SLE133 Chemistry in our World

Week 7

Chemical Bonding and Molecular Structure

Week 7

We will be covering Chapter 6 of Chemistry: Core Concepts.

6.1 Fundamentals of Bonding
6.2 Ionic Bonding
6.3 Lewis Structures
6.4 Valence Shell Electron Pair Repulsion (VSEPR)
6.5 Properties of Covalent Bonds

Not Covered in SLE133:
6.4 Trigonal Bipyramidal and Octahedral Geometries – p327 – 332 (SLE155)
6.6 Valence Bond Theory (SLE155)
Chemistry – 4th Edition: Molecular Orbital Theory (2nd Year)

Learning Goals

1. Explain how electronegativity influences the nature of bonding molecules.
2. Describe the structure and lattice energy of ionic solids.
3. Construct Lewis structures for small molecules by considering how valence electrons form covalent bonds and lone pairs.
4. Predict the geometries adopted by different molecules and ions.
5. Identify and explain properties of covalent bonds.

Fundamentals of Bonding

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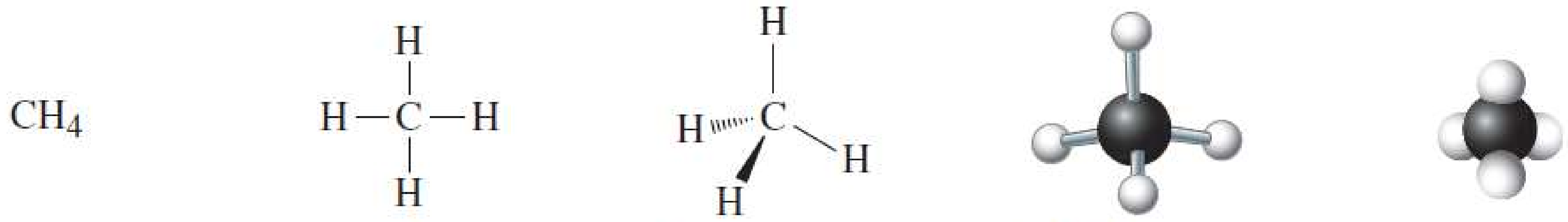
Fundamentals of Bonding

Recall week 1: an atom consists of a nucleus containing protons and neutrons, surrounded by a cloud of electrons.

- Electrons are most important to how atoms interact with each other

FIGURE 2.1 Different ways of representing the chemical species methane. Each representation is used for a different purpose to communicate relevant information about the structure.



Chemical formula | Structural formula | 3-D structural formula | Ball-and-stick model | Space-filling model

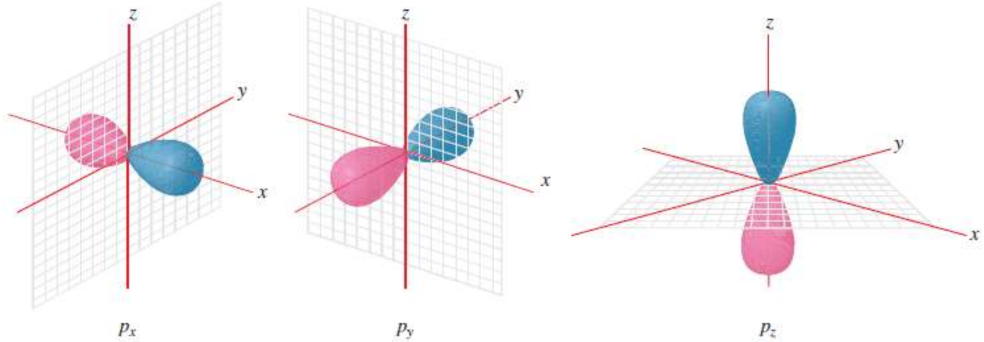
Fundamentals of Bonding

Last week: orbitals describe ***regions in space where there is a probability of finding an electron***.

We are mostly concerned with electrons in *s* and *p* orbitals

FIGURE 5.26 Boundary surface diagram of the 1*s* orbital

FIGURE 5.27 Boundary surface diagrams of the three 2*p* orbitals. The three orbitals have the same overall electron distribution, but each is oriented perpendicular to the other two. The nodal plane in each case is illustrated by the grey hatched surface.

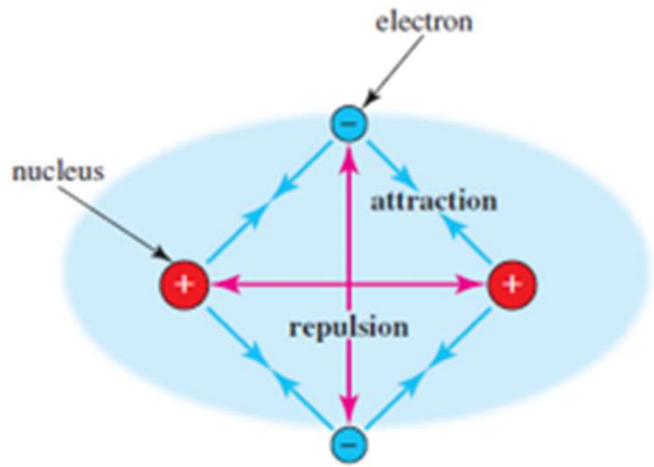


Fundamentals of Bonding

- There are three types of interactions within a molecule:
- Electrons and nuclei attract one another.
- Electrons repel each other.
- Nuclei repel each other.

Example: H_2

FIGURE 6.2 When electrons are in the region between two hydrogen nuclei, attractive electrostatic forces exceed repulsive electrostatic forces, leading to the stable arrangement of a chemical bond



Fundamentals of Bonding

These three interactions (1 attraction, 2 repulsions) are balanced to give the molecule its greatest stability.

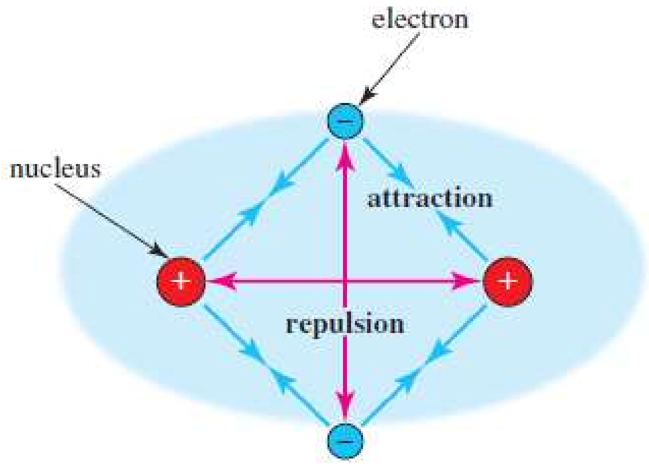
Balance is achieved when electron density is located between the nuclei of bonded atoms.

Shared electron density is called a **covalent bond.**

Fundamentals of Bonding

- **Example:** Hydrogen – H_2
- Both nuclei are attracted to the same electrons
- Overlap of orbitals occurs to give egg shape
- Two electrons shared between the nuclei provide $1s^2$ configuration of helium for each of the H atoms.

FIGURE 6.2 When electrons are in the region between two hydrogen nuclei, attractive electrostatic forces exceed repulsive electrostatic forces, leading to the stable arrangement of a chemical bond



Bond length and bond energy:

Bond length is the distance at which the molecule has the maximum energetic advantage over the separated atoms.

Bond energy is the energy required to break the bond (in kJ mol^{-1}), it is always positive.

Each different chemical bond has a characteristic bond length and energy.

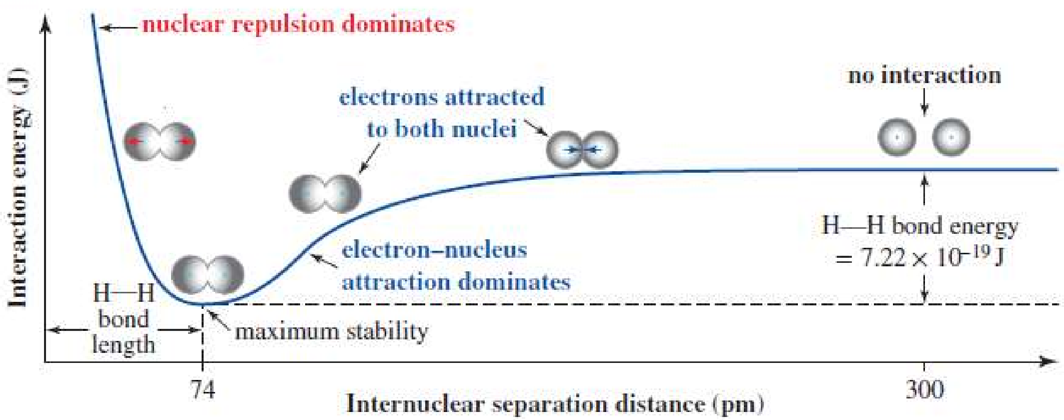
Fundamentals of Bonding – Bond Length

Bond length

The separation distance at which the molecule has the maximum energetic advantage over the separated atoms (optimal distance)

Example: H_2, two H atoms bonded to each other.

FIGURE 6.3 The interaction energy of two hydrogen atoms depends on the distance between the nuclei



300 pm apart = no interaction

74 pm = <u>maximum stability</u>

Closer than that has too much repulsion!

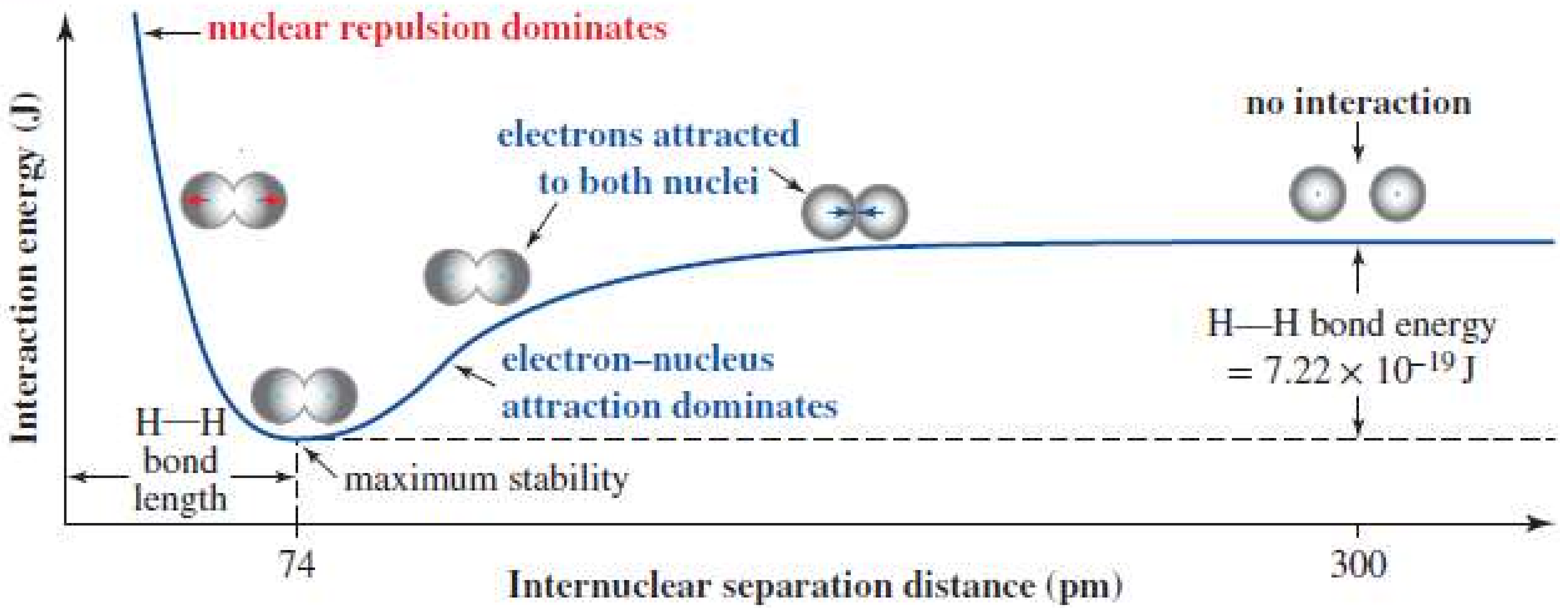
Fundamentals of Bonding – Bond Length

Sigma (σ) bonds

The most probable position of the electrons is between the two nuclei.

Example: H_2, two H atoms bonded to each other.

FIGURE 6.3 The interaction energy of two hydrogen atoms depends on the distance between the nuclei



Fundamentals of Bonding

Other diatomic molecules: F_2

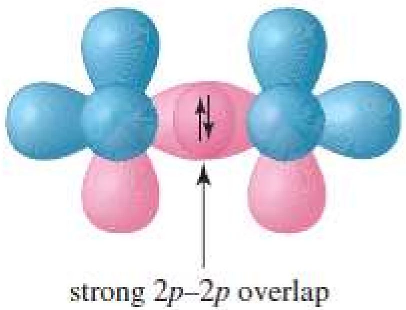
H_2 has only two electrons total – what about more?

Even when the atoms within a molecule contain many electrons, covalent bond

formation is still considered as the *sharing of only two electrons*.

• The resulting bond is also a sigma bond.

FIGURE 6.4 Two adjacent fluorine atoms each have three 2*p* atomic orbitals, each pointing at right angles to one another. The chemical bond in F_2 forms from strong electrostatic attraction of the electron in the fluorine 2*p* orbital that points directly at the neighbouring nucleus.



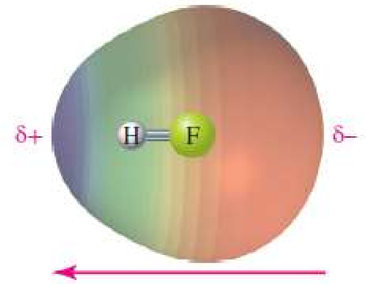
Unequal electron sharing

In a chemical bond between any two identical atoms, the nuclei share the bonding electrons equally.

When it is two different atoms, unequal attractive forces lead to an unsymmetrical distribution of the bonding electrons.

This results in a **polar covalent bond.**

FIGURE 6.5 Unequal sharing of electron density in HF results in a polar covalent bond. The colour gradient represents the variation in electron density shared between the atoms.



Unequal electron sharing

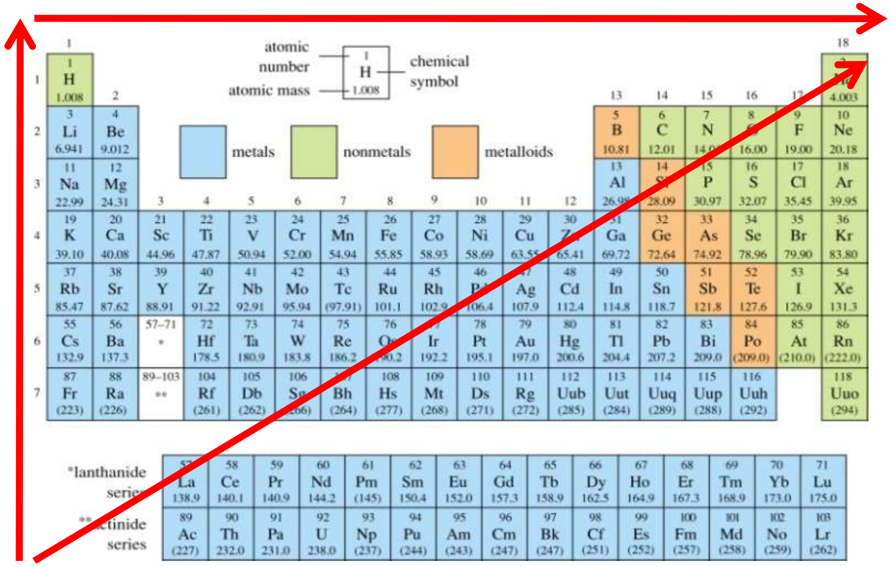
Electronegativity gives a numerical value of how strongly an atom attracts the electrons in a chemical bond.

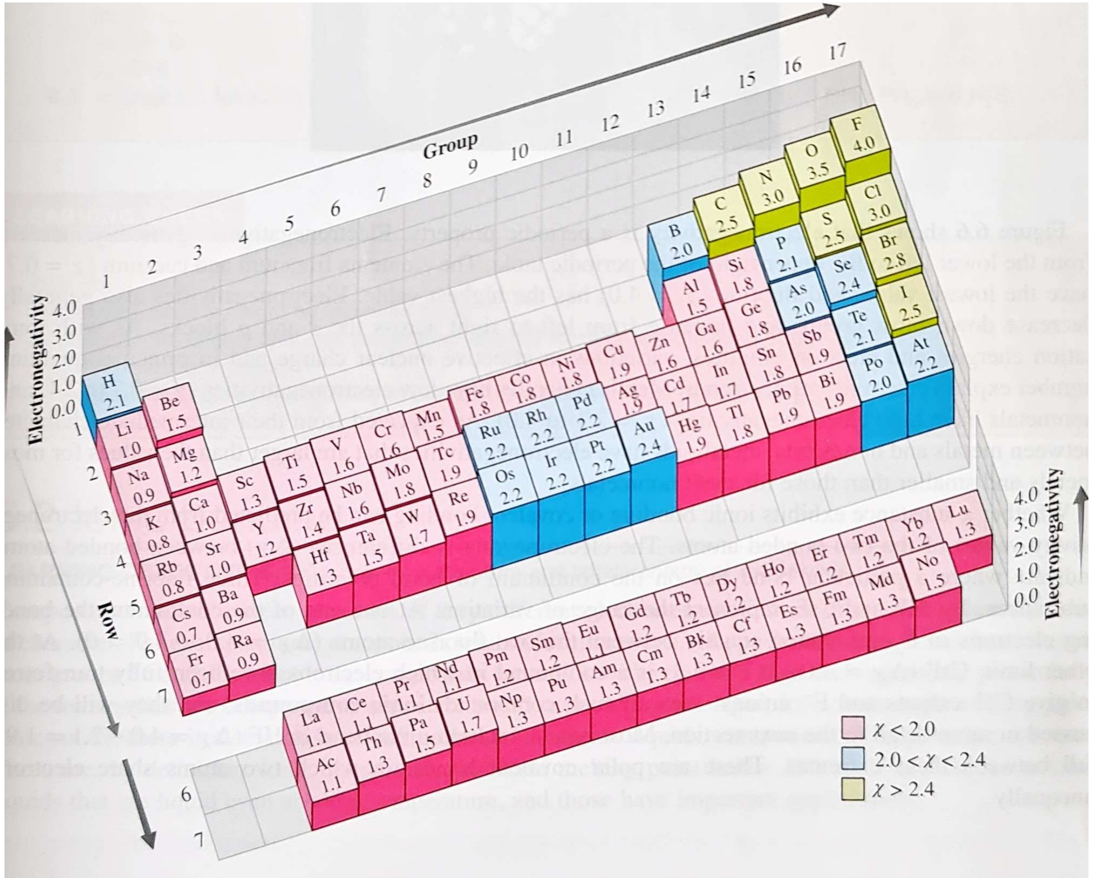
Symbolised by χ (no units).

Trend in the periodic table.

The more **electronegative** atom in a polar bond attracts a greater share of the electron density.

Fundamentals of Bonding - Electronegativity





In a covalent bond formed between the following atoms, which tends to attract electron density?

1) C and O

2) N and H

3) Cu and I

4) S and N

Fundamentals of Bonding

The number of covalent bonds typically formed by main group elements.

Row number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H $1s^1$																	2 He $1s^2$
													main group (p block)					
2													5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3														14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4														32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5															51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$

Quick Check

How many valence electrons does sulfur have?

a) 4

b) 6

c) 16

d) 10

Ionic Bonding

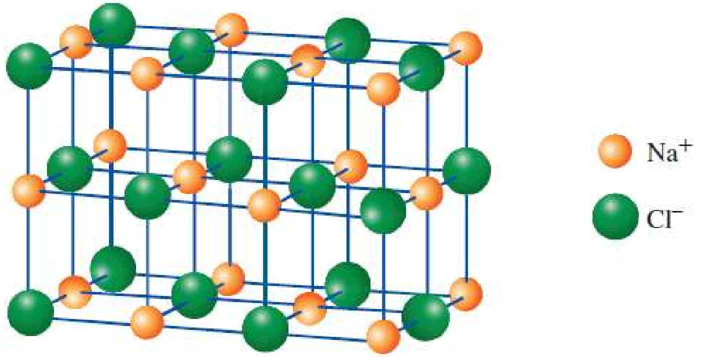
Ionic Bonding

Compounds formed between elements of very different electronegativities are **ionic.**

Most ionic compounds are solids with *high* melting points.

They are held together by the attractive forces between oppositely charged ions.

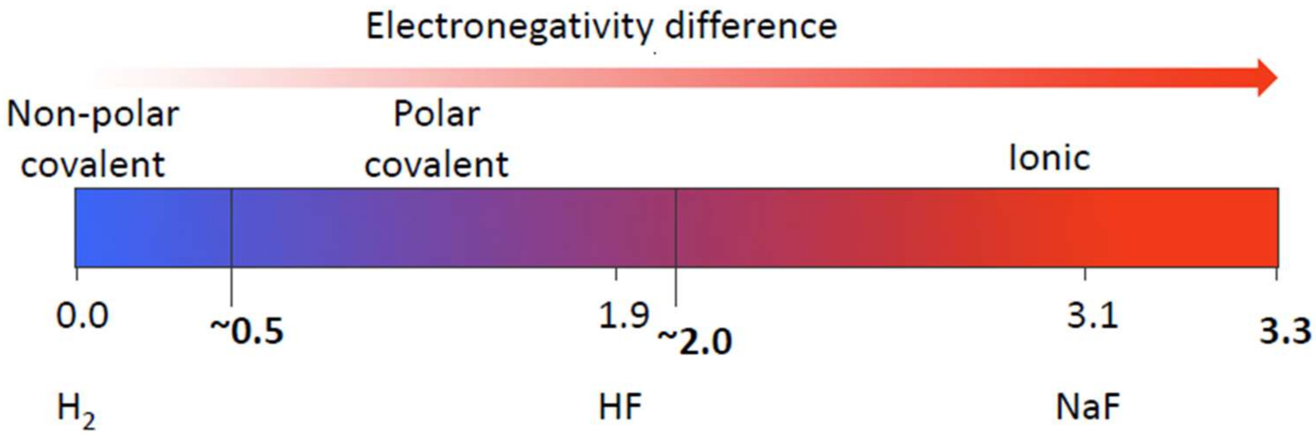
FIGURE 6.8 Representation of part of the structure of sodium chloride, NaCl. Note that each Na^+ cation is surrounded by six Cl^- anions, and each Cl^- anion is surrounded by six Na^+ cations.



Fundamentals of Bonding – Types of Bonding

Types of bonding

- Covalent
- Polar Covalent
- Ionic



What type of bonds do the following compounds contain?

1) CS_2

2) $NaBr$

3) H_2O

Lewis Structures

Lewis Structures

The conventions:

An atom is represented by its elemental symbol.

Only the valence electrons appear.

A line represents one pair of electrons that is shared between two atoms (double bond: 2 lines, triple bond: 3 lines).

Dots represent the nonbonding electrons on that atom (nonbonding pairs are called lone pairs).

Lewis Structures

FIGURE 6.10 The Lewis structure conventions for hydrogen fluoride

1. Elemental symbols represent atoms.	H	F
2. Only valence electrons appear.	1s $\uparrow$	2s $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ 2p
3. Lines represent bonds.	H—F	
4. Dots represent nonbonding electrons.	$\mathrm{H{-}\ddot{\underset{\cdot\cdot}{F}}\colon}$	

Lewis Structures – Steps for Drawing a Lewis Structure

Building Lewis structures:

Step 1: Count the valence electrons.

Step 2: Assemble the bonding framework using single bonds.

Step 3: Place three nonbonding pairs of electrons on each outer atom except H.

Step 4: Assign the remaining valence electrons to inner atoms.

Step 5: Minimise formal charges on all atoms.

Lewis Structures – Drawing a Lewis Structure

Step 1: Count the valence electrons. If the species is an ion, add or subtract one electron for each negative or positive charge respectively.

Example: SO_2

S – 6 valence electrons

O – 6 valence electrons

SO_2 – [6 + (2 x 6)] = 18 valence electrons

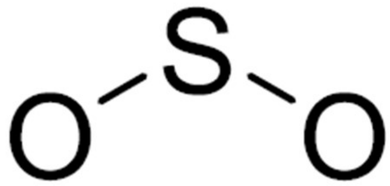
Lewis Structures – Drawing a Lewis Structure

Step 2: Assemble the bonding framework using single bonds.

Example: SO_2

- Outer atoms are usually the more electronegative.
- Usually one inner atom attached to two or more other atoms.
- Is sulfur or oxygen more electronegative?

18 valence electrons
– 4 electrons (bonding)
14 electrons leftover



Lewis Structures – Drawing a Lewis Structure

Step 3: Place three nonbonding pairs of electrons on each outer atom except H.

Example: SO_2

- Nonbonding electron pairs are called *lone pairs*.

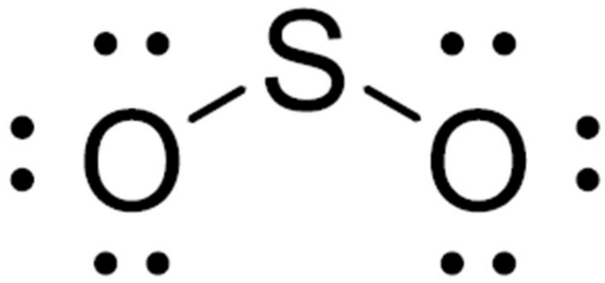
18 valence electrons

– 4 electrons (bonding)

= 14 electrons

– 12 electrons (lone pairs)

= 2 electrons

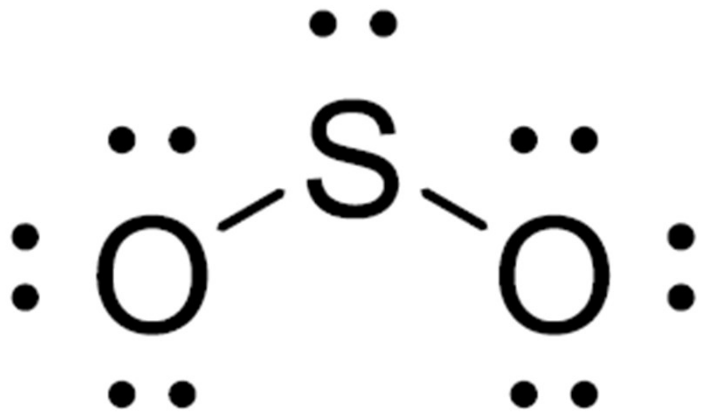


Lewis Structures – Drawing a Lewis Structure

Step 4: Assign the remaining valence electrons to inner atoms.

Example: SO_2

- We have assigned 16 electrons in steps 2-3, and SO_2 has 18 valence electrons (step 1). Therefore 2 electrons are left.



18 valence electrons
– 4 electrons (bonding)
= 14 electrons
– 12 electrons (lone pairs)
= 2 electrons
– 2 electrons (lone pairs)
= 0 electrons

Lewis Structures – Drawing a Lewis Structure

Step 5: Minimise formal charges on all atoms.

Example: SO_2

- Making sure our structure makes sense!

    Formal charge = (valence electrons of free atom) – (electrons assigned to atom in Lewis structure)

- Lone pair electrons are assigned to the atom.
- Electrons in bonds are shared between the atoms.

Electrons assigned to atom in Lewis structure – **all** lone pairs and ½ of bonding pairs

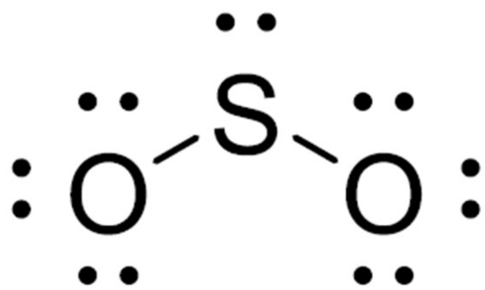
Lewis Structures – Drawing a Lewis Structure

Step 5: Minimise formal charges on all atoms.

Example: SO_2

S	Valence electrons of atom	6
	Electrons assigned in Lewis structures	
	Lone pair electrons on sulfur	
	½ of bonding pair electrons	
	Formal Change	

O	Valence electrons of atom	6
	Electrons assigned in Lewis structures	
	Lone pair electrons on oxygen	
	½ of bonding pair electrons	
	Formal Change	



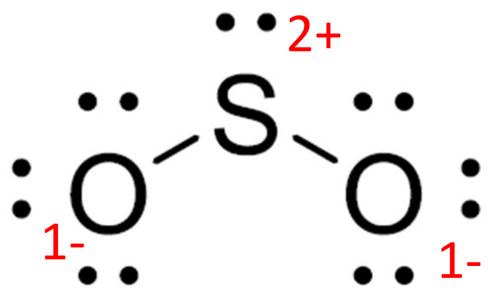
Lewis Structures – Drawing a Lewis Structure

Step 5: Minimise formal charges on all atoms.

Example: SO_2

S	Valence electrons of atom	6
	Electrons assigned in Lewis structures	
	Lone pair electrons on sulfur	2
	½ of bonding pair electrons	2
	Formal Change: 6 – 2 – 2	+2

O	Valence electrons of atom	6
	Electrons assigned in Lewis structures	
	Lone pair electrons on oxygen	6
	½ of bonding pair electrons	1
	Formal Change: 6 – 6 – 1	-1



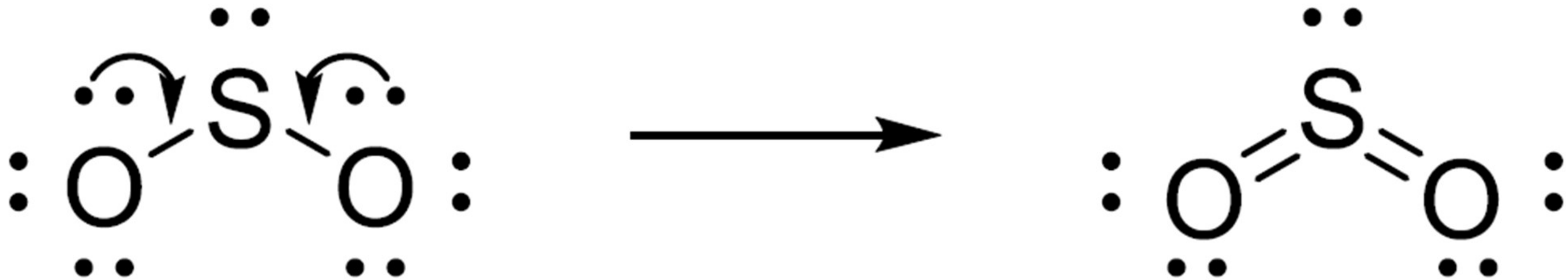
We can minimise these formal charges to give a better structure

Lewis Structures – Drawing a Lewis Structure

Step 5: Minimise formal charges on all atoms.

Example: SO_2

- Convert one lone pair from each O into a bond
- Two double bonds



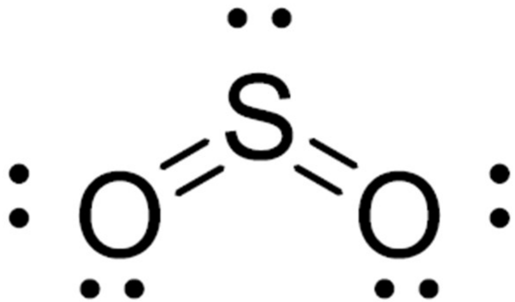
Lewis Structures – Drawing a Lewis Structure

Step 5: Minimise formal charges on all atoms.

Example: SO_2

S	Valence electrons of atom	6
	Electrons assigned in Lewis structures	
	Lone pair electrons on sulfur	2
	½ of bonding pair electrons	4
	Formal Change: 6 – 2 – 2	0

O	Valence electrons of atom	6
	Electrons assigned in Lewis structures	
	Lone pair electrons on oxygen	4
	½ of bonding pair electrons	2
	Formal Change: 6 – 6 – 1	0



This is the final, “best” Lewis structure for SO_2

Lewis Structures – Formal Charge

Formal charges

Formal charges can't always equal zero

Make sure negative formal negative charges are on the more electronegative atoms.

Only atoms with access to *d* orbitals can be assigned more than 8 electrons.

Formal charges are NOT THE SAME as **partial charges** (δ+ or δ-)

eg: H_2O versus OH^-

Quick Check

How many valence electrons does carbon dioxide (CO2) have?

a) 16

b) 6

c) 12

d) 10

Construct the Lewis structure for the compound CO_2

Lewis Structures – Resonance Structures

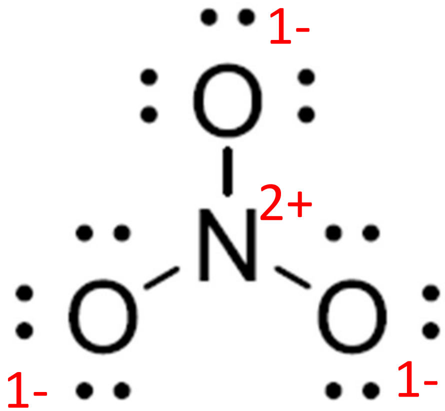
Resonance structures:

Sometimes more than one “best” Lewis structure is possible.

Resonance structures are composites of equivalent Lewis structures.

Resonance structures differ only in the position of the electrons, not atoms.

Example: NO_3^-



24 valence electrons

- Three N-O bonds use 6 electrons
- Three lone pairs on each O uses another 18 Formal charges: O = -1, N = +2

We can minimise these formal charges

Lewis Structures – Resonance Structures

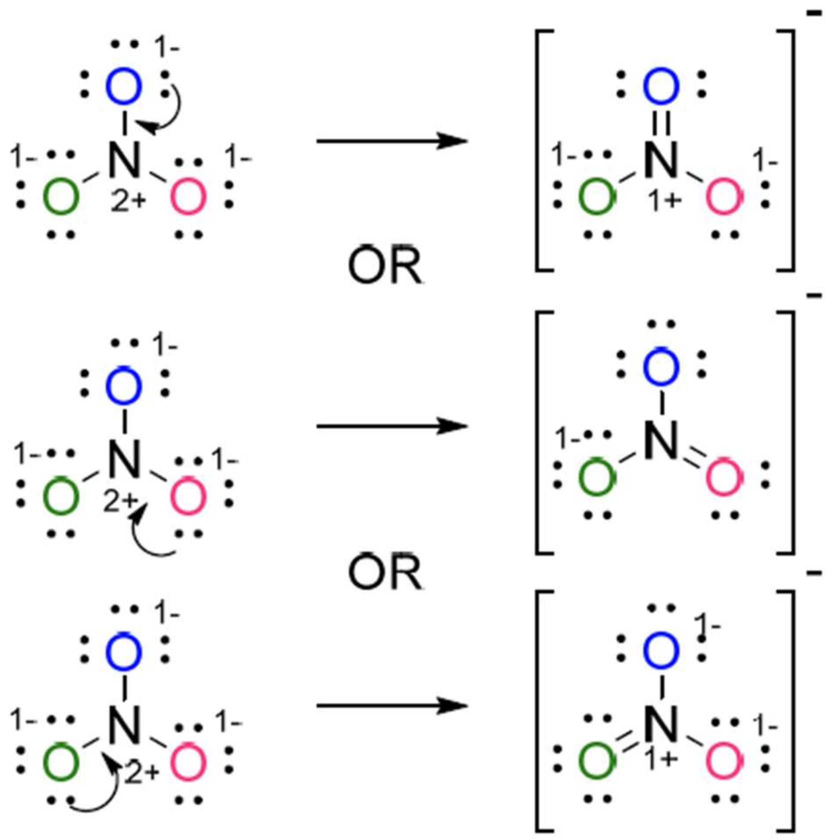
Resonance structures:

Example: NO_3^-

Move one lone pair from O to form a bond

We can do that three times!

But which one is right?



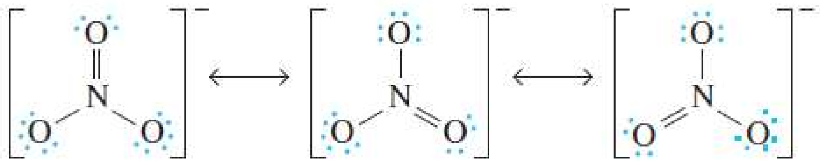
Lewis Structures – Resonance Structures

Resonance structures:

No *single* resonance structure is an accurate representation of NO_3^-.

Experiments show each N-O bond is of equal length (between length of normal double and single bonds).

FIGURE 6.13 The possible resonance structures of NO_3^-



Double-headed arrow emphasises that a complete depiction requires ALL the resonance structures.

Electrons don’t ‘flip back and forth’.

Worked Example

Determine the possible resonance structures of the nitrite ion, NO_2^-.

Valence Shell Electron Pair Repulsion

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Valence Shell Electron Pair Repulsion

VSEPR:

The **V**alence **S**hell **E**lectron **P**air **R**epulsion theory considers that molecular shape is determined by repulsions between pairs of electrons.

To minimise these repulsions, electron pairs around an inner atom within a molecule will be situated as far apart as possible.

The repulsions are in the order:

LP-LP	>	BP-LP	>	BP-BP
Greatest repulsion				*Less repulsion*

Valence Shell Electron Pair Repulsion

Electronic geometry

Describes the geometry of the electron pairs (both bonding and lone pairs).

Determined only by the total number of electron pairs.

TABLE 6.2 Optimum geometry of sets of electron pairs

Number of sets of electron pairs	Geometry of sets of electron pairs
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

Valence Shell Electron Pair Repulsion

Molecular shape

Describes the shape of the molecule.

Dependant on the proportion of bonding vs. lone pairs of electrons.

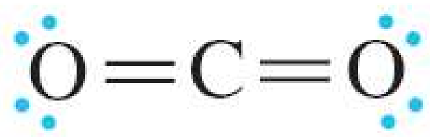
VSEPR – Linear Electronic Geometry

Two sets of electron pairs = linear electronic geometry

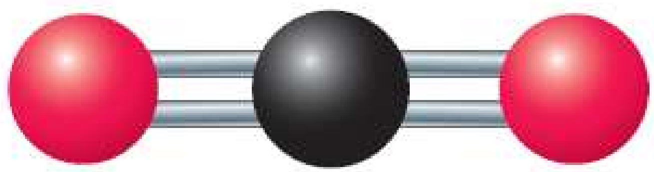
The two sets of electron pairs need to be situated as far apart as possible.

- Linear molecular shape

Example: CO_2



two sets of electron
pairs around the C atom

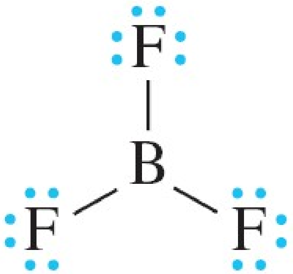


linear shape
bond angle = 180°

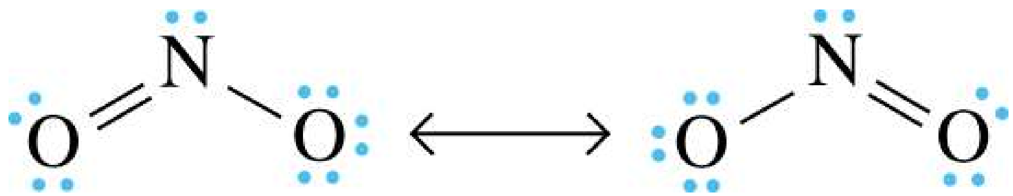
VSEPR – Trigonal Planar Electronic Geometry

Three sets of electron pairs = trigonal planar electronic geometry

- The three sets of electron pairs around an inner atom need to be situated as far apart as possible.
  - 2 molecular shapes – trigonal planar (0 LP), or bent (1 LP).
- **Examples:** BF_3 and NO_2



Trigonal planar geometry
Trigonal planar shape
120° bond angle



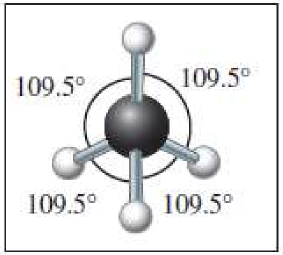
Trigonal planar geometry
Bent shape
<120° bond angle

VSEPR – Tetrahedral Electronic Geometry

Four sets of electron pairs = tetrahedral electronic geometry

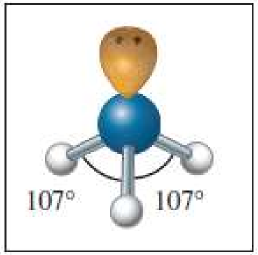
- 3 molecular shapes – tetrahedral (0 LP), trigonal pyramidal (1 LP), and bent (2 LP).

Examples: CH_4, NH_3, and H_2O



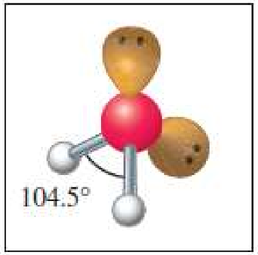
CH_4

Tetrahedral geometry
Tetrahedral shape
109.5° bond angle



NH_3

Tetrahedral geometry
Trigonal pyramidal shape
107° bond angle



H_2O

Tetrahedral geometry
Bent shape
104.5° bond angle

Quick Check

What is the electronic geometry of NO_2^-? What is its molecular shape?

A) Tetrahedral geometry, trigonal pyramidal shape

B) Trigonal planar geometry, bent shape

C) Tetrahedral geometry, tetrahedral shape

D) Tetrahedral geometry, trigonal pyramidal shape

Quick Check

What is the electronic geometry of H_3O^+? What is its molecular shape?

A) Tetrahedral geometry, trigonal pyramidal shape

B) Tetrahedral geometry, tetrahedral shape

C) Trigonal planar geometry, trigonal planar shape

D) Trigonal planar geometry, bent shape

Properties of Covalent Bonds

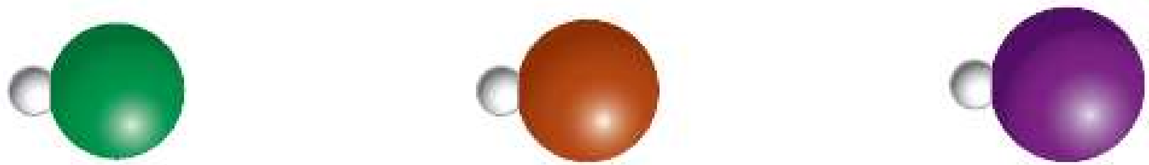
Properties of Covalent Bonds – Dipole Moment

Dipole moment:

Most chemical bonds are polar (one end slightly positive, the other slightly negative).

Bond polarities can lead to molecules with *dipole moment*.

Dipole moment depends on bond polarities ($\Delta\chi$) and on molecular shape.



HCl
$\Delta\chi = 1.9$
$\mu = 3.57 \times 10^{-30}$ C m

HBr
$\Delta\chi = 0.7$
$\mu = 2.64 \times 10^{-30}$ C m

HI
$\Delta\chi = 0.4$
$\mu = 1.27 \times 10^{-30}$ C m

Properties of Covalent Bonds – Dipole Moment

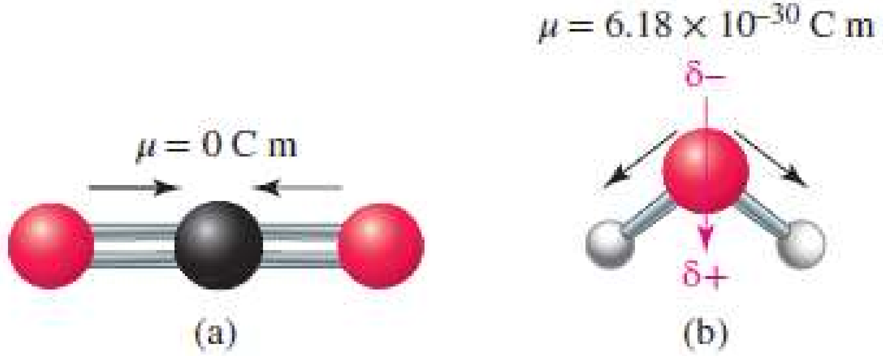
Dipole moment:

Most chemical bonds are polar (one end slightly positive, the other slightly negative).

Bond polarities can lead to molecules with *dipole moment*.

Dipole moment depends on bond polarities (Δχ) and on molecular shape.

FIGURE 6.23 (a) When identical polar bonds point in opposite directions, as in CO_2, their polarity effects cancel, giving a zero net dipole moment. (b) When two identical polar bonds do not point in exactly opposite directions, as in H_2O, there is a net dipole moment.



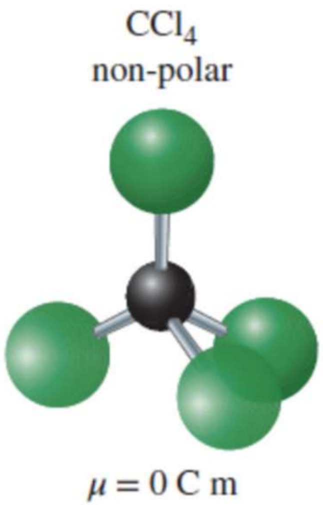
Properties of Covalent Bonds – Dipole Moment

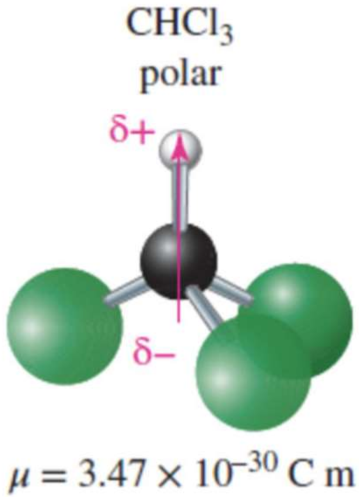
Dipole moment:

Most chemical bonds are polar (one end slightly positive, the other slightly negative).

Bond polarities can lead to molecules with *dipole moment*.

Dipole moment depends on bond polarities (Δχ) and on molecular shape.





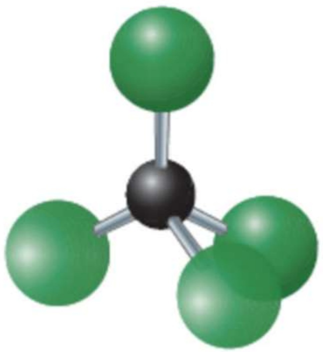
Properties of Covalent Bonds – Dipole Moment

Dipole moment:

For a molecule to have dipole moment, it must have polar bonds that do not cancel each other.

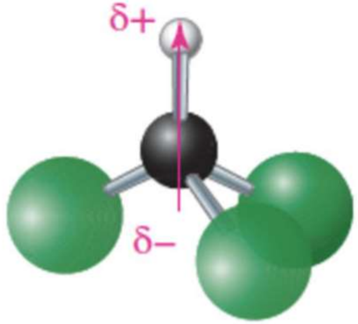
Small, symmetrical molecules will likely *not* have dipole moment due to polar bonds cancelling.

CCl_4
non-polar



$\mu = 0$ C m

$CHCl_3$
polar



$\mu = 3.47 \times 10^{-30}$ C m

Worked Example

Does the hydronium ion (H_3O^+) exhibit a dipole moment?

Properties of Covalent Bonds – Bond Length

Bond length:

Bond length of a covalent bond is the nuclear separation distance at which the molecule is most stable.

At this distance, attractive interactions are maximised relative to repulsive interactions.

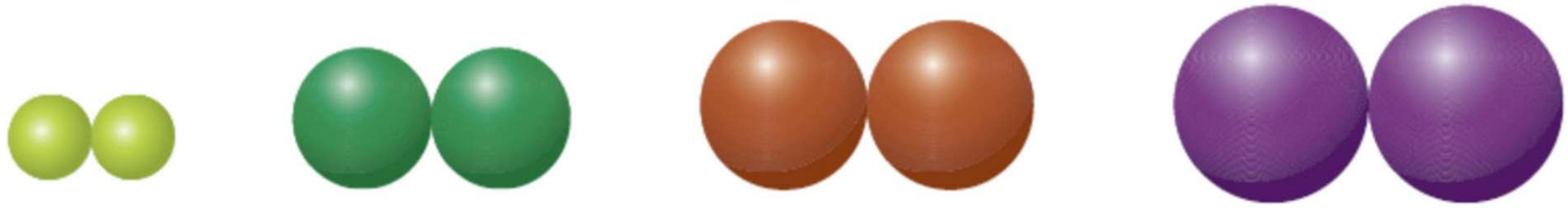
Bond lengths vary between 70 and 250 pm (1 pm = 10^{-12} m).

Properties of Covalent Bonds – Bond Length

Bond length:

Bond length increases as atom size increases.

Example: Diatomic halogens.



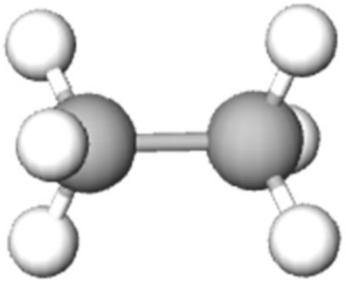
	F_2	Cl_2	Br_2	I_2
Bond length (pm)	142	199	228	267

Properties of Covalent Bonds – Bond Length

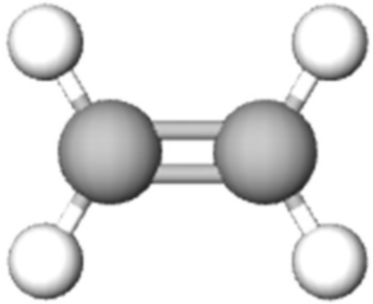
Bond length:

A multiple bond is shorter than a single bond between the same two atoms.

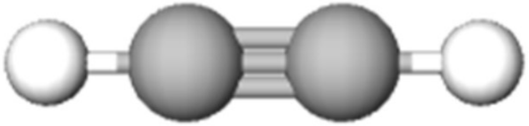
Example: carbon-carbon bonds



Ethane
Single bond between C atoms
Bond length: 154 pm



Ethene
Double bond between C atoms
Bond length: 133 pm



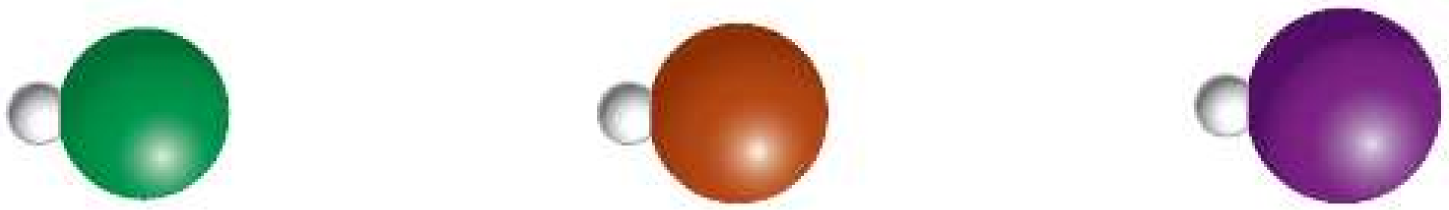
Ethyne
Triple bond between C atoms
Bond length: 120 pm

Properties of Covalent Bonds – Bond Length

Bond length:

Atoms that are joined by the same type of bond (i.e. either all single, double, or triple) and are of different types will have varying bond lengths.

The larger the difference in electronegativity between the two atoms, the shorter the bond.



HCl	HBr	HI
$\Delta\chi = 1.9$	$\Delta\chi = 0.7$	$\Delta\chi = 0.4$
$\mu = 3.57 \times 10^{-30}$ C m	$\mu = 2.64 \times 10^{-30}$ C m	$\mu = 1.27 \times 10^{-30}$ C m

Properties of Covalent Bonds – Bond Length

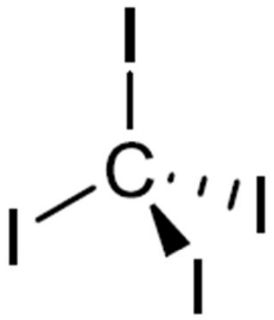
Bond length:

- The smaller the atomic radius, the shorter the bond length.
- For a given pair of atoms, the more electrons in the bond (single (2 e-); double (4 e-); triple (6 e-)) between them, the shorter the bond.
- For two atoms joined by the same type of bond (single, double or triple), the larger the electronegativity difference between the bonded atoms, the shorter the bond.

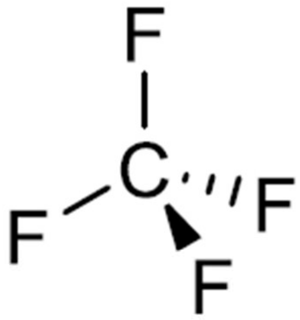
You must take all factors into account when evaluating bond length!

Quick Check

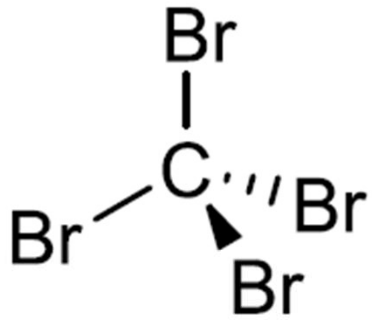
Which of the following molecules has the greatest bond length?



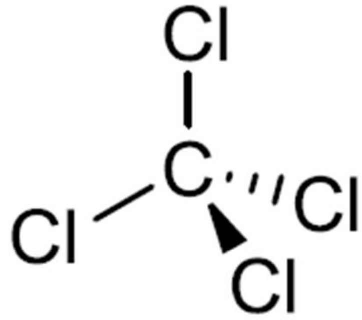
A



B



C



D

Which of the following molecules has the greatest bond length?

A. P-F

B. H-Cl

Which of the following molecules has dipole moment?

A) H_2O

B) N_2O

C) $CHCl_3$

D) CO_2

Next Week

Next week, we will cover chapter 7 from Core Concepts:

7.1 States of matter

7.2 Intermolecular forces

7.3 Gases

7.4 Gas Mixtures

7.5 Gas stoichiometry

7.6 Liquids

7.7 Solids

7.8 Phase Changes to page 430