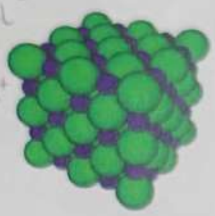
Bonding

When atoms or ions are strongly attracted to one another, we say that there is a **chemical bond** between them.

In chemical bonds, electrons are shared or transferred between atoms.

Types of chemical bonding include:

IONIC Bonding | COVALENT Bonding | METALLIC Bonding

Cl^-

Na^+


H_2O molecule


Ca Ca Ca

$NaCl_{(s)}$ | Ice $H_2O_{(s)}$ | Calcium $Ca_{(s)}$

electrostatic attraction between oppositely charged cations and anions

mutual attraction of atoms for a "shared" pair of electrons

electrons delocalized throughout a lattice of close-packed metal atoms.

Lewis symbols

Electrons involved in bonding are called *valence electrons*, and are found in the incomplete, outermost shell of an atom. We can represent these by use of **Lewis symbols.**

Place electrons on four sides of a square around the element's symbol e.g. for phosphorus, [Ne] $3s^2 3p^3$ we write: $:\dot{\underset{\cdot}{P}}\cdot$

The octet rule

An octet consists of full s and p subshells

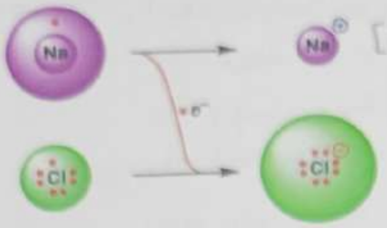
(electrons in filled d or f orbitals are NOT considered valence)

We know that s^2p^6 is a noble gas configuration. Atoms tend to gain, lose or share electrons until they are surrounded by **eight** electrons (four electron pairs).

This is known as the <u>octet rule</u>

Ionic bonding

A metal reacts with a non-metal by losing electrons to the non-metal, until both achieve the electron configuration of the noble gas (full octet) with the closest atomic number.



[Ne] 3s¹

[Ne] 3s² 3p⁵

[Ne]
Na^+ cation

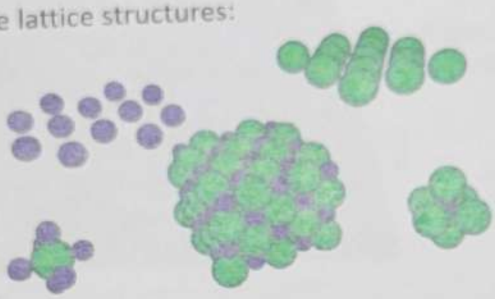
[Ne] 3s² 3p⁶ = [Ar]
Cl^- anion

Ionic structures

Ionic compounds have lattice structures:

Layer of Na^+ cations

Each Cl surrounded by 6 Na^+



Layer of Cl^- anions

Each Na^+ surrounded by 6 Cl^-

Portion of the NaCl lattice

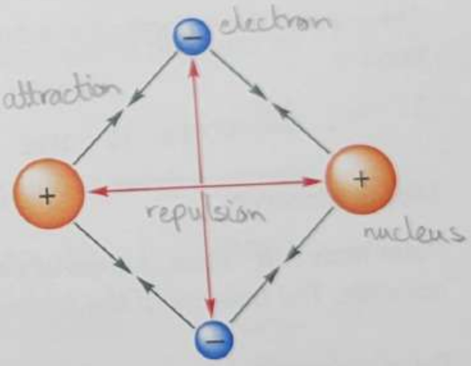
Covalent Bonding

In these bonds atoms share electrons. There are several electrostatic interactions in these bonds:

Attractions between electrons and nuclei

Repulsions between nuclei

Repulsions between electrons

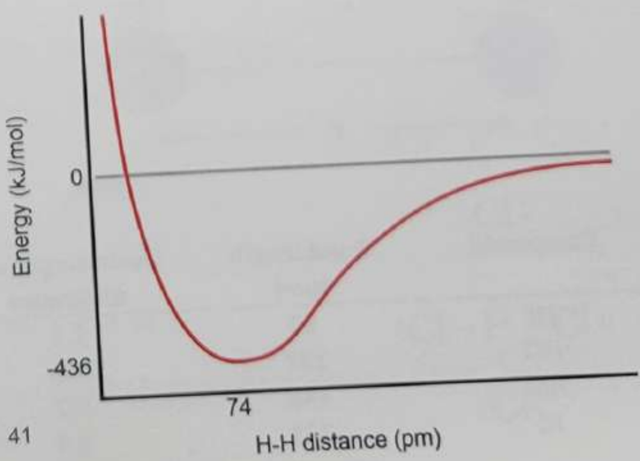


Formation of covalent bonds

The change in potential energy as two hydrogen atoms approach each other to form the H_2 molecule:

The minimum in the energy at 74 pm represents the equilibrium bond length

= distance at which attractive forces between opposite charges balance repulsive forces between like charges



Polar covalent bonds

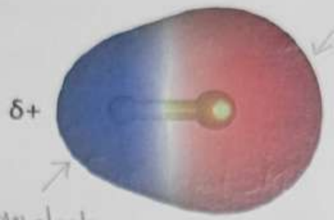
In a **nonpolar** covalent bond (e.g. F_2), electrons are shared equally, but more often they are unequally shared between different atoms:

polar
covalent
bond

one atom attracts bonding electrons more than the other

HF

high electron density



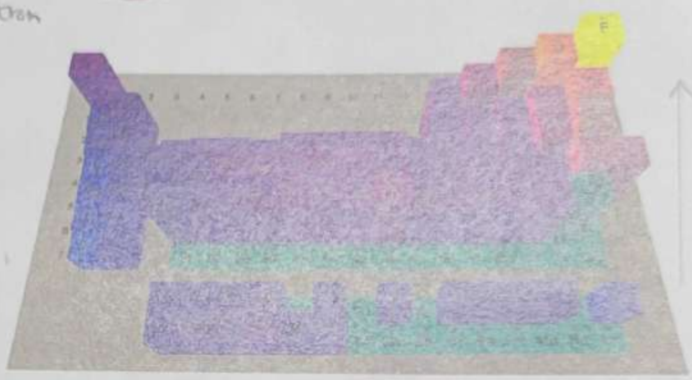
low electron density

$\delta+$ $\delta-$ = partial charges

Electronegativity

The ability of an atom *in a molecule* to attract electrons to itself is its **electronegativity**.

- related to ionization energy and electron affinity
- scale ranges from 0.7 (Cs) to 4.0 (F)



electronegativity increases to the right and up the periodic table

The greater the difference in electronegativity between two atoms, the more polar the bond is.

If the difference is large enough, an ionic bond forms (e.g. NaCl)

Dipole Moments

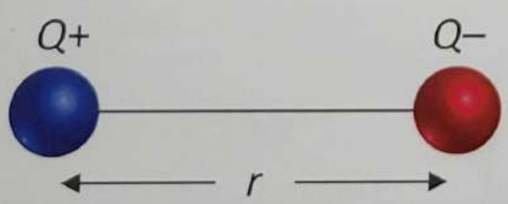
Polar molecules have centers of positive and negative charge that do not coincide. The polarity of the molecule can be indicated:

$\overset{\delta^+}{H} - \overset{\delta^-}{F}$

The dipole moment, μ, produced by two equal but opposite charges separated by a distance, *r*, is calculated:

$\mu = \underset{\text{electronegativity difference}}{Q}\ \underset{\text{bond length}}{r}$

measured in debyes (D)



Compound	Bond length (pm)	Electronegativity difference	Dipole moment (D)
HF	92	1.9	1.82
HCl	127	0.9	1.08
HBr	141	0.7	0.82
HI	161	0.4	0.44

Ionic: > 2

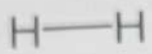
Polar Covalent: 0.5 - 2

Non-polar: < 0.5

Lewis Structures

Lewis structures are representations of molecules showing all valence electrons, bonding and nonbonding.

Show each electron pair shared between atoms as a line and unshared electron pairs as dots

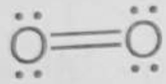


Each pair of shared electrons constitutes one chemical bond

Multiple Bonds

It is possible for more than one pair of electrons to be shared between two atoms (i.e. **multiple bonding**).

Two shared pairs is a double bond e.g O_2, three is a triple bond e.g N_2



Multiple bonds are shorter than single bonds

We will learn how to construct a Lewis structure using the example of phosphorus trichloride, PCl_3:

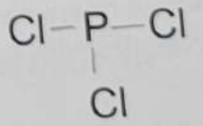
1. Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.

If an anion, add one electron for each negative (−) charge

If a cation, subtract one electron for each positive (+) charge

For PCl_3 : 5 (for P) + (3 × 7) (for Cl_3) = 26 valence electrons

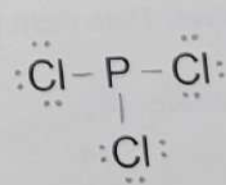
2. The central atom is generally, **but not always**, less electronegative than the atoms surrounding it.



Draw a line from the central atom to the outer ones

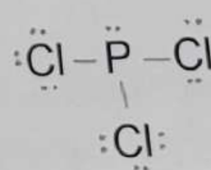
Each line (= bond) uses 2 electrons

Keep track of the electrons: 26 − 6 = 20



3. Fill the octets of the outer atoms

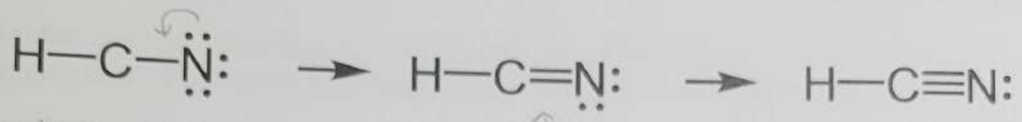
20 − (3×6) = 20 − 18 = 2



4. Fill the octet of the central atom

2 − 2 = 0

5. If you run out of electrons before the central atom has an octet...

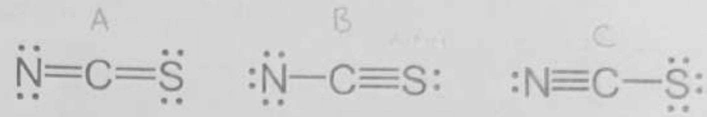


For HCN : 1 + 4 + 5 = 10

... form multiple bonds until central atom has an octet.

Then assign **formal charges.** For each atom, count the electrons in lone pairs and **half** the electrons it shares with other atoms. Subtract that from the number of valence electrons for that atom. The difference is its **formal charge**.

- helps us choose between alternative Lewis structures, e.g [NCS]⁻



	A			B			C		
valence electrons:	5	4	6	5	4	6	5	4	6
−(electrons assigned to atom):	6	4	6	7	4	5	5	4	7
formal charge:	-1	0	0	-2	0	+1	0	0	-1

Best: the one with the fewest absolute number of charges (A or C)

Best: puts a negative charge on the most electronegative atom (A)

Exceptions to the Octet Rule

There are three types of ions or molecules that do not follow the octet rule:

1- Those with an odd number of electrons

2- Those with less than an octet

3- Those with more than eight valence electrons (an "expanded octet")

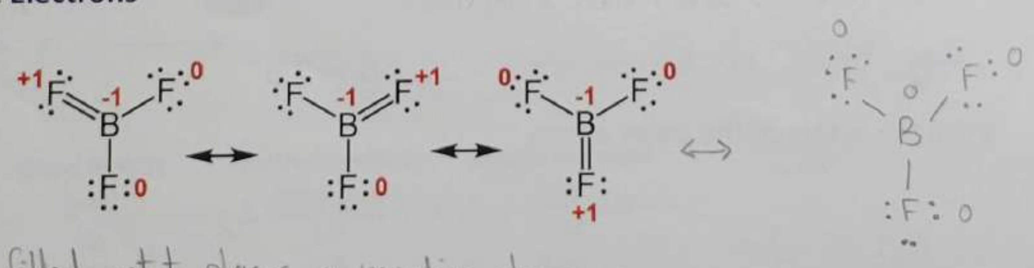
Odd number of electrons

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons, e.g. ClO_2, O_2^-, NO.

all atoms except one have an octet

Fewer Than Eight Electrons

Consider BF_3:



Giving boron a filled octet places a negative charge on the boron and a positive charge on fluorine

most important

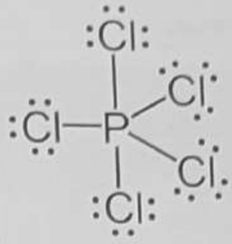
Structures that put a double bond between boron and fluorine are much less important in describing BF_3 than the one that leaves boron with only 6 valence electrons.

If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom:

then DON'T fill the octet of the central atom!

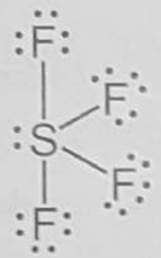
More Than Eight Electrons

The only way PCl_5 can exist is if P >8 electrons around it:

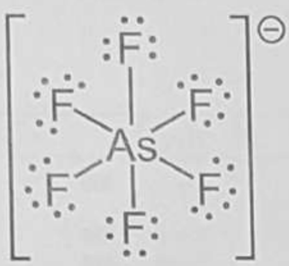


10 electrons

Atoms from the third period and beyond can accommodate more than an octet, e.g. SF_4 and AsF_6^-:



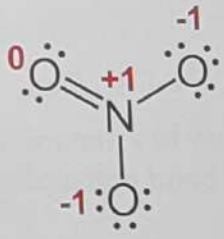
10 electrons

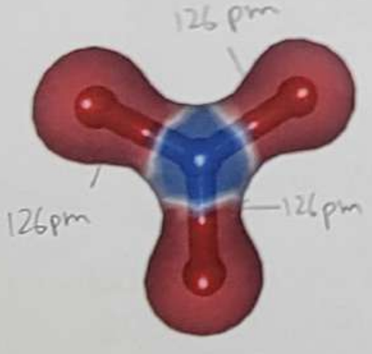


12 electrons

Resonance Structures

This is the Lewis structure we would draw for the nitrate ion, NO_3^-:

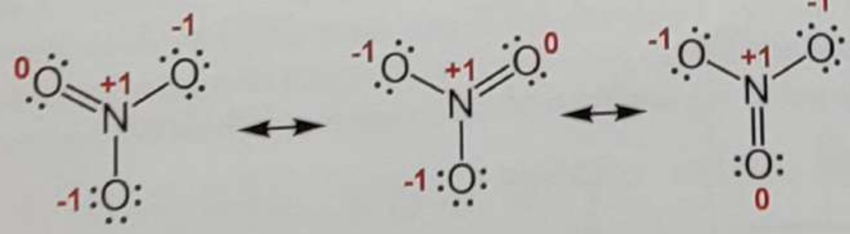


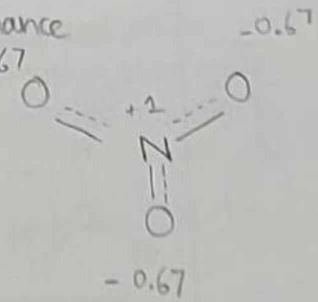


But in the observed structure of nitrate all N-O bonds are the same length, and all outer oxygens have the same partial negative charge

One Lewis structure cannot accurately capture the bonding in the nitrate ion, so we use multiple structures, **resonance** structures, to describe it:

use a double headed arrow, ↔, to indicate resonance





resonance structures of NO_3^-

average structure

Strengths of Covalent Bonds

The strength of a bond is measured by determining how much energy is required to break the bond: the **bond enthalpy**. A common symbol is D, for bond Dissociation energy.

$$:\ddot{\underset{..}{Cl}}—\ddot{\underset{..}{Cl}}:(g) \longrightarrow 2\ :\ddot{\underset{..}{Cl}}\cdot(g)$$

D(Cl - Cl) = 242 kJ mol^{-1}

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

bond enthalpies are positive, because bond breaking is an endothermic process

NOTE: Most of these are average bond enthalpies, not absolute bond enthalpies: i.e the C-H bonds in methane, CH_4, will be a bit different than the C-H bond in chloroform, $CHCl_3$

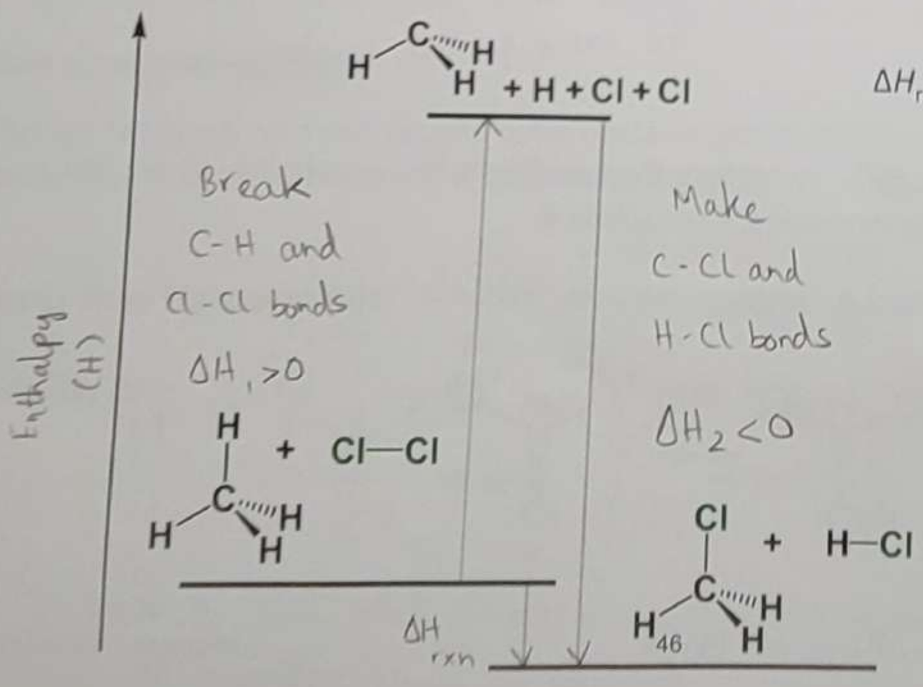
Some values are exact: Cl_2, O_2, F_2, Br_2, I_2, H_2, HF etc

Note how multiple bonds are stronger than single bonds

A way to estimate ΔH for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed. Consider the reaction

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$\Delta H_{rxn} = \Sigma(\text{enthalpies of bonds broken}) - \Sigma(\text{enthalpies of bonds formed})$$



$$\Delta H_{rxn} = [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})]$$

$$= [(413) + (242)] - [(328) + (431)]$$

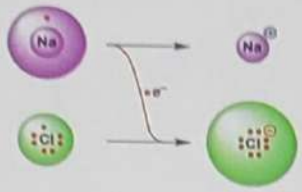
$$= (655) - (759)$$

$$= -104 \text{ kJ mol}^{-1}$$

Ionic bond strength and lattice energy

An ionic compound is stable because of the electrostatic attraction between positive and negative ions.

495 kJ mol^{-1} to remove electron from sodium



394 kJ mol^{-1} back by giving electron to chlorine

Reaction of sodium metal and chlorine gas to form sodium chloride is violently exothermic:

The "missing" energy comes from the **lattice energy**, the energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

Energy associated with electrostatic interactions is governed by Coulomb's law:

$$E_{el} = K\frac{Q_1 Q_2}{d}$$

$K = 8.99 \times 10^{9}\ J.m/C^2$ $Q_1 Q_2$ = charges d = distance

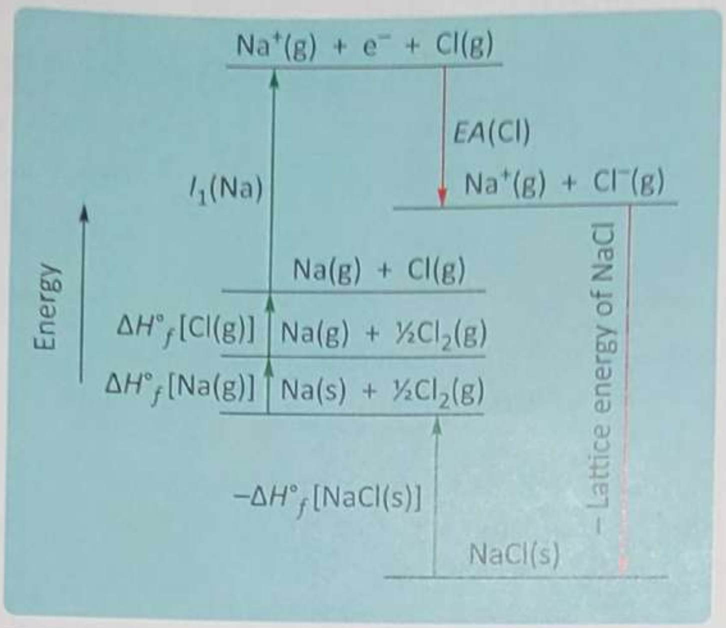
Note how lattice energy increases as $Q_1 \times Q_2$ increases, and as the distance between ions decreases:

Compound	Lattice energy (kJ/mol)	Compound	Lattice energy (kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$ 2x1	2127
LiI	730		
NaF 1x1	910	MgO	3795
NaCl	788	CaO 2x2	3414
NaBr	732	SrO	3217
NaI	increasing d 682		
KF	808	ScN 3x3	7547

increasing Q x Q

By accounting for all three energies (ionization energy, electron affinity, and lattice energy), we can get a good idea of the energetics involved in the formation of an ionic compound from its elements. We also need to take into account the energy required to convert the elements in their normal state into gas-phase atoms.

A Born-Haber cycle is used to analyze factors contributing to stability of ionic compounds:



elemental sodium

elemental chlorine

sodium chloride

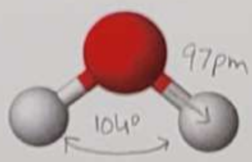
Molecular Shapes

Lewis structures give atomic **connectivity** (which atoms are physically connected).

The description of the shape of a molecule depends on its bond angles

The shape of a molecule plays an important role in its reactivity

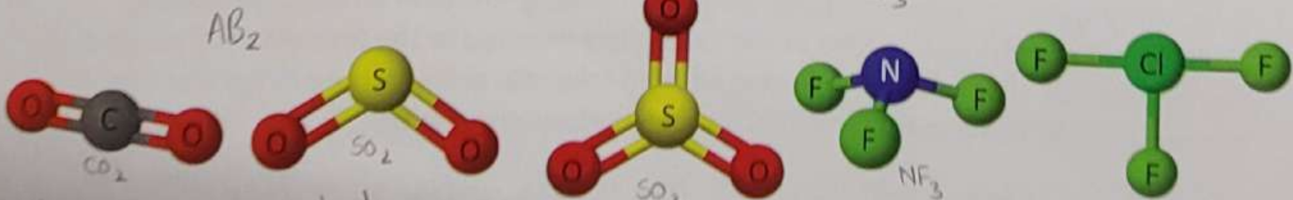
To describe the three dimensional shape of a molecule, we use bond lengths (in picometers) and bond angles (in degrees).



By noting the number of bonding and nonbonding electron domains we can predict the shape of the molecule. Here are some descriptions of molecular shapes.

'general formula'

AB_2 AB_3



CO_2 linear

SO_2 bent

SO_3 trigonal planar

NF_3 trigonal pyramidal

ClF_3 T-shaped

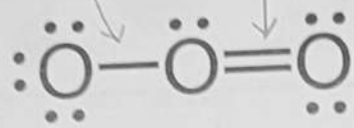
The VSEPR Model

"valence-shell electron-pair repulsion"

By assuming the valence electron domains are placed as far as possible from each other, we can predict the shape of the molecule.

An electron domain = region occupied by electrons

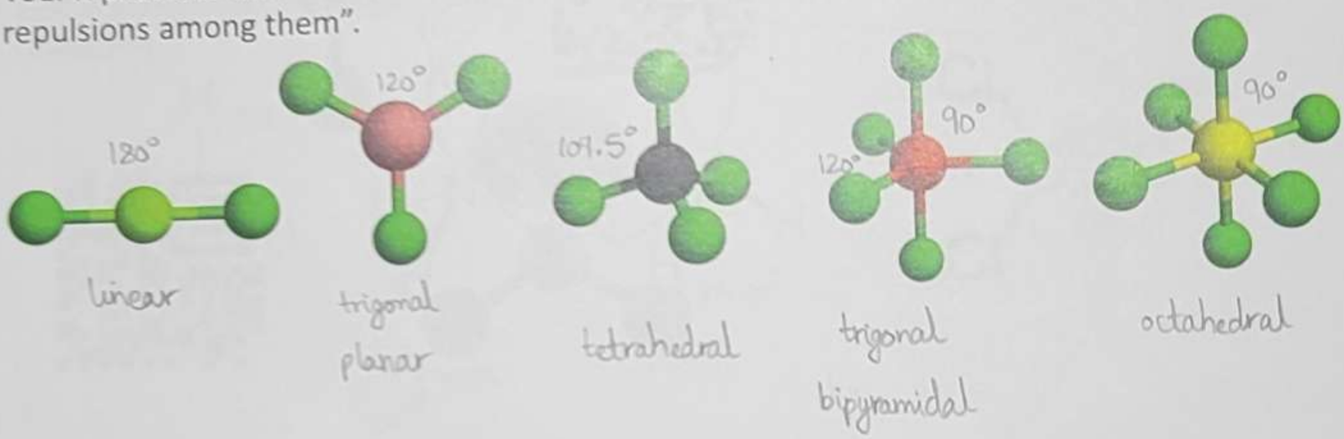
Each **nonbonding pair, single bond** or **multiple bond** produces an electron domain about the central atom.



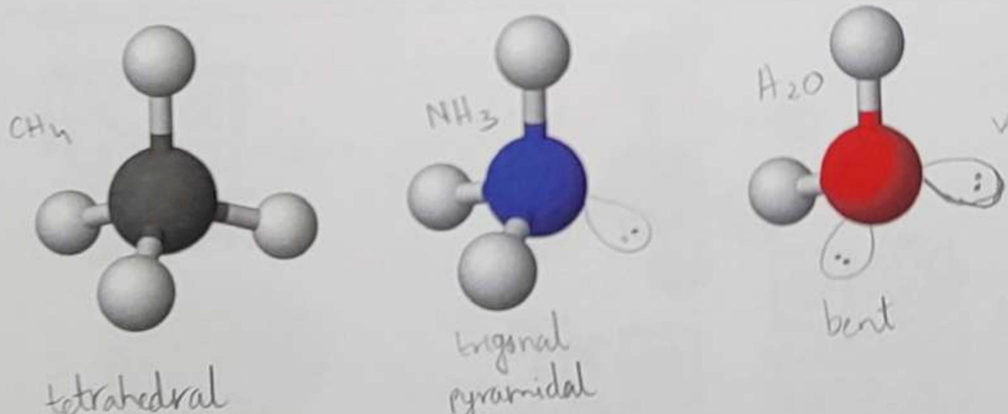
3 domains about central O

or "lone pair" of electrons: an electron domain located principally on one atom

VSEPR predicts that "the best arrangement of electron domains is the one that minimizes the repulsions among them".



The shape of any particular AB_n molecule can usually be derived from one of these 5 fundamental shapes. For example, starting from a tetrahedron:

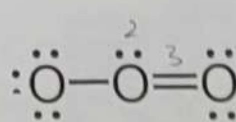


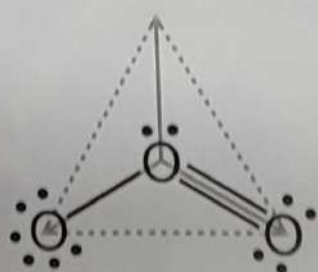
lone pairs affect the structure

We use the electron domain geometry to help us predict the molecular geometry.

1- Draw Lewis structure, count electron domains

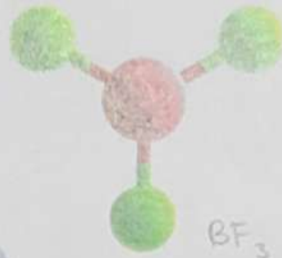
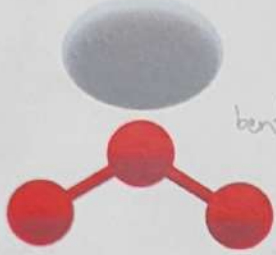
2- Arrange electron domains to minimize repulsion

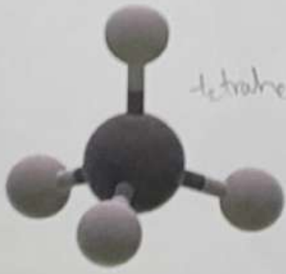
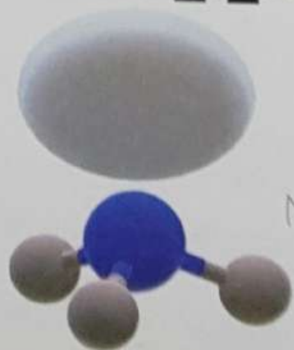
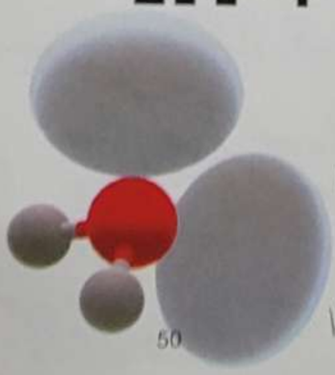




trigonal planar

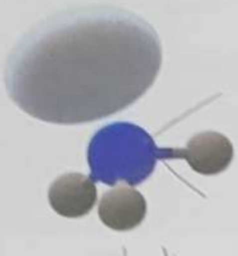
3 - Inspect arrangement of atoms to determine molecular geometry

# of electron domains	Electron domain geometry	# of non-bonding domains	Molecular geometry/ MolecularAR code
2	linear	0	 linear BeF_2
3	trigonal planar	0	 trigonal planar BF_3
3	trigonal planar	1	 bent O_3

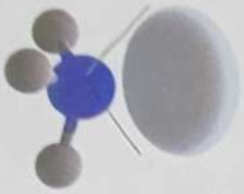
# of electron domains	Electron domain geometry	# of non-bonding domains	Molecular geometry/ MolecularAR code
4	tetrahedral	0	 tetrahedral CH_4
4	tetrahedral	1	trigonal pyramidal  NH_3
4	tetrahedral	2	 bent H_2O

Effect of nonbonding electrons and multiple bonds on bond angles

Nonbonding pairs are physically larger than bonding pairs:



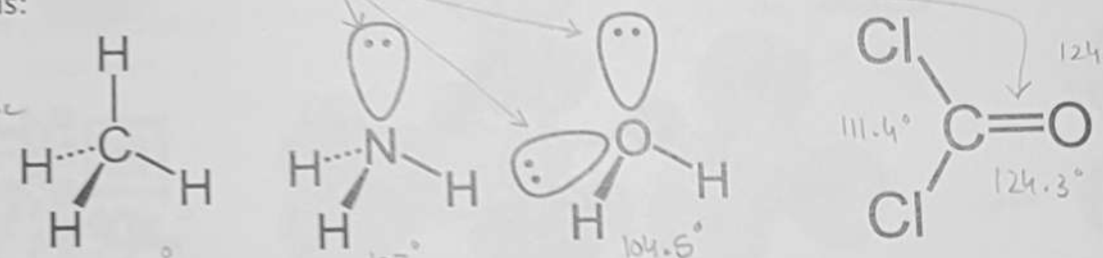
bonding pair

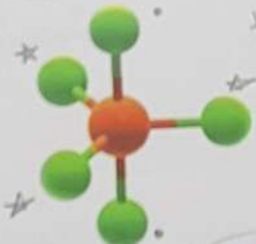
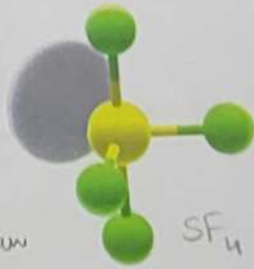
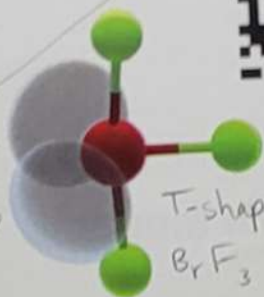
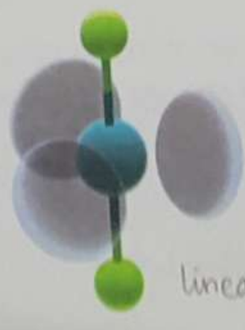


non-bonding pair

Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule

Electrons in nonbonding pairs and in multiple bonds repel **more** than electrons in single bonds:

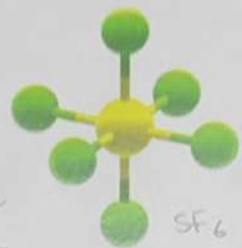
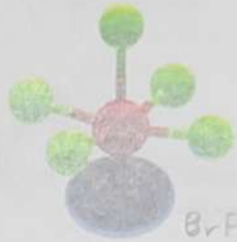
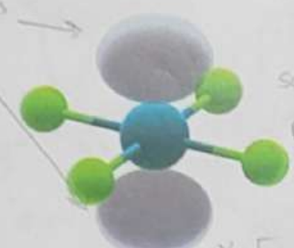


# of electron domains	Electron domain geometry	# of non-bonding domains	Molecular geometry/ MoleculAR code
5	trigonal bipyramidal	0	 trigonal bipyramidal PF_5
5		1	 see-saw SF_4
5		2	 T-shaped BrF_3
5		3	 linear XeF_2

☆ = equatorial

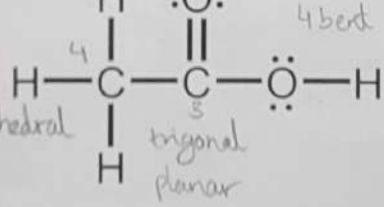
• = axial

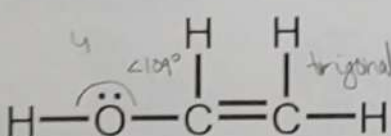
note position of lone pairs: always in least crowded equatorial positions

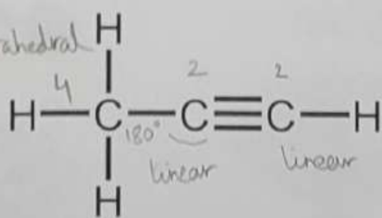
# of electron domains	Electron domain geometry	# of non-bonding domains	Molecular geometry/ MoleculAR code
6	octahedral	0	
6		1	
6		2	

Shapes of larger molecules

The interior atoms of more complicated molecules can be dealt with in turn using the VSEPR model.







Molecular polarity and dipole moment

(non-polar molecules do not interact with electric field)

Polar molecules interact with electric fields. Binary compounds are polar if their centers of negative and positive charge **do not** coincide.

If two charges, equal in magnitude and opposite in sign, are separated by a distance d, then a dipole is established

CO_2

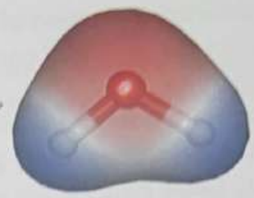
δ^+ δ^+

← A dipole is a vector quantity →

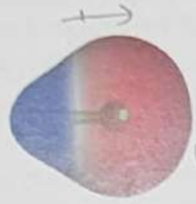
H_2O

= 0 ← overall dipole moment →

← electrostatic potentials →
(red = high, blue = lows)



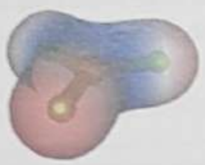
The orientation of the individual bond dipole moments determines whether a molecule has an overall dipole moment



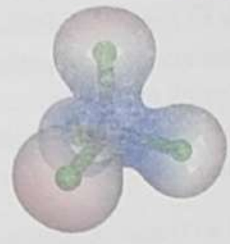
HCl
polar

NH_3
polar

CH_3Cl
polar

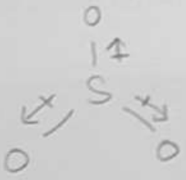


BF_3
non-polar



CCl_4
non-polar

SO_3



overall dipole moment = 0