

A DOT STRUCTURE FOR A MOLECULE WITH DELOCALIZED BONDS O_3

O_3 (OZONE)

① Count valence electrons

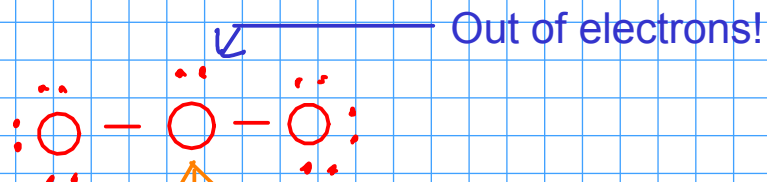
② Pick central atom and draw skeletal structure

- central atom is usually the one that needs to gain the most electrons!

- skeletal structure has all atoms connected to center with single bonds

③ Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

④ Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.



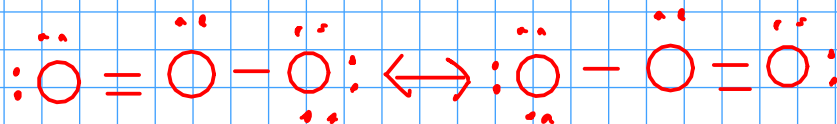
This oxygen atom only has six electrons!



This structure suggests that one of the outer oxygen atoms is closer to the central oxygen atom than the other one!

Experimentally, we observe that both outer oxygen atoms are the SAME distance from the center.

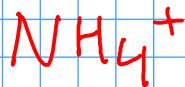
In the molecule, electrons are actually being shared between ALL THREE oxygen atoms. This is a DELOCALIZED bond!



These are RESONANCE structures. The real structure is an "average" of these two. The "double bond"'s electrons are shared between all three oxygen atoms!

A DOT STRUCTURE FOR A POLYATOMIC ION

1) Count valence electrons


$$\hline 9$$
$$- 1$$
$$\hline 8$$

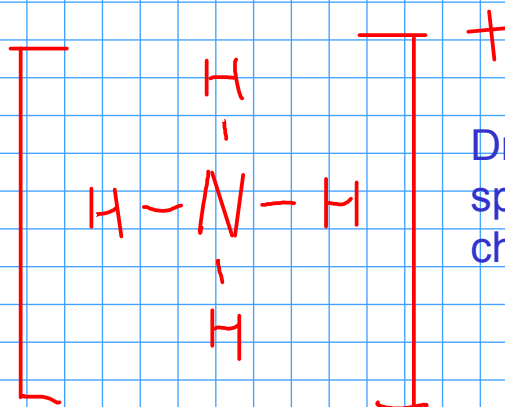
An odd number of electrons? But Lewis structures deal in PAIRS of electrons!

Subtract one electron from the total to get the correct charge (+1) on the ion.

2) Pick central atom and draw skeletal structure

- central atom is usually the one that needs to gain the most electrons!

- skeletal structure has all atoms connected to center with single bonds



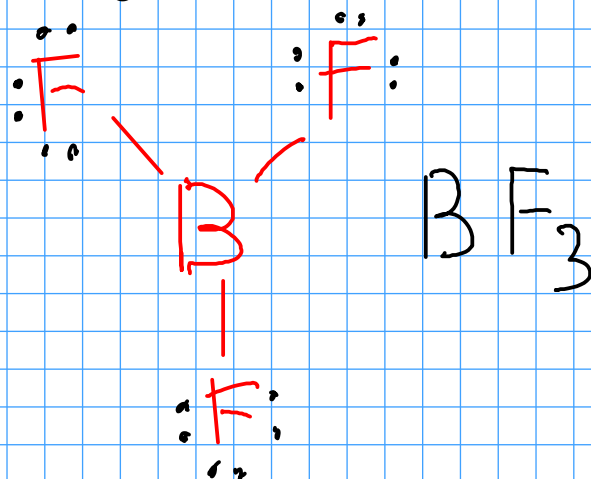
Draw brackets around charged species and indicate the overall charge!

3) Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

4) Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

EXPANDED VALENCE and other exceptions to the "octet rule"

- Some atoms do not always obey the octet rule. A few, like BORON, will bond in such a way that they end up with less than eight electrons.



... but many more bond in such a way that they end up with a share in MORE THAN EIGHT electrons!

- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

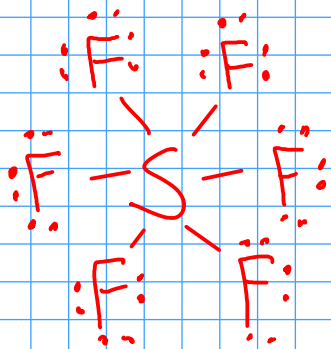
... these atoms have unfilled "d" orbitals that may participate in bonding!

- All noble gas compounds (example: XENON compounds with oxygen and fluorine) exhibit this behavior!

EXAMPLES:

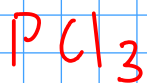


$$\begin{array}{r} \text{S: } 6 \\ \text{F: } \frac{7 \times 6}{48} \end{array}$$

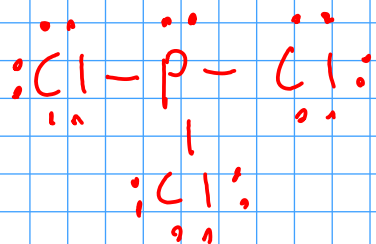


The sulfur atom ends up with a share in twelve electrons, not eight!

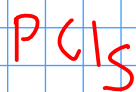
The shape of the sulfur hexafluoride molecule suggested by this structure checks with experimental data.



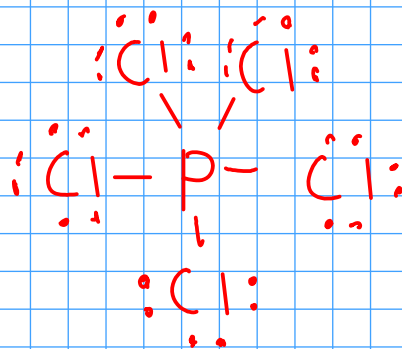
$$\begin{array}{r} \text{P: } 5 \\ \text{Cl: } \frac{7 \times 3 = 21}{26} \end{array}$$



THIS compound obeys the octet rule!



$$\begin{array}{r} \text{P: } 5 \\ \text{Cl: } \frac{7 \times 5 = 35}{40} \end{array}$$



This molecule does NOT obey the octet rule - phosphorus ends up with a share in ten electrons!

FORMAL CHARGE

- You can often draw more than one structure for a molecule that appears correct. How can you determine which one is more likely?

- USE FORMAL CHARGE!

- Formal charge is a hypothetical charge on each atom in a structure. It assumes:

- ① All bonding electrons are shared EQUALLY between atoms
- ② Lone pairs are NOT shared.

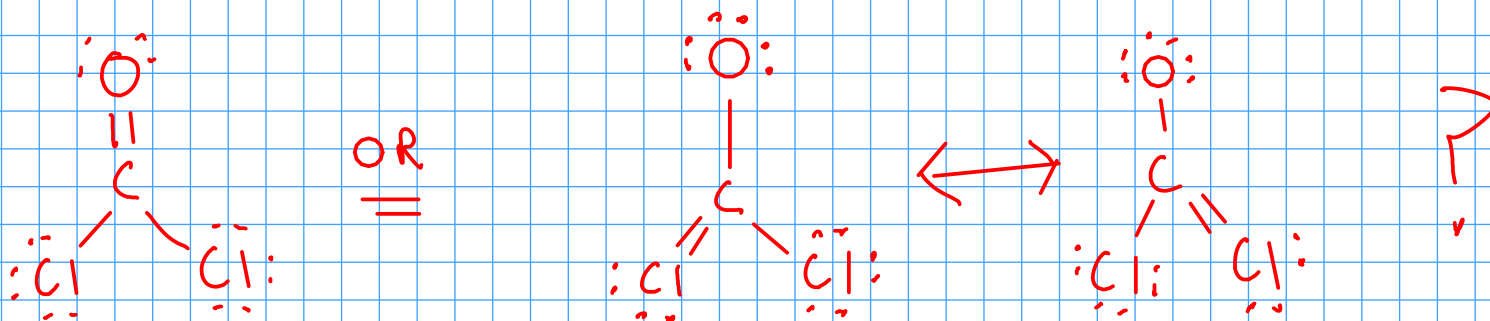
$$\text{FORMAL CHARGE} = \text{ORIGINAL \# OF VALENCE ELECTRONS} - \text{NUMBER OF BONDS} - \text{NUMBER OF UNSHARED ELECTRONS}$$

* The sum of the formal charges of all atoms in a structure should equal to the charge of the molecule (0 for neutral molecules)

The "better" Lewis structure will have:

- Lower magnitudes of formal charge (0 0 is better than +2 -2)
- Negative formal charges on ELECTRONEGATIVE atoms, or positive formal charges on atoms that are less electronegative.

EXAMPLE: COCl_2



... calculate formal charges to tell which structure is more likely!

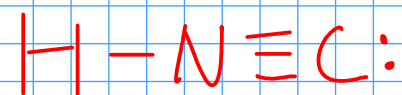
✓

$$\begin{array}{l} \text{O} \quad 6 - 2 - 4 = 0 \\ \text{C} \quad 4 - 4 - 0 = 0 \\ \text{Cl} \quad 7 - 1 - 6 = 0 \\ \text{Cl} \quad 7 - 1 - 6 = 0 \end{array}$$

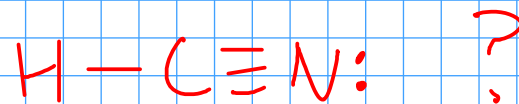
$$\begin{array}{l} \text{O} \quad 6 - 1 - 6 = -1 \\ \text{C} \quad 4 - 4 - 0 = 0 \\ =\text{Cl} \quad 7 - 2 - 4 = +1 \\ -\text{Cl} \quad 7 - 1 - 6 = 0 \end{array}$$

* The sum of the formal charges of a correct Lewis structure will sum to the overall CHARGE of the molecule.

We think the structure on the left is preferred. It has LOWER formal charges, AND it does not have a positive formal charge on something as electron-greedy as CHLORINE!



vs



?

... we can determine which of these structures is more likely by calculating formal charges!

$$\text{H} \quad 1 - 1 - 0 = 0$$

$$\text{C} \quad 4 - 3 - 2 = -1$$

$$\text{N} \quad 5 - 4 - 0 = +1$$

$$\text{H} \quad 1 - 1 - 0 = 0$$

$$\text{C} \quad 4 - 4 - 0 = 0$$

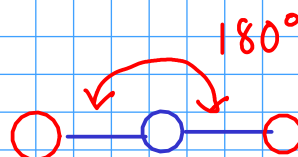
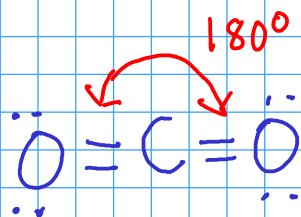
$$\text{N} \quad 5 - 3 - 2 = 0$$

PREDICTING MOLECULAR SHAPE

The shape of simple molecules (and parts of larger molecules) can be easily predicted using the VSEPR model

VSEPR = Valence Shell Electron Pair Repulsion Model

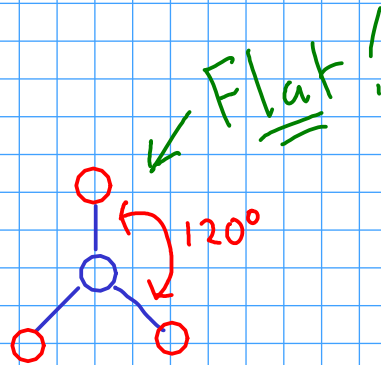
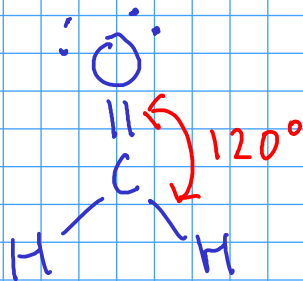
- Each BOND or LONE PAIR OF ELECTRONS around an atom will try to move itself as far away from other bonds or lone pairs as possible!



For the two red circles to be farthest apart, they must be 180 degrees apart

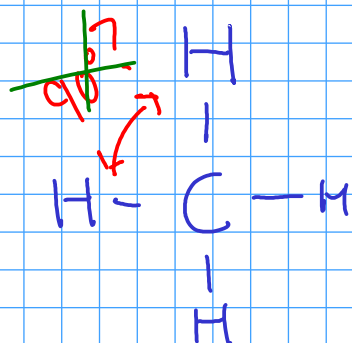
LINEAR
MOLECULES

ANY diatomic (two-atom) molecule is linear, but only some three-atom molecules are!



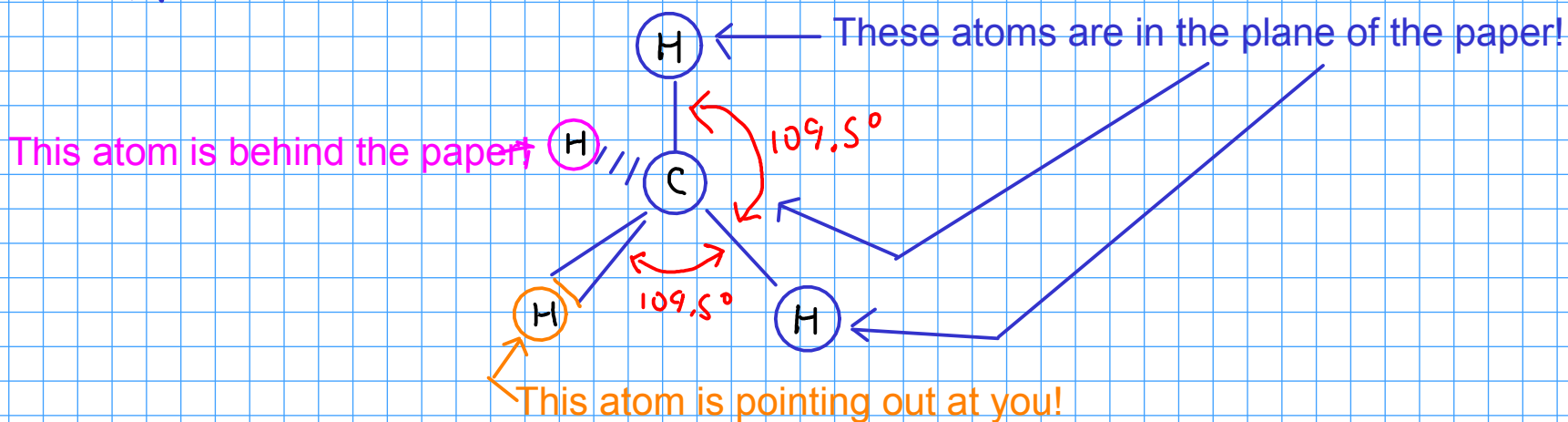
For the three red circles to be farthest apart, they spread out so that each is 120 degrees from the others!

TRIGONAL
PLANAR
MOLECULES



These hydrogen atoms might appear at first glance to be 90 degrees apart, but remember that molecules exist in **THREE DIMENSIONS**, not two!

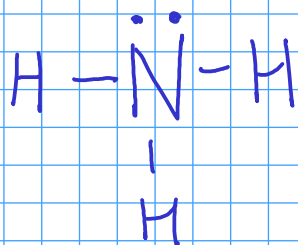
Each hydrogen atom is actually 109.5 degrees apart, forming a **TETRAHEDRON**.



To see the tetrahedron in three dimensions **WITHOUT** buying a molecular model kit, just take four balloons, blow them up, and then tie them together. The knot will be the central atom, and the balloons will line themselves up to be 109.5 degrees apart.

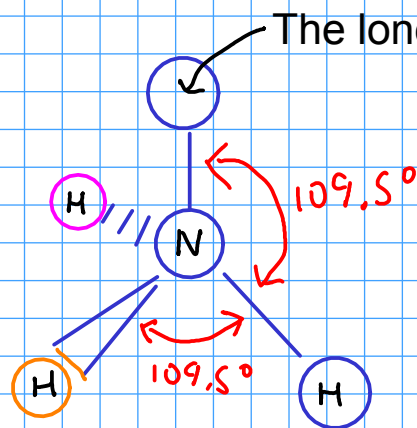
DERIVATIVES OF THE TETRAHEDRON

- What if there are lone pairs? The way the shape of a molecule is described depends on the ATOMS in the molecule, even though lone pairs play a role in the positions of the atoms.

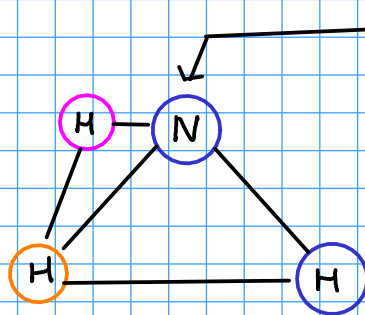


Since there are four "things" around the nitrogen atom, we would expect them to be approximately 109.5 degrees apart (in other words, TETRAHEDRAL). BUT ... only three of these things are atoms.

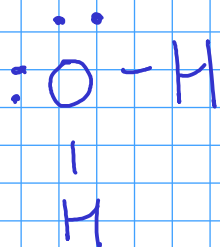
The atoms are arranged in a PYRAMID shape, so we call this molecule PYRAMIDAL!



The lone pair takes one position in the tetrahedron



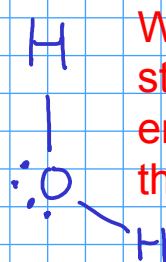
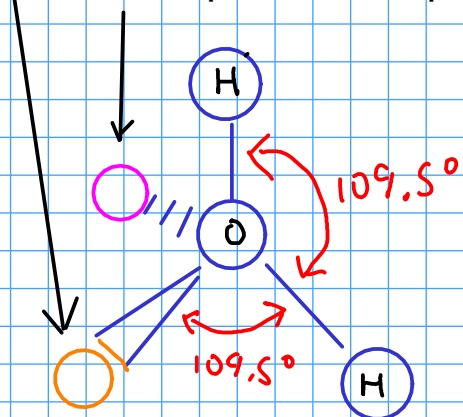
By just looking at the atoms, you can see the pyramid - with the central nitrogen atom as the top and the hydrogen atoms forming the base of the pyramid.



Since there are four "things" around the oxygen atom, we would expect them to be approximately 109.5 degrees apart (in other words, TETRAHEDRAL). BUT... only two of these things are atoms.

The atoms are all in a single plane, but they are not lined up in a straight line. We call this shape "BENT".

Lone pairs take up two positions in the tetrahedron



We sometimes draw the Lewis structure of water this way to emphasize the "bent" nature of the molecule!

* These atoms are in the same plane, like carbon dioxide. But they are not arranged linearly!

Notice that this molecule has two "sides", one with the oxygen atom and one with hydrogen atoms.

