy and electron affinity

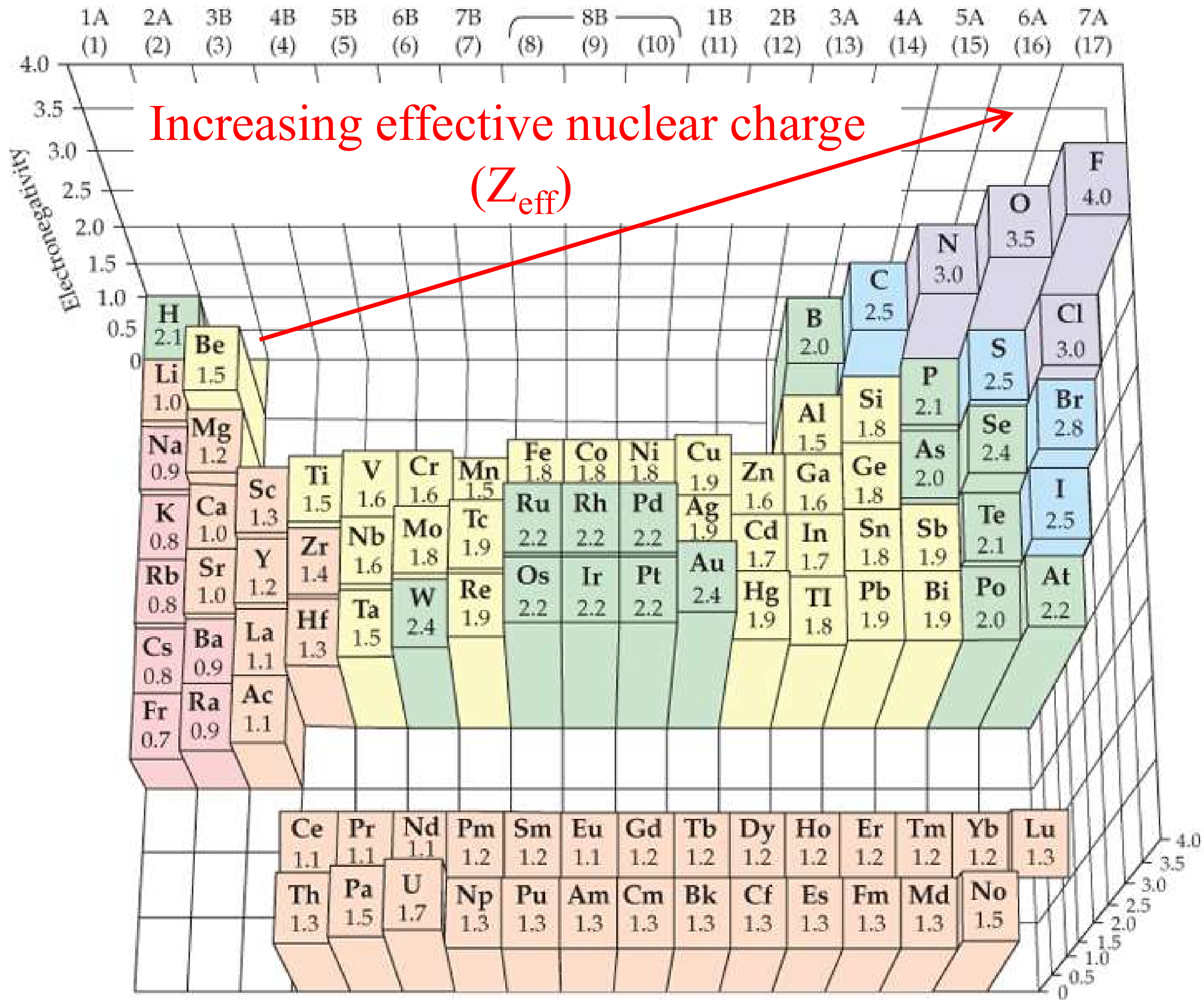


Figure 6. Electronegativities of the elements.

Electronegativity Difference (ΔEN)

Gives an insight into the amount of polar character in a covalent bond.

Electronegativity difference related to “percent ionic character”. Unequal sharing on spectrum, use threshold of 50% (ΔEN ~1.5) for ionic vs covalent bond.

$$\Delta EN = |\ EN_A - EN_B\ |$$

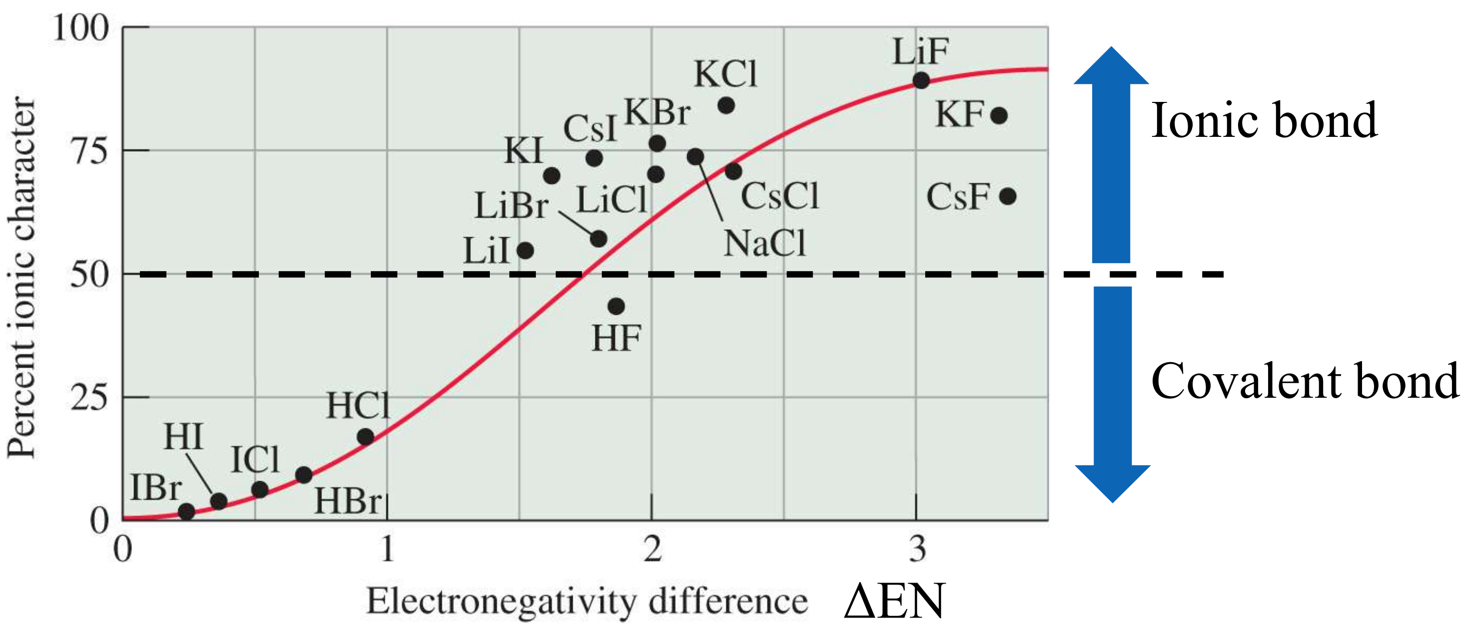


Figure 7: Percent ionic character of a chemical bond as a function of electronegativity difference.