

Depicting Molecules and Ions with Lewis Structures

The first step toward visualizing what a molecule looks like is to convert its molecular formula into its **Lewis structure**.

Applying the Octet Rule to Write Lewis Structures

To write a Lewis structure, we place bonded atoms adjacent to one another and distribute the total number of valence electrons as bonding electron pairs and lone electron pairs.

Molecules with Single Bonds

Let's use NF_3 as an example . . .

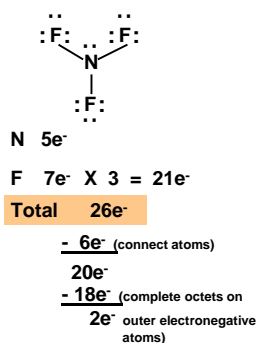
Step 1: Place the least electronegative atom at the center and place the other atoms around.

Step 2: (Available Electrons) Determine the total number of valence electrons.

Note: For polyatomic ions, add one electron for each negative charge or subtract one electron for each positive charge.

Step 3: Draw the single covalent bonds and subtract those valence electrons used in covalent bonds from the total number of valence electrons.

Step 4: Distribute the remaining electrons as lone pairs on the atoms so that each atom ends up with 8 valence electrons with the exception that hydrogen atoms only have 2 valence electrons.



Sample Problem 10.1 – Write the Lewis structure for CCl_2F_2 .

Sample Problem 10.2 – Write the Lewis structure for methanol (molecular formula CH_4O).

Molecules with Multiple Bonds

Sometimes, you'll find that, after Steps 1 to 4, there are not enough electrons for the central atom (or one of the central atoms). This usually means that a multiple bond is present and you will need to perform an additional step.

Step 5: If after Step 4, a central atom still does not have an octet of valence electrons, make a multiple bond by changing a lone electron pair from one of the surrounding atoms into a bonding electron pair to the central atom.

Write Lewis structure for the following:

(a) Ethylene (C_2H_4)

(b) Nitrogen (N_2)

Resonance: Delocalized Electron-Pair Bonding

We can often write more than one Lewis structure, each with the same relative placement of atoms. Consider the possible Lewis structures for ozone, O_3 .

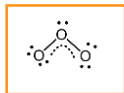


In fact, neither Lewis structure depicts O_3 accurately. Bond length and bond energy measurements indicate that the two oxygen-oxygen bonds in O_3 are **identical** – not an isolated $\text{O}-\text{O}$ single bond and an isolated $\text{O}=\text{O}$ double bond but something in between.

The molecule is depicted more correctly with two Lewis structures, called **resonance structures**, and a two-headed arrow (\leftrightarrow) between them.

Resonance structures are not real bonding depictions.

In reality, the electron density is spread out, or **delocalized**, over the entire molecule and the molecule exists as a **resonance hybrid**. In the case of O_3 , we draw the resonance hybrid with a curved dashed line to indicate the delocalized electron pairs. . .

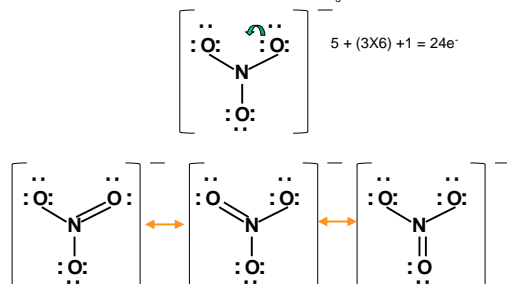


Electron delocalization diffuses electron density over a greater volume, which reduces electron-electron repulsions and thus stabilizes the molecule.

Fractional Bond Orders. Partial bonding in resonance hybrids leads to fractional bond orders. For the oxygen-oxygen bond in O_3 , we have

$$\text{Bond order} = \frac{3 \text{ shared electron pairs}}{2 \text{ bonded - atom pairs}} = 1 \frac{1}{2}$$

Draw the resonance structures for the nitrate ion, NO_3^- , and find the bond order.



$$\text{Bond order} = \frac{4 \text{ shared electron pairs}}{3 \text{ bonded - atom pairs}} = 1 \frac{1}{3}$$

Formal Charge: Selecting the More Important Resonance Structure

Often one resonance structure is more important than the others that may be written for a molecule.

One way to select the more important resonance structure is to determine the atom's **formal charge** – that is, the charge each atom would have if the bonding electrons were equally shared.

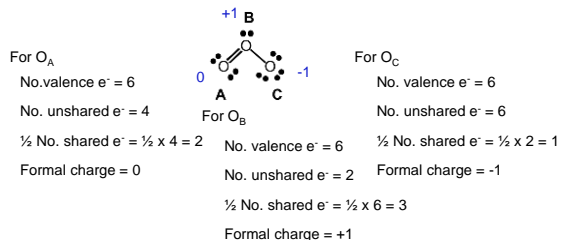
Formal charge of atom =

No. valence e^- - (no. unshared e^- + $\frac{1}{2}$ no. shared e^-)

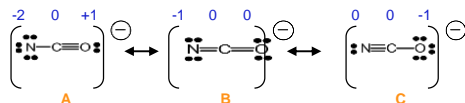
No. valence e^- - (no. e^- 's in lone pairs + no. of bonds)

Example: Calculate the formal charge on O_3 .

Formal charge of atom = No. valence e^- - (no. unshared e^- + $\frac{1}{2}$ no. shared e^-)



Write the resonance structures of the cyanate anion NCO^- and use formal charges to select the more important resonance structure(s).



Three criteria help us choose the more important resonance structure(s):

1. Smaller formal charges (positive or negative) are preferable to larger ones.
2. Like formal charges on adjacent atoms are not desirable – unless formal charge is zero.
3. A more negative formal charge should reside on the more electronegative atom.

Form A has a large negative formal charge on the nitrogen making it a less preferable resonance structure.

Form C has a negative formal charge on O which is more electronegative than N, therefore **Form C** contributes the most to the resonance hybrid.

Lewis Structures for Exceptions to the Octet Rule

Some molecules do not follow the octet rule. Typically, these exceptions are observed for molecules containing electron-deficient atoms, odd-electron atoms and atoms with expanded valence levels.

Molecules with Electron-Deficient Atoms

Gaseous molecules containing beryllium or boron as the central atom are often **electron-deficient** - that is, they have fewer than eight valence electrons around the Be or B atoms.

Example: $BeCl_2$ and BF_3

Molecules with Odd-Electron Atoms

A few molecules contain a central atom with an odd number of valence electrons. These species are called **free radicals**, contain an unpaired electron and are extremely reactive.

Example: Nitrogen dioxide, NO_2

Expanded Valence Shells

Many molecules and ions have more than eight valence electrons around a central atom. A central atom can accommodate additional electrons by using empty d orbitals. Therefore, expanded valence levels only occur when central atom is from Period 3, Period 4 and so on.

Example: Sulfur hexafluoride, SF_6

Write the Lewis structure for H_3PO_4^- .

Valence – Shell Electron – Pair Repulsion (VSEPR) Theory and Molecular Shape

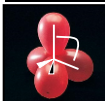
To construct a molecule's three-dimensional shape from the Lewis structure, we employ **valence-shell electron-pair repulsion (VSEPR) theory**.

Each group of valence electrons, be they a lone pair or involved in a covalent bond, around the central atom is located as far away as possible from the others to minimize electron –electron repulsions.

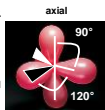
Electron Group Arrangements and Molecular Shapes

There are five electron-group arrangements of minimum energy

Electron Pairs	Bond Angle	Arrangement Name
2	180°	linear
3	120°	trigonal planar
4	109.5°	tetrahedral

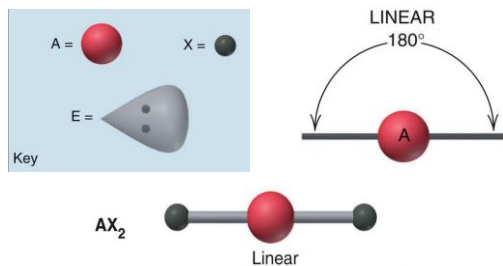


No. Electron Pairs	Bond Angle	Arrangement Name
5	90°/120°	trigonal bipyramidal
6	90°	octahedral



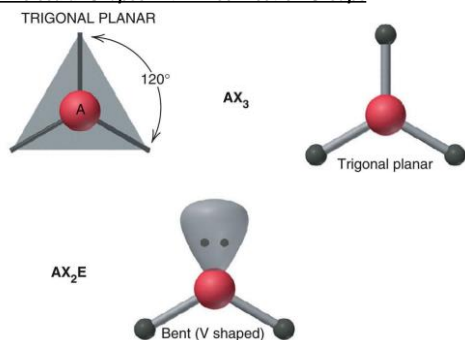
The molecular shape is defined by the relative positions of the atomic nuclei.

Note: The same electron-group arrangement can give rise to different molecular shapes depending on whether the electron pairs are bonded to another atom or are just lone pairs.

The Molecular Shape with Two Electron Groups

Example: $BeCl_2$ (molecule containing single bonds)

Example: Carbon dioxide, CO_2 (molecule containing double bonds)

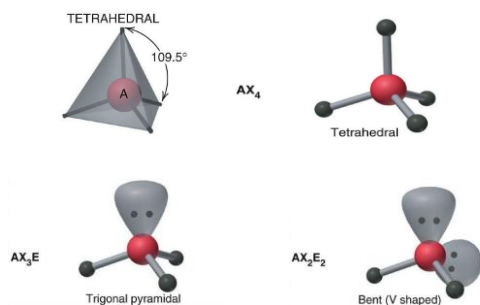
The Molecular Shapes with Three Electron Groups

Example: BF_3 (molecule containing single bonds)

Example: CH_2O (molecule containing isolated double bond)

Example: SnCl_2 (molecule containing one lone pair)

The Molecular Shapes with Four Electron Groups

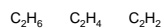


Example: Methane, CH_4 (molecule containing single bonds)

Example: Ammonia, NH_3 (molecule containing one lone pair)

Example: Water, H_2O (molecule containing two lone pairs)

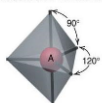
Give the number of valence electrons, draw the structure, predict the shape around each carbon atom and describe the orbital hybridization for the carbon on each of the following molecules.



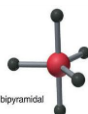
What type of orbital holds the lone pair of electrons on nitrogen in H_2CNH ?

The Molecular Shapes with Five Electron Groups

TRIGONAL BIPYRAMIDAL



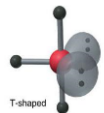
Trigonal bipyramidal



Seesaw



T-shaped



Linear



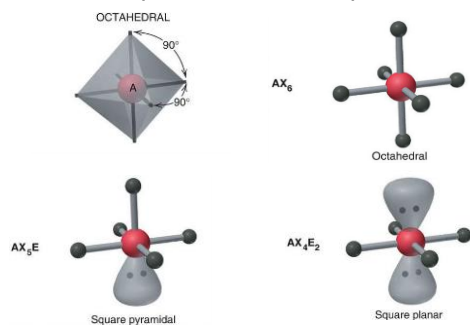
Example: PCl_5 (molecule containing single bonds)

Example: SF_4 (molecule containing one lone pair)

Example: BrF_3 (molecule containing two lone pairs)

Example: I_3^- (ion containing three lone pairs)

The Molecular Shapes with Six Electron Groups



Example: SF_6 (molecule containing single bonds)

Example: IF_5 (molecule containing one lone pair)

Example: XeF_4 (molecule containing two lone pairs)

Molecular Shape and Molecular Polarity

Knowing the shape of a substance's molecules is key to understanding its physical and chemical behavior. One important effect of molecular shape is **molecular polarity**, which is determined by both charge imbalance and bond polarity.

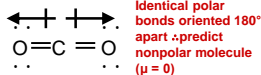
The **dipole moment** (μ) is the product of all the partial charges, arising from charge imbalance and bond polarity, and the distances between them. The dipole moment is typically measured in units of **debye (D)**.

$$1 \text{ D} = 3.34 \times 10^{-30} \text{ C m}$$

Bond Polarity, Bond Angle and Dipole Moments

When determining molecular polarity, we must take molecular shape/symmetry into account. . .

Examples: Carbon dioxide, CO_2



Water, H_2O



Polar bonds do not cancel plus lone pair electrons \therefore predict polar molecule ($\mu \neq 0$)

Carbon tetrachloride CCl_4 and Trichloromethane CHCl_3

