COVALENT BONDING

[MH5; Chapter 7]

- **Covalent** bonds occur when electrons are equally shared between two atoms.
- The electrons are not always equally shared by both atoms; these bonds are said to be **polar covalent**.
- We assume that only electrons in the **valence shell** are involved in forming covalent bonds.
- These electrons are simultaneously attracted to both nuclei; a favourable, lower - energy, arrangement.
- The nuclei are "insulated" from each other by electrons; so the electrons feel attraction of 2 nuclei.
- Two bonded atoms are in a lower energy state than two separate atoms; resulting in the formation of a stable covalently bonded molecule:

$$\mathbf{H(g) + H(g) \rightarrow H_2\,(g)}$$

- Two electrons are shared; a single bond is formed.

- Lewis dot structure: H• X H → H—H

- Since each H atom has electron configuration $1s^1$, H atoms form only **one** bond:

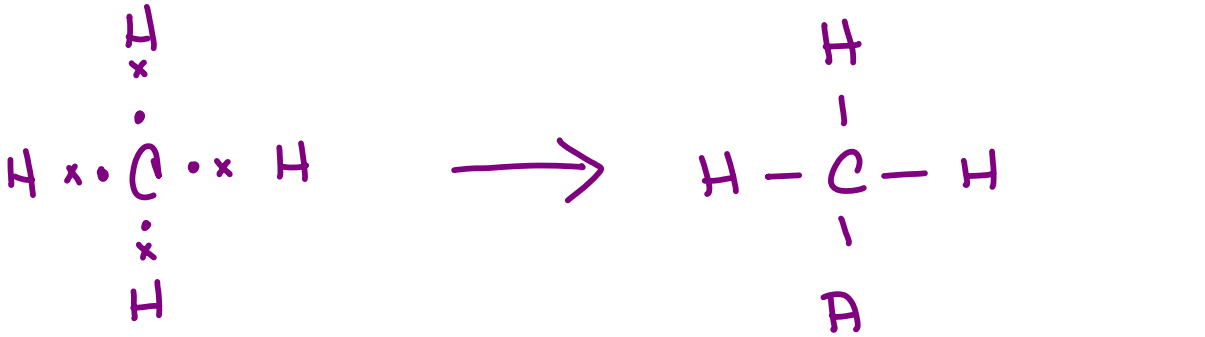
EXAMPLES:

H — H H — Cl H₂O

LEWIS STRUCTURES; THE OCTET RULE [MH5; 7.1]

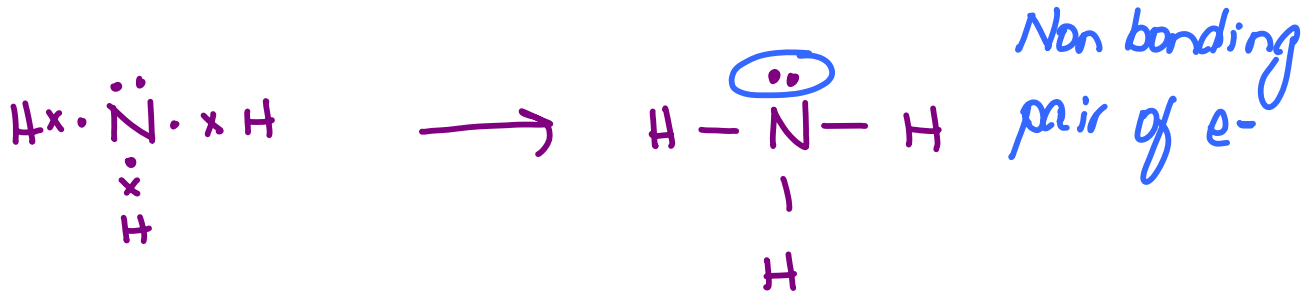
- G.N. Lewis suggested the idea of the covalent bond by pointing out that the electron configuration of the inert gases seemed to be extremely stable.
- His idea was that non metal atoms may share electrons to form bonds; by doing so they acquire the same electron configuration as an inert gas.
- As only valence electrons are involved in forming bonds, first-row elements Li through F form a maximum of four bonds, (4 electron pairs), which fill the 2s and 2p orbitals.
- **Lewis Structures** are diagrams which show how many bonds there are in a covalently bonded molecule and the location of any non bonding electron pairs.
- We sometimes use a generic notation to show how many bonds (and possibly non bonding electron pairs) there are placed around a "central" atom.
- This is the AXE notation, where A represents the central atom, X represents the number of bonds (or bonding pairs of electrons) and E represent the number of any non bonding (or "lone") pairs of electrons located on the central atom.

Methane; CH_4 $C: 2s^2 2p^2$ $4H: 1s^1$



AX_4

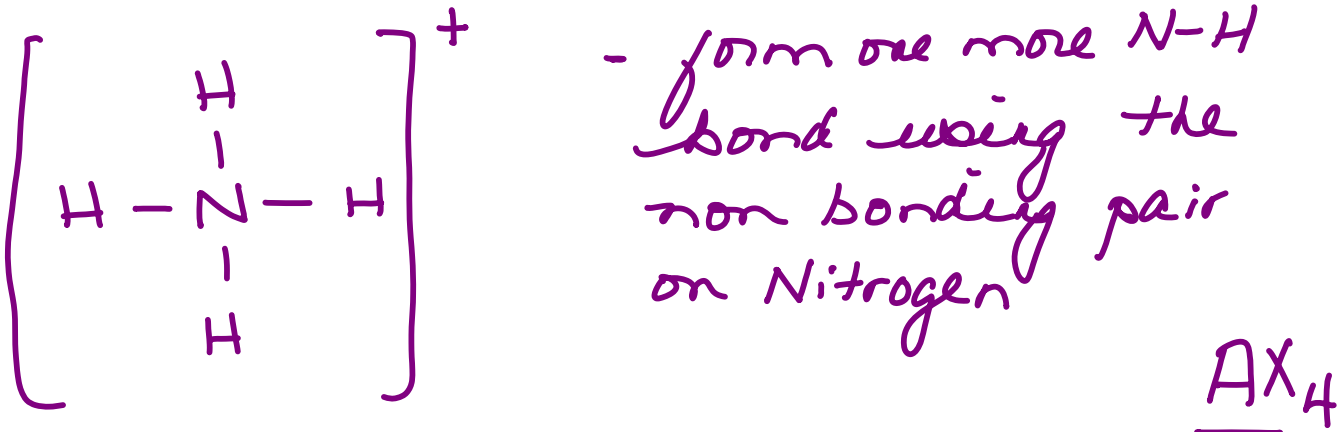
Ammonia; NH_3 $N: 2s^2 2p^3$ $3H: 1s^1$



AX_3E

- By adding H^+, we change the NB pair into a bonding pair (without changing the electron arrangement) adding +1+ (no electrons) doesn't change the # of e-

Ammonium ion; NH_4^+

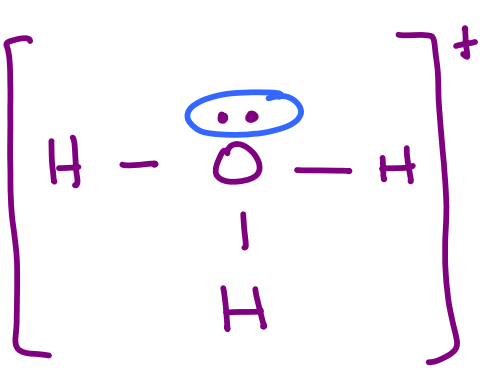


AX_4

Water; H_2O $O: 2s^2 2p^4$ $2H: 1s^1$

AX_2E_2

- H^+ may be added.....**Hydronium ion;** H_3O^+

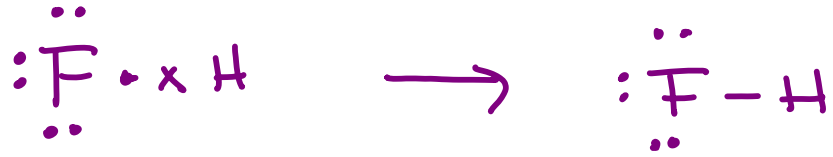


O-H bond formed using 1 non bonding pr from Oxygen

AX_3E

Hydrogen Fluoride; HF

$F: 2s^2 2p^5$ $H: 1s^1$



1 Bonding pair, 3 N.B. prs on F

Neon atom; Ne $2s^2 2p^6$

- 4 non bonding pairs

- No unpaired electrons, no vacancies, so no tendency to bond formation.
- This behaviour is summarized in the **Octet Rule**:
  "In a first - row element, bond formation does not go beyond a total

of four e^- pairs (bonding + non-bonding) in the valence shell."

- There are 103 elements. The octet rule applies to **only 8** of them - but they include some important elements !

∴ maximum of 4 bonds

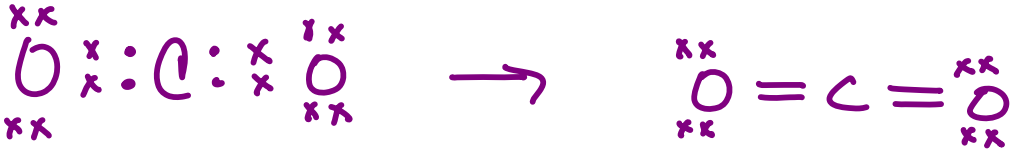
- Second - Row elements are NOT limited by the octet rule because a 3d orbital is available.....they may form more than 4 bonds as the 3d orbital allows for the formation of more electron pairs.

- All these examples contain single bonds - the sharing of one e^- pair.
- Many compounds contain double bonds, which involve the sharing of two pairs of electrons.....

EXAMPLE:

Carbon dioxide, CO_2

C: $2s^2 2p^2$ O: $2s^2 2p^4$



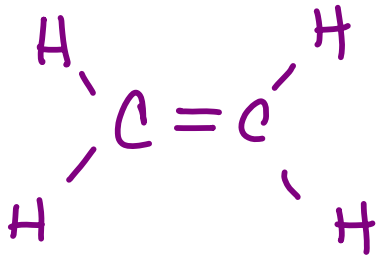
What is wrong with O—C—O ?

1) No atom has an octet

2) Each O has an unpaired electron

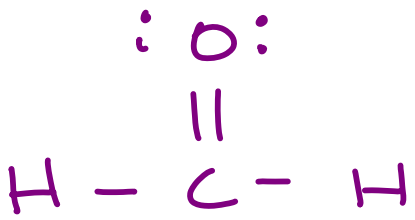
- In the correct structure O = C = O, all electrons are paired up through the formation of double bonds.

EXAMPLES:



Ethylene

Formaldehyde



- A triple bond has 3 electron pairs shared.

EXAMPLES:

: N ≡ N :	Nitrogen gas, 4 pairs on each N
H – C ≡ C – H	Acetylene
H – C ≡ N:	Hydrogen cyanide

Note:

- Bond length (= nucleus-to-nucleus distance) decreases in the order: Single Bond > Double Bond > Triple Bond (for same linked atoms);

EXAMPLES:

C - C	C = C	C ≡ C
0.154 nm	0.134 nm	0.120 nm
N - N	N = N	N ≡ N
0.145 nm	0.125 nm	0.110 nm

Handy to Remember....

H : 1 bond

O : 2 bonds, 2 NB pairs

C : 4 bonds

N : 3 bonds, 1 NB pr

F : 1 bond, 3 NB prs

(other halogens do this too!)

Rules for writing Lewis Structures

1) Count the number of valence electrons of all atoms (and add or subtract electrons for an overall –ve and +ve charge , respectively)

$SiCl_4$ $4 + 4(7) = 32$

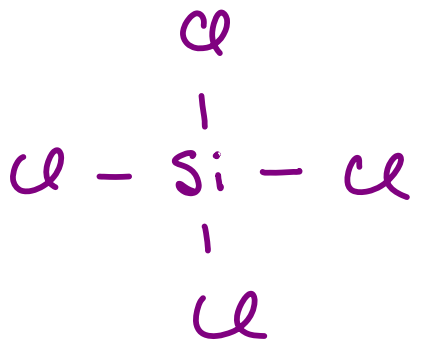
NO_2^+ $5 + 2(6) - 1 = 16$

HCN $1 + 4 + 5 = 10$

BrO_4^- $7 + 4(6) + 1 = 32$

2) Put the atoms in their correct relative positions.
To do this, you need to know which is the **central atom**.
This will usually be a unique atom and/or the heaviest atom or the least electronegative atom.
The order of symbols will give the skeleton..... (e.g.).
It **can't** be H !! Then put in a skeleton of single bonds (—-).

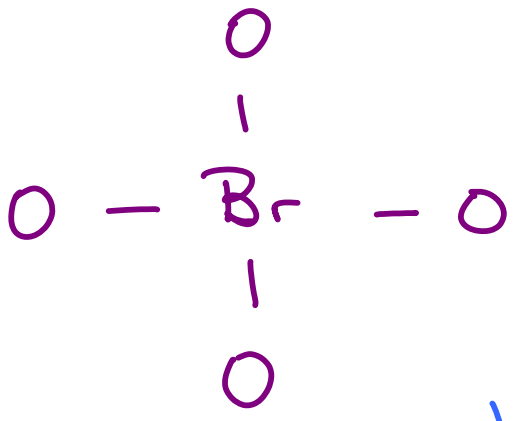
EXAMPLES:



$32e^- - 4(2e^-) = 24e^-$

$10e^- - 2(2e^-) = 6e^-$

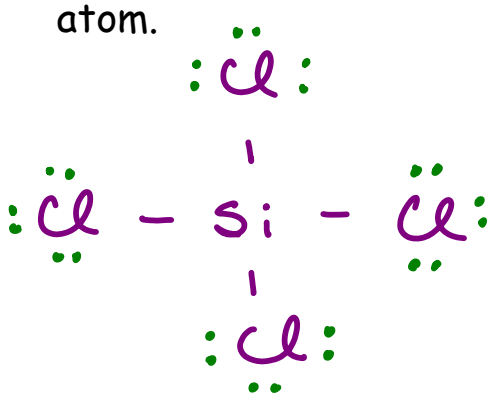
$16e^- - 2(2e^-) = 12e^-$

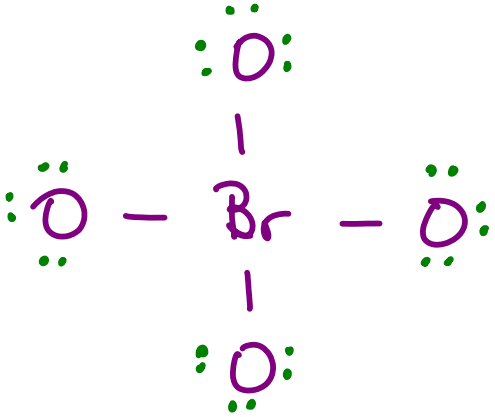


$32e^- - 4(2e^-) = 24e^-$

3) Count up the number of valence electrons used in the bonds; it's 2 electrons per bond.
   Subtract the number of electrons in the bonds from the total number of electrons to find the number of non bonding electrons to be distributed.

4) Distribute the remaining electrons to first give octets to terminal (end of chain) atoms (except H), then put the rest on the central atom.

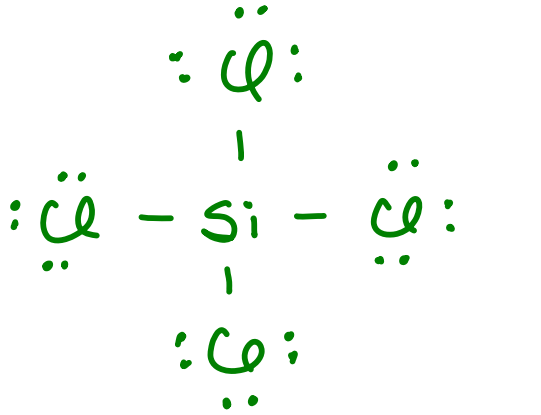




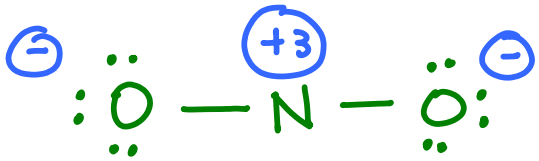
5) Assign **Formal Charges**.

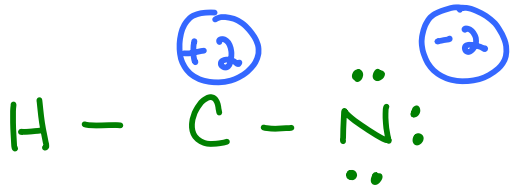
The Formal Charge on an atom is the difference between the number of electrons an isolated atom has and the number assigned to it in the Lewis Structure.

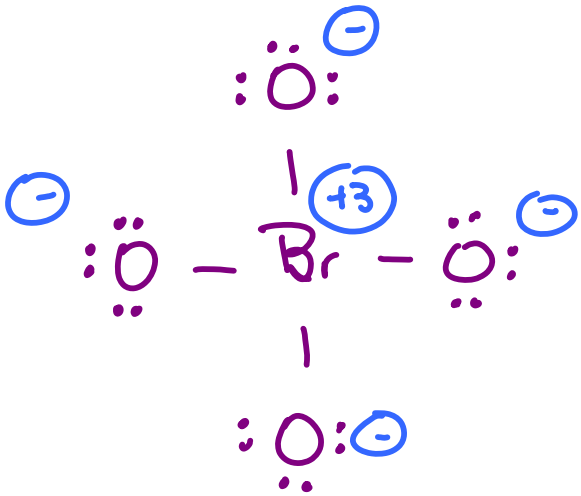
Assigned electrons include lone pairs **on** the atom, and the number of electrons that the atom donated to the covalent bond. (This is usually one electron.)



No formal charges
∴ Done

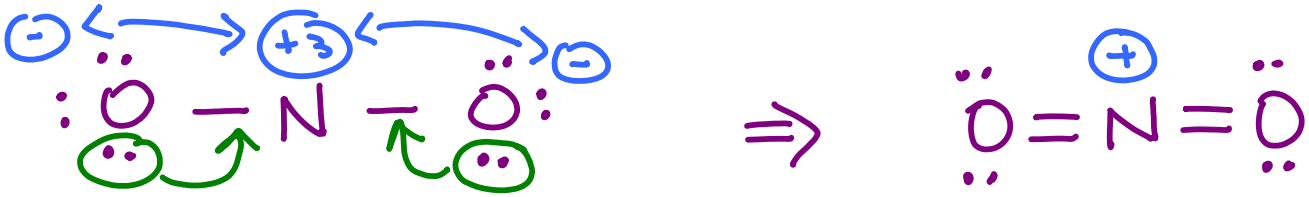


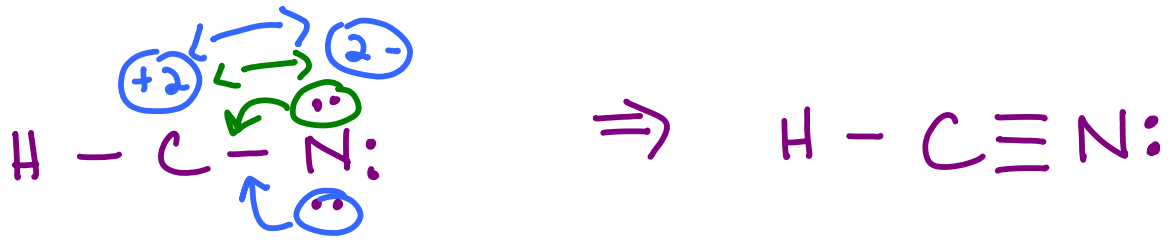


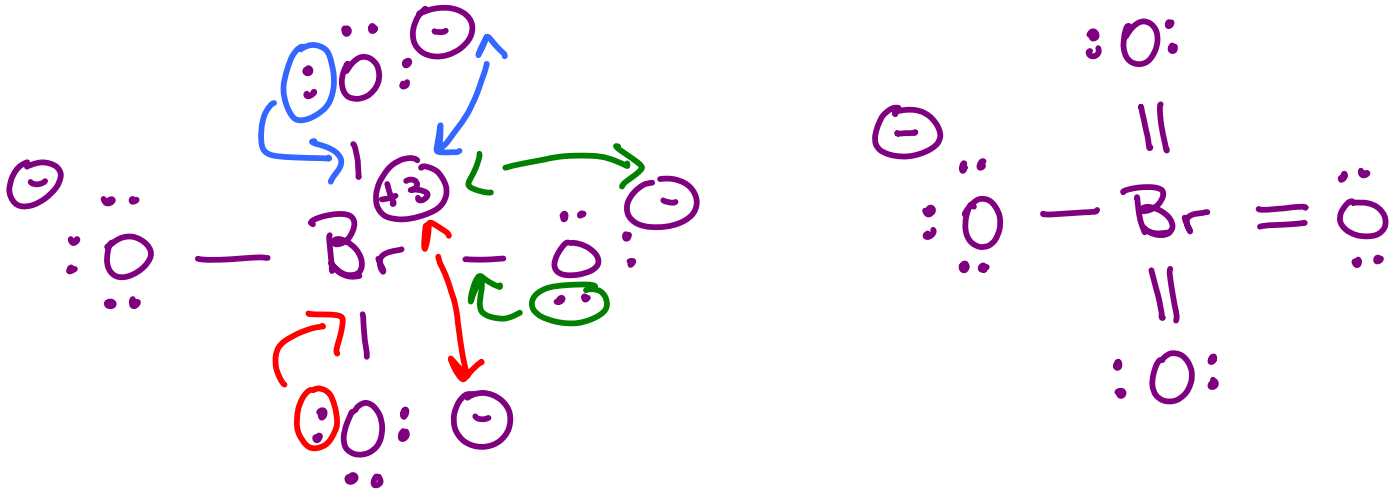


Note that the Sum of formal charges = overall charge on species

6) **If** the central atom does not have an octet of electrons (at least), convert lone pairs on terminal C, N, O or S atoms into pairs shared with the central atom.
Doing this forms a double bond. (Do it twice for a triple bond!)
Usually, the central atom will have a +ve Formal Charge and the terminal atoms will have -ve Formal Charges.
So....if you have a +ve, a -ve, and a non bonding pair of electrons, you can form a double bond.



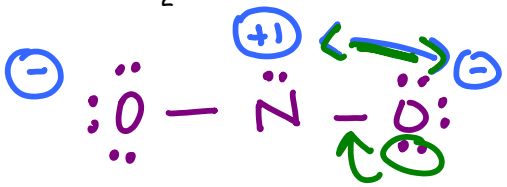




7) Does your structure make sense?
If there appear to be several possibilities for a structure, the most stable is that with:
Formal charges as close to zero as possible;
-ve formal charges on the **most** electronegative atoms;
+ve charges on the **least** electronegative atoms.

MORE EXAMPLES:

NO_2^-: # e^- = 5 + 2(6) + 1 = 18 e^- − 2(2e^-) = 14 e^-



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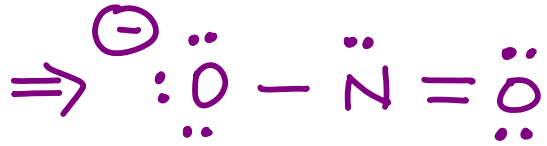
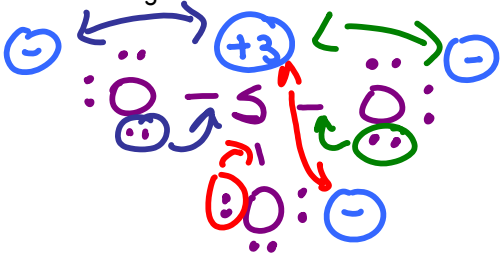


AX_2E

SO_3: 6 + 3(6) = 24 e^- − 3(2e^-) = 18 e^-



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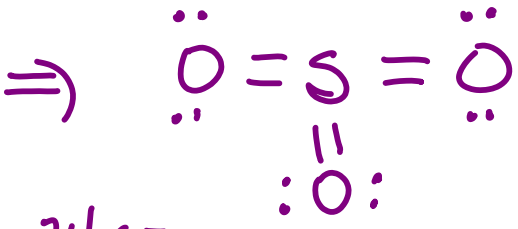
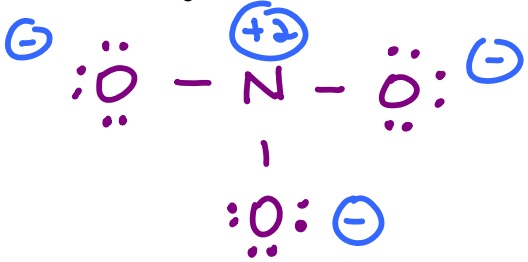


NO_3^-: 5 + 3(6) + 1 = 24 e^- − 3(2e^-) = 18 e^-



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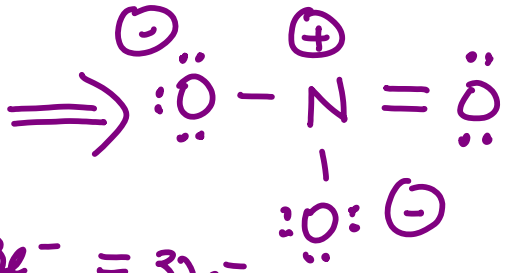
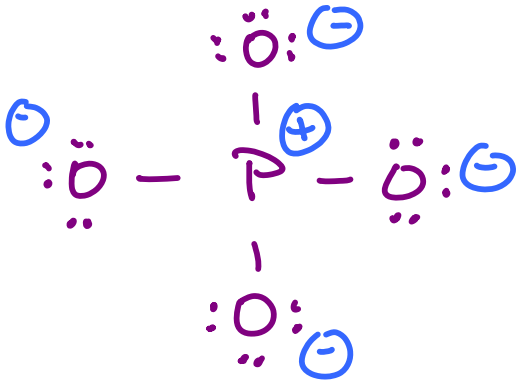


N - 1st row ∴ max 4 bonds

PO_4^{3-}: 5 + 4(6) + 3e^- = 32e^- − 4(2e^-) = 24 e^-



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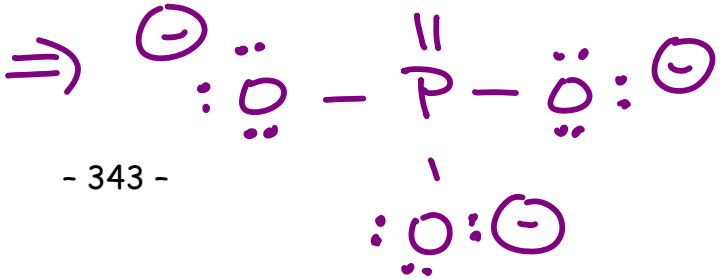
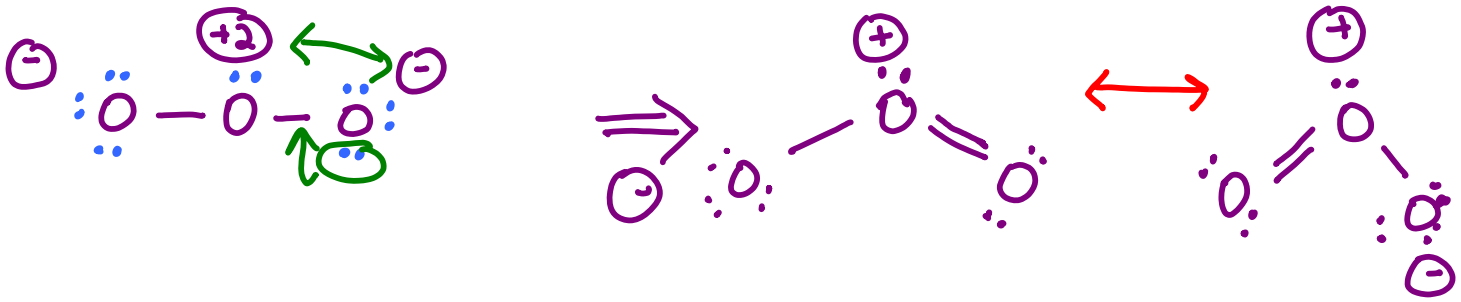


Contributing , or Resonance Structures

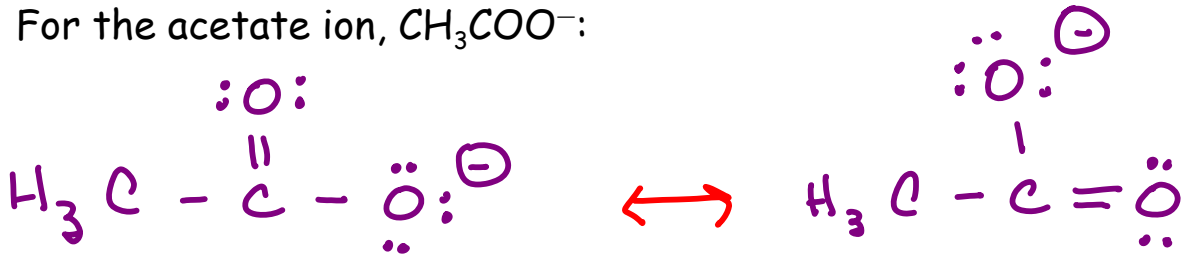
- We write contributing structures if more than one reasonable valence bond structure is possible.
- In the case of ozone: O_3 : $18e^- - 2(2e^-) = 14e^-$



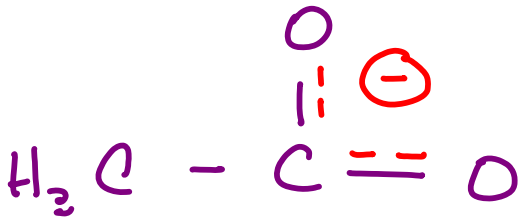
- Often, two or more equivalent contributing structures are possible, differing only in the position of the electrons.

- extra electrons in double bond
- double bond moves around

- For the acetate ion, CH_3COO^-:

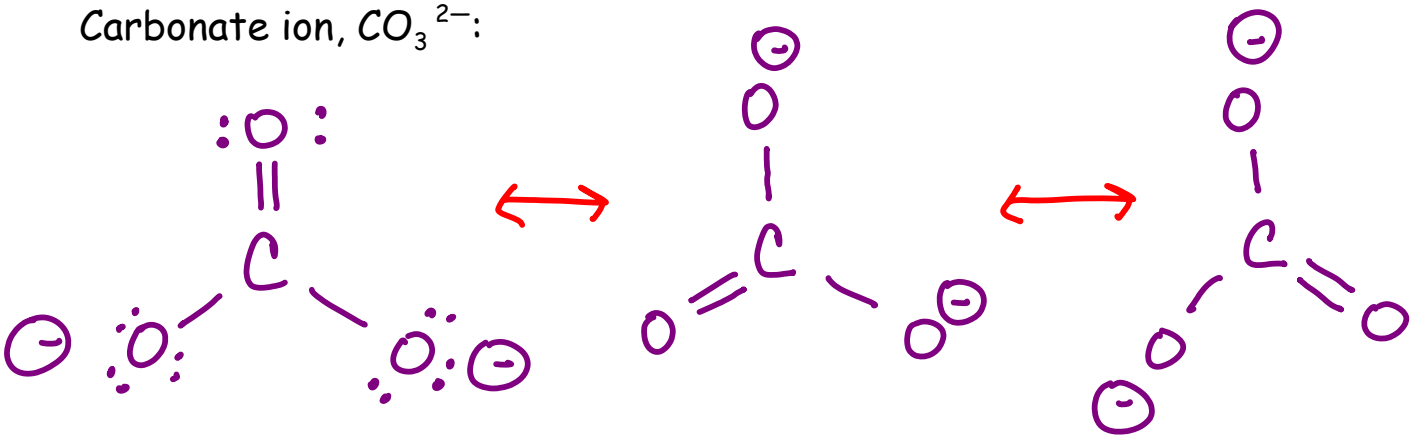


- In fact both C–O bonds are identical.
- Neither Lewis dot structure is correct !
- In practice each may be considered to be 'contributing' to the actual structure (often called "**resonance structures**") and the ↔ symbol is used to indicate this.
- Actual structure is an average.....

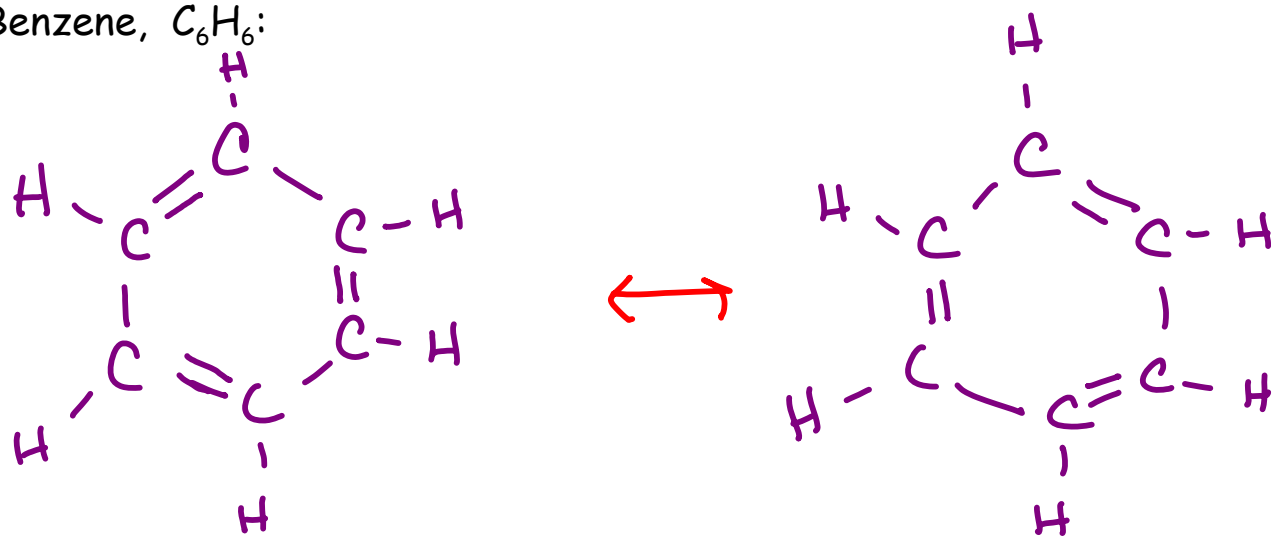


<u>MORE EXAMPLES:</u>

Carbonate ion, CO_3^{2-}:



Benzene, C_6H_6:



- Non-equivalent resonance structures.....

- In general, the existence of resonance structures implies that the species so described is of increased, or greater stability than might be expected.
- This is especially true in the delocalization of negative charge over several O atoms. ClO_4^-

  - 4 possible structures

- Stable anions mean strong acids:

$$HNO_3 \rightarrow H^+ + NO_3^-$$

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

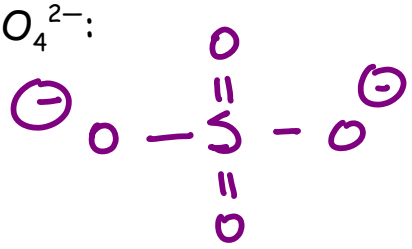
- Finally, note that resonance structures must have exactly the same nuclear positions/connectivity - you cannot move atoms around, whereas you can move electrons around.

Bond Order

- Normally, the bond order of an atom - atom linkage is an integer: 1 for C - C, 2 for C = C etc.
- In resonance structures, all the linkages for the same atoms are identical, neither single or double bonds.
- We assign these linkages fractional bond orders; in SO_4^{2-}, instead of 2 linkages of bond order 1, and 2 linkages of bond order 2; we say each of the four linkages has bond order 1.5.

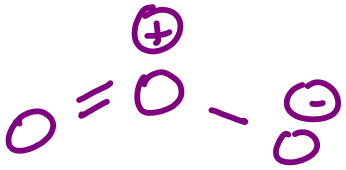
EXAMPLES:

SO_4^{2-}:



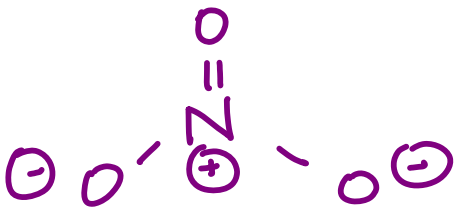
2 of B.O. 2 (S=O) = 4
2 of BO 1 (S-O) = 2
Av. B.O = $\frac{6}{4\text{ (\# bonds)}}$ = 1.5

O_3:



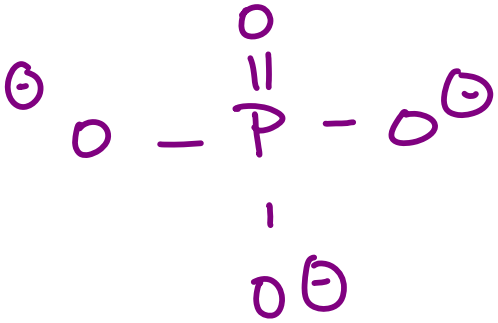
1 of BO 1 (O-O) = 1
1 of BO 2 (O=O) = 2
Av. BO = $\frac{3}{2}$ = 1.5

NO_3^-:



1 of BO 2 (N=O) = 2
2 of BO 1 (N-O) = 2
Av. BO = $\frac{4}{3}$ = 1 1/3

PO_4^{3-}:



1 of BO 2 (P=O) = 2
3 of BO 1 (P-O) = 3
Av. BO = $\frac{5}{4}$ = 1 1/4

EXCEPTIONS TO THE OCTET RULE

Electron Deficient Molecules

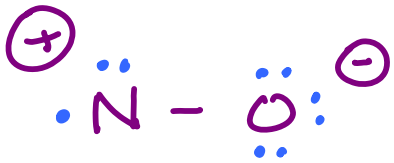
- Some molecules contain odd numbers of electrons.

EXAMPLES:

	NO	NO_2	ClO_2,	O_2^-
Valence e^-	11	17	19	13

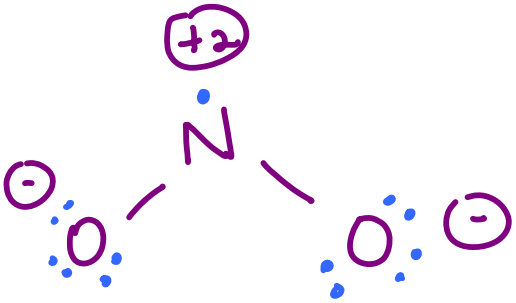
- Obviously, all of these molecules will have an unpaired electron somewhere.....
- These molecules are often called **free radicals** and are very reactive !

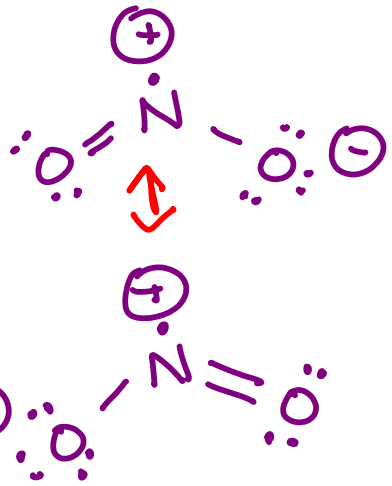
NO: 11 e⁻ - 2 e⁻ (1 bond.) = 9 e⁻



- N still has an unpaired e⁻

NO_2: 17 e⁻ - 2(2 e⁻) = 13 e⁻

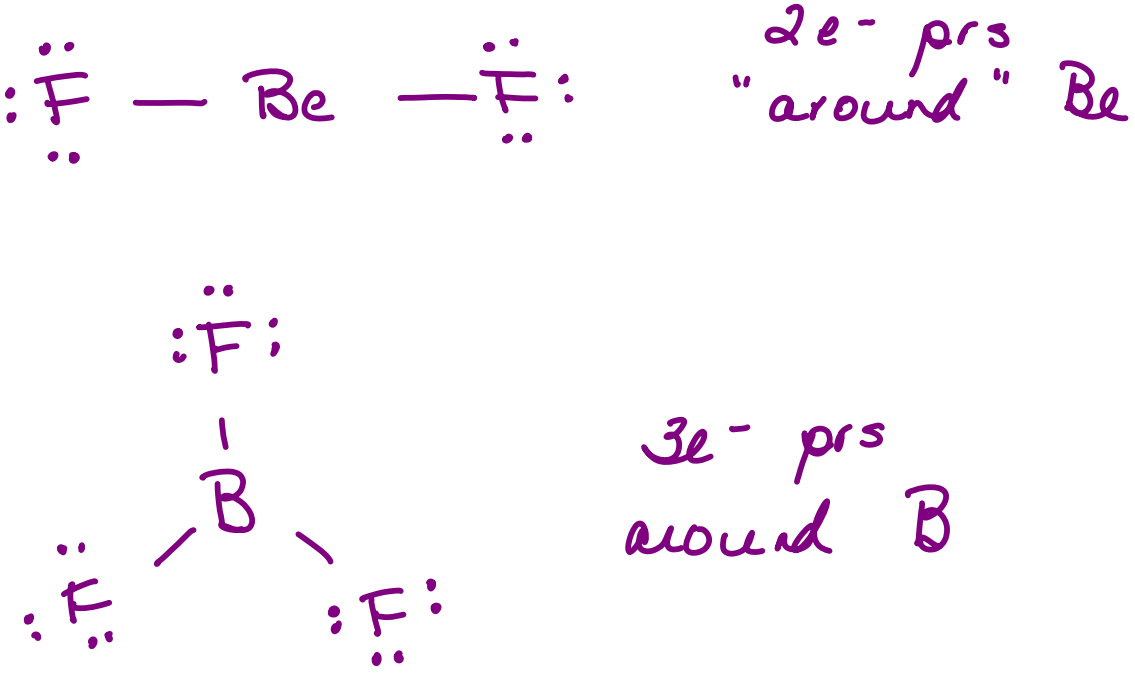




- There are a few compounds in which the central atom does not obey the Octet Rule.....it is surrounded by 2 or 3 pairs of electrons instead of 4 pairs of electrons.

- The fluorides of beryllium and boron are BeF_2 and BF_3.

- Experimental evidence shows their structures as follows:

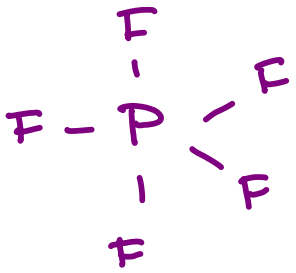


Expanded Octets

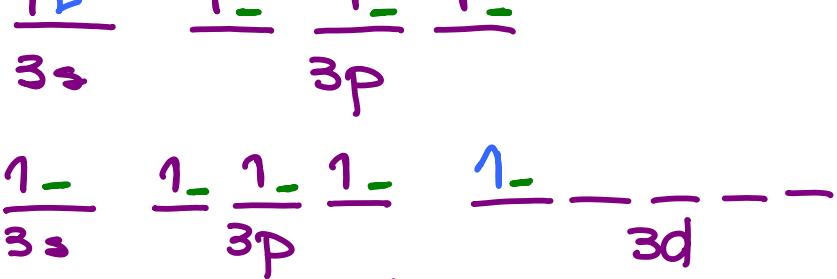
- As was mentioned earlier, second row elements do not have to obey the octet rule; they can form more than four bonds.
- We say that the central atoms in these molecules have **expanded octets.**
- These atoms have d orbitals available for bonding; this is where the extra electron pairs are located.

EXAMPLES:

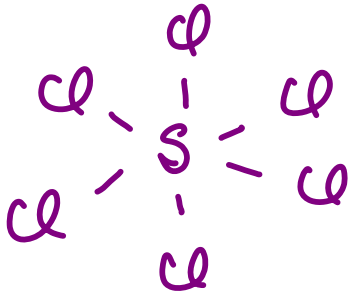
PF_5:



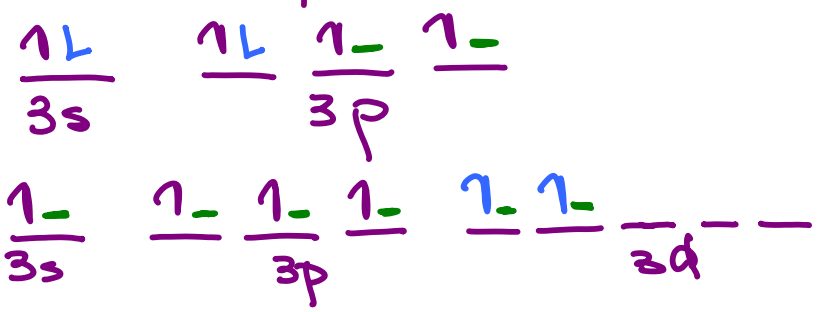
P: $3s^2\ 3p^3$



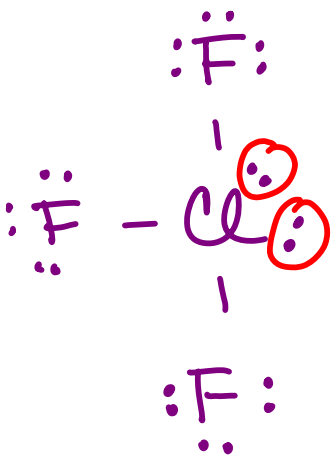
SCl_6:



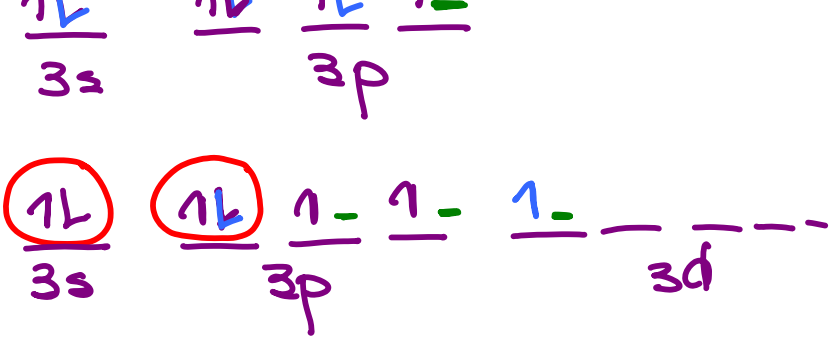
S: $3s^2\ 3p^4$



ClF_3:



Cl: $3s^2\ 3p^5$



MOLECULAR GEOMETRY; (VSEPR Theory) [MH5; 7.2]

- Lewis structures tell us the number and type of bonds around a central atom; also the location of any non bonding electron pairs.
- They do not tell us the 3 - D arrangement of either the bonding or non bonding electron pairs around the central atom.
- The **V**alence **S**hell **E**lectron **P**air **R**epulsion Theory (commonly known as "**VSEPR**") was developed to predict molecular stereo-chemistry, or 3 - D shape.
- VSEPR Theory is based on four main assumptions:

  1) Electrons, in pairs, are placed in the valence shell of the "central" atom.
  2) Both bonding and non-bonding (NB) pairs are included.
  3) Electron pairs repel each other and try to obtain the maximum possible separation.
  4) NB electron pairs repel more strongly than bonding pairs.

- Molecular or ionic shapes are therefore determined by the total number of electron pairs in the valence shell of the central atom.
- To find the number of electron pairs:

1) Add up the # of valence electrons on the free central atom.

2) Add 1 for each singly bonded atom.

3)Add 1 for each -ve charge; subtract 1 for each +ve charge.

4) Divide by 2 (to get number of electron **pairs!**)

5) NOTE: This does not work if there are terminal Oxygen (or Nitrogen) atoms in the molecule....you must use Lewis structure rules !

EXAMPLES:

BCl_3 B: $2s^2 2p^1$ ⇒ 3e⁻ from B

1 e⁻ from each of 3 B–Cl bonds = 3e⁻

Total = 6 e⁻ ⇒ 3 prs

SF_5^+ S: 6 valence e⁻

5 S–F bonds

Total = 6 + 5 − 1 = 10 e⁻ = 5 prs

PF_5 P: 5 valence e⁻

5 P–F bonds

Total = 5 + 5 = 10 e⁻ = 5 prs

SCl_5^- S: 6 valence e⁻

5 S–Cl bonds

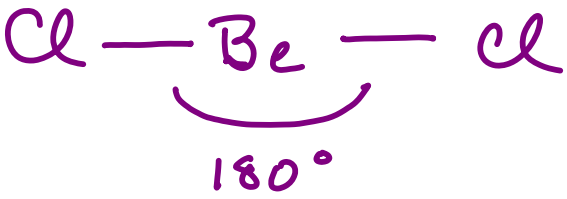
Total = 6 + 5 + 1 = 12 e⁻ = 6 prs

- We will use the $AX_n E$ notation to describe the basic shape of the molecule or ion; **A** represents the central atom and **X** represents the terminal atoms, which are singly bonded to the central atom. "**n**" indicates the number of terminal atoms.
- For the moment, we will look at molecules that have no non bonding pairs of electrons on the central atom, **A**. (So we will disregard E for the moment.)
- To see how this works, we will work through molecules where n = 1.....6.

- 1 pair; **AX**: a trivial case, the molecule is linear: **H — H**
- 2 pairs; **AX_2**; the maximum separation is at 180°

EXAMPLE: **$BeCl_2$**

Be : 2 e⁻ + 2 (bonds)
= 4 e⁻ ⇒ 2prs



AX_2

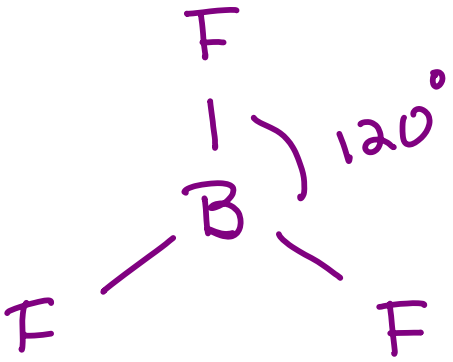
- Only the electrons on the central atom Be determine the electron pair geometry; other electron pairs on Cl are ignored.
  The geometry (or shape) for this molecule is **linear**.

- 3 pairs; **AX_3**: the maximum separation is at 120°.
- The shape of this molecule is **triangular (or trigonal) planar**.

EXAMPLE: **BF_3**

B : 3 val e⁻ + 3 bonds
= 6 e⁻ = 3prs

AX_3

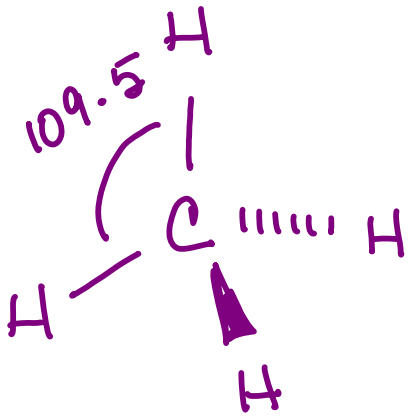


- Any distortion out of the plane would decrease the F–B–F angles.....

- 4 pairs; AX_4; this is a three dimensional molecule with bond angles of 109.5°.
- The shape of this molecule is called **tetrahedral**.

EXAMPLE: CH_4

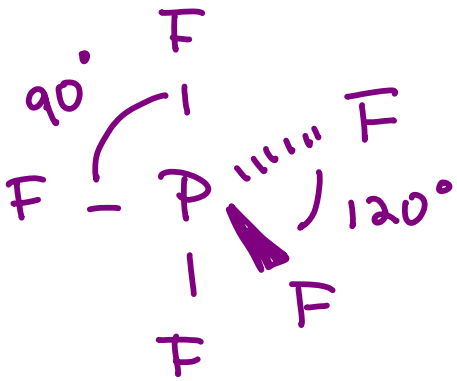
C: 4 val e⁻ + 4 bonds
= 8 e⁻ = 4 prs AX_4



- 5 pairs; AX_5; the **trigonal bipyramidal** shape

EXAMPLE: PF_5

P: 5 val e⁻ + 5 bonds
= 10 e⁻ = 5 prs AX_5



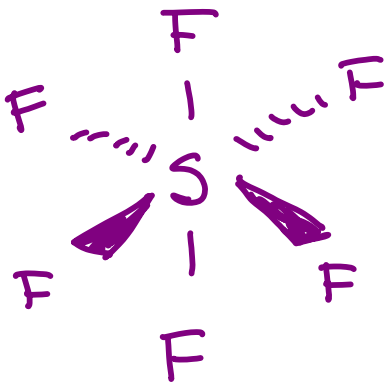
- There are two pyramids stuck base to base.
  There are three equatorial X atoms in a planar triangle and two axial X atoms above and below the central atom.

- 6 pairs; **AX_6**; the **octahedral** geometry

EXAMPLE: **SF_6**

S: 6 val e- + 6 bonds
= 12 e- = 6 prs

AX_6



all 90° angles

- The octahedron consists of two square based pyramids; base to base.
- It has 8 faces, 12 edges and 6 corners.

- What happens when there are non bonding pairs of electrons located on the central atom?
- VSEPR theory is easily expanded to determine the shapes of these species.
- The geometry of the **electron pairs** is roughly the same as what we see when only single bonds are involved.

- Because non bonding electron pairs take up more space than do bonding pairs, the angles for the bonding pairs will be a bit smaller.
- The actual **shape**, or **geometry**, of the **molecule** will be quite different when non bonding electron pairs are present.
- The number of non bonding electron pairs will influence the shape of the molecule.

- To determine the shapes of molecules containing non bonding electron pairs on the central atom, we expand our AX_n notation.....

- Determine the total number of electron pairs around the central atom as before.
- Subtract the number of bonding pairs (indicated by the number of bonds, or terminal atoms) from the total number of electron pairs.
- The difference is the number of non bonding electron pairs, which is denoted by **E**.

EXAMPLE: NH_3 N: $2s^2 2p^3$

Total number of electrons:

5 valence e- (N) + 3e- (bonds)

= 8 e- = 4 prs

Number of bonding pairs: 3 N-H bonds

∴ 3 bonding prs

Number of non bonding pairs:

4 - 3 = 1

Notation is: AX_3E

This indicates 3 bonding pairs and 1 non bonding pair.

- Now we will look at all the combinations of bonding and non bonding pairs for our previously determined shapes.....

- 2 pairs; **AX_2** or **AXE**; both must be **linear**

EXAMPLES:

BeF_2 F — Be — F AX_2 (2e- prs)

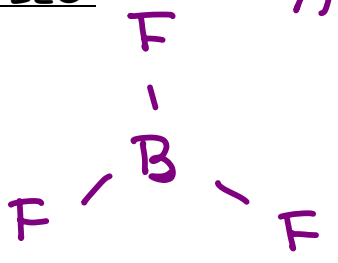
BF B : 3e- + 1 (bond) = 4e- = 2 prs

:B — F AXE (2e- prs, 1 bond, 1 n.b.)

- 3 pairs; **AX_3**, **AX_2E**, or **AXE_2**

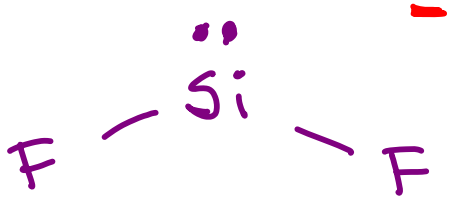
EXAMPLES:

BF_3 AX_3 = 3 bonding prs



Triangular or Trigonal planar

SiF_2 AX_2E = 2 bonding prs



Bent

NF

1 bonding pr

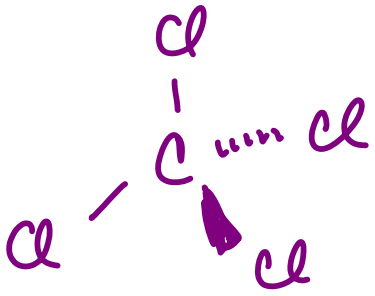
∴ 2 n.b. prs

AXE_2 Linear

- 4 pairs; AX_4, AX_3E or AX_2E_2

EXAMPLES:

CCl_4 4 bonding prs

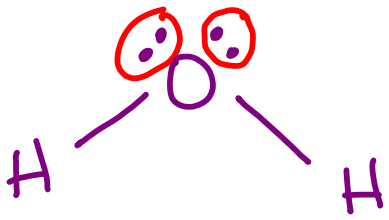


AX_4 Tetrahedral.

NF_3 3 bonding prs, ∴ 1 n.b. pair

AX_3E Triangular Pyramid.

H_2O 2 bonding prs ∴ 2 n.b. prs

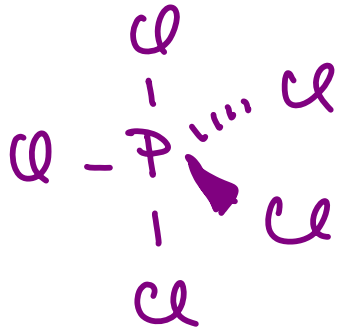


AX_2E_2 Bent

- 5 pairs; AX_5, AX_4E, AX_3E_2 or AX_2E_3

EXAMPLES:

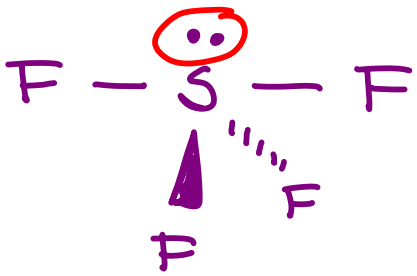
PCl_5 5 Bonding prs AX_5



Trigonal Bipyramid

SF_4 4 Bonding prs, 1 n.b pair

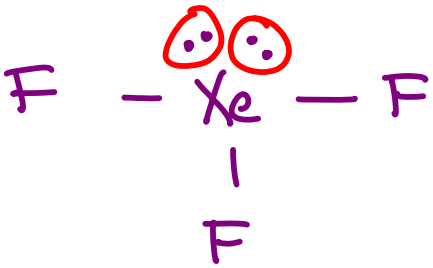
AX_4E



See Saw

XeF_3^+ 3 Bonding prs, 2 nb pairs

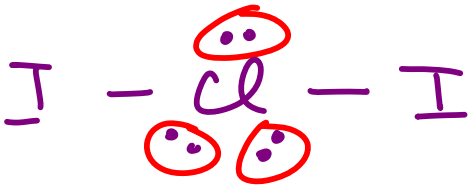
AX_3E_2



T shaped

I_2Cl^- 2 bonding prs, 3 n.b pairs

AX_2E_3

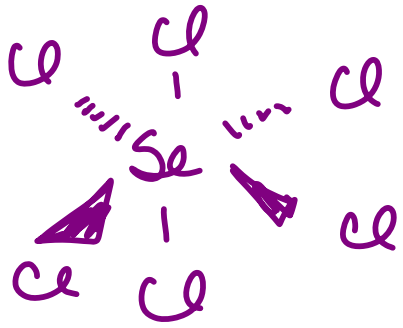


Linear

- 6 pairs; AX_6 , AX_5E or AX_4E_2

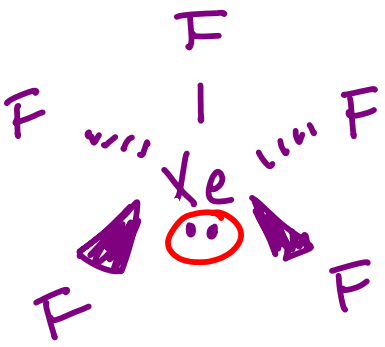
EXAMPLES:

$SeCl_6$ 6 bonding pairs AX_6



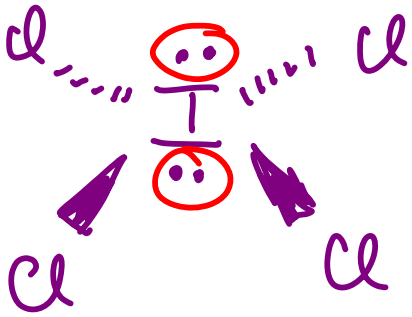
Octahedron

XeF_5^+ 5 bonding pairs, 1 n.b. pr AX_5E



Square Pyramid

ICl_4^- 4 bonding prs, 2 nb prs AX_4E_2



Square Planar

Molecules with Double or Triple Bonds

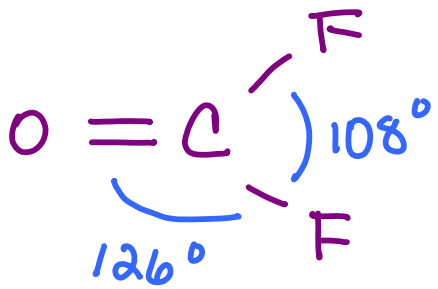
- In determining molecular shape, treat a double or triple bond like a single bond.
- An atom joined by a double bond occupies one "coordination site" around the central atom.
- Consider CO_2, carbon dioxide...
- The Lewis dot structure will be:

- VSEPR predicts two bonds, 180° apart, and linear.

$\therefore AX_2$

- C is central atom
- each double bond counts as a "bond"

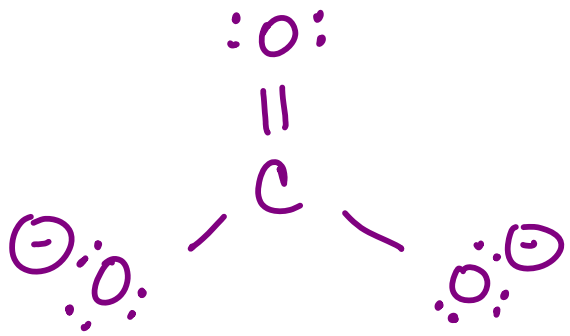
- Double bonds take up a little more space.
  For example, carbonyl fluoride COF_2:



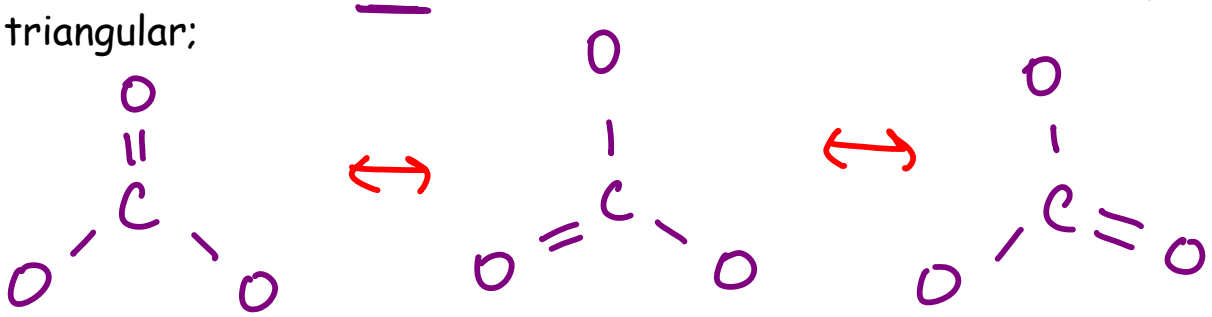
AX_3

Trigonal planar

- A planar triangular structure but the angles are not 120°



- The carbonate ion, CO_3^{2-}, (isoelectronic with COF_2) is also planar triangular;



but here the bond angles are exactly 120° because of the three resonance structures.

- Similarly we deal with triple bonds.....

H – C ≡ C – H a linear molecule

linear AX_2 linear AX_2

- A molecule or ion may have both double bonds and NB pairs.

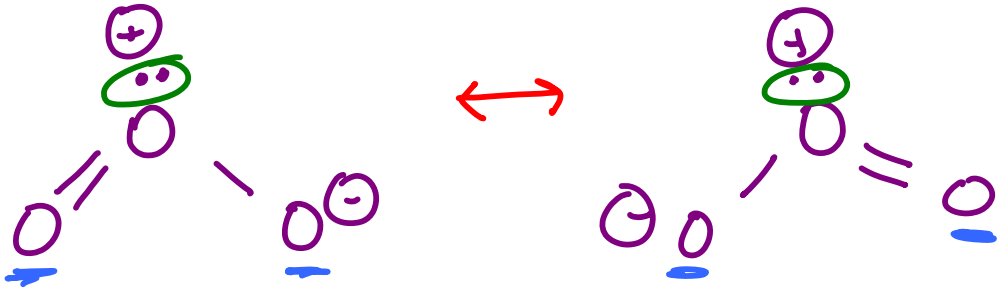
EXAMPLE:

Nitrite ion NO_2^-

AX_2E "Bent"

which is isoelectronic with ozone, O_3

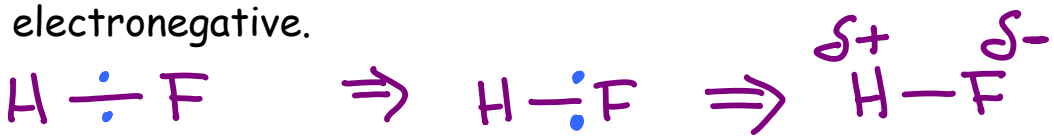
AX_2E



but the bond angles are less than 120° due to repulsion from the lone pair.

MOLECULAR POLARITY [MH5; 7.3]

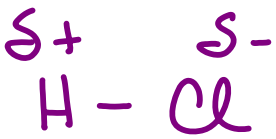
- If two different atoms are covalently bonded, the bonding electron pair is not equally shared between them.
- The atom with the greater attraction for the electron pair is said to be more electronegative.

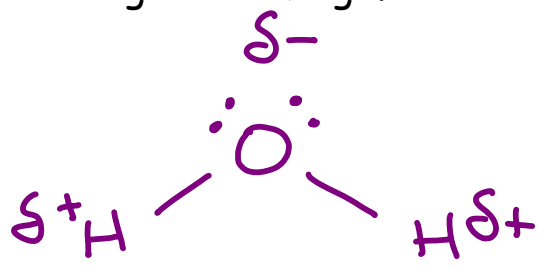


- Electronegativity is a property of an element in a bonding situation, not of an isolated atom.
- It cannot be defined exactly; various scales have been described. [MH5; Table 6.5]

H	B	C	N	O	F
2.2	2.0	2.5	3.0	3.5	4.0
		Si	P	S	Cl
		1.9	2.2	2.6	3.2
				Se	Br
				2.5	3.0
					I
					2.7

- This is only important for reactive, non-metallic elements.
- Covalent bonds are therefore polarized with the more electronegative atom bearing a partial negative charge.





- Such molecules are affected by an electric field and will try to line up.

- The lower 'unaligned' molecule will try to rotate in the electric field.

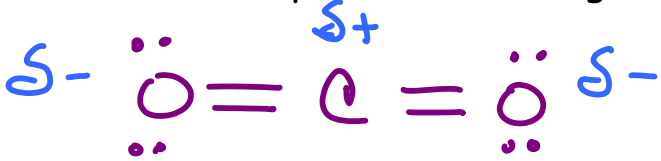
- It has a "dipole moment" which can be measured experimentally.
- A molecule of this type is a polar molecule.

- For a molecule to be polar, at least one polar bond must be present:

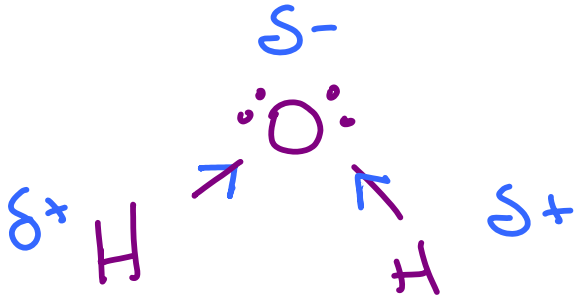
H—H O=O Cl— Cl

are non-polar molecules, not affected by an electric field.

- However, a molecule may be non-polar because the effects of the polar bonds cancel out.
- This depends on the shape or molecular geometry.....

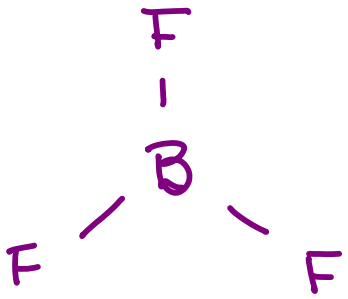


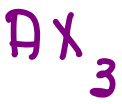
- Linear molecules of this type are non-polar (the polar bonds are equal and opposite).
- But bent molecules.....



- Here the bond polarities do not cancel out (vector sum is not zero), and the molecules are polar.

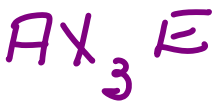
MORE EXAMPLES:

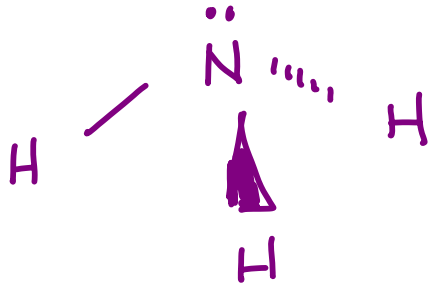


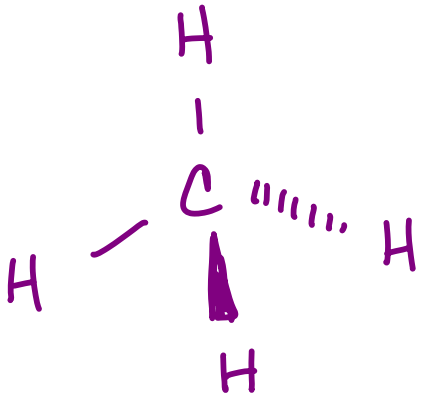


BF_3
A non-polar molecule.
The effect of three B-F bonds cancels out.
The molecule is planar.

NH_3
A polar molecule because it is non-planar, and the bond dipoles do not cancel !



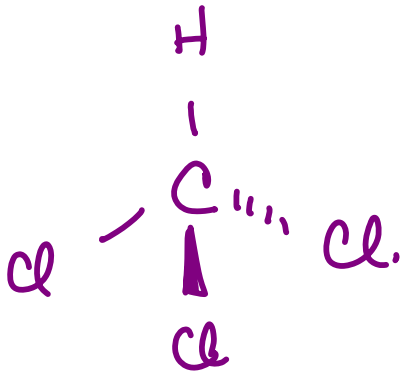


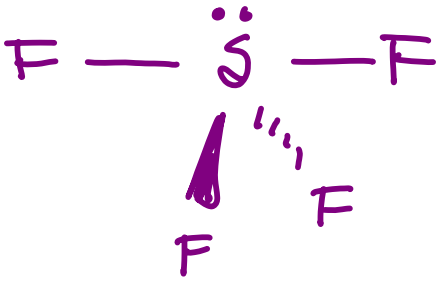


CH_4
Tetrahedral, non-polar

AX_4

$CHCl_3$
Polar, because C - H has a different polarity from C - Cl.



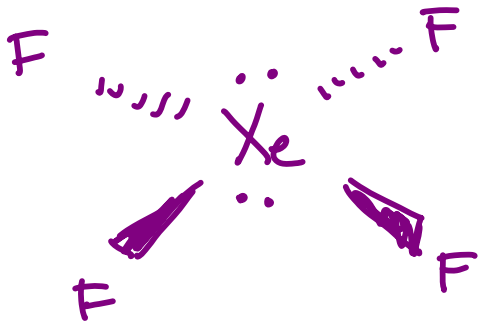


AX_4E

SF_4
Polar, because shape is irregular.

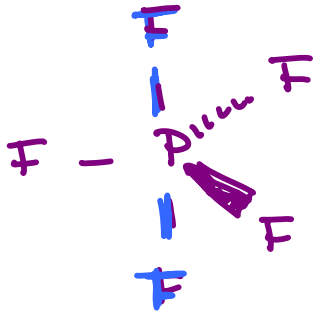
AX_4E_2

XeF_4
Non-polar; bond dipoles cancel in square planar shape.



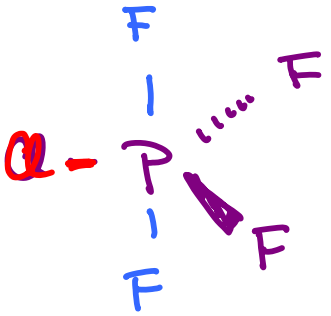
- Check the following:

PF_5: non-polar AX_5

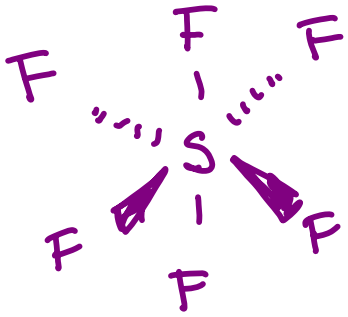


PF_4Cl; polar

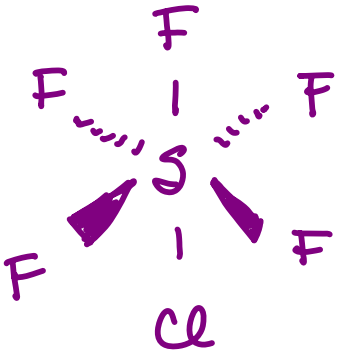
$P-F \neq P-Cl$



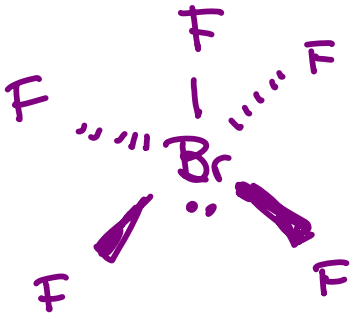
SF_6; non-polar AX_6



SF_5Cl, **BrF_5**; polar

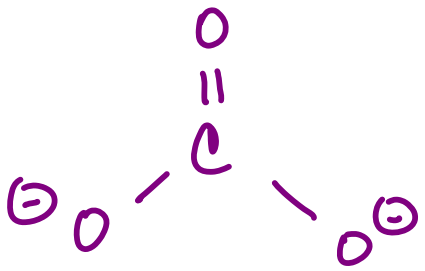


BrF_5 (AX_5E)



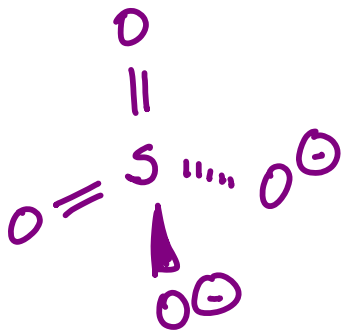
- Overall polarity is 'averaged out' in a set of resonance structures:

CO_3^{2-} AX_3



Planar, non - polar

SO_4^{2-} AX_4



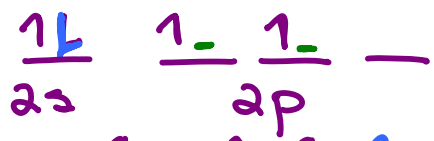
Tetrahedral, non - polar

ATOMIC ORBITALS; HYBRIDIZATION [MH5; 7.4]

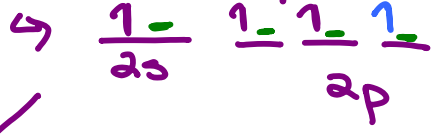
- How is molecular shape related to the orbitals in the valence shell ?

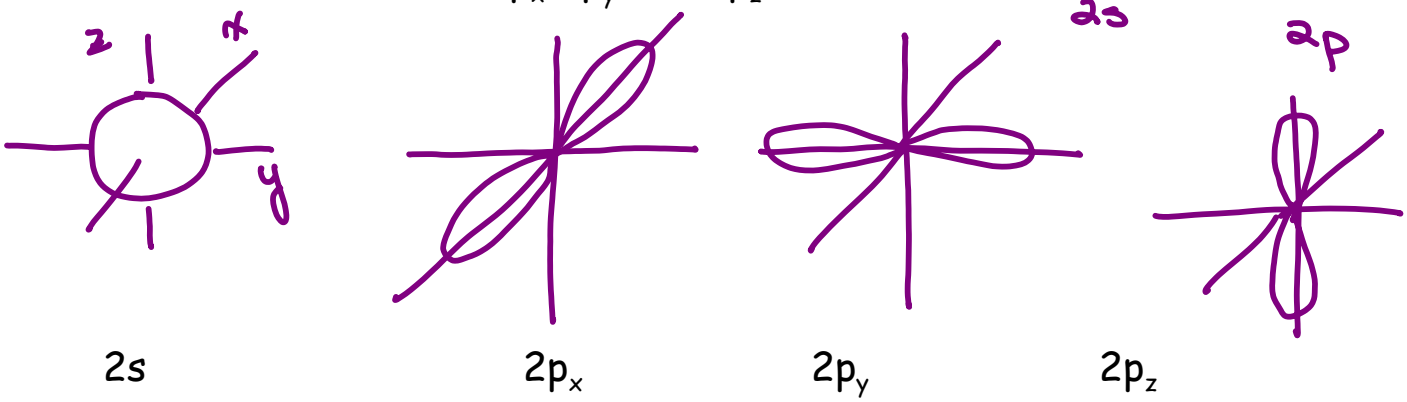
- Consider methane, CH_4;

$2s^2\ 2p^2$



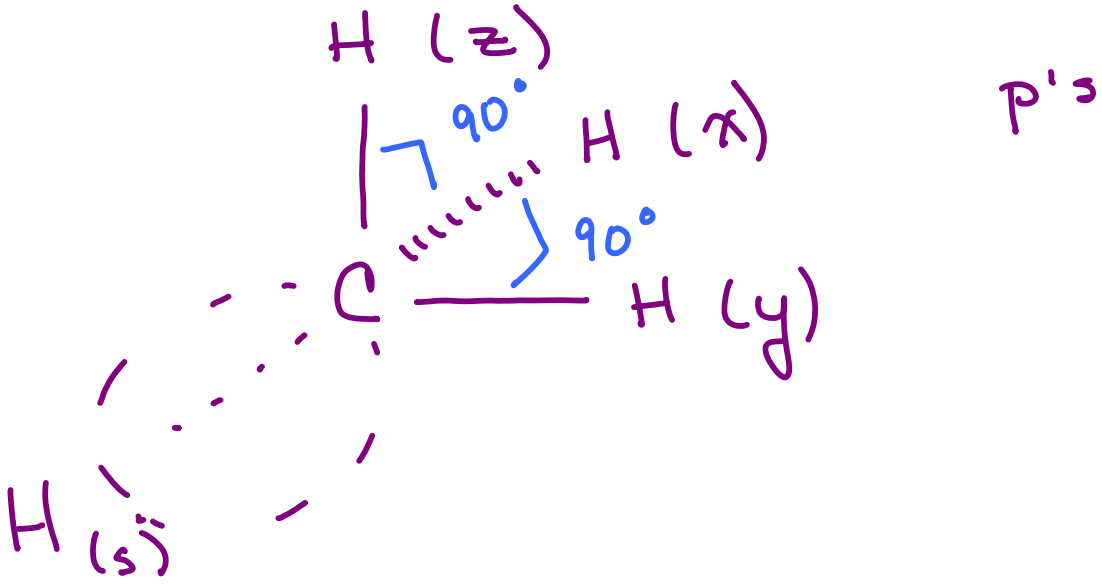
Carbon uses the 2s and $2p_x$ $2p_y$ and $2p_z$ orbitals...





2s $2p_x$ $2p_y$ $2p_z$

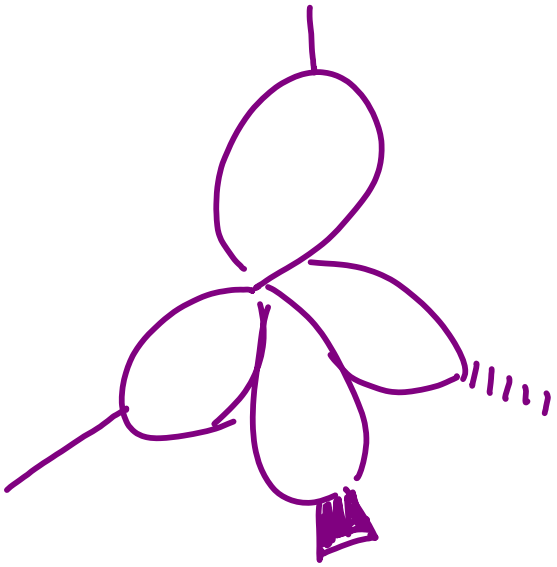
- These pictures result from plotting out the ψ^2 equation representing each orbital.
- But are the bonding electrons in CH_4 still in these orbitals ?
- Applying the "logic" used earlier, we suppose an electron configuration $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$.
- That would give us the imaginary structure:



- This is NOT the correct structure, which we know to be tetrahedral !
- What has happened is that the 2s and three 2p atomic orbitals are **hybridized**, or mixed and averaged to give a set of four equivalent **sp^3 hybrid** orbitals arranged at the tetrahedral angles of 109.5 °.

- Each sp^3 hybrid orbital contains 2 electrons: they may be bonding (in methane) or..... both bonding and non bonding (as in NH_3 and H_2O).

1 from C
1 from each H (or whatever)



Possible orbital combinations

There are five hybrid types only -

1) one **s** plus one **p** → **sp hybrids**
   The two sp hybrid orbitals are directed 180° apart.
   Each can hold an electron pair, bonding or non-bonding.
   The resulting geometry is linear:

EXAMPLES: **Cl—Be — Cl**

H—C≡C—H or **O=C=O**

s + p ⟶ 2 sp hybrids
(2 "pure" p orbitals left over)

2) one **s** plus two **p** → **sp^2 hybrids**

1s + 2p → 3 sp^2

There are three of these, 120° apart.

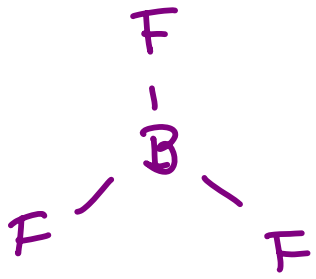
Three electron pairs can be accommodated.

- 1 pure p orbital left over

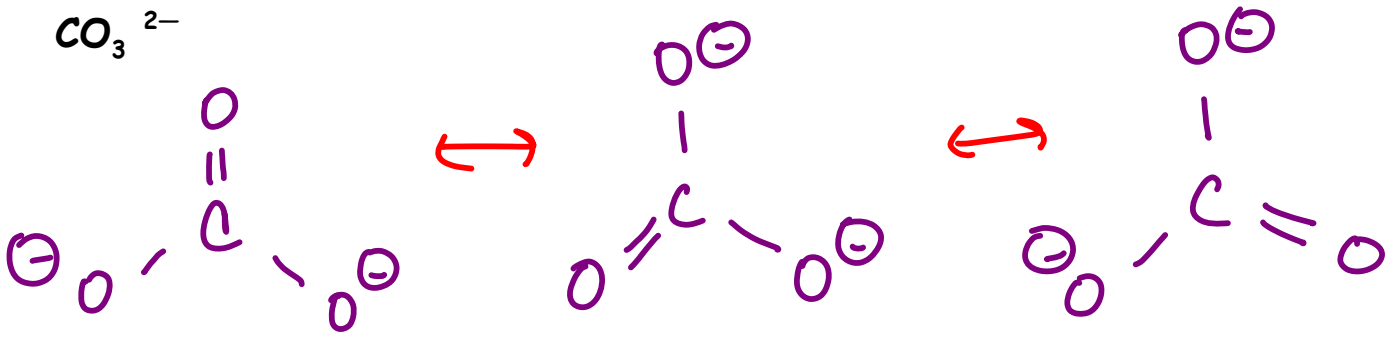
The molecular geometry is planar triangular.

EXAMPLES:

BF_3



CO_3^{2-}



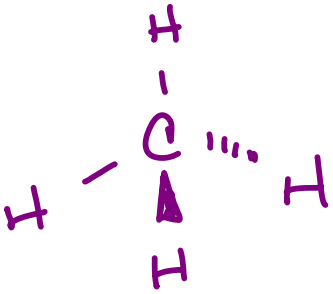
3) one **s** plus three **p** → **sp^3 hybrids**

Already described for methane.

With sp^3 hybrids, the electron pair arrangement is always tetrahedral, but the shape may differ if NB pairs are present.

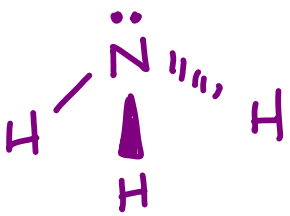
EXAMPLES:

CH_4 AX_4



4 bond. prs

NH_3 AX_3E



3 bond. pr, 1 nb pr

H_2O AX_2E_2

2 bond pr
2 nb pr.

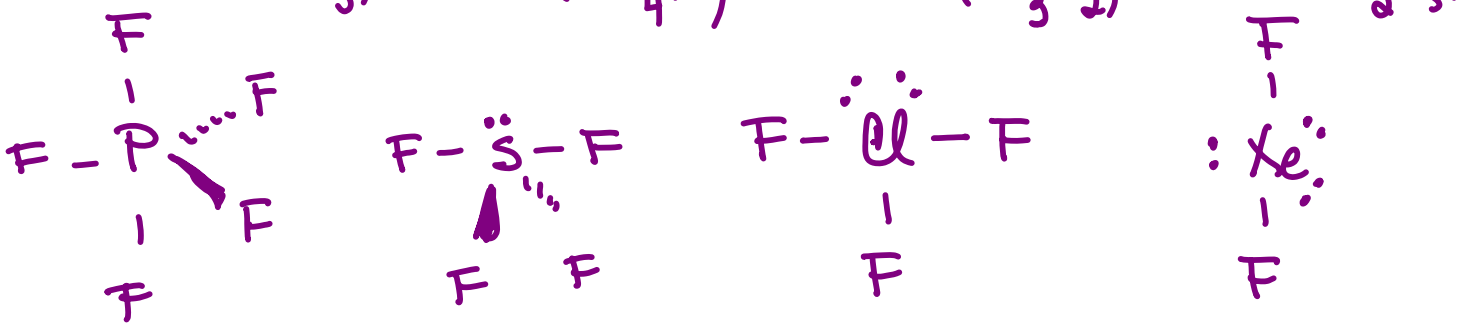
4) one **s** plus three **p** plus one **d** → **sp^3d** (or **dsp^3**)

The electron arrangement is always **trigonal bipyramidal**

(5 electron pairs) $1s + 3p + 1d \longrightarrow 5\ sp^3d \Rightarrow AX_5$

EXAMPLES:

PF_5 (AX_5) **SF_4** (AX_4E) **ClF_3** (AX_3E_2) **XeF_2** (AX_2E_3)



5 BP 4BP,1NB 3BP,2NB 2BP,3NB

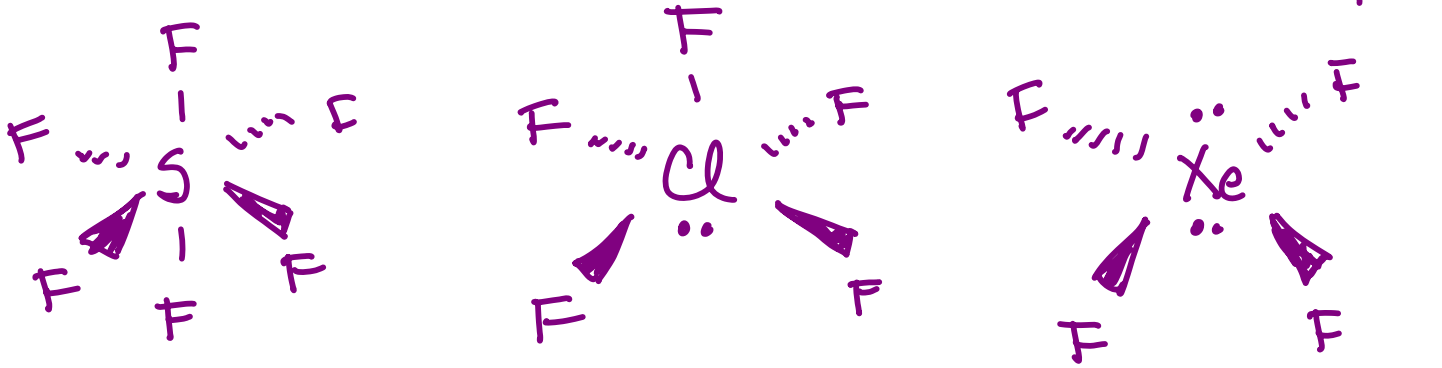
5) one **s** plus three **p** plus two **d** → **sp^3d^2** (or **d^2sp^3**)

Here the electron arrangement is octahedral, with 6 electron pairs.

$1s + 3p + 2d \longrightarrow 6\ sp^3d^2 \Rightarrow AX_6$

EXAMPLES:

SF_6 (AX_6) **ClF_5** (AX_5E) **XeF_4** (AX_4E_2)



6BP 5BP,1NB 4BP,2NB

- The VSEPR approach uses hybrid orbitals....

- To decide upon the hybridization at the central atom, look at the total number of electron pairs on the central atom, counting one pair for each bond (single, double or triple), and one pair for each NB pair of electrons.
- You need as many hybrid orbitals as you have pairs of electrons.

SUMMARY:

2 e- prs $\longrightarrow$ 2 sp (AX_2)

3 e- prs $\longrightarrow$ 3 sp^2 (AX_3)

4 e- prs $\longrightarrow$ 4 sp^3 (AX_4)

5 e- prs $\longrightarrow$ 5 sp^3d (AX_5)

6 e- prs $\longrightarrow$ 6 sp^3d^2 (AX_6)

Sum of $s^1p^xd^y$

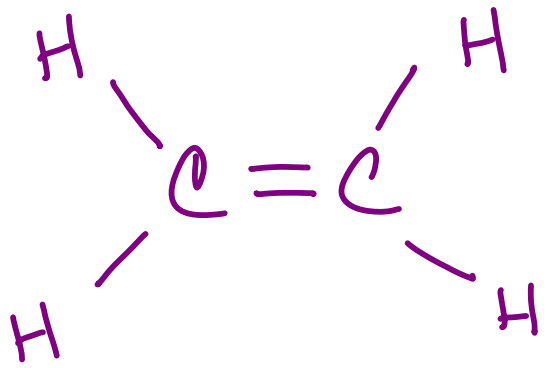
$1 + x + y$ = # e- prs

= # hybrid orbitals

Hybridization and Multiple Bonds

- Recall that when the geometry of a molecule is being determined, we count a multiple (be it double or triple) as **one bond**.
- We do this because the extra electron pairs in the double or triple bond have no effect on the geometry of the molecule.
- These extra electron pairs are **not** located in the hybrid orbitals; and it is the hybrid orbitals that determine the geometry of the molecule.
- So where are those extra electrons, and how do they make a multiple bond?

- We'll look at alkenes first; for example, C_2H_4.



- If we look at **each** carbon atom as a "central" atom, we see that there are 3 bonds (counting the double bond as one bond).
- What geometry (AXE) does this imply?

AX_3

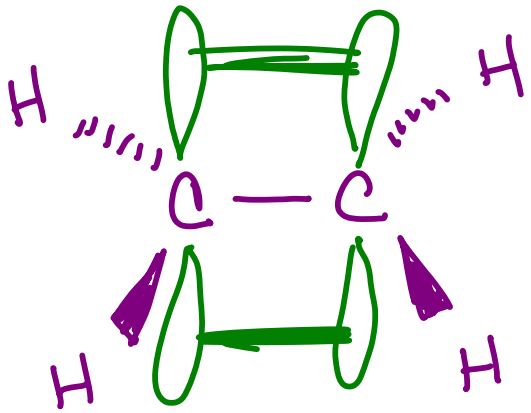
- What type of hybrid orbitals are used for this geometry?

sp^2 (3 of them)

- These 3 hybrids form three single, or **sigma bonds (σ-bonds)**. - used 3 prs of electrons
- What happens to the p-orbital which was not used in making the hybrid orbitals?

- "houses" an extra pair of electrons
- called a "pure" p orbital (did not take part in hybridization)

- These un-used p-orbitals are called pi (π) bonding orbitals and are located above and below the sigma bond axis.
- The overlap of these orbitals creates another bond, the π bond.
- It is the **sum** of the σ and π bonds that creates what we call a "double bond".



sp^2 hybrid orbitals (σ bond)

- A similar approach can be used with alkynes (a triple bond); eg, C_2H_2

$H-C\equiv C-H$ Linear

- 2 e- prs in 2 sp hybrids

- What is the AXE type for this molecule?

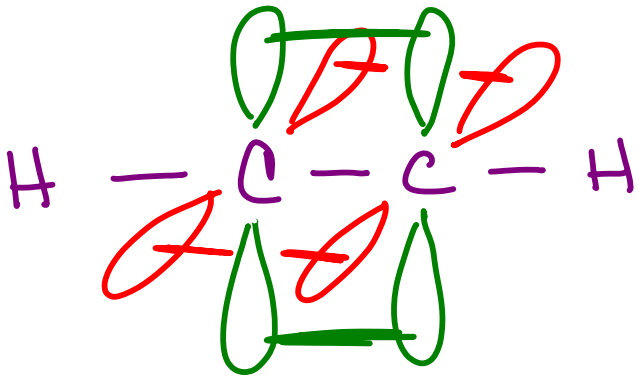
AX_2

- What hybrid orbitals are being used to form σ bonds?

- 2 sp hybrids → form σ bonds

- How may pi bonding orbitals are there?

∴ 2 π bonding orbitals (use the pure p orbitals)



σ bonds

π bond

π bond

- A triple bond consists of one σ and two π bonds.