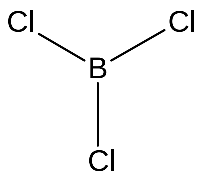
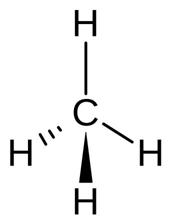
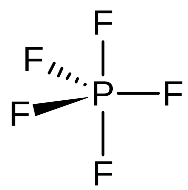
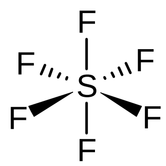
2.24 Shapes of Molecules

The shape of simple covalent molecules is determined by the number of bonding pairs of electrons and the number of lone pair of electrons.

In determining shape the electron pairs repel away from each other, and will move as far away as possible.

There are five basic shapes and then variations on each shape where lone pairs replace bond pairs

Name	No bonding pairs	Diagram
linear	**2**	Cl—Be—Cl
Trigonal planar	**3**	
Tetrahedral	**4**	
Trigonal Bipyramidal	**5**	
Octahedral	**6**	

We need to be able to work out for any simple molecule how many bond pairs and lone pairs there will be. There is a simple method for compounds with single covalent bonds below that I will set out below in a tabular form

This is the same as the Periodic Table group number, except in the case of the noble gases which form compounds, when it will be 8.

if the ion has a 1- charge, add one more electron. For a 1+ charge, deduct an electron.

Add first three rows together

Divide total electrons by 2

The bonding pairs will be the number of other atoms that are joined to the central atom.

Number of Electrons on central atom	
Add one electron from each atom being bonded in	
Add or subtract electron if the molecule has a charge	
Total electrons	
Total pairs of electrons	
Number of bonding pairs	
Number of lone pairs	

The lone pairs will be the difference between the total pairs and bonding pairs

Example: SiF_4 and SF_4 Are they the same shape?

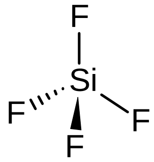
SiF_4 Si in group 4

Number of Electrons on central atom	4
Add one electron from each atom being bonded in	4
Add or subtract electron if the molecule has a charge	-
Total electrons	8
Total pairs of electrons	4
Number of bonding pairs	4
Number of lone pairs	0

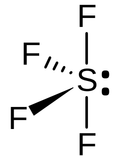
SF_4 S in group 6

Number of Electrons on central atom-	6
Add one electron from each atom being bonded in	4
Add or subtract electron if the molecule has a charge	-
Total electrons	10
Total pairs of electrons	5
Number of bonding pairs	4
Number of lone pairs	1

So SiF_4 has a shape based on 4 bond pairs which is tetrahedral



SF_4 has a shape based on 5 pairs of electrons which is trigonal bipyrimidal where one pair is lone pair

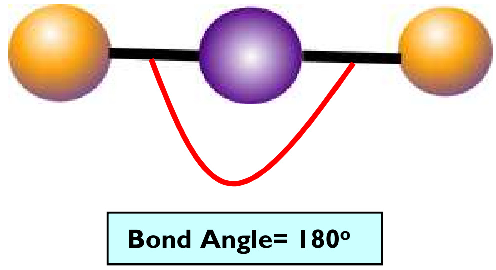


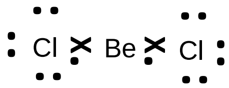
Let us look in more detail at each shape.

Linear shape : 2 bonding pairs

$BeCl_2$

Number of Electrons on central atom	2
Add one electron from each atom being bonded in	2
Add or subtract electron if the molecule has a charge	-
Total electrons	4
Total pairs of electrons	2
Number of bonding pairs	**2**
Number of lone pairs	**0**





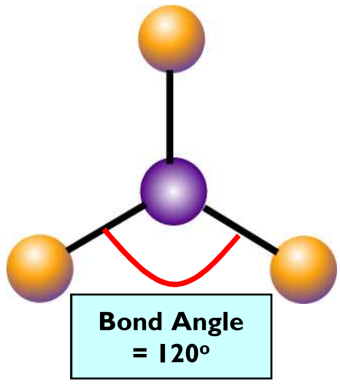
Note Be does not have a full outer shell in this compound. It does not agree with the octet rule

Cl—Be—Cl

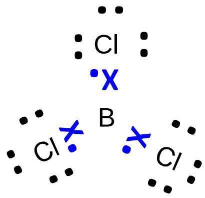
Trigonal planar: 3 bonding pairs of electrons

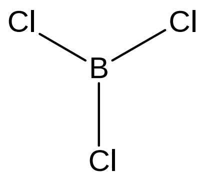
BCl_3

Number of Electrons on central atom	3
Add one electron from each atom being bonded in	3
Add or subtract electron if the molecule has a charge	-
Total electrons	6
Total pairs of electrons	3
Number of bonding pairs	**3**
Number of lone pairs	**0**



[B only has 6 electrons in its outer shell: it also has an incomplete octet.]

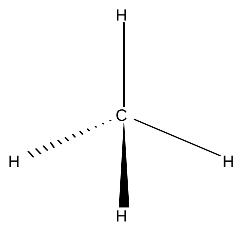


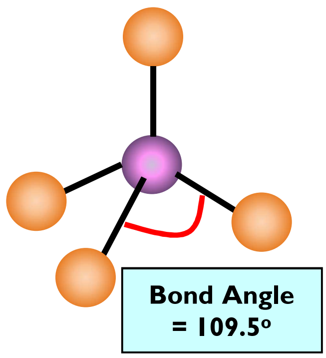


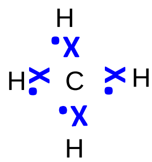
Tetrahedral: 4 bonding pairs of electrons

CH_4

Number of Electrons on central atom	4
Add one electron from each atom being bonded in	4
Add or subtract electron if the molecule has a charge	-
Total electrons	8
Total pairs of electrons	4
Number of bonding pairs	**4**
Number of lone pairs	**0**





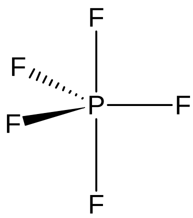


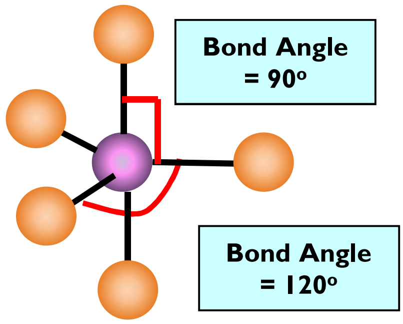
The next two shapes have more than 8 electrons on the central atom's outer shell. We say the octet has expanded. This can happen with period 3,4,5 elements where the availability of empty d subshells allow more than 8 electrons to be on the central atom. This cannot happen with period 2 elements such as C,N,O because there is not a 2d electron shell.

Trigonal bipyrimidal: 5 bonding pairs of electrons

PF_5

Number of Electrons on central atom	5
Add one electron from each atom being bonded in	5
Add or subtract electron if the molecule has a charge	-
Total electrons	10
Total pairs of electrons	5
Number of bonding pairs	**5**
Number of lone pairs	**0**

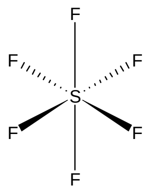




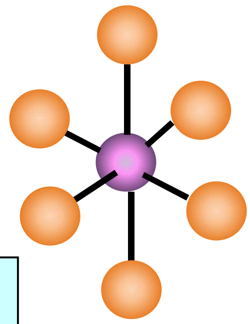
Octahedral: 6 bonding pairs of electrons

SF_6

Number of Electrons on central atom	6
Add one electron from each atom being bonded in	6
Add or subtract electron if the molecule has a charge	-
Total electrons	12
Total pairs of electrons	6
Number of bonding pairs	**6**
Number of lone pairs	**0**



Bond Angle = 90°



Shapes with lone pairs

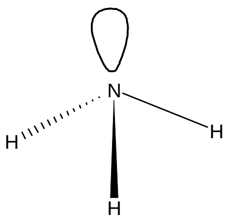
All the standard shapes above can have lone(non bonding) pairs of electrons in place of bonding pairs of electrons. Lone pairs of electrons repel more than bonding pairs. This pushes the remaining bonding pairs closer together reducing the bond angles between bonding pairs. As a rule of thumb, the presence of a lone pair in a shape will reduce the bond angle between the bonding pairs by 2 to 2.5°

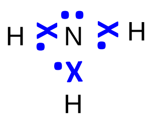
At A-level, the most common shapes that include lone pairs are the following two shapes where lone pairs in place of bonding pairs in a tetrahedral shape.

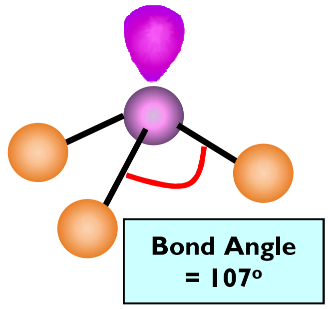
Trigonal pyramidal: 3 bonding pairs and 1 lone pair

Ammonia: NH_3

Number of Electrons on central atom	5
Add one electron from each atom being bonded in	3
Add or subtract electron if the molecule has a charge	-
Total electrons	8
Total pairs of electrons	4
Number of bonding pairs	**3**
Number of lone pairs	**1**





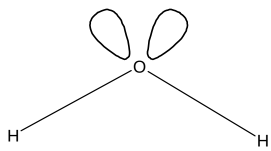


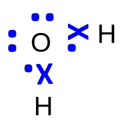
The repulsion of the lone pair of electrons pushes the N-H bonds closer together than in CH_4, so the H-N-H bond angle is 107°

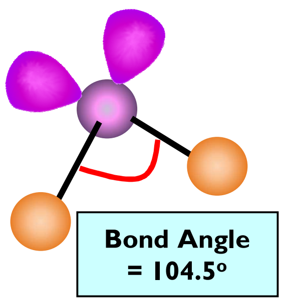
Bent line: 2 bonding pairs and 2 lone pairs

water: H_2O

Number of Electrons on central atom	6
Add one electron from each atom being bonded in	2
Add or subtract electron if the molecule has a charge	-
Total electrons	8
Total pairs of electrons	4
Number of bonding pairs	**2**
Number of lone pairs	**2**





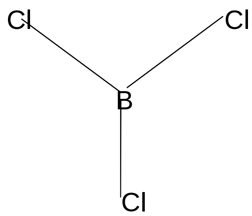
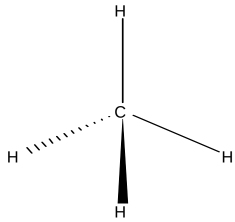
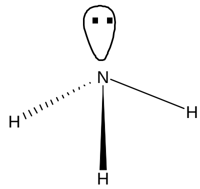
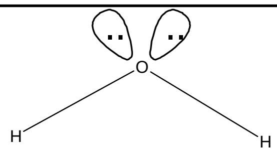
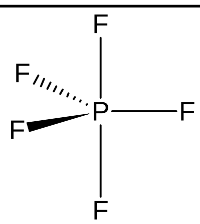
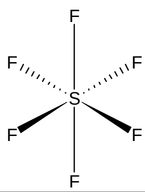


<u>How to explain shape</u>

1. State number of bonding pairs and lone pairs of electrons.
2. State that electron pairs repel and try to get as far apart as possible (or to a position of minimum repulsion.)
3. If there are no lone pairs state that the electron pairs repel equally
4. If there are lone pairs of electrons, then state that lone pairs repel more than bonding pairs.
5. State actual shape and bond angle.

Remember lone pairs repel more than bonding pairs and so reduce bond angles (by about 2.5° per lone pair in above examples)

Summary of most common shapes of molecules

Name	No bonding pairs	No lone pairs	Diagram	Bond angle	Examples
linear	**2**	**0**		**180**	CO_2, CS_2, HCN, BeF_2
Trigonal planar	**3**	**0**		**120**	BF_3, $AlCl_3$, SO_3, NO_3^-, CO_3^{2-}
Tetrahedral	**4**	**0**		**109.5**	$SiCl_4$, SO_4^{2-}, ClO_4^-, NH_4^+
Trigonal pyramidal	**3**	**1**		**107**	NCl_3 ,PF_3 ,ClO_3 ,H_3O^+
Bent	**2**	**2**		**104.5**	OCl_2, H_2S, OF_2 , SCl_2
Trigonal Bipyramidal	**5**	**0**		**120 and 90**	**PCl_5**
Octahedral	**6**	**0**		**90**	**SF_6**

Exercise 1: Work out the shapes of the following molecules a)CH_4 b)NH_3 c) $BeCl_2$ d)H_2O e) PF_5 f)NH_4^+ g)CCl_4 h)BCl_3 l) SF_6 j)H_2S k)BF_3 m)NCl_3 n)AsH_3 o)PH_3 p) PH_4^+ q)$AsCl_3$ r)BF_4^- s)AlF_2^+ t)H_2Se u) PCl_5

Exercise 2: Work out the shapes of the following molecules a) H_3O^+ b)PCl_4^+ c)$AlCl_4^-$ d)$BeCl_4^{2-}$ e)CH_2 f)CH_3^+ g)CH_3^- h)CCl_2 i) NH_2^- j)PF_4^+ k)PF_6^- l)AsF_5 m)CCl_2F_2 n)Cl_2O o)PH_2^- p)$InBr_3^{2-}$ r)NHF_2 s) AsF_6^- t)$TlCl_2^+$ u)$TlBr_5^{2-}$ v)CS_2 w) NF_3 x) AlH_4^-

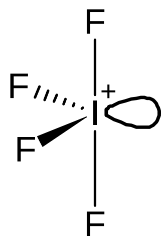
More Complex Shapes

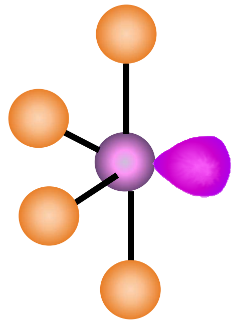
Occasionally more complex shapes are seen that are variations of octahedral and trigonal bipyramidal where some of the bonds are replaced with lone pairs. You do not need to learn the names of these but ought to be able to work out these shapes using the method below.

Variations of Trigonal bipyrimidal shape

IF_4^+ **distorted tetrahedron**

Number of Electrons on central atom	7
Add one electron from each atom being bonded in	4
Add or subtract electron if the molecule has a charge	-1
Total electrons	10
Total pairs of electrons	5
Number of bonding pairs	**4**
Number of lone pairs	**1**

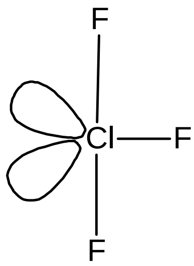


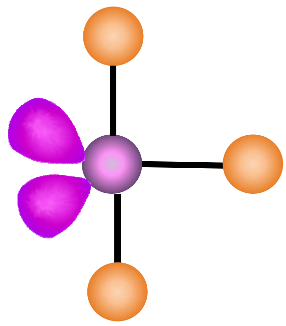


Bond angles ~119 + 89^{O}
(Reduced by lone pair)

ClF_3 **T-shaped**

Number of Electrons on central atom	7
Add one electron from each atom being bonded in	3
Add or subtract electron if the molecule has a charge	0
Total electrons	10
Total pairs of electrons	5
Number of bonding pairs	**3**
Number of lone pairs	**2**

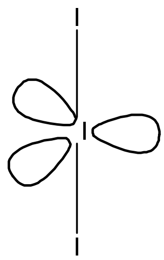


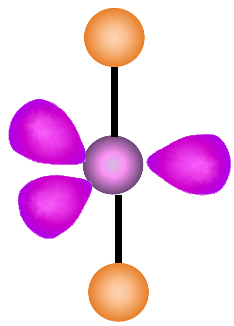


Bond angle ~89^{O}

I_3^- **linear**

Number of Electrons on central atom	7
Add one electron from each atom being bonded in	2
Add or subtract electron if the molecule has a charge	1
Total electrons	10
Total pairs of electrons	5
Number of bonding pairs	**2**
Number of lone pairs	**3**





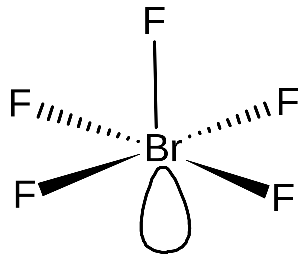
Bond angle 180^{O}

The even distribution of the lone pairs leads to no reduction in the bond angle in this shape

Variations of Octahedral shape

BrF_5 **square pyramidal**

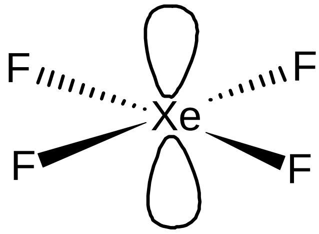
Number of Electrons on central atom	7
Add one electron from each atom being bonded in	5
Add or subtract electron if the molecule has a charge	
Total electrons	12
Total pairs of electrons	6
Number of bonding pairs	**5**
Number of lone pairs	**1**



Bond angle ~89^{O}

XeF_4 **square planar**

Number of Electrons on central atom	8
Add one electron from each atom being bonded in	4
Add or subtract electron if the molecule has a charge	
Total electrons	12
Total pairs of electrons	6
Number of bonding pairs	**4**
Number of lone pairs	**2**



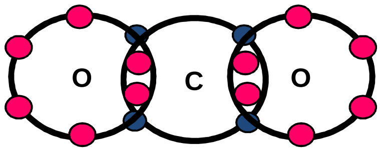
Bond angle 90^{O}

The even distribution of the lone pairs leads to no reduction in the bond angle in this shape

Exercise 3: Work out the shapes of the following molecules a) BrF_3 b) XeF_4 c) IF_5 d)ClF_2^+ e)IF_4^- f)IF_4^+ g)ClF_3 h) SF_4 i)BrF_4^- j) ICl_3 k) XeF_2 l) XeF_5^+ m) Cl_3^+ n) XeF_5^-

Double and Triple bonds

Double and triple bonds act like single bonds in determining the shape of the molecule. So CO_2 acts like it has two bonded pairs of electrons.



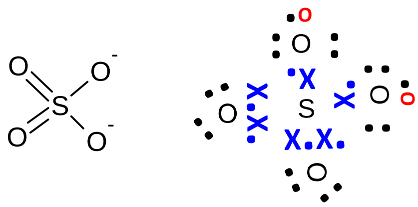
It is more appropriate to explain the shape in terms of '**number of regions of negative charge**'. CO_2 has **two regions of negative charge**, and has the linear shape of $BeCl_2$.

O=C=O

The method we used above with the table does not work so easily where double and triple bonds are involved. The best method is to try and draw a dot and cross diagram and work out how many double bonds, single bonds and lone pairs there are.

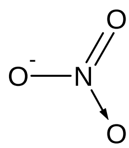
As a rule of thumb if the molecule is neutral assume the oxygen atoms are double bonded to the central atom. If the molecule has a minus charge, the extra electrons will be on the oxygen atom rather than the central atom and these oxygen atoms will have single bonds to the central atom. There may well be a combination of single and double bonds to oxygen atoms

SO_4^{2-} has a -2 charge so has two single bonds to O's that hold the minus charges. The other two oxygen atoms are double bonded to the S. Each oxygen has a full shell of 8 electrons but the central S has more than 8. It can do this because it is in period 3 and can 'expand its octet'.



For the purpose of determining shape this is 4 regions of bonds and no lone pairs so is a tetrahedral shape

Nitrogen and Carbon are in period 2 and cannot expand their octets. Nitrogen to oxygen compounds can have unusual bonding structures.



The nitrate ion has a double bond, a single bond and a dative covalent bond. Delocalisation however occurs and the bonds all become equal in strength

Exercise 4: Work out the shapes of the following molecules a) CO_3^{2-} b)SO_4^{2-} c)SO_2 d)SO_3 e)SO_3^{2-} f)NO_3^- g)NO_2 h)NO_2^- i)$POCl_3$ j) PO_4^{3-} k)ClO_4^- l)$SOCl_2$ m) $XeOF_4$ n)XeO_3 o)ClO_2 p)ClO_2^-

This exercise is hard and really pushing beyond A-level in most cases. You must first try to work out how many double and single bonds there are, then work out if there are lone pairs.