Chemical bonding & structure

Ionic bonding and structure
Covalent bonding
Covalent structures
Intermolecular forces
Metallic bonding

Ms. Thompson - SL Chemistry
Wooster High School

Topic 4.3
Covalent structures

- Lewis (electron dot) structures show all the valence electrons in a covalently bonded species.
- The "octet rule" refers to the tendency of atoms to gain a valence shell with a total of 8 electrons.
- Some atoms, like Be and B, might form stable compounds with incomplete octets of electrons.
- Resonance structures occur when there is more than one possible position for a double bond in a molecule.
- Shapes of species are determined by the repulsion of electron pairs according to VSEPR theory.
- Carbon and silicon form giant covalent/network covalent structures.

Covalent structures

Nature of science

- Scientist use models as representations of the real world – the development of the model of molecular shape (VSEPR) and to to explain observable properties.

Covalent structures

Lewis (electron dot) structures

- Based on the formation of the covalent bond and the molecule
- Each pair of electrons can be represented in a number of different ways - by two dots, two crosses (or a combination of a dot and a cross), or by a line.

Covalent structures

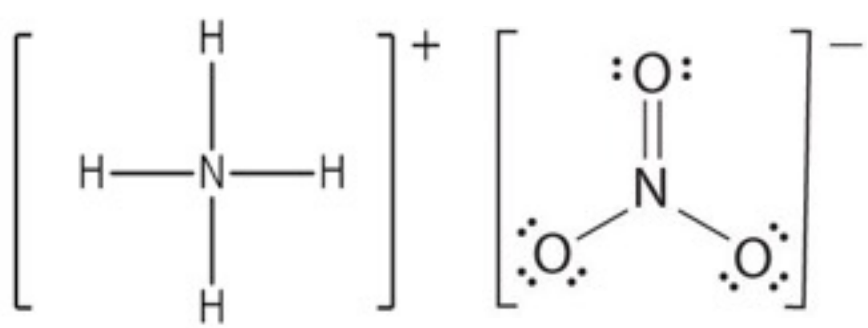
Lewis (electron dot) structures

- In the previous representations it is important to distinguish between:
  - **Bonding pairs of electrons** (showing the covalent bond as single, double, or triple bonds)
  - **Non-bonding pairs of electrons**, often call **lone pairs**, which are pairs of electrons not involved in the bonding
- Help us understand the different types of covalent bond (single, double, or triple bonds) and the existence of lone pairs in molecules.
- Tell us nothing about the actual shapes of molecules
- May be drawn with a geometrical arrangement that differs completely from its real shape in space.
- So we rely on the **valence shell electron pair repulsion theory (VSEPR)** to deduce the shape of molecules and predicting molecular geometries.

Covalent structures

Lewis structures of cations and anions and ionic compounds

- Can be written for neutral molecules as well as cations and anions
- Notice that *within* the cations and anions there can be covalent bonds but the bonding *between* the cation and anion is ionic.



covalent bonds in the cation

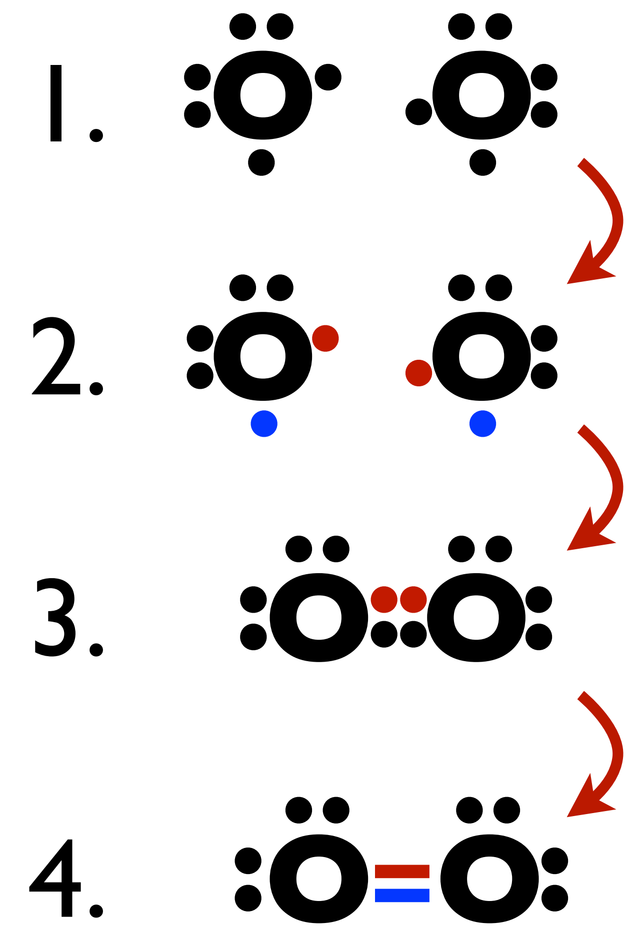
covalent bonds in the anion

Ionic bonds between the cation and anion – So the compound overall is ionic

Covalent structures

Lewis Dot Structure

- **Oxygen, O_2**
  - Group 16 and has six valence electrons
  - Needs to acquire two more electrons for a full octet and to attain noble gas configuration.
    - If two oxygen atoms share two electrons with each other, each oxygen atom gains two more electrons to attain a complete octet of electrons, which results in the formation of a covalent bond between the two oxygen atoms.
    - A **double, covalent bond** is formed and the shared pair of electrons can be represented by two lines.



Oxygen has 4 non-bonding pair of electrons (lone pairs) and two pair that bonds

Covalent structures

Valence shell electron pair repulsion (VSEPR) theory

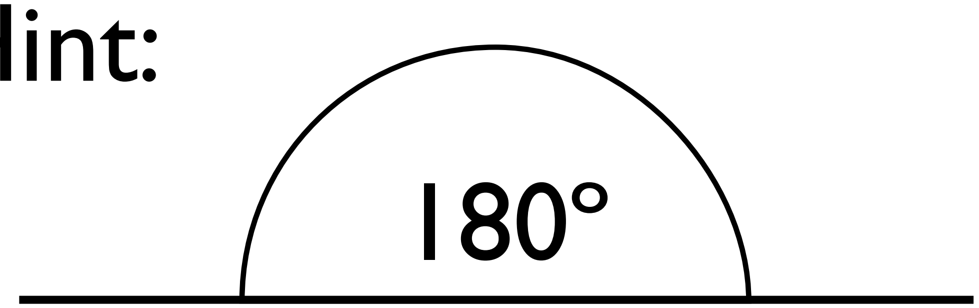
- Every molecule has a particular shape therefore, we need to have the ability to think in three-dimensional.
- Lewis structures are two-dimensional representations and tell us nothing about the shape.
- **Valence shell electron pair repulsion theory (VSEPR)** can be used to deduce the shapes of covalent molecules.
  - Since electrons are negatively charged subatomic particles, *pairs of electrons repel one another to be as far apart as possible in space*

Covalent structures

Valence shell electron pair repulsion (VSEPR) theory

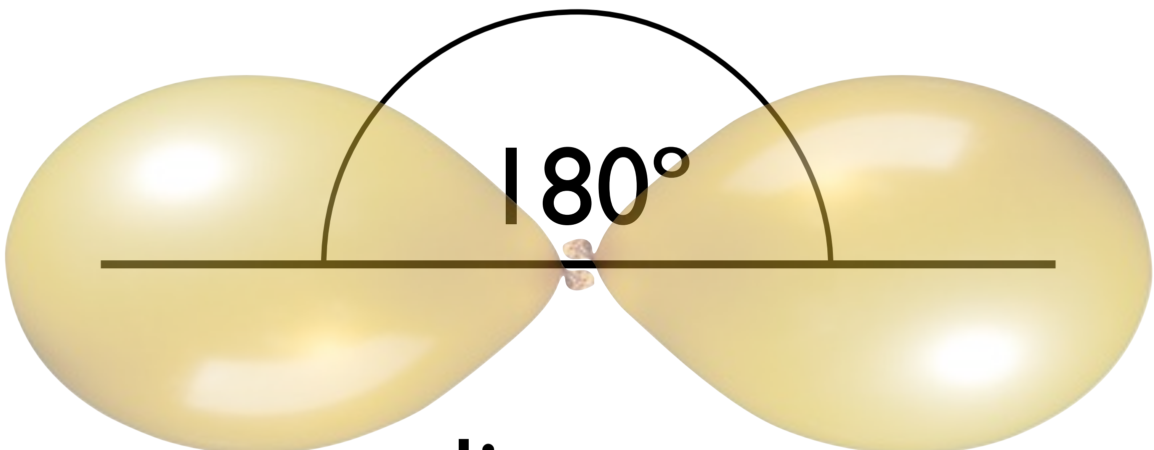
- **Get into groups of four**
- **Send one person to grab nine balloons from the front**
  - **Tie two balloons together**
  - **Tie three balloons together**
  - **Tie four balloons together**
- ***Estimate the angles between the balloons using a protractor***

Hint:

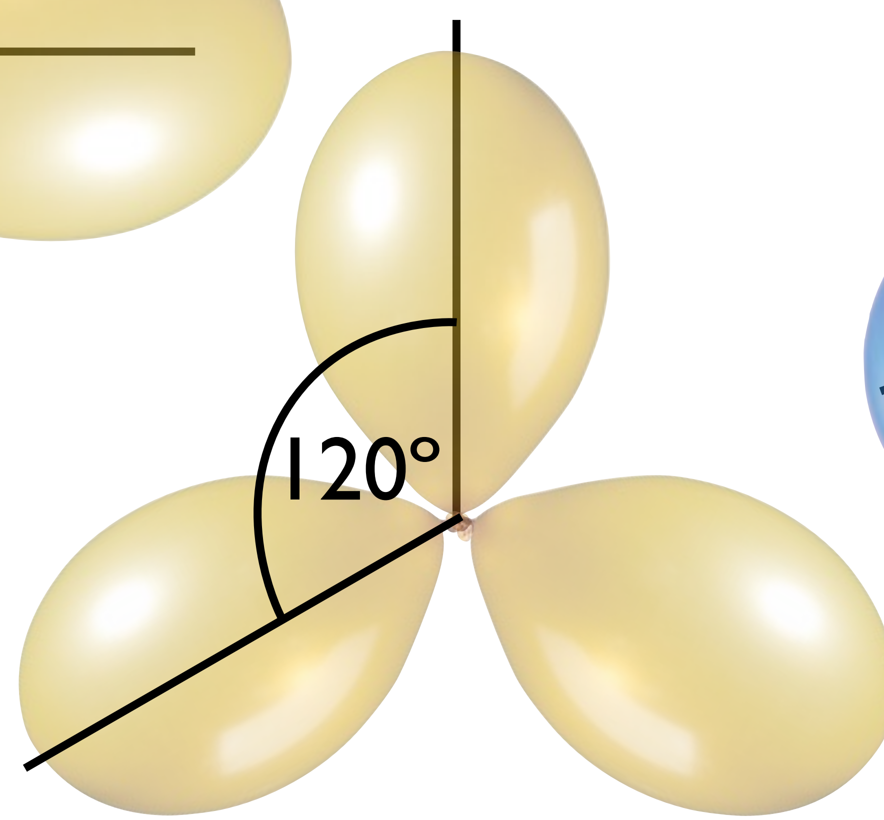


Covalent structures

Valence shell electron pair repulsion (VSEPR) theory



linear



trigonal planar

tetrahedral

Covalent structures

Valence shell electron pair repulsion (VSEPR) theory

- The basic molecular geometries can therefore be summarized on the basis of two, three, or four pairs of electrons. Each pair of electrons is described as occupying an **electronic domain** - a field of electronic density.

Number of electron domains	**Molecular geometry**	**Bond angle**	**Examples of molecules or ions having this shape**
two	 linear	180°	**AB_2** $BeCl_2$, CO_2
three	 trigonal planar	120°	**AB_3** BF_3, $[NO_3]^-$
four	 tetrahedral	109.5°	**AB_4** CH_4, $[NH_4]^+$, $[ClO_4]^-$

Covalent structures

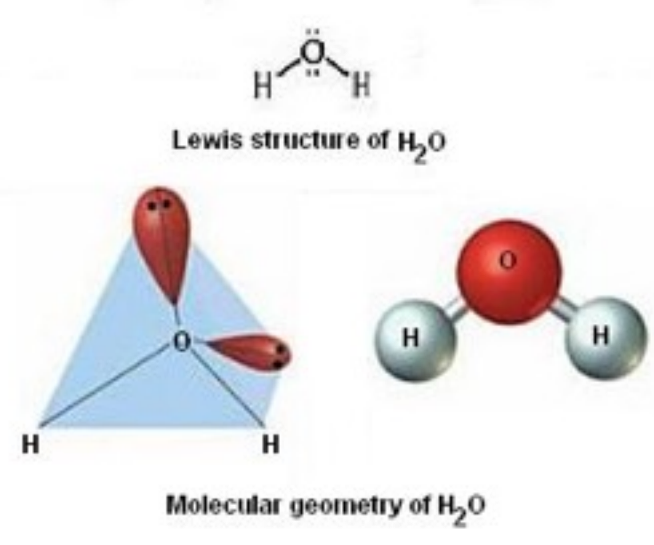
Valence shell electron pair repulsion (VSEPR) theory

- Additional shapes can be deduced for species with fewer bonding pairs of electrons than the number of domains present.
- **Electron domains not occupied by bonding pairs of electrons are filled by non-bonding pairs of electrons (lone pairs)**
  - AB_2E (v-shaped), AB_3E (trigonal pyramidal), and AB_2E_2 (v-shaped or bent) where represents a lone pair of electrons
- **Electron domain geometry:** based on total number of electron domains predicted by VSEPR theory
- **Molecular geometry:** gives the shape of the molecule

Covalent structures

Valence shell electron pair repulsion (VSEPR) theory

Number of electron domains	Electron domain geometry	Molecular geometry	Bond angle	Examples of molecules or ions having this shape
three	trigonal planar **AB_2E**	v-shaped (bent)	<120°	$[NO_2]^-$, SO_2
four	tetrahedral **AB_3E**	trigonal pyramidal	<109.5°	NH_3, $[SO_3]^{2-}$, H_3O^+
four	tetrahedral **AB_2E_2**	v-shaped (bent)	<109.5°	H_2O, $[NH_2]^-$



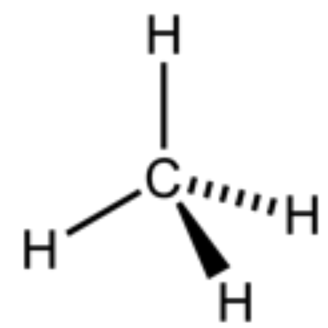
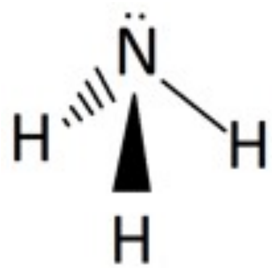
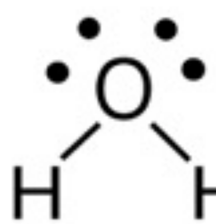
Covalent structures

Bond angles in molecular geometries

- Lone pairs of electrons affect bond angles in a molecule
- *Lone pairs occupy* **more** *space than bonding pairs so they decrease the bond angle between bonding pairs.*
- Degree of electron pair-electron pair repulsion follows this order:
  - LP|LP > LP|BP > BP|BP
- Angles are not uniform across the board! **Electronegativity and multiple bonds can affect bond angles.**
  - *i.e. PH_3 has AB_3E structure and is trigonal pyramidal but its angle is 93.5º due to the greater electronegativity effect from Phosphorus.*

Covalent structures

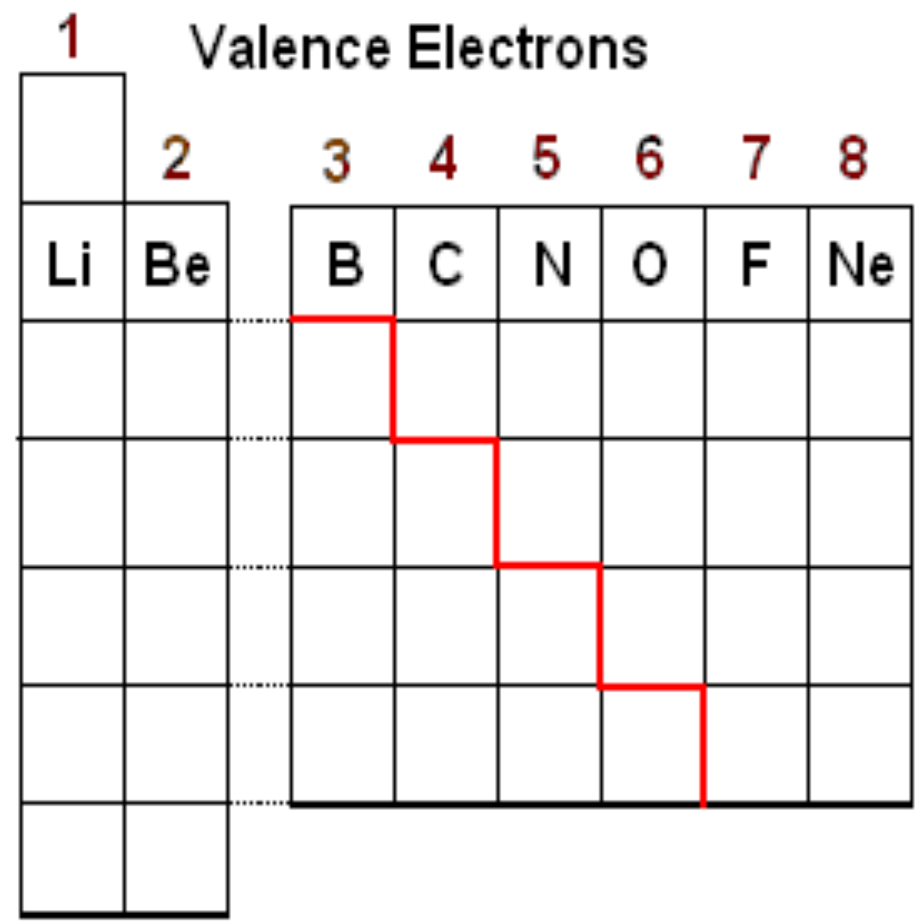
Bond angles in molecular geometries

Molecule	Number of electron domains	Molecular geometry	Bond angle
CH_4	four	 tetrahedral (AB_4)	109.5°
NH_3	four	 trigonal pyramidal (AB_3E)	107°
H_2O	four	 v-shaped (AB_2E_2)	104.5°

Covalent structures

Writing Lewis dot structures and electron domain and molecular geometries

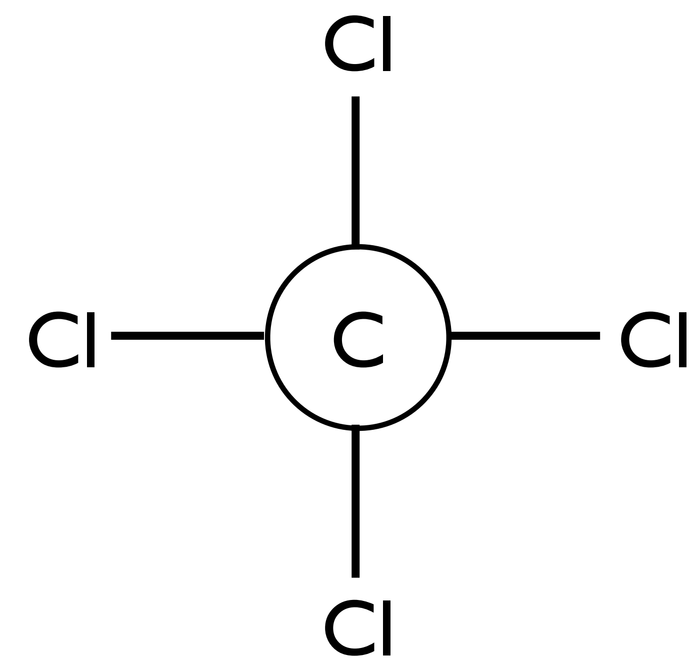
- *Writing dot structures is a process:*
  - Determine the number of valence electrons each atom contributes to the structure
  - The number of valence electrons can usually be determined by the column in which the atom resides in the periodic table



Covalent structures

Writing Lewis dot structures and electron domain and molecular geometries

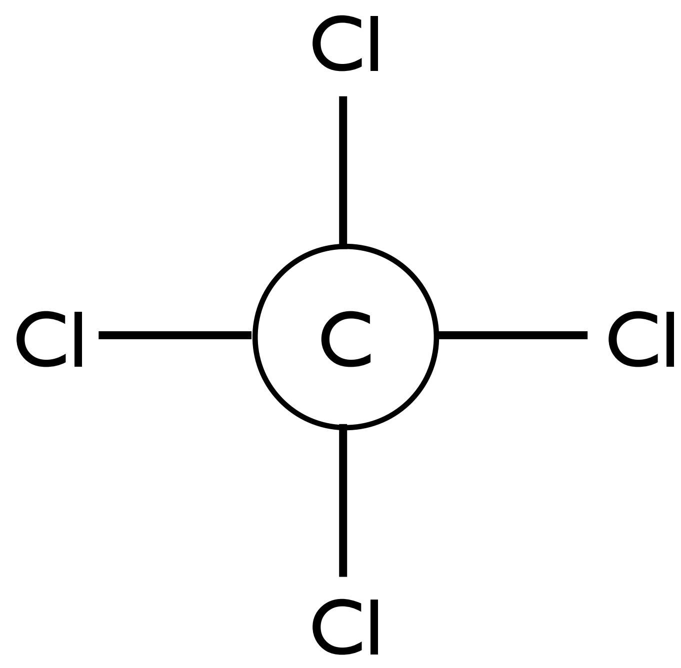
1. Draw ball and stick diagram, identifying central atom.
   - Each stick represents a pair of bonding electrons
   - For oxoanions (anions containing oxygen) put negative charge on terminal oxygen atoms
   - Remaining bonds should be converted into double bonds
   - For other non-oxoanions put brackets around ion and put charge outside these.



Covalent structures

Writing Lewis dot structures and electron domain and molecular geometries

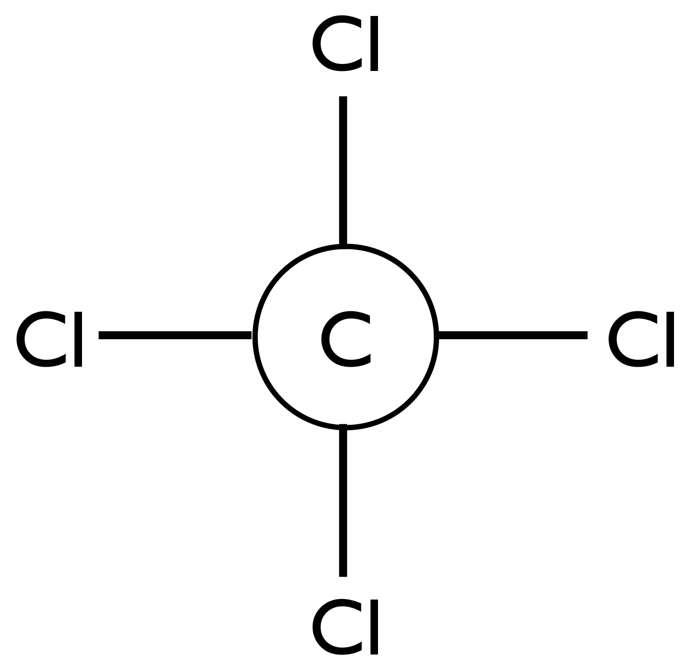
2. Make the atom that is fewest in number the central atom. For the central atom the number of valence electrons comes from periodic table.
3. Count number of sticks, these are single bonds designated as sigma (σ) bonds (add these). You subtract double (pi π bonds).
   a. Carbon has four valence electrons and four sigma bonds (no pi bonds) so number of valence electrons is eight



Covalent structures

Writing Lewis dot structures and electron domain and molecular geometries

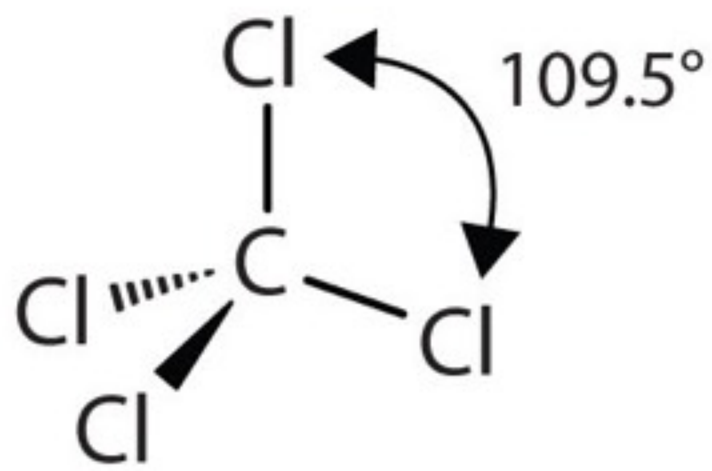
4. Add one electron for a negative charge and subtract one for a positive charge *(exclude this for oxoanions as you already localized them)*
5. Combine steps 2-4 and divide this number by two to obtain the number of electron pairs, which equals the number of electron domains
   a. 8 valence electrons/2 = four electron domains
6. Deduce the electron domain geometry
   a. Thus, the electron domain geometry is tetrahedral, AB_4



Covalent structures

Writing Lewis dot structures and electron domain and molecular geometries

7. Determine number of lone pairs present, if applicable and deduce molecular geometry. Draw exact representation taking into account the order of electron-pair repulsion:
   a. LP|LP > LP|BP > BP|BP
8. Draw Lewis structure completing the octets on all terminal atoms, except Hydrogen. Remember square brackets on anions and cations.
9. Draw resonance structures, if applicable.

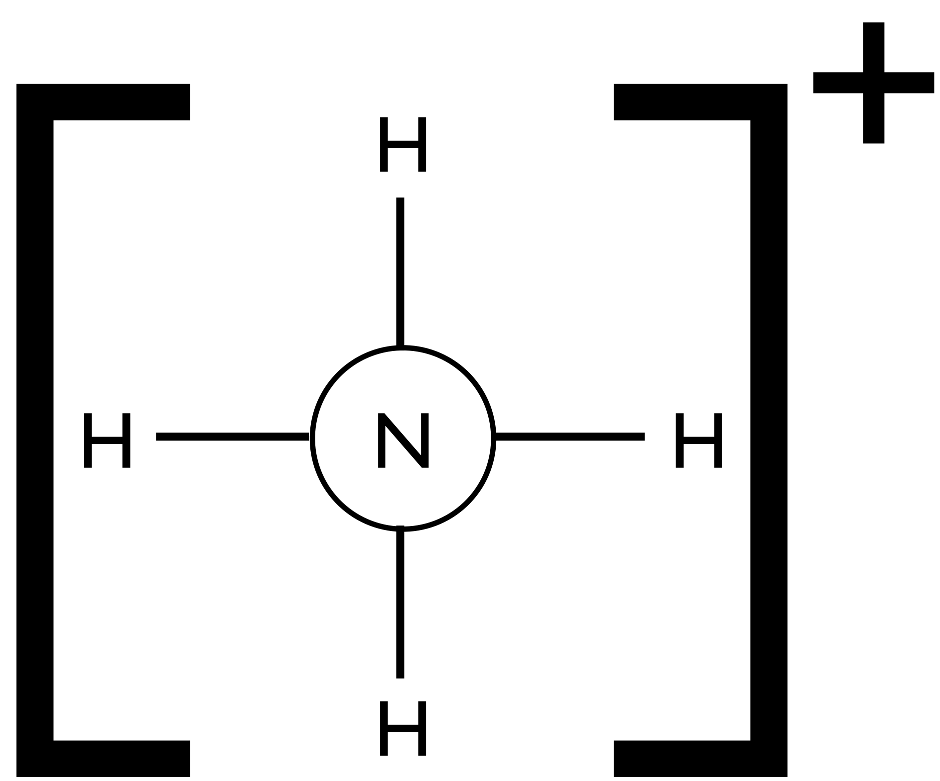


Practice Problem

... I Do ...

Determine the Lewis structure, electron domains, and molecular geometries for $[NH_4]^+$

First, draw the ball and stick diagram for the ammonium ion. Be sure to include the cation's charge in this step!



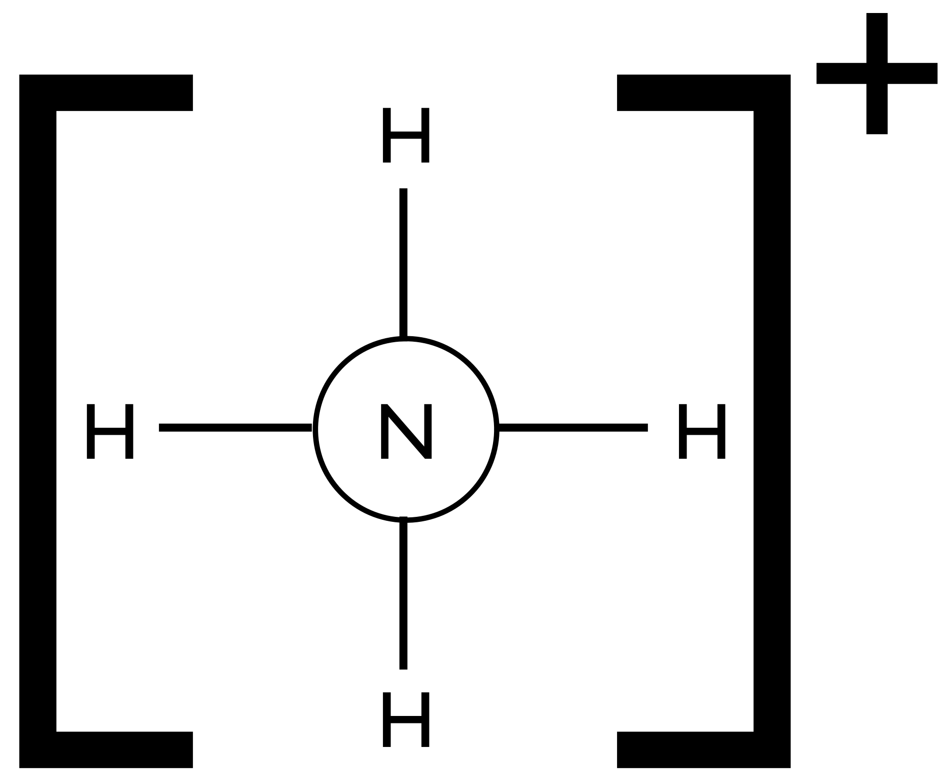
Practice Problem

... I Do ...

Determine the Lewis structure, electron domains, and molecular geometries for $[NH_4]^+$

Second, count the number of valence electrons of the central atom (N) and the number of sigma (single) bonds, add them up and divide by two to obtain the number of electron domains.

- N has five valence electrons
- $[NH_4]^+$ has four sigma bonds
- $[NH_4]^+$ has eight valence electrons
- 8/2= 4 electron domains for $[NH_4]^+$



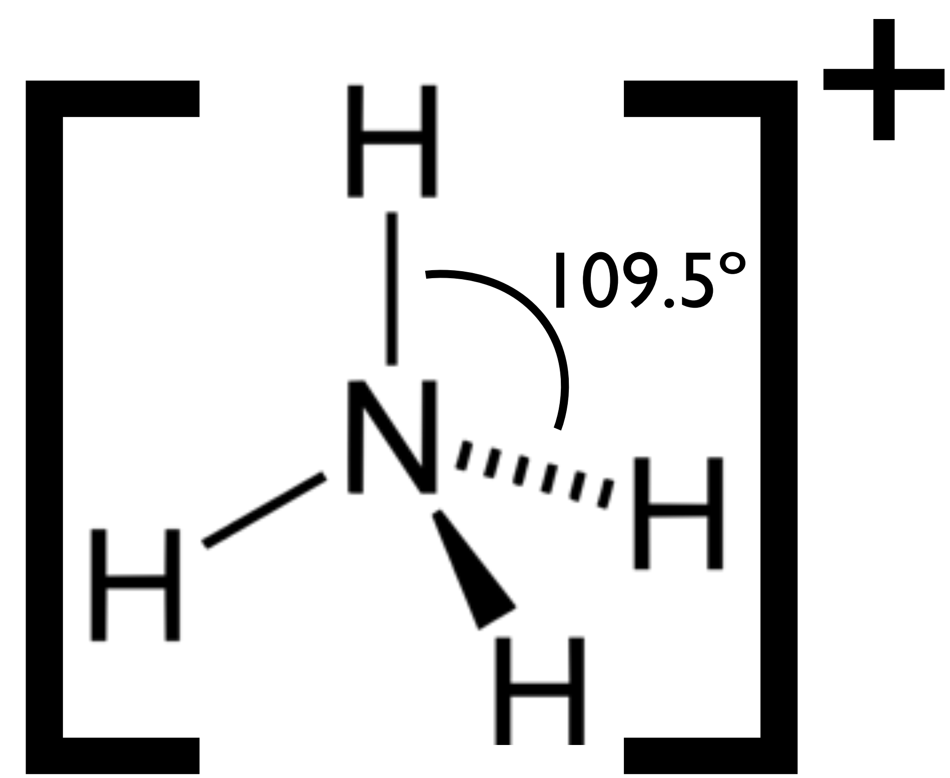
- Electron domain geometry is tetrahedral, AB_4.

Practice Problem

... I Do ...

Determine the Lewis structure, electron domains, and molecular geometries for $[NH_4]^+$

Last, draw the actual structure taking into consideration shape due to electron-pair repulsion. $[NH_4]^+$ has no lone pairs therefore it is truly tetrahedral with bond angles of 109.5°



Practice Problem

... We Do ...

Determine the Lewis structure, electron domains, and molecular geometries for NF_3

Practice Problem

20 mins

... You Do ...

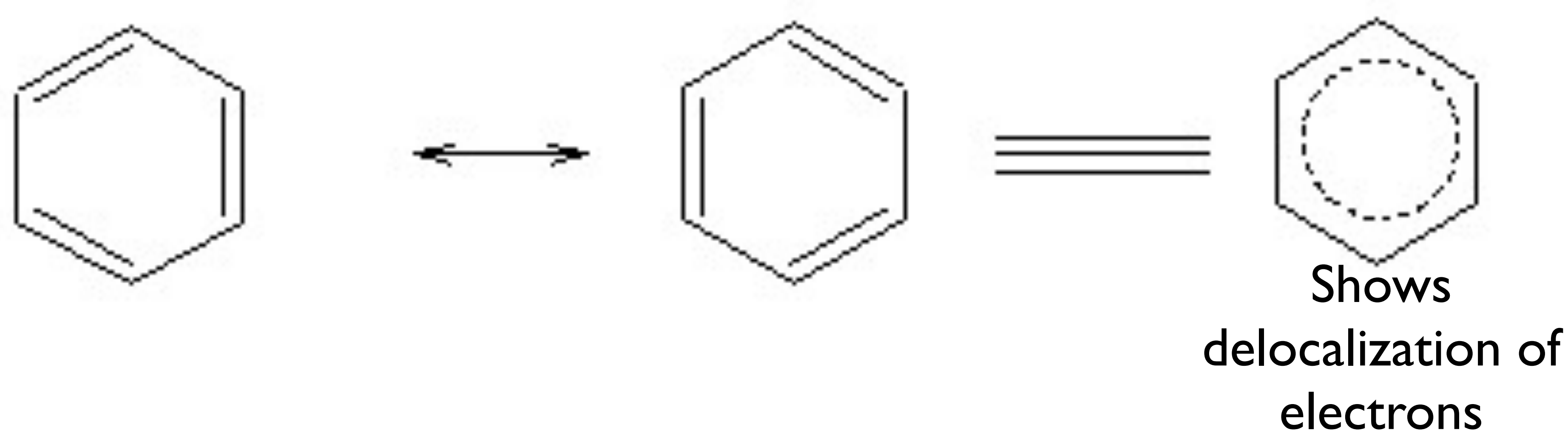
Work with a partner and answer the following question:

Determine the Lewis structure, electron domains, and molecular geometries for SF_2, $[NO_2]^-$, and $[SO_3]^{2-}$

Covalent structures

Resonance structures

- Individual Lewis structures that contribute to overall structure are called **resonance forms**.
- Actual *electronic* structure of a species is called a **resonance hybrid** of these resonance forms.
  - Shown using double headed arrow - will look at in more detail in Topic 10.
- Best known example is Benzene.

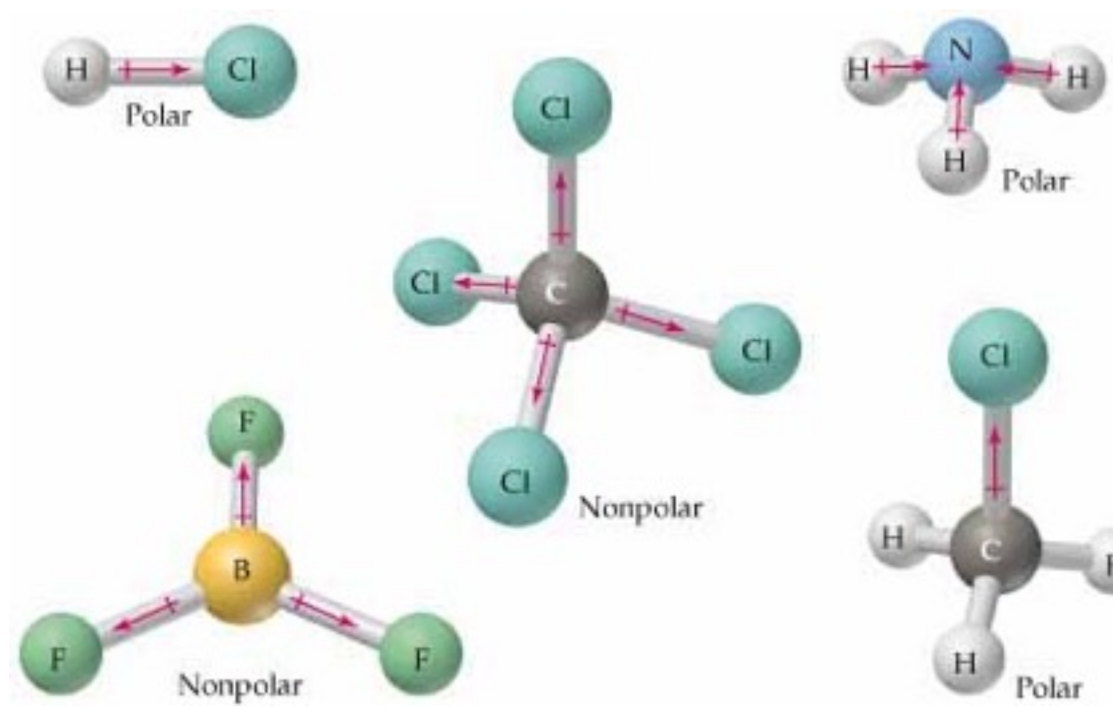


Covalent structures

Molecular polarity

- Unlike bond polarity, **molecular polarity** looks at whether the whole molecule is polar or non-polar.
  - Non-polar molecule may have polar bonds
  - Follow these steps to determine molecular polarity:

1. Using VSEPR theory, deduce the molecular geometry.
2. For each bond present, using electronegativity differences, $\Delta\chi_P$, deduce the bond polarity for each bond present and draw the associated dipole moments; these are best represented as vectors.
3. Using vector addition, sum all the dipole moments present to establish whether there is a net dipole moment, μ, for the molecule. If so, the molecule is polar.



Practice Problem

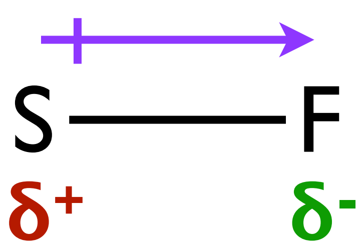
Turn to section 8 of your data booklet!!

... We Do ...

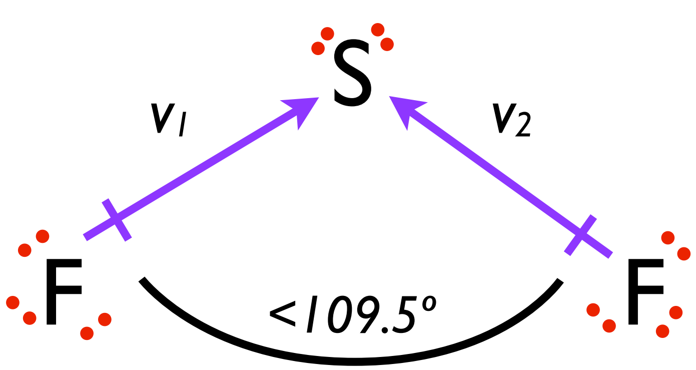
Deduce the molecular polarities of the following: SF_2.

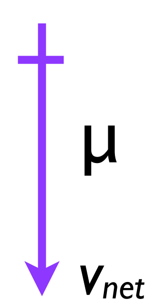
$\chi_P(S) = 2.6$
$\chi_P(F) = 4.0$

Fluorine is more electronegative than sulfur and the S-F bond is polar with the following dipole moment:



To deduce molecular polarity, we sum the two S-F vectors. The SF_2 molecule is v-shaped so we add the two vectors using the **parallelogram law**.





$v_1 + v_2 = v_{net}$

This results in a net dipole moment, μ; the molecule is polar

Practice Problem

Turn to section 8 of your data booklet!!

... You Do ...

Deduce the molecular polarities of the following:

CO_2.

Covalent structures

Allotropes

- Different structural modifications of the same element.
  - Can vary in both physical and chemical properties.
  - Carbon is most fascinating elements of periodic table and life forms on Earth are all based on carbon.
    - Has a number of allotropes: *graphite, graphene, and C_{60} fullerene*.

Covalent structures

Allotropes

- **Covalent solid networks**
  - Graphite, diamond, and graphene are examples of covalent solid networks.
    - *Atoms are held together by covalent bonds in a giant three-dimensional lattice structure*
  - **Graphite**
    - Layers of hexagonal rings consisting of carbon atoms.
    - Connected by weak intermolecular forces of attraction **(London Forces)**
      - Used as a lubricant and in pencils
  - **Diamond**
    - Each carbon atom is bonded to four other carbon atoms in a tetrahedral arrangement.
    - Strength is due to covalently bonded interlocking structural arrangement of tetrahedra.

Covalent structures

Allotropes

- **Graphene - the super material!**
  - Not only the thinnest and strongest of known materials but first two-dimensional crystal ever discovered.
  - Differs from graphite because it is single planar sheet of carbon atoms arranged hexagonally and is only *ONE ATOM* thick!!!!
  - 1mm piece of graphite consists of 3 million sheets of graphene, stacked on top of each other.
  - When folded into sphere, becomes fullerene.
- **C_{60} fullerene**
  - Not a covalent solid network
  - Composed of individual molecules with strong covalent bonds but with weak London forces between molecules.

Covalent structures

Silicon dioxide, SiO_2 (quartz)

- Often called silica, usually found in its **amorphous** form as sand.
  - Solid with no ordered structure.
- Quartz is another example of a three-dimensional covalent network solid.
  - Consists of arrays of SiO_4 tetrahedra arranged in a lattice
- Both cyrstalline and amorphous dioxide are insoluble in water and solid SiO_2 does not conduct electricity or heat (no delocalized electrons present)

Covalent structures

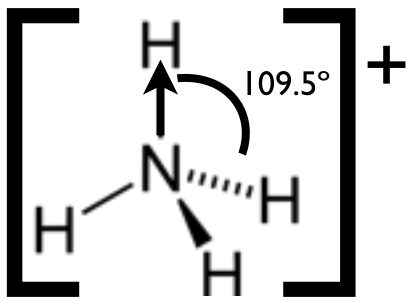
Coordinate covalent bonding

- Another type of covalent bonding
  - In a typical covalent bond, the shared pair of electrons originate from both atoms that form the bond
  - One atom contributes an electron to share and so does the other atom
  - In coordinate covalent bonding, the shared pair of electrons comes from only one of the atoms; this atoms donates both electrons to the shared pair
    - i.e. $[NH_4]^+$, $[H_3O]^+$, CO, Al_2Cl_6 and transition metal complexes

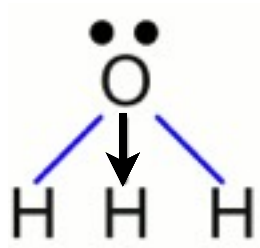
Covalent structures

Coordinate covalent bonding

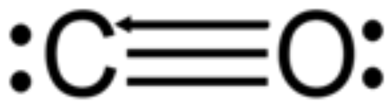
- **Ammonium cation**
  $H_3N + H^+ \text{-->} [NH_4]^+$
  Lone pair on nitrogen combines with proton to form ammonium cation



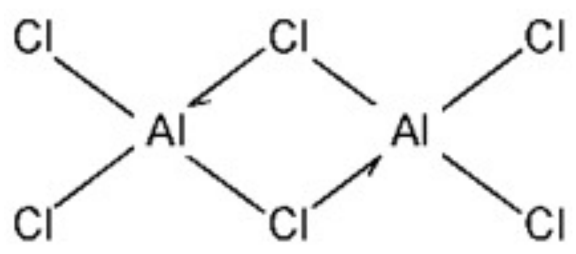
- **Hydronium cation**
  $H_2O + H^+ \text{-->} [H_3O]^+$
  Lone pair on oxygen combines with proton to form hydronium cation



- **Carbon monoxide, CO**



- **Dimer of aluminum chloride**



The coordinate covalent bond is represented by an arrow to signify the origin of the electrons in the bond. Once formed, however, all the bonds are equivalent (whether coordinate covalent or normal covalent).

Previously, the term dative covalent bonding was used for this type of bond but this term is now largely obsolete.

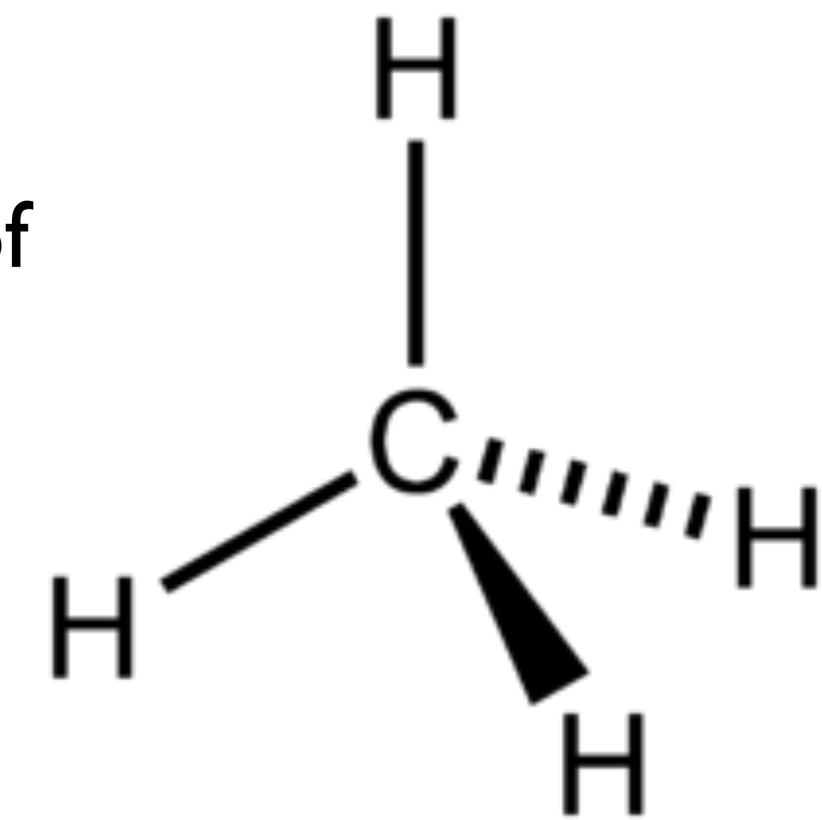
Covalent structures

Representations of structures

For tetrahedral structures it is common to use wedge and dash notation to show the various planes:

- A wedge indicates that the bond is in front of the defining plane (coming towards you)
- A dash indicates that the bond is behind the defining plane (facing away from you)
- A solid line indicates that the bond lies on the defining plane

For example, the tetrahedral structure of methane, CH_4, can be represented as follows using this notation



Topic 4.3
Covalent structure

- ➡Lewis (electron dot) structures show all the valence electrons in a covalently bonded species.
- ➡The "octet rule" refers to the tendency of atoms to gain a valence shell with a total of 8 electrons.
- ➡Some atoms, like Be and B, might form stable compounds with incomplete octets of electrons.
- ➡Resonance structures occur when there is more than one possible position for a double bond in a molecule.
- ➡Shapes of species are determined by the repulsion of electron pairs according to VSEPR theory.
- ➡Carbon and silicon form giant covalent/network covalent structures.