

# CHEM1011

# BONDING: WEEKS 5-6

Dr Alex Donald ([w.donald@unsw.edu.au](mailto:w.donald@unsw.edu.au); Dalton 221)

Senior Lecturer

UNSW Chemistry

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***Please ask questions,  
drop by during feedback hours  
or schedule an appointment***

**Feedback hours:**

Friday at 2:00-3:00 pm,  
My office  
02 9385 8827



# BONDING LECTURE 1: LEWIS STRUCTURES

Dr Alex Donald ([w.donald@unsw.edu.au](mailto:w.donald@unsw.edu.au); Dalton 221)

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GN Lewis  
Discoverer of the covalent bond

Was Prof and Dean of Chemistry  
at Berkeley



# Bonding: Weeks 4-6 – Chapter 5

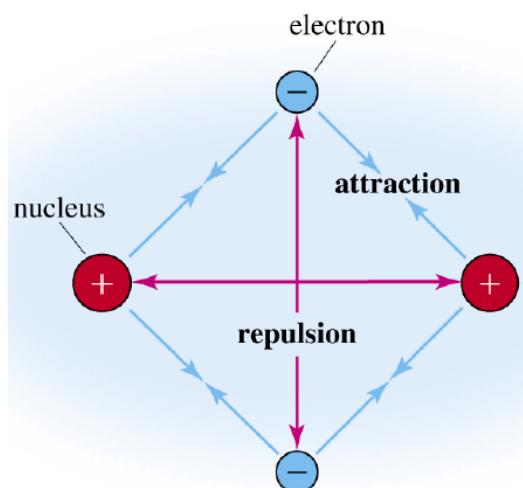
Content	Blackman Book	Learning Objectives
Bonding	5.3-5.5	
Lewis diagrams; Electron deficient & expanded valence shell species Lewis structures Resonance structures	5.6	Draw Lewis diagrams for simple molecules Identify species where the octet rule is violated Assign formal charges and use to select most likely Lewis structure Draw multiple Lewis structures for species where the distribution of electrons is ambiguous
VSEPR Theory and molecular shape Polarity of molecules		Use VSEPR theory to predict the shapes of molecules/ions Predict whether molecules are polar or non-polar
Valence bond theory Hybridized orbitals		Assign hybridized orbitals to central atoms in molecules and polyatomic ions Sketch the overlap between orbitals on adjacent atoms which gives rise to bonding
Sigma and pi bonds Multiple bonds delocalisation		Identify species where extended orbital overlap gives rise to delocalisation of electrons

# Blackman Chapter 5 - Bonding

- Fundamentals of bonding
- Lewis structures
- Valence shell electron pair repulsion (VSPER) theory
- Properties of covalent bonds
- Valence bond theory
- Sigma and pi bonding, electron delocalization, multiple bonding

# Introduction to bonding

- What is a chemical bond?
- Two atoms in close proximity
- Atomic orbitals distort to minimize energy



Competition between attractive and repulsive forces leads to a ***minimum energy configuration***

# Types of bonding

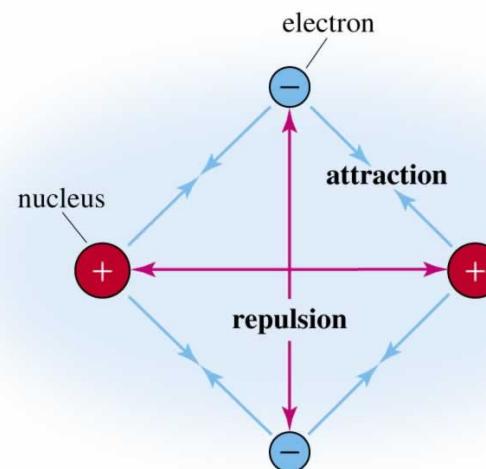
1. Covalent bonding

2. Ionic bonding

3. Metallic bonding

# Molecules: Fundamentals

- Electron density shared between atoms (COVALENT BOND)
- Polar bond – sharing electrons between dissimilar atoms (one atom wins the electron tug-o-war)
- Ionic bonding – extreme example of a polar covalent bond



[See video](#)

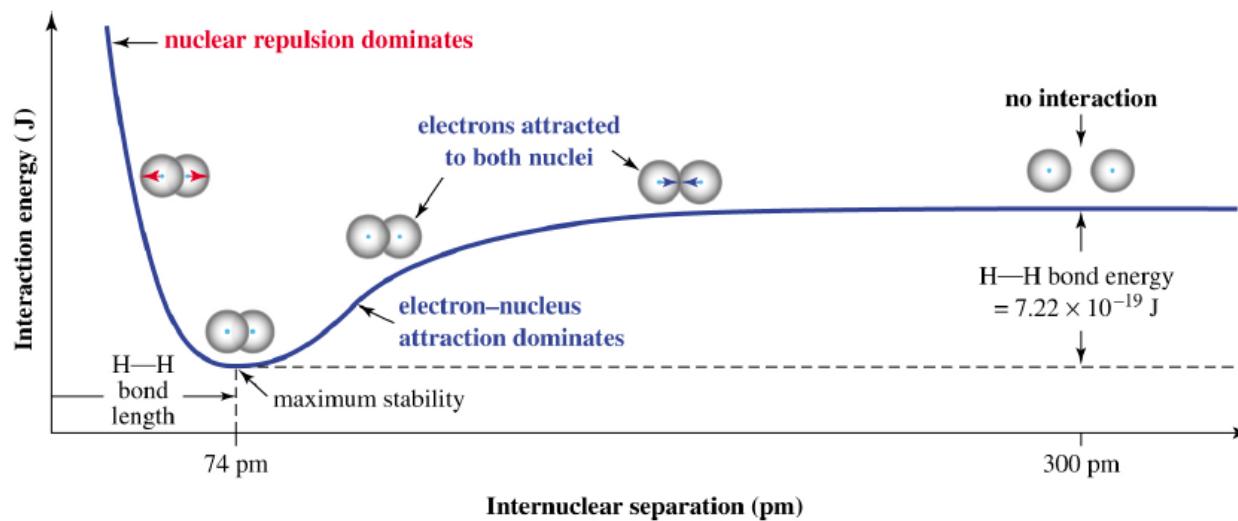
# Molecules: Fundamentals

- Equilibrium bond length is at the distance where the energy is at a minimum w/ equilibrium between attractive and repulsive forces
  - Typical bond length of 100-200 pm

- H<sub>2</sub> is the simplest of all molecules

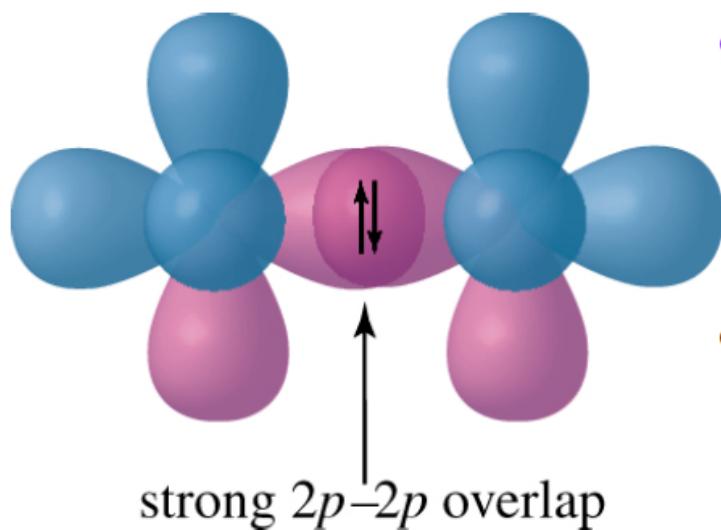
- H<sub>2</sub> bond length = 74 pm

$$(6.023 \times 10^{23}) \times (7.22 \times 10^{-19}) = 435 \text{ kJmol}^{-1}$$



# Molecules: Fundamentals

- $F_2$  is also a covalent diatomic molecule.
- electronic configuration F:  $1s^22s^22p^5$

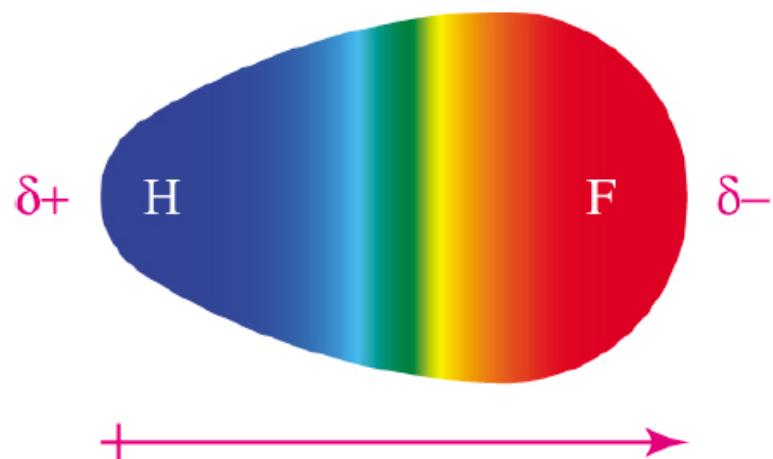


- the interacting valence orbitals are  $2 \times 2p$  orbitals.
- if the 2 orbitals are allowed to overlap & the atoms share the electrons, each F shares a closed  $2s^22p^6$  shell.

See demo on board.

# Molecules: Fundamentals

- diatomic molecules need not be **homonuclear**.
- for molecules X-Y, there may be unequal sharing of the electrons.



- the result is polarity in the bond.
- H-F is a strongly polar covalent bond.

# Models for chemical bonding

- Lot's of different models
  - All can be rationalized to a first approximation by charge-charge attraction/repulsion (Coulomb's law)
- We want to be able to predict:
  - molecular shapes.
  - molecular dipole moments and polarised bonds.
  - strength of bonding.
- We will look at theories of increasing sophistication:
  - Lewis structures.
  - Valence bond theory.
    - Atomic orbitals.
    - Hybridised orbitals.
  - VSEPR = Valence shell electron pair repulsion theory

# Lewis structures

- a Lewis electron-dot symbol shows the symbol for the element surrounded by dots to represent the valence electrons of the atom.



- covalent bonding between two atoms is shown by one or more pairs of electrons between the symbols, with each pair indicating one bond.



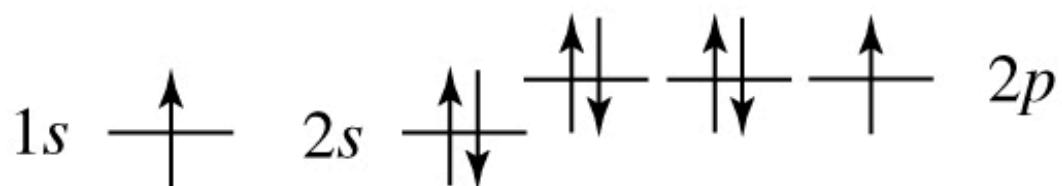
- when all electrons have been placed, each shared pair (**bonding pair**) is replaced by a line between the symbols to represent a covalent bond.

# Lewis structures

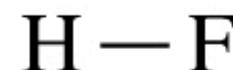
1. Elemental symbols represent atoms



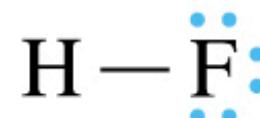
2. Only valence electrons appear



3. Lines represent bonds



4. Dots represent nonbonding electrons



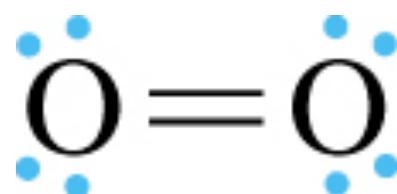
# Lewis structures

- atoms can share more than one pair of electrons.

- consider O<sub>2</sub>:

What is the Lewis structure of N<sub>2</sub> or ethene, CH<sub>2</sub>CH<sub>2</sub>?

each oxygen has 8 electrons (VALENCE?):



Lewis structure:

**Bond order** is equal to the number of shared electron pairs between two atoms: A single bond has a bond order of one, a double bond has a bond order of two, and a triple bond has a bond order of three.

# Lewis structures: The octet rule

- suggested (G.N. Lewis) to explain the number of bonds formed by many compounds:

*"An atom (other than hydrogen) usually forms enough bonds so that it becomes surrounded by eight valence electrons"*

- the octet rule is applied when drawing a Lewis dot structure of a compound.
- What is the structure of HCN?

# Lewis structures: The octet rule

- HCN....

1. Decide which atoms are connected to which other atoms (the **connectivity**).
2. Add up the number of valence electrons on all the atoms in the molecule.

$$H + C + N = 1 + 4 + 5 = 10 \text{ electrons.}$$

3. Draw a single bond from the central atom to the surrounding atoms; take away 2 electrons from the electron total, for each bond drawn ( $10 - 4 = 6$  left).



4. Allocate the remaining electrons in pairs to each surrounding atom (except hydrogen) until either they run out, or until each has an octet. Any left-over electrons go on the central atom.
5. If the central atom does not have an octet, change lone pairs on surrounding atoms to bonding pairs (creating multiple bonds) until the central atom has an octet.

# Lewis structures: Final tips....

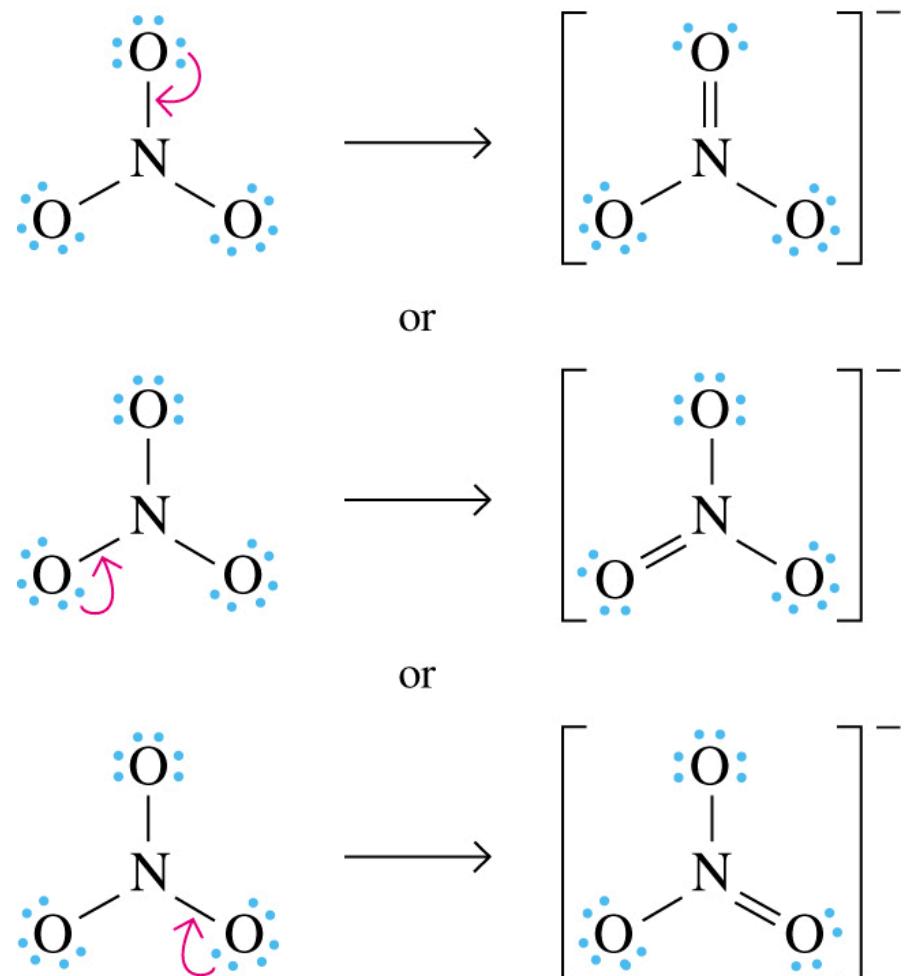
1. In drawing a Lewis structure it is important to have the **correct connectivity** – determining the central atom is important (usually apparent from the formula).
2. H cannot be the central atom in almost all of its compounds. Unlike other atoms, H requires the share of just one electron pair – not an octet.
3. The central atom is usually the first atom in the formula: e.g.  $\text{NO}_3^-$  (and many other oxyanions),  $\text{CH}_4$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{NH}_3$  – but there are some exceptions, e.g.  $\text{H}_2\text{O}$ ,  $\text{Cl}_2\text{O}$ .  
*The reason for the above is that formulae are usually written with the more electropositive element first – electropositive elements are more able to attract multiple attachments of bonding pairs.*
4. When summing valence electrons of an anion, remember to add an extra electron for each negative charge. e.g.  $\text{SO}_4^{2-}$  is  $6 + (4 \times 6) + 2 = 32$ .
5. When summing valence electrons of a cation, remember to subtract an electron for each positive charge. e.g.  $\text{NH}_4^+$  is  $5 + (4 \times 1) - 1 = 8$ .

# Lewis structures: Examples

- Draw the Lewis structure of  $\text{OF}_2$
- Draw the Lewis structure of carbonyl diiodide,  $\text{Cl}_2\text{O}$
- How about the tetrafluoroborate ion  $\text{BF}_4^-$ ?

# Resonance structures

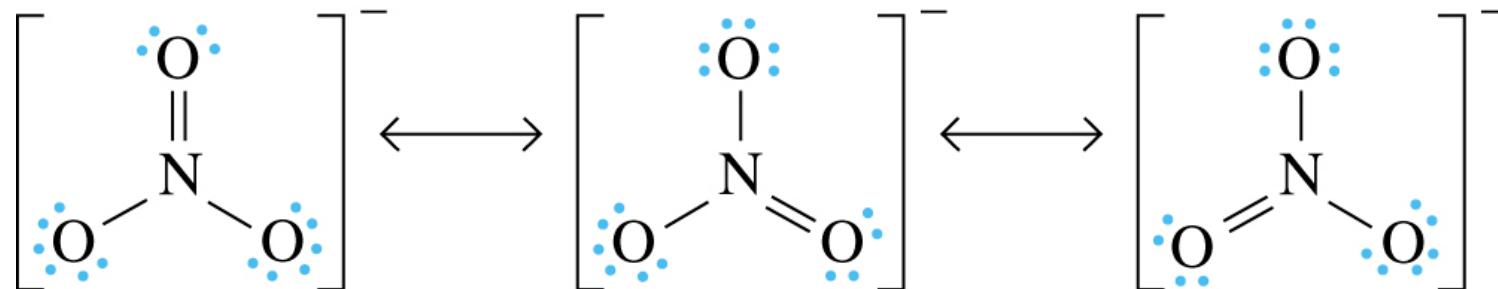
- Lewis diagrams do not give numerical values for bond lengths or strengths, but they do give an indication of bond order.



- For some molecules it is possible to draw several valid Lewis structures. For example, **three** valid structures are possible for the nitrate ion,  $\text{NO}_3^-$ :

# Resonance structures: $\text{NO}_3^-$

- each structure implies that one bond (the double bond) should be shorter than the other two - but experiments show that all bonds are equal, and of length between a single and a double.

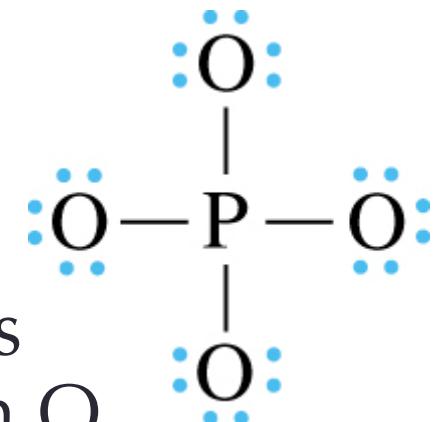


- The real structure of  $\text{NO}_3^-$  is said to be a **resonance hybrid** of the three Lewis **resonance structures**.

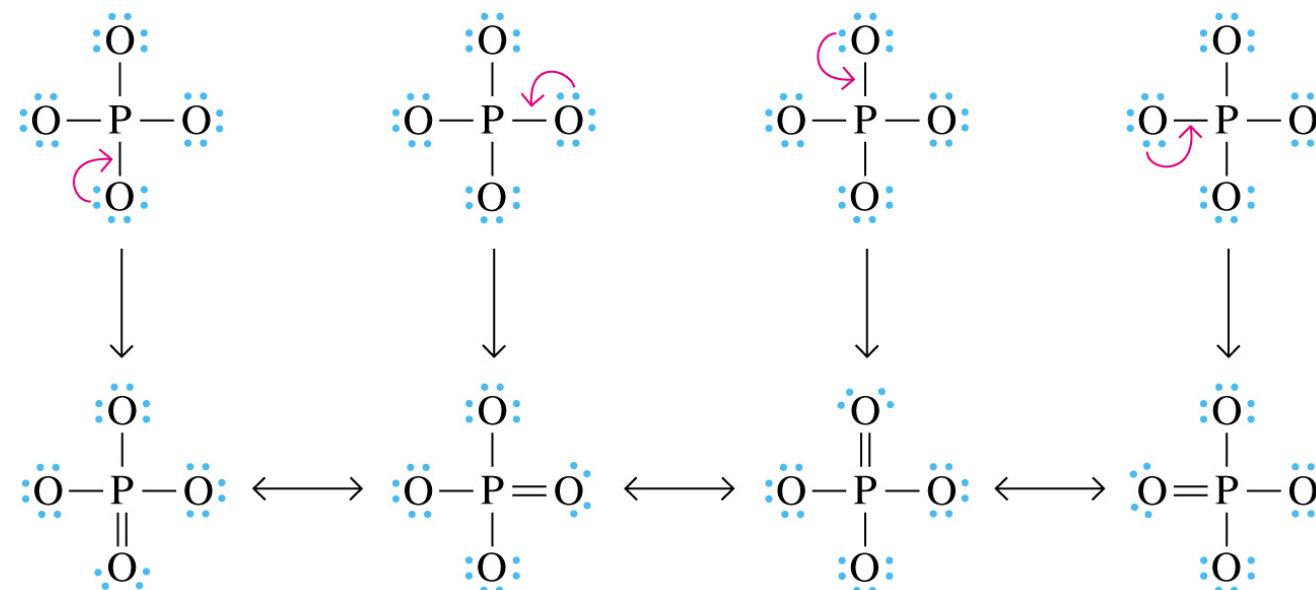
Resonance structures are needed when a single, simple, Lewis structure cannot be drawn for a molecule.

# resonance structures: $\text{PO}_4^{3-}$

- 32 electrons in total:  $5 + (4 \times 6) + 3 = 32$



- each O is formally -1 & the P is +1 in this structure. By turning one lone pair on an O into a bonding pair, the +ve charge on the P is removed & the -ve charge on that O too.



this leads to 4 possible resonance structures

# formal charges in Lewis structures

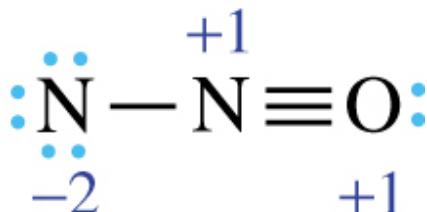
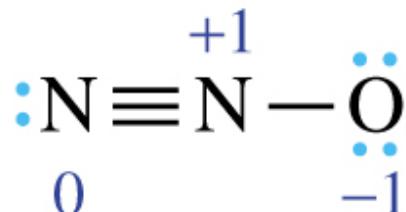
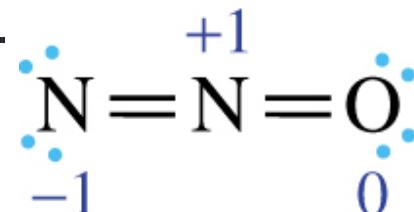
- The rules for drawing Lewis structures are indiscriminate and sometimes lead to resonance structures that are unlikely to contribute much to the character of the real molecule.

Sensible conclusions about the likely structure can, however, be reached.

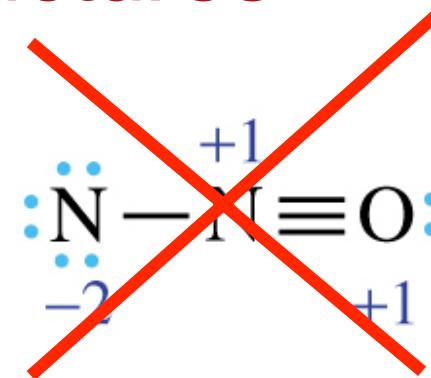
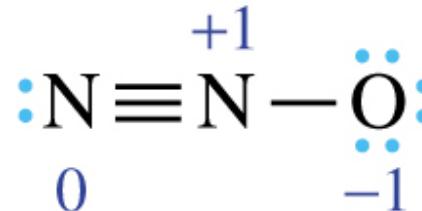
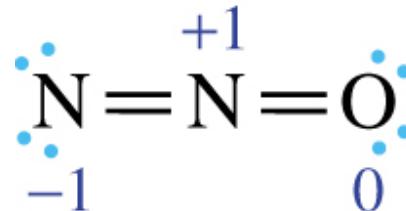
e.g. 3 valid Lewis structures can be drawn for dinitrogen oxide, N<sub>2</sub>O:



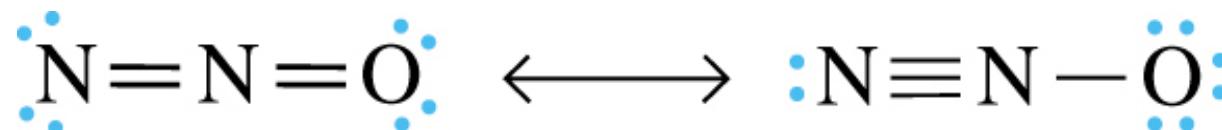
(a gas used as an anaesthetic, foaming agent & propellant for whipped cream).



# formal charges in Lewis structures



1. Lewis structures with the smallest formal charges will resemble the real molecular structure more closely.
2. Lewis structures with like charges on adjacent atoms will not contribute much to the real structure.
3. Structures having negative charges on more electronegative atoms like F, O, Cl, N will contribute more to the real structure.



# BONDING LECTURE 2: LEWIS STRUCTURES CONTINUED...

Dr Alex Donald ([w.donald@unsw.edu.au](mailto:w.donald@unsw.edu.au); Dalton 221)

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GN Lewis  
Discoverer of the covalent bond

Was Prof and Dean of Chemistry  
at Berkeley



# Today

- Lewis structures continued...
  - exceptions to the octet rule (e.g., free radicals, expanded octets, etc.)
  - minimizing formal charge (recap)
- Molecular shapes & polarity
- Valence bond theory [if time permits]

# Lewis structures: The octet rule (RECAP)

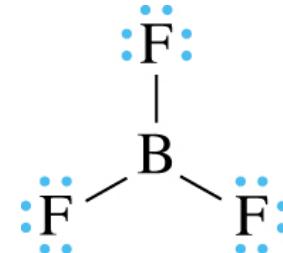
- suggested (G.N. Lewis) to explain the number of bonds formed by many compounds:

*"An atom (other than hydrogen) usually forms enough bonds so that it becomes surrounded by eight valence electrons"*

- the octet rule is applied when drawing a Lewis dot structure of a compound.

# electron-deficient molecules

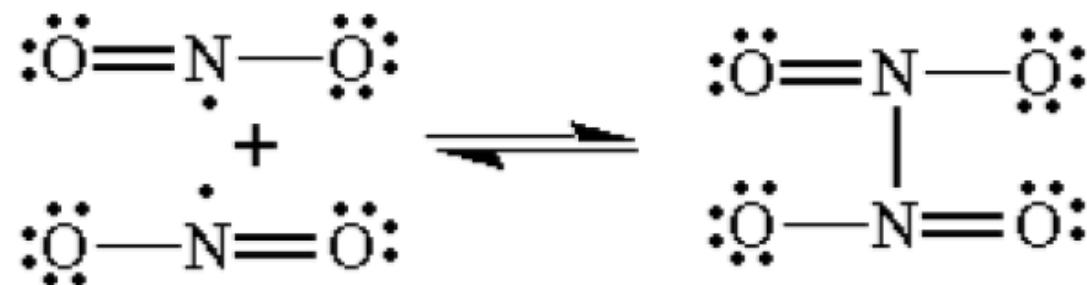
- The octet rule works well for compounds containing second period elements like C, O, N, F.
- However, Be and B can form covalent compounds that are stable without a full octet. Such compounds are called ***electron-deficient***.



- In gaseous  $\text{BeCl}_2$ , the Be has only  $4\text{ e}^-$  around it, and  $\text{BF}_3$  has only  $6\text{ e}^-$ .
- both B and Be are not very *electronegative*. They are therefore less able to pull lone pairs from the attached halogen atoms to form the multiple bonds needed to complete the octet.

# Free radicals

- On rare occasions stable molecules (free radicals) contain an odd number of electrons - and thus, not all can be paired. A good example is NO<sub>2</sub>.
- Although stable on their own, free radicals are very reactive to other molecules, owing to their unpaired electron.
- Free radicals can dimerise by pairing their single electrons, but the bond may be weak, and may break to form the free radicals again.



# Example question

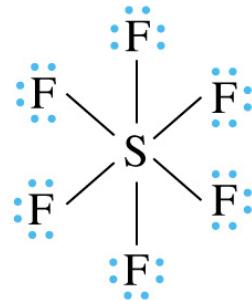
Consider CO and NO. Which are a free radical species?

- (a) CO
- (b) NO
- (c) Both CO and NO
- (d) Neither CO or NO

# expanded valence shell

- Elements of the 3rd and lower periods can form compounds with more than an octet around them.
  - This usually takes the form of more single bonds than four, or by forming multiple bonds to one or more of the four atoms bonded to them.
- These elements are said to have an ***expanded valence shell***. Typical central atoms that do this are **S, P, As, Cl, Br, I, Xe**.
  - The valence electrons of such elements are at a greater radius from the nucleus than those in 2nd row, so  $e^-$ - $e^-$  repulsions between the  $e^-$  clouds of adjacent bonds are weaker, allowing more than 4 bonds to fit around the atom.

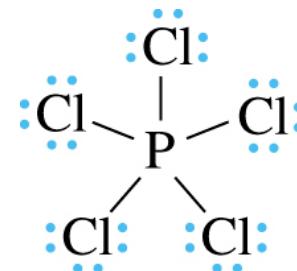
# expanded valence shells



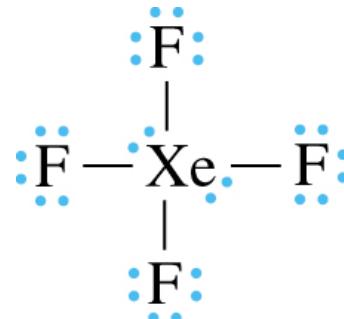
sulfur hexafluoride



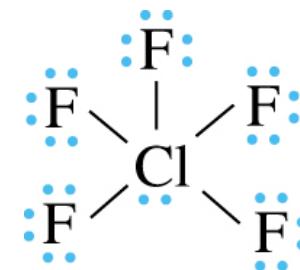
triiodide anion,  $\text{I}_3^-$



phosphorus pentachloride



xenon tetrafluoride



chlorine pentafluoride

# expanded valence shells

	$\text{H}_2\text{SO}_4$ <b>Sulfuric acid</b>	$\text{SO}_4^{2-}$ <b>Sulfate anion</b>	$\text{SO}_2$ <b>Sulfur dioxide</b>	$\text{SO}_3$ <b>Sulfur trioxide</b>
<b>Octet structures</b>	$\begin{array}{c} \text{:O} - \text{H} \\   \\ \text{:O} - \text{S} - \text{O}: \\   \\ \text{H} - \text{O}: \end{array}$	$\begin{array}{c} \text{:O:}^{2-} \\   \\ \text{:O} - \text{S} - \text{O}: \\   \\ \text{:O:} \end{array}$	$\begin{array}{c} \text{:O:} \\   \\ \text{:S} \\    \\ \text{:O:} \end{array}$ <p>plus other resonance structures</p>	$\begin{array}{c} \text{:O:} \\   \\ \text{S} = \text{O} \\   \\ \text{:O:} \end{array}$ <p>plus other resonance structures</p>
<b>Bond types</b>	4 single bonds	4 single bonds	2 intermediate bonds	3 intermediate bonds
<b>Optimised structures</b>	$\begin{array}{c} \text{:O} - \text{H} \\   \\ \text{O} = \text{S} = \text{O} \\   \\ \text{H} - \text{O}: \end{array}$	$\begin{array}{c} \text{:O:}^{2-} \\   \\ \text{O} = \text{S} = \text{O} \\   \\ \text{:O:} \end{array}$ <p>plus other resonance structures</p>	$\begin{array}{c} \text{:O:} \\    \\ \text{:S} \\    \\ \text{:O:} \end{array}$	$\begin{array}{c} \text{:O:} \\    \\ \text{S} = \text{O} \\    \\ \text{:O:} \end{array}$
<b>Bond types</b>	2 single bonds, 2 double bonds	4 intermediate bonds	2 double bonds	3 double bonds

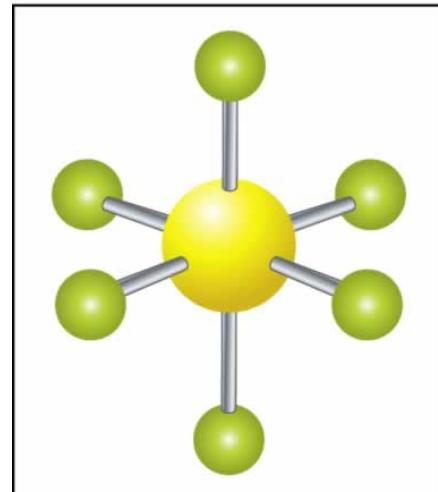
# Final notes on Lewis structures: Remember!

- When you are finishing a Lewis structure:
  - Double check: (1) octet “rule” and (2) formal charges on atoms
  - For 3<sup>rd</sup> row elements and below -> better to expand octet to reduce formal charges (e.g. SO<sub>4</sub><sup>2-</sup>)
  - For 2<sup>nd</sup> row elements, octet CANNOT be expanded (but can be deficient), *better to have a deficient octet with minimal formal charges, than an octet with formal charges* (e.g. BF<sub>3</sub>)

# MOLECULAR SHAPES

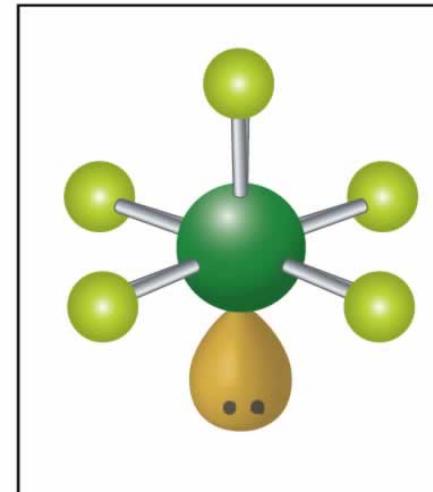
Dr Alex Donald ([w.donald@unsw.edu.au](mailto:w.donald@unsw.edu.au);  
Dalton 221)

octahedral



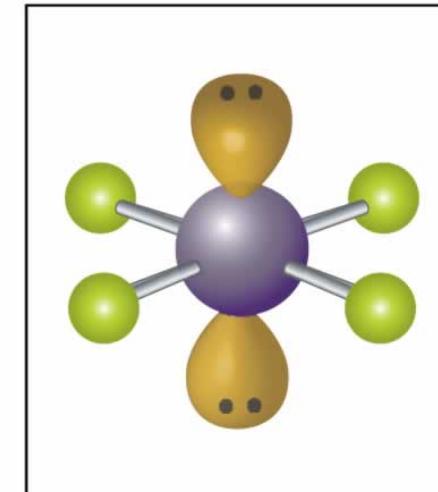
$\text{SF}_6$   
lone pairs = 0

square pyramidal



$\text{ClF}_5$   
lone pairs = 1

square planar

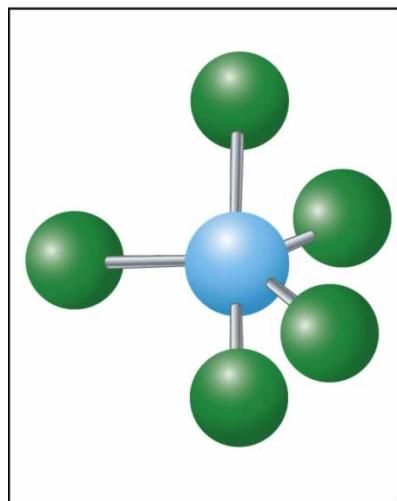


$\text{XeF}_4$   
lone pairs = 2

# How to use Lewis structures to predict the shapes of molecules

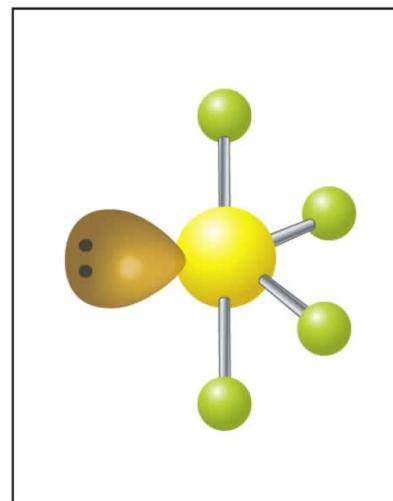
From a simple molecular formula, you will learn how to predict the shapes of molecules

trigonal bipyramidal



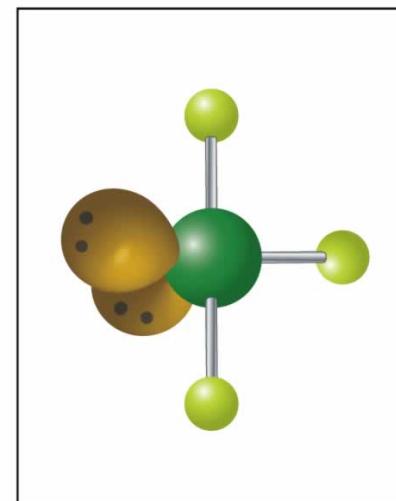
PCl<sub>5</sub>  
lone pairs = 0

seesaw



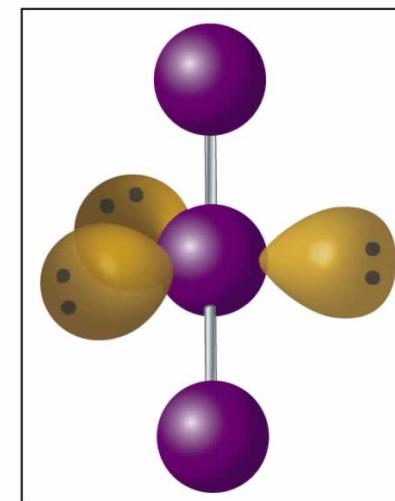
SF<sub>4</sub>  
lone pairs = 1

T-shaped



ClF<sub>3</sub>  
lone pairs = 2

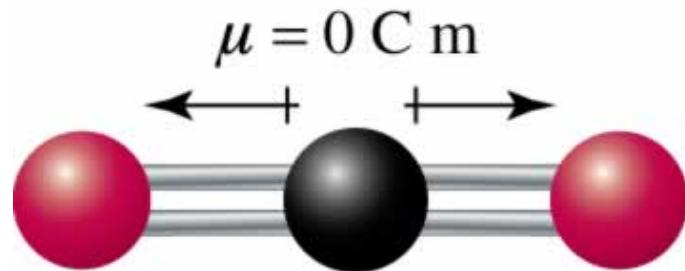
linear



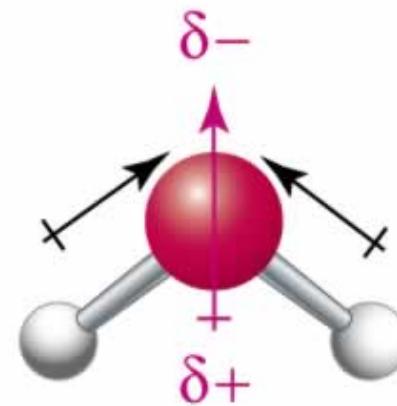
I<sub>3</sub><sup>-</sup>  
lone pairs = 3

# Molecular shape is important

$$\mu = 6.18 \times 10^{-30} \text{ C m}$$



Carbon dioxide = gas



Water = liquid

# VSEPR Theory



Australian chemist Sir Ronald Sydney Nyholm (born in Broken Hill, NSW)

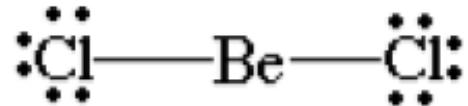


Ronald J. Gillespie

# Valence Shell Electron Pair Repulsion (VSEPR) Theory

- allows us to go from Lewis structures to molecular shapes
- VSEPR theory supposes that electron pairs (bonding and lone pairs) about an atom will arrange themselves to minimise repulsions.
- the final arrangement of bonding pairs thus dictates the shape of the molecule by dictating where the terminal atoms are located about the central atom.

# VSEPR



## EXAMPLE:

$\text{BeCl}_2$  has only two electron pairs around the central Be atom.

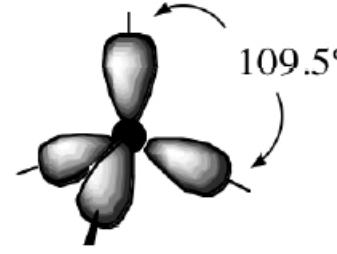
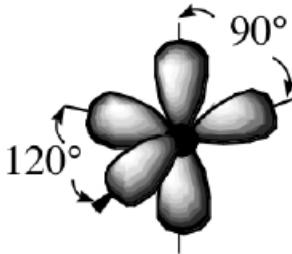
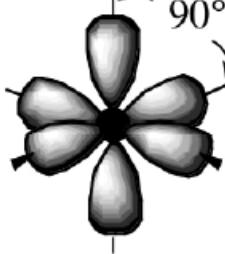
By their mutual repulsion, these pairs will position themselves on opposite sides of the Be atom, to minimize their repulsions.

The resulting angle between the bonding pairs will be  $180^\circ$ .

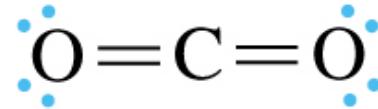
Each bonding pair is between the Be and Cl nuclei, so the molecule, as a whole, will be **linear**.

# VSEPR

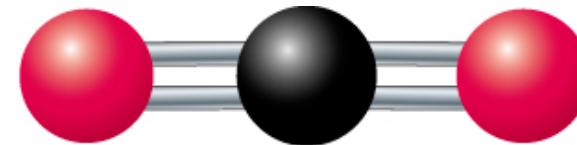
- for given numbers of electrons, there are specific **minimum energy** arrangements:

Number of pairs	Arrangement of pairs	Number of pairs	Arrangement of pairs	Number of pairs	Arrangement of pairs
2	 linear	3	 trigonal planar	4	 tetrahedral
5	 trigonal bipyramidal	6	 octahedral		

# VSEPR: double bonds



two sets of electron  
pairs around the C atom

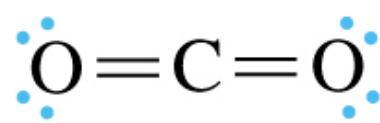


linear shape  
bond angle = 180°

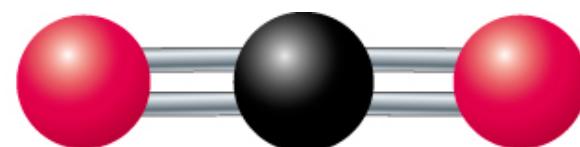
- the two e<sup>-</sup> pairs of a double bond both lie in the region of space between two nuclei (although not quite *exactly* the same region).
- for VSEPR purposes, they act like one region of e<sup>-</sup> density, and are treated like one bonding pair during the VSEPR analysis of shape.

# VSEPR: double bonds

- the Lewis structure of  $\text{CO}_2$  shows that the only regions of electron density around the central C atom are the two double bonds.
- each double bond is considered as one region of electron density.
- two regions of electron density repel one-another so they will prefer to lie at  $180^\circ$  bond angles — so the  $\text{CO}_2$  molecule is linear:



two sets of electron pairs around the C atom



linear shape  
bond angle =  $180^\circ$

# e<sup>-</sup> pairs in VSEPR

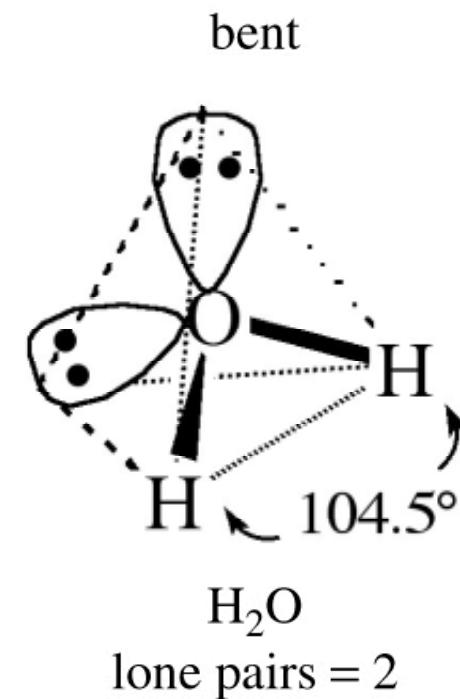
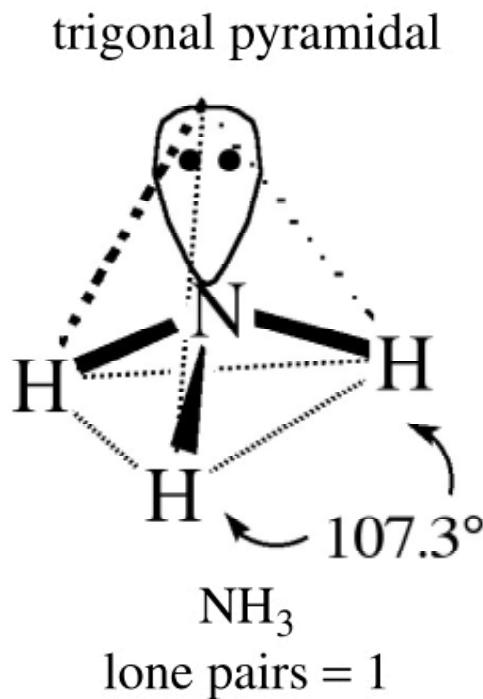
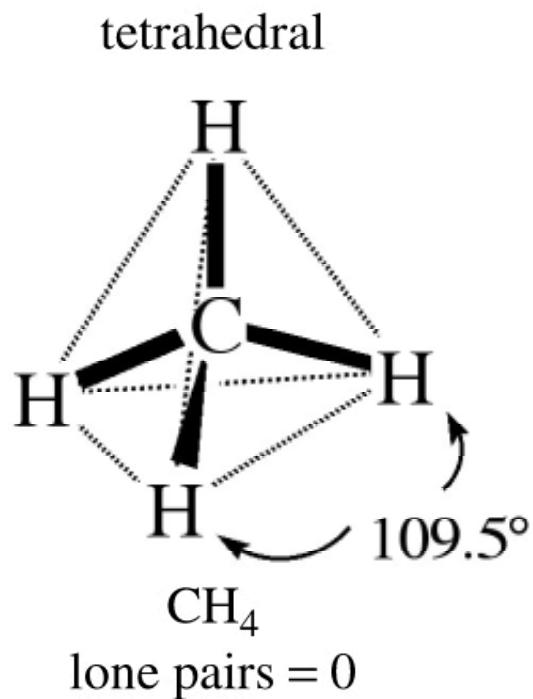
- ***lone pairs*** are very important in determining the shape of molecules
  - they are predominantly located on just one atom & so form a region of high e<sup>-</sup> density
- ***bonding pairs*** however are stretched between nuclei
  - as such they present a lower density e<sup>-</sup> cloud

as a result, **lone pairs** are more demanding of space than bonding pairs.

**lone pairs** help determine molecular shape, but they are not part of our final description of that shape as a description of the shape is solely of nuclei positions.

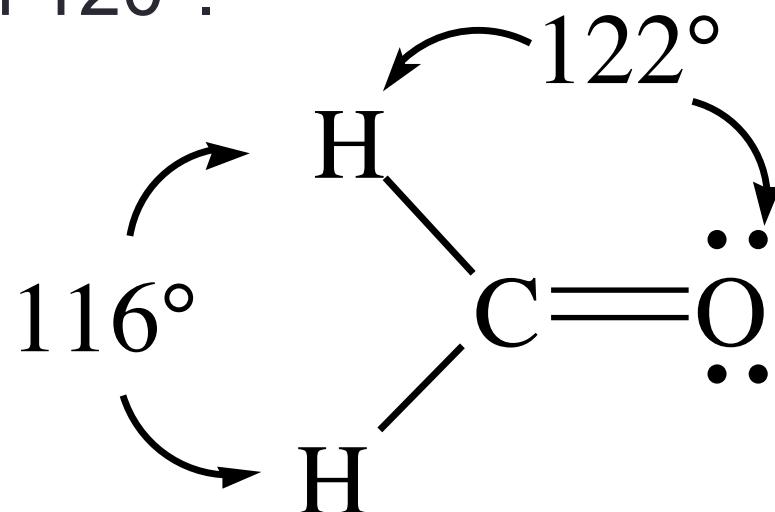
**Q: why do the hydrides of C, N & O have different shapes?**

**A:**  $\text{CH}_4$ ,  $\text{NH}_3$  &  $\text{H}_2\text{O}$ .....



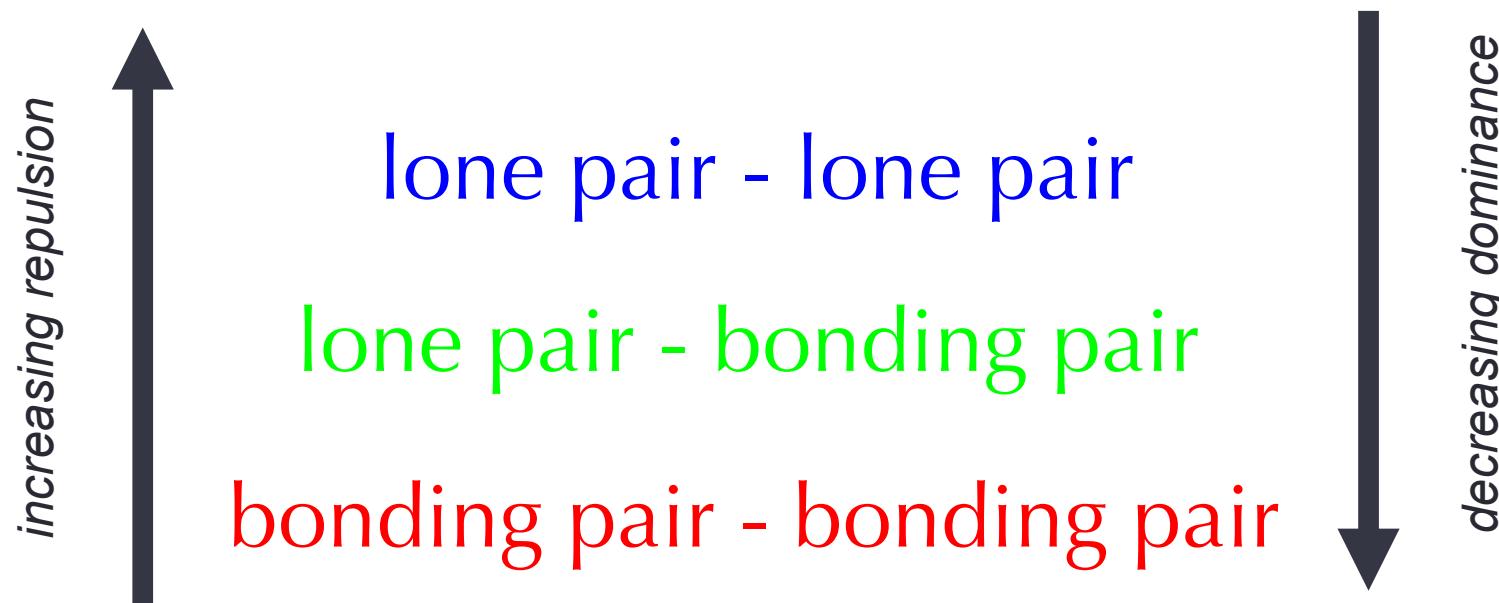
# VSEPR: multiple bonds & bond angles

- multiple bonds have *fatter* e<sup>-</sup> clouds than single bonds
  - so they repel neighbouring e<sup>-</sup> pairs more strongly than a single bond.
- in formaldehyde, CH<sub>2</sub>O, the H-C-O bond angle is larger than 120°, and the H-C-H bond angle is smaller than 120°.



# VSEPR: molecular shapes

- shapes of molecules dictated by relative strength of electron pair repulsions:

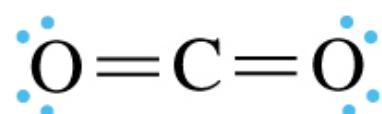


# molecular shapes: $\text{AX}_2$

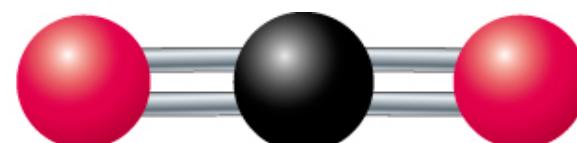
## 1. MOLECULES WITH TWO REGIONS OF ELECTRON DENSITY.

- $\text{AX}_2$  always have **LINEAR** shape, with the two bonding pairs preferring to be on opposite sides of the central atom.

e.g.  $\text{BeCl}_2$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{HCN}$ .



two sets of electron pairs around the C atom

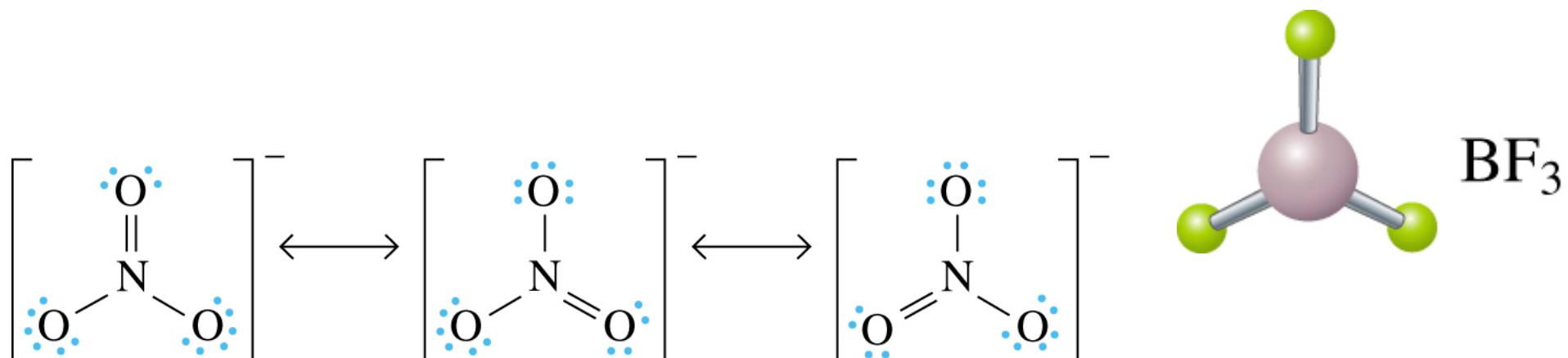


linear shape  
bond angle =  $180^\circ$

# molecular shapes: $\text{AX}_3$

## 2. MOLECULES WITH THREE REGIONS OF ELECTRON DENSITY.

- $\text{AX}_3$  always have **TRIGONAL PLANAR** shape, with the three bonding pairs at  $120^\circ$  to one-another.  
e.g.  $\text{BCl}_3$ ,  $\text{BF}_3$ ,  $\text{SO}_3$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_2\text{O}$ .



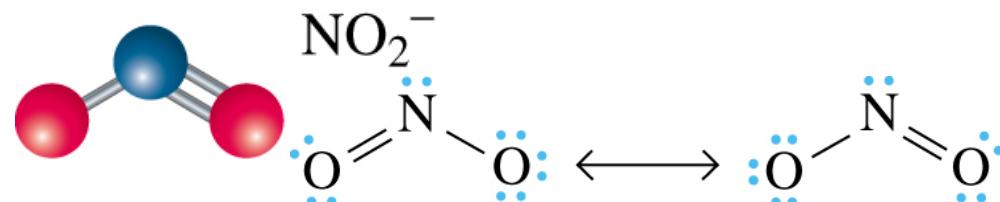
# molecular shapes: AX<sub>2</sub>E

## 2. MOLECULES WITH THREE REGIONS OF ELECTRON DENSITY.

- AX<sub>2</sub>E, two bonding pairs plus one lone pair - **TRIGONAL PLANAR**
  - final description of the molecular shape is **BENT** or **V-SHAPED**, since only the atom positions are used to specify the molecular shape.

the X-A-X bond angle is less than 120°.

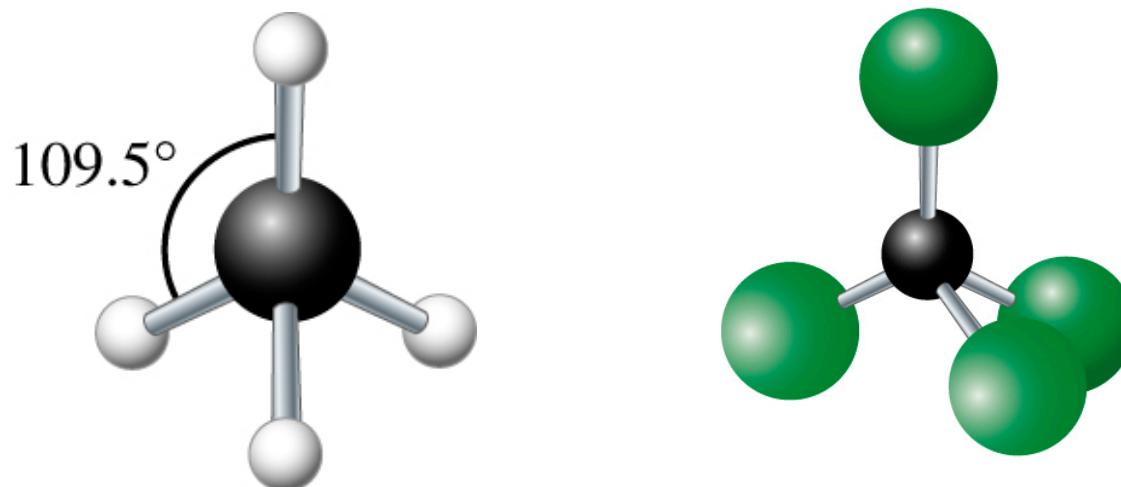
e.g. O<sub>3</sub>, SnCl<sub>2</sub>, SO<sub>2</sub>, PbCl<sub>2</sub>, NO<sub>2</sub><sup>-</sup>.



# molecular shapes: $\text{AX}_4$

## 3. MOLECULES WITH FOUR REGIONS OF ELECTRON DENSITY.

- $\text{AX}_4$  always have **TETRAHEDRAL** shape.  
e.g.  $\text{CH}_4$ ,  $\text{SiF}_4$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{ClO}_4^-$ ,  $\text{POCl}_3$ ,  $\text{BF}_4^-$ .



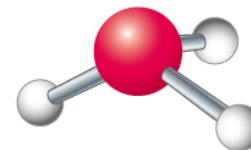
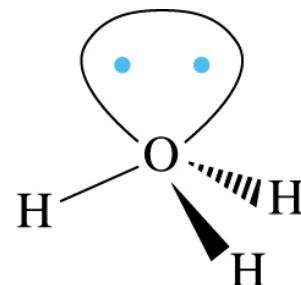
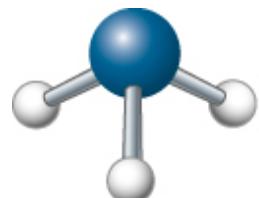
# molecular shapes: $\text{AX}_3\text{E}$

## 3. MOLECULES WITH FOUR REGIONS OF ELECTRON DENSITY.

- $\text{AX}_3\text{E}$ , three bonding pairs plus one lone pair - **TETRAHEDRAL**
  - final description of the molecular shape is **TRIGONAL PYRAMIDAL**, since only the atom positions are used to specify the molecular shape.

the X-A-X bond angle is less than  $109.5^\circ$ .

e.g.  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{ClO}_3^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{SO}_3^{2-}$ .



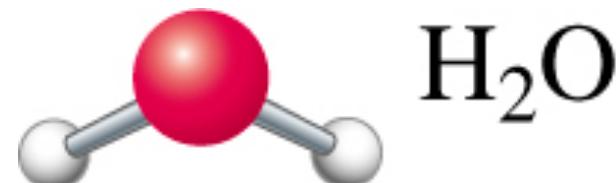
# molecular shapes: $\text{AX}_2\text{E}_2$

## 3. MOLECULES WITH FOUR REGIONS OF ELECTRON DENSITY.

- $\text{AX}_2\text{E}_2$ , two bonding pairs plus two lone pairs - **TETRAHEDRAL**
  - final description of the molecular shape is **BENT** or **V-SHAPED**, since only the atom positions are used to specify the molecular shape.

the X-A-X bond angle is less than  $109.5^\circ$ .

e.g.  $\text{H}_2\text{O}$ ,  $\text{OF}_2$ ,  $\text{SCl}_2$ ,  $\text{ClO}_2^-$ .



# molecular shapes: $\text{AX}_5$

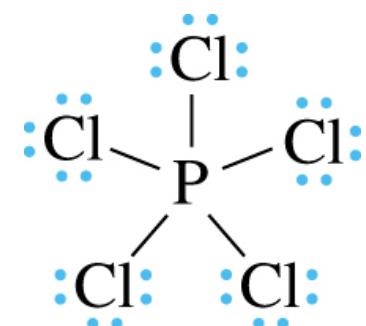
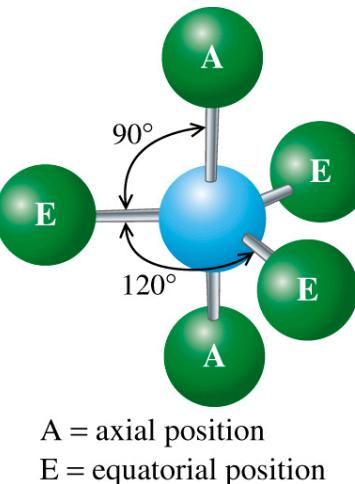
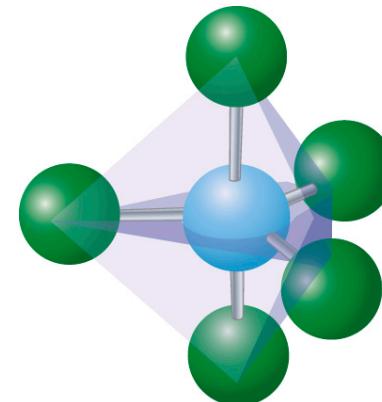
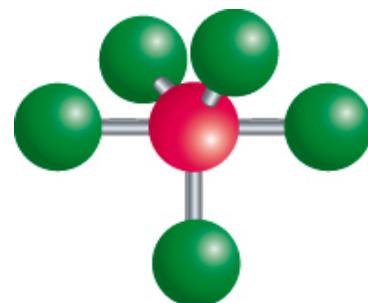
## 4. MOLECULES WITH FIVE REGIONS OF ELECTRON DENSITY.

- $\text{AX}_5$  always are **TRIGONAL BIPYRAMIDAL**.

Bond angles in this structure are:

$$\text{X}_{(\text{equat})}\text{-A-X}_{(\text{equat})} = 120^\circ \text{ and } \text{X}_{(\text{equat})}\text{-A-X}_{(\text{axial})} = 90^\circ.$$

e.g.  $\text{PF}_5$ ,  $\text{PCl}_5$ ,  $\text{SOF}_4$ .



# molecular shapes: $\text{AX}_4\text{E}$

## 4. MOLECULES WITH FIVE REGIONS OF ELECTRON DENSITY.

- $\text{AX}_4\text{E}$ , four bonding pairs plus one lone pair - **TRIGONAL BIPYRAMIDAL**
  - final description of the molecular shape is described as a '**SEE-SAW**'.

lone pair goes into equatorial position, as major repulsions are two  $90^\circ$  interactions with the axial A–X bonding pairs.  
(If the lone pair went into an equatorial site instead, it would have three  $90^\circ$  repulsions with the three equatorial A–X pairs). The actual X–A–X bond angles are  $<120^\circ$  and  $<90^\circ$ .

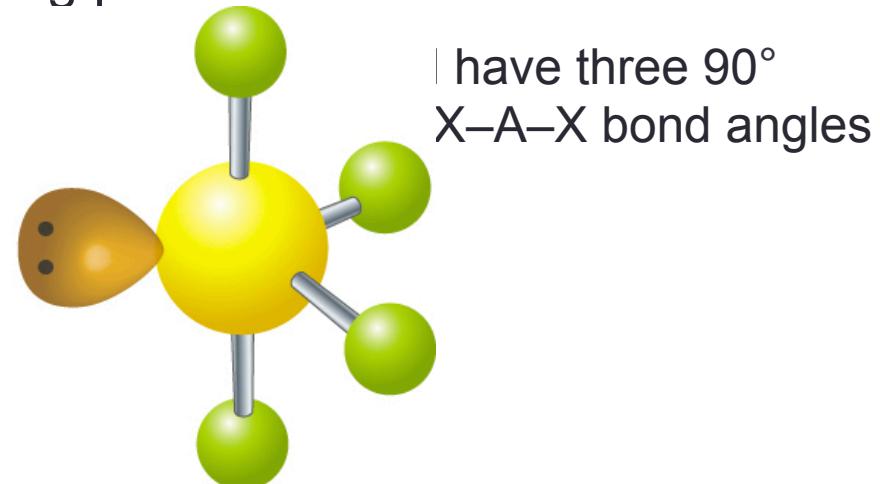
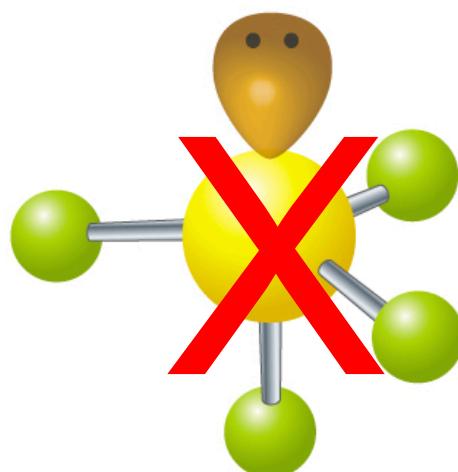
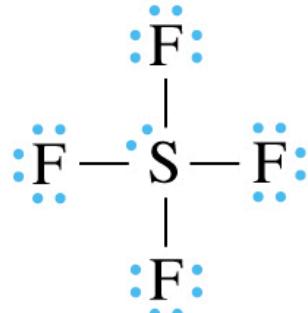
e.g.  $\text{SF}_4$ ,  $\text{XeOF}_4$ ,  $\text{IF}_4^+$ ,  $\text{IO}_2\text{F}_2^-$ .

# molecular shapes: $\text{AX}_4\text{E}$

## 4. MOLECULES WITH FIVE REGIONS OF ELECTRON DENSITY.

- $\text{AX}_4\text{E}$ , four bonding pairs plus one lone pair - **TRIGONAL BIPYRAMIDAL**
  - final description of the molecular shape is described as a '**SEE-SAW**'.

lone pair goes into equatorial position, as major repulsions are two  $90^\circ$  interactions with the axial A–X bonding pairs.

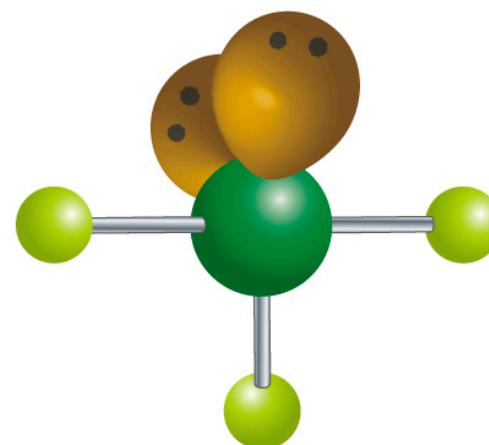


# molecular shapes: $\text{AX}_3\text{E}_2$

## 4. MOLECULES WITH FIVE REGIONS OF ELECTRON DENSITY.

- $\text{AX}_3\text{E}_2$ , three bonding pairs plus two lone pairs -  
**TRIGONAL BIPYRAMIDAL**
  - final description of the molecular shape is **T-SHAPED**.  
the lone pairs adopt equatorial positions & the X-A-X bond angle is less than  $90^\circ$ .

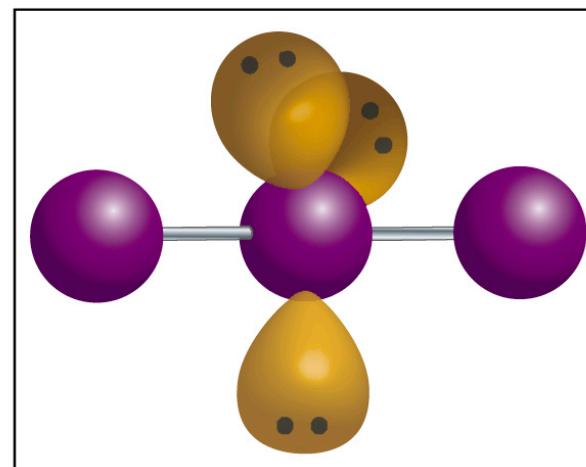
e.g.  $\text{ClF}_3$ ,  $\text{BrF}_3$ .



# molecular shapes: $\text{AX}_2\text{E}_3$

## 4. MOLECULES WITH FIVE REGIONS OF ELECTRON DENSITY.

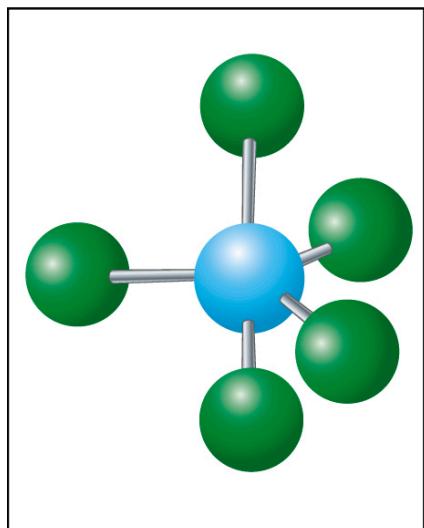
- $\text{AX}_2\text{E}_3$ , two bonding pairs plus three lone pairs - **TRIGONAL BIPYRAMIDAL**
    - final description of the molecular shape is **LINEAR**.  
the X-A-X bond angle is  $180^\circ$ .
- e.g.  $\text{I}_3^-$ ,  $\text{XeF}_2$ ,  $\text{IF}_2^-$ .



# remember!

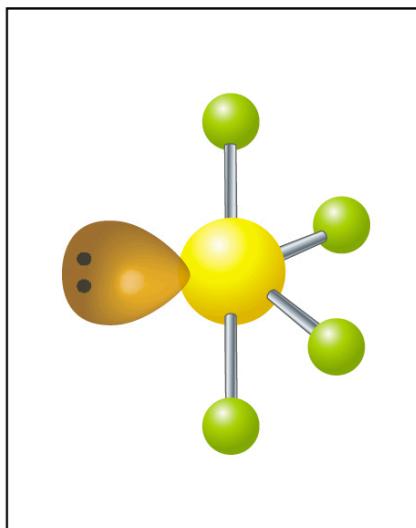
## 4. MOLECULES WITH FIVE REGIONS OF ELECTRON DENSITY.

trigonal bipyramidal



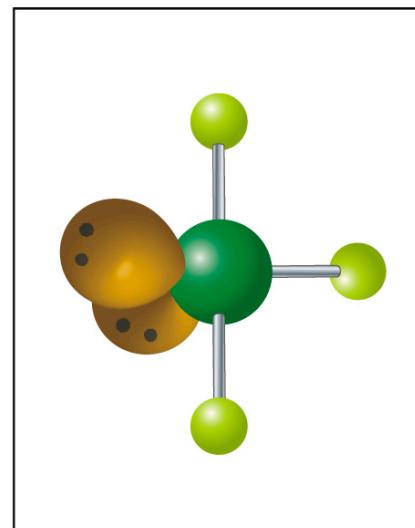
$\text{PCl}_5$   
lone pairs = 0

seesaw



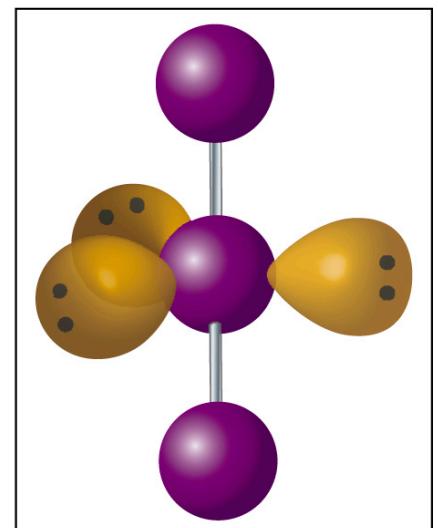
$\text{SF}_4$   
lone pairs = 1

T-shaped



$\text{ClF}_3$   
lone pairs = 2

linear



$\text{I}_3^-$   
lone pairs = 3

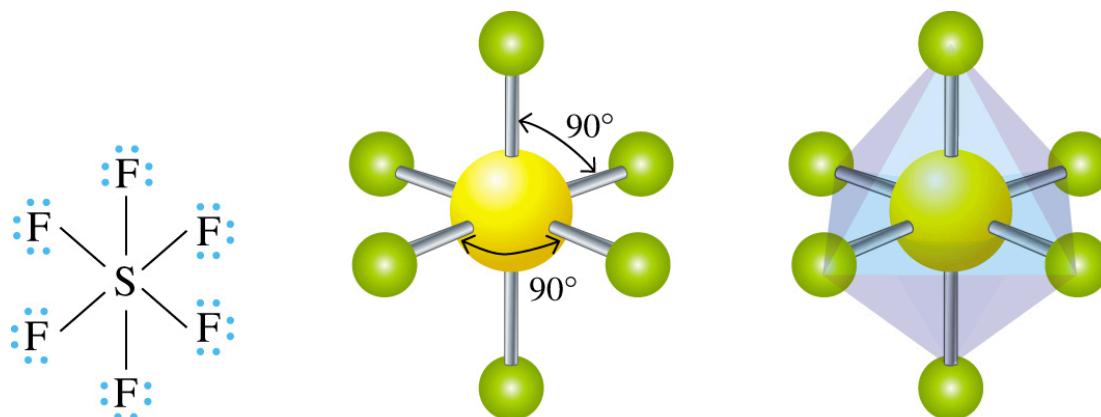
# molecular shapes: $\text{AX}_6$

## 5. MOLECULES WITH SIX REGIONS OF ELECTRON DENSITY.

- $\text{AX}_6$  always are **OCTAHEDRAL**.

Bond angles :  $\text{X}_{(\text{equat})}-\text{A}-\text{X}_{(\text{equat})}=90^\circ$   
and  $\text{X}_{(\text{equat})}-\text{A}-\text{X}_{(\text{axial})}=90^\circ$ .

e.g.  $\text{SF}_6$ ,  $\text{IOF}_5$ ,  $\text{PF}_6^-$ ,  $\text{SiF}_6^{2-}$ ,  $\text{AlF}_6^{3-}$ .



# molecular shapes: $\text{AX}_5\text{E}$

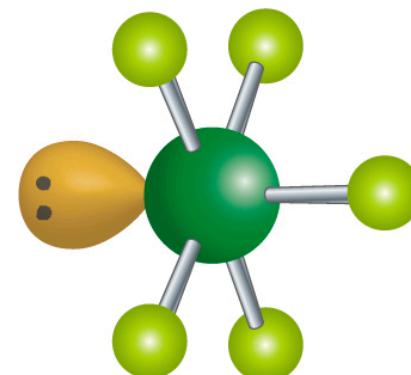
## 5. MOLECULES WITH SIX REGIONS OF ELECTRON DENSITY.

- $\text{AX}_5\text{E}$ , five bonding pairs plus one lone pair - **OCTAHEDRAL**
  - final description of the molecular shape is described as a '**SQUARE PYRAMIDAL**'.

lone pair goes into any of the equivalent octahedral positions.

the actual X-A-X bond angles are less than  $90^\circ$ .

e.g.  $\text{BrF}_5$ ,  $\text{TeF}_5$ ,  $\text{XeOF}_4$ .



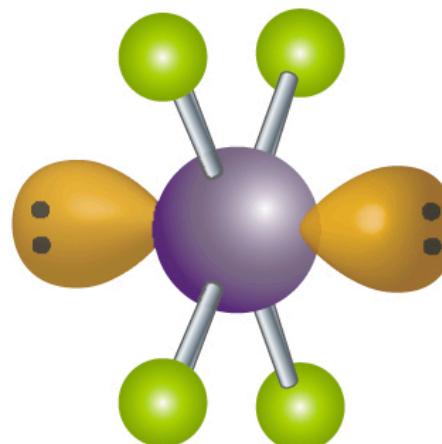
# molecular shapes: $\text{AX}_4\text{E}_2$

## 5. MOLECULES WITH SIX REGIONS OF ELECTRON DENSITY.

- $\text{AX}_4\text{E}_2$ , four bonding pairs plus two lone pairs - **OCTAHEDRAL**
  - final description of the molecular shape is described as '**SQUARE PLANAR**'.

lone pairs go into two opposite octahedral sites.

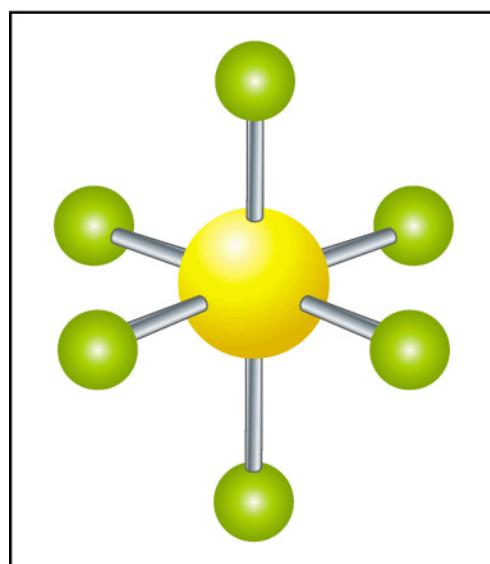
e.g.  $\text{XeF}_4$ ,  $\text{ICl}_4^-$ .



**remember!**

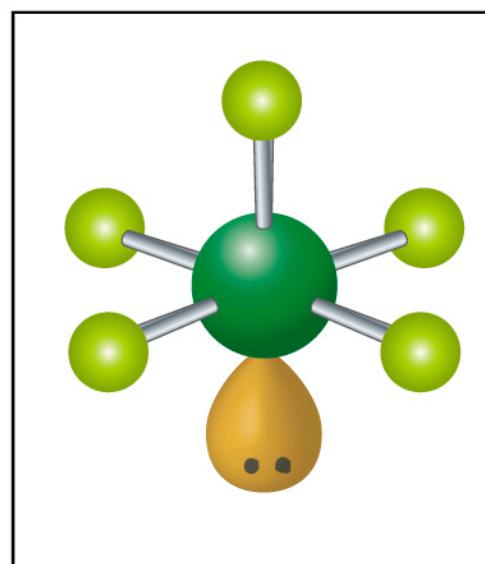
## 5. MOLECULES WITH SIX REGIONS OF ELECTRON DENSITY.

octahedral



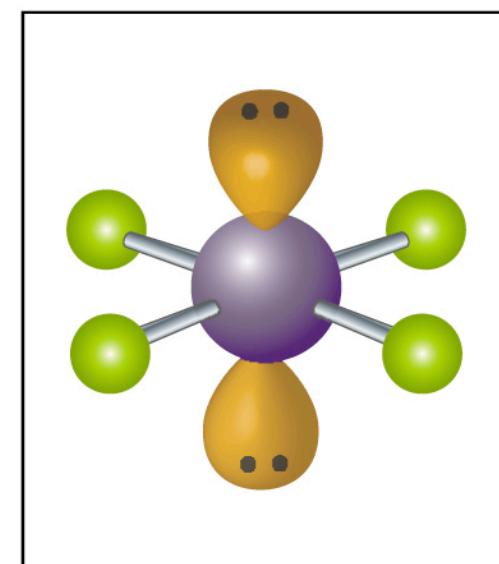
$\text{SF}_6$   
lone pairs = 0

square pyramidal



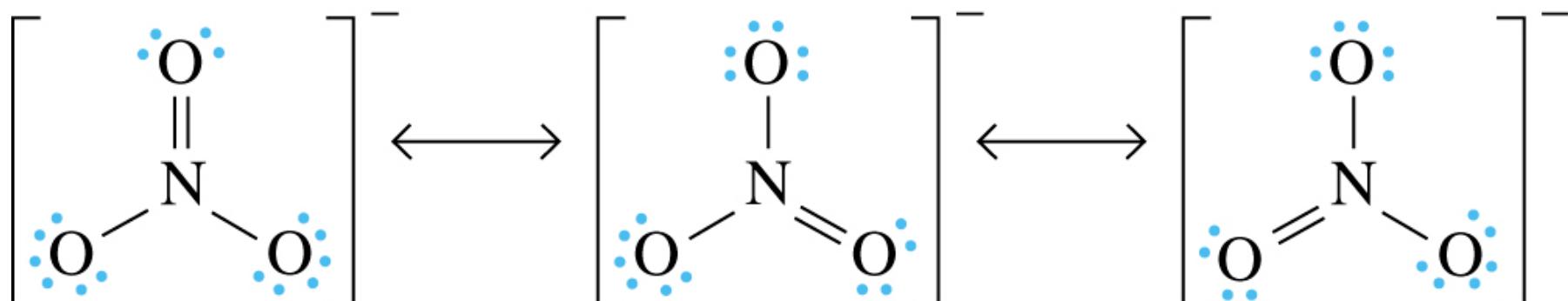
$\text{ClF}_5$   
lone pairs = 1

square planar

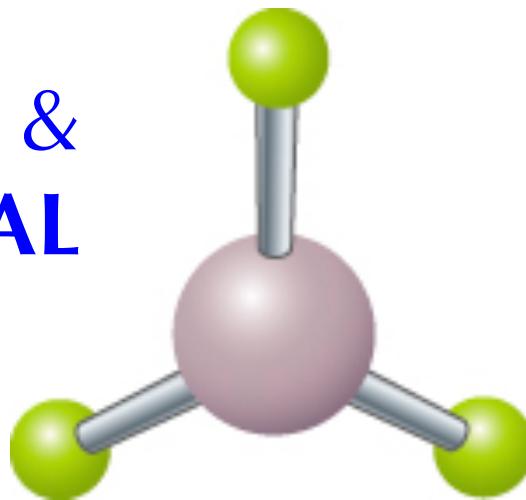


$\text{XeF}_4$   
lone pairs = 2

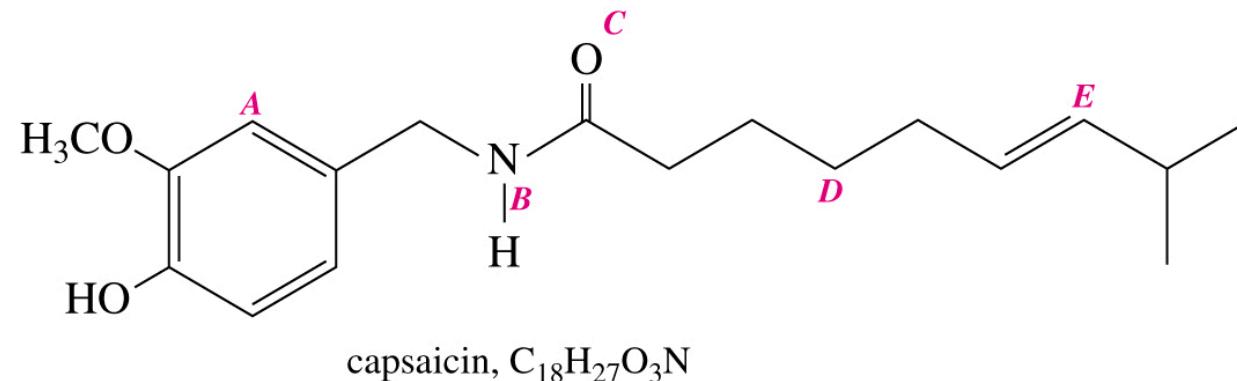
remember: for resonant structures, the pair of e<sup>-</sup>'s that is different in each structure is spending a fraction of the time delocalised across the bonds



all bond lengths &  
angles are **EQUAL**



# VSEPR in large molecules



- VSEPR rules can be applied to describe the *local* shape within a complex molecule
  - what shapes would *A*, *B*, *C*, *D* & *E* have?
- in this way the complete shape of the molecule could be built up....

# VSEPR in large molecules

In this example, carbon = black; oxygen = red; hydrogen = grey; nitrogen = blue.

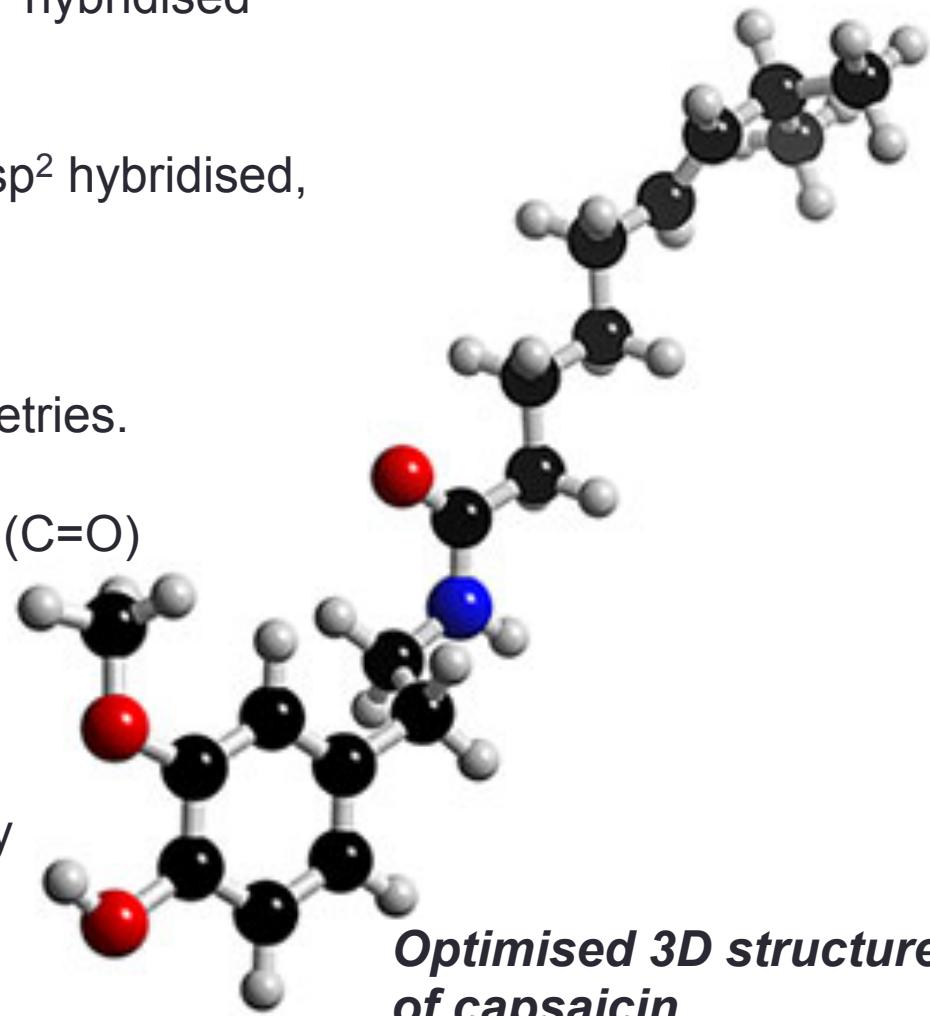
You can see the carbon atoms (black) are  $sp^3$  hybridised (tetrahedral geometries) in the alkyl chain.

In contrast, the carbon atoms in the ring are  $sp^2$  hybridised, forming a linear ring.

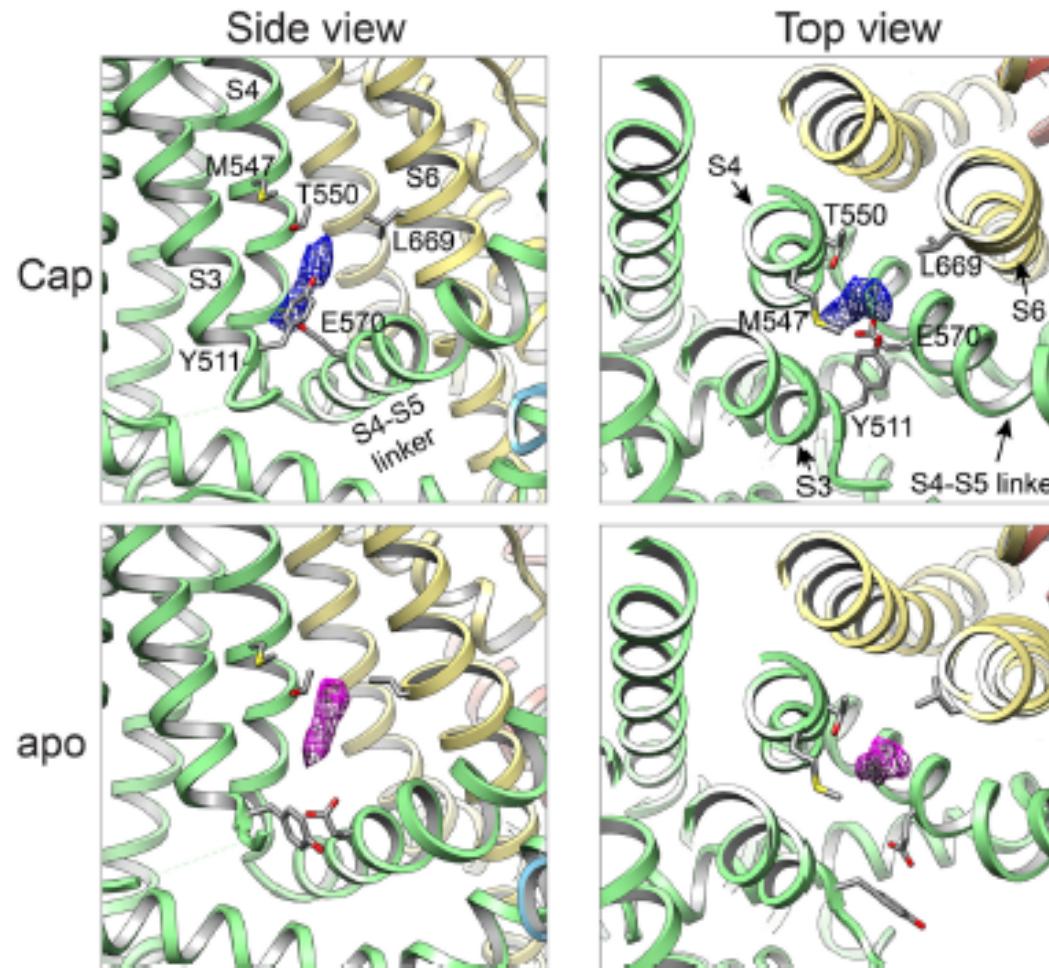
O-atoms attached to ring are  $sp^3$  hybridised (with 2 lone pairs) so they adopt “bent” geometries.

The O-atom on the alkyl chain terminates ( $sp^2$  hybridised, two lone pairs). The carbonyl (C=O) carbon is also  $sp^2$  hybridised forming, forming a plane between the O, N and other C atoms that it bonds with.

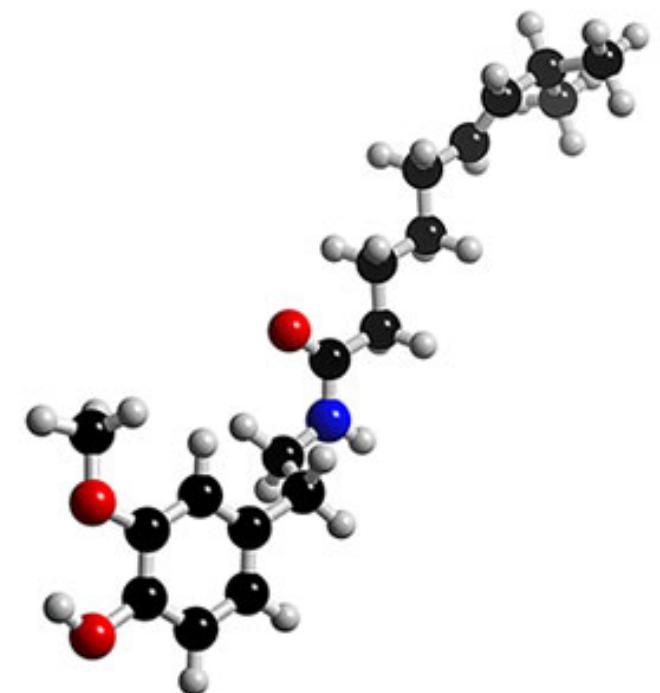
By applying VSEPR to each atom, a relatively accurate three dimensional structure is obtained (subject to rotations about bonds and other factors). Why is this important?



# VSEPR in large molecules



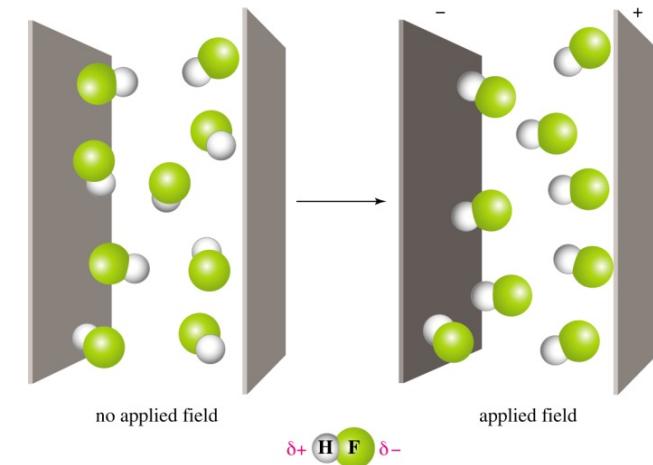
*Optimised 3D structure  
of capsaicin*



Basically, capsaicin has a three dimensional structure that fits perfectly in the binding site of a protein complex in nerve cells in your mouth, which triggers an electrical impulse to your brain...causing a burning sensation

# molecular shape & polarity

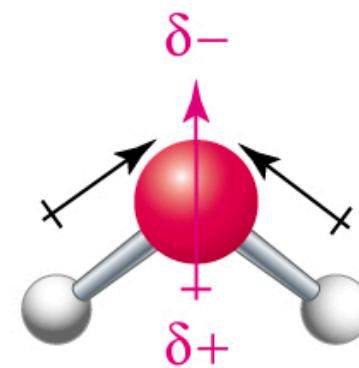
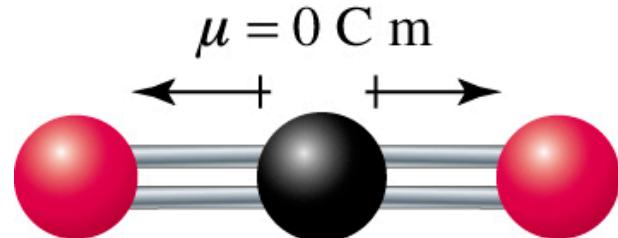
- as we have seen, some molecules can display permanent dipole moments
- the molecular dipole moment is a measure of how unevenly charge (on average) is distributed over the molecule.
- the molecular dipole is the vector sum of the individual bond dipoles of the molecule  
(units of debye, 1 D =  $3.34 \times 10^{-30}$  Cm)



# molecular shape & polarity

- we have seen that  $\text{CO}_2$  is linear and that  $\text{H}_2\text{O}$  is bent; this has a direct bearing on the overall dipole moment of the molecules:

$$\mu = 6.18 \times 10^{-30} \text{ C m}$$

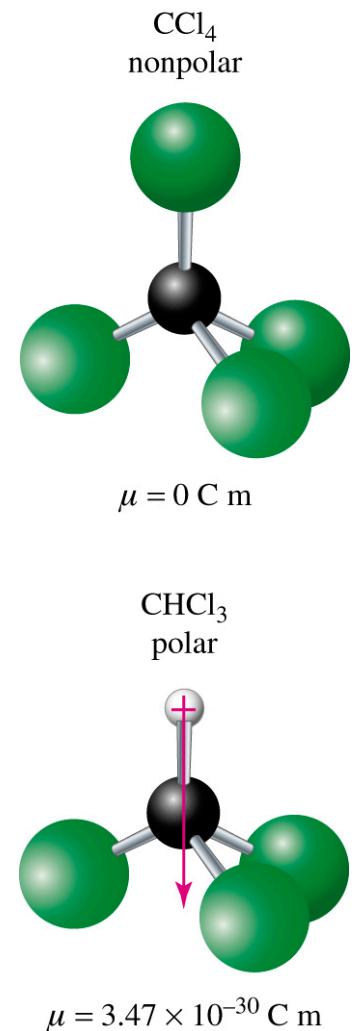


# molecular shape & polarity

- different molecules that have the same shape can be either non-polar or polar
- the sum of the individual bond polarities will then give the overall molecular dipole moment:

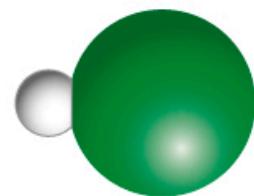
both carbon tetrachloride & chloroform are  $T_d$ ;

however only  $\text{CHCl}_3$  has a dipole moment!



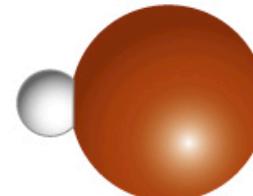
# recap: bond polarity

- the polarity of a bond can be related directly to the difference in the electronegativities ( $\chi$ ) of the bonded atoms:



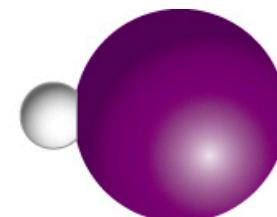
HCl

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



HBr

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



HI

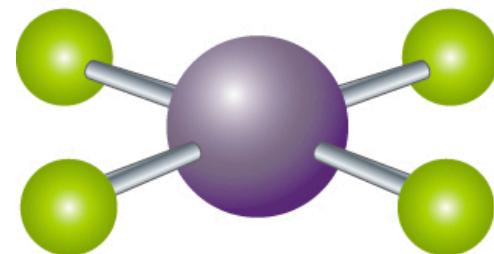
$$\Delta \chi = 0.4$$
$$\mu = 1.27 \times 10^{-30} \text{ C m}$$

$\chi$  tends to decrease down a Group;

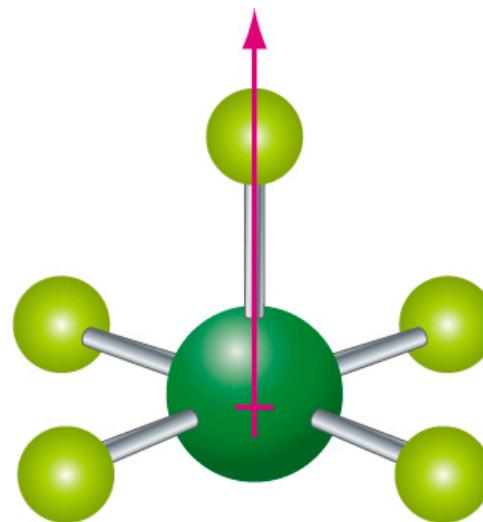
halo-hydrides should be less polar as  $Z \uparrow$

# molecular shape & polarity

- more complex molecular shapes obtained by VSEPR theory behave in exactly the same way:



$\text{XeF}_4$   
nonpolar



$\text{ClF}_5$   
polar

# BONDING LECTURE 4: VALENCE BOND THEORY

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Dr Alex Donald ([w.donald@unsw.edu.au](mailto:w.donald@unsw.edu.au); Dalton 221)

## Example – Recap question from last week

- What is the molecular shape of ozone,  $O_3$ ?
- Does  $O_3$  have a permanent dipole moment?
- What is the O-O-O bond angle?

# Chapter 5: Chemical bonding and molecular structure

- fundamentals of bonding.
- Lewis structures.
- valence shell electron pair repulsion (VSPER) theory.
- properties of covalent bonds.
- valence bond theory.

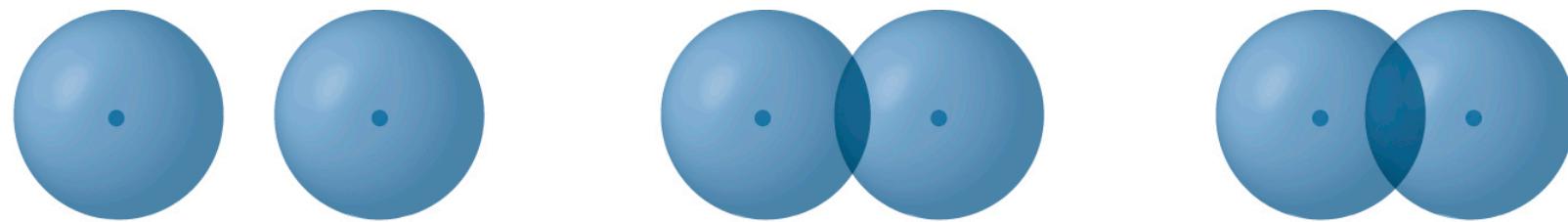
***You will learn how to use valence bond theory  
to visualise bonding between atoms (molecular  
orbitals)***

# Valence Bond theory

- Lewis structures & VSEPR theory are usually good predictors of molecular shapes and bond orders, **BUT** they do not:
  - describe the shape of molecular orbitals
  - how electrons are specifically shared between atoms to form single, double and triple bonds
- more detailed models of bonding are needed: VB theory is a simple extension of VSEPR & AO theories
- Just like we need atomic orbitals to visualise how electrons are distributed in atoms, we need an orbital view to understand how electrons are distributed in molecules

# Valence Bond theory

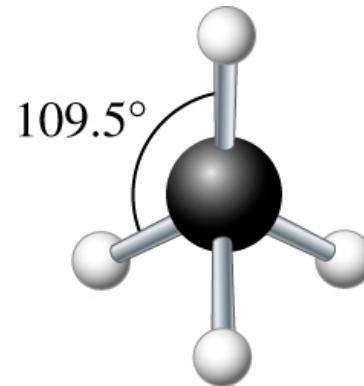
- bonding in  $\text{H}_2$  can be thought of as overlap between the  $1s^1$  electrons (in  $1s$  AOs) on each H atom:



- in the internuclear region, the electrons pair up to form a bonding pair

# Valence Bond theory

- but what of  $\text{CH}_4$ ?



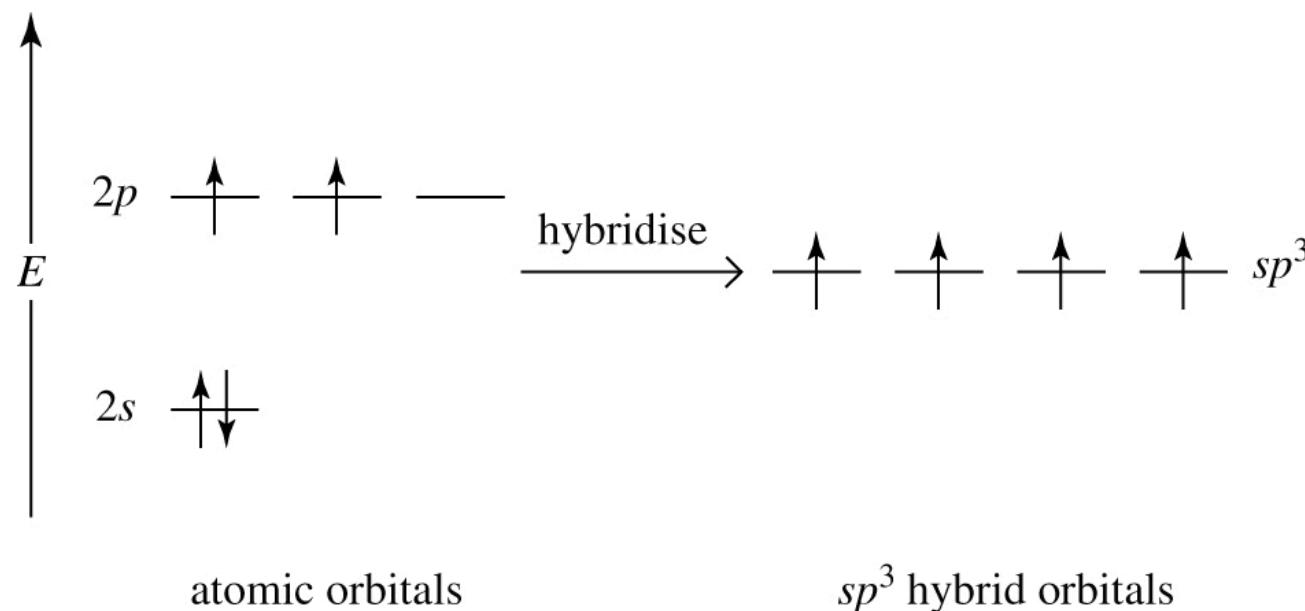
- in  $\text{CH}_4$  the  $1s$  electron in each H atom is now interacting with the  $n = 2$  electrons ( $2s^22p^2$ ) of carbon.....
- Lewis structures treat all valence electrons equally - carbon has  $2 + 2 = 4$ .....why?

# Valence Bond theory: hybridisation

- valence electrons on atoms can be considered to hybridise
  - that is to say that they can mix to give a hybrid orbital type in which all electrons are equivalent
- remember that for multi-electron atoms, the  $2s$  electrons lie lower in energy than the  $2p$ .
- hybridisation makes all electrons involved equal in energy
  - that is to say that they can mix to give a hybrid orbital type in which all electrons are equivalent

# hybridisation: $sp^3$

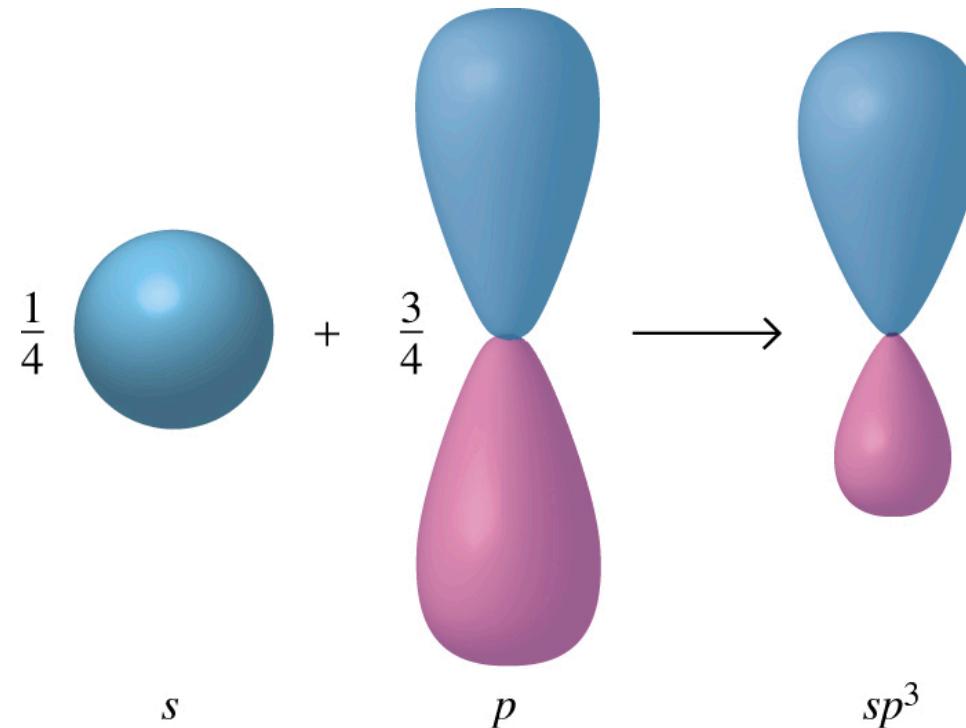
- the  $s$  orbital, containing 2 electrons, can mix with the three  $p$  orbitals to form a set of  $sp^3$  hybrid orbitals
- this re-distributes the 4 valence electrons of carbon (for example) into equivalent orbitals (Hund's rules):



# hybridisation: $sp^3$

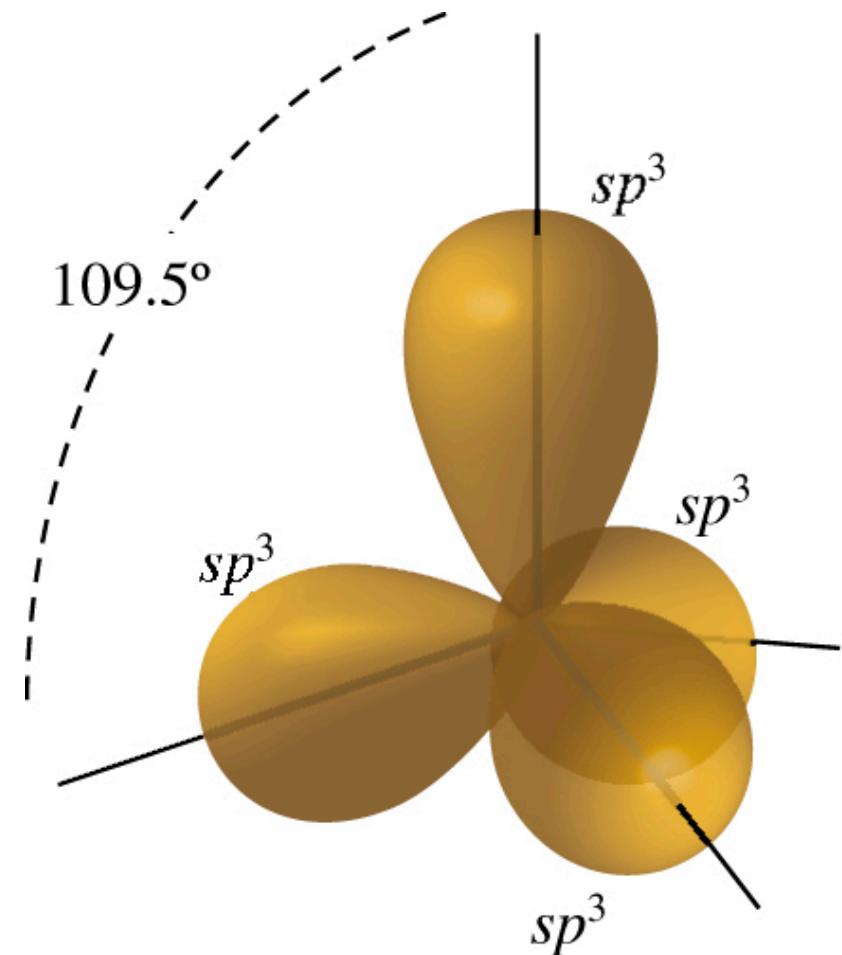
- $sp^3$  hybrid orbitals have a physical shape that reflects the constituent pure atomic orbitals:

$$4 \times sp^3 = (1 \times s) + (3 \times p)$$

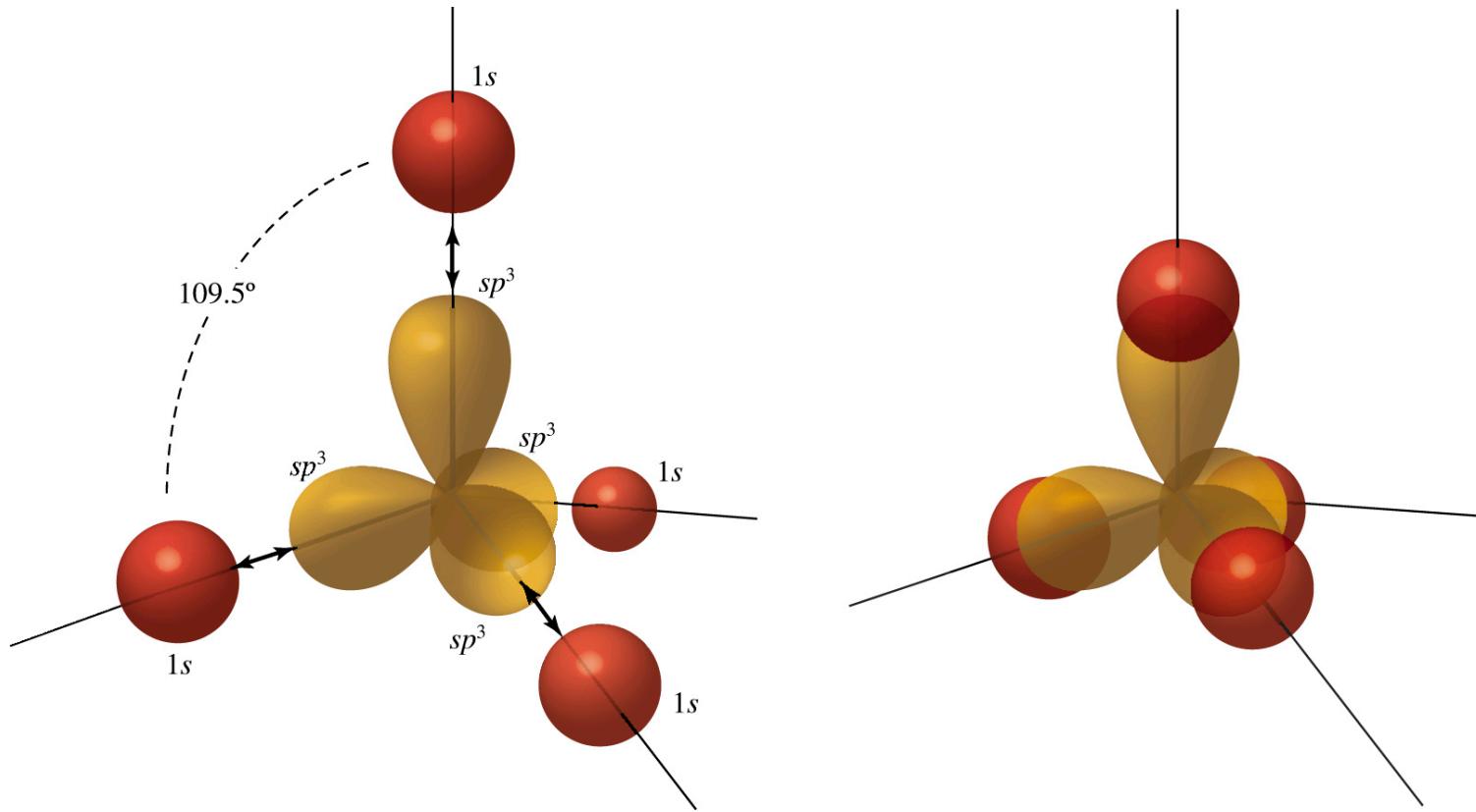


# hybridisation: $sp^3$

- $sp^3$  orbitals
  - mixing of  $1 \times s$  &  $3 \times p$  valence orbitals
  - four large lobes
  - orbitals have **tetrahedral** geometry
  - each lobe presents only a **single sign** of the wavefunction



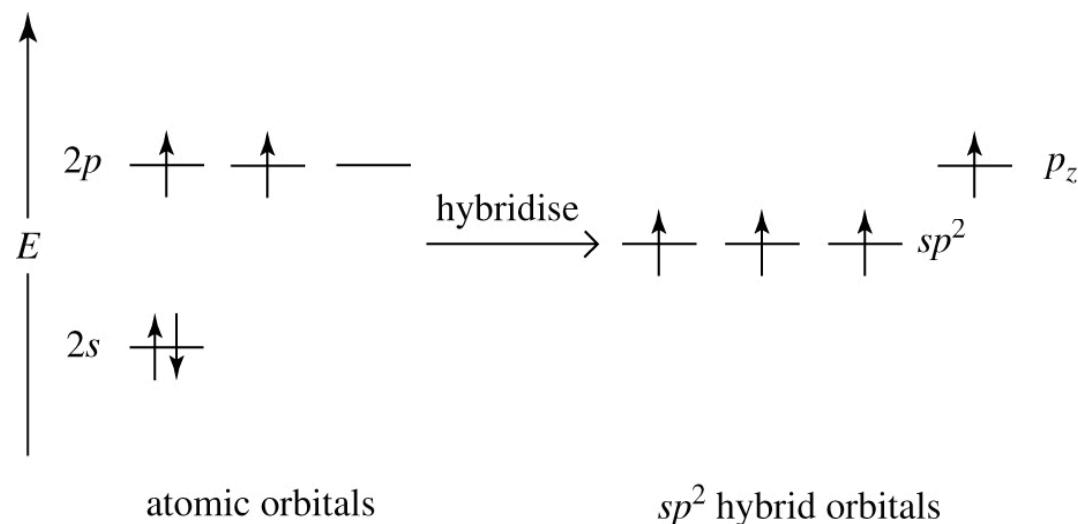
# hybridisation: $sp^3$



- the 4 ( $n = 2$ )  $sp^3$  orbitals of C can efficiently overlap with the 1s orbitals of H
  - this gives rise to methane,  $\text{CH}_4$

# hybridisation: $sp^2$

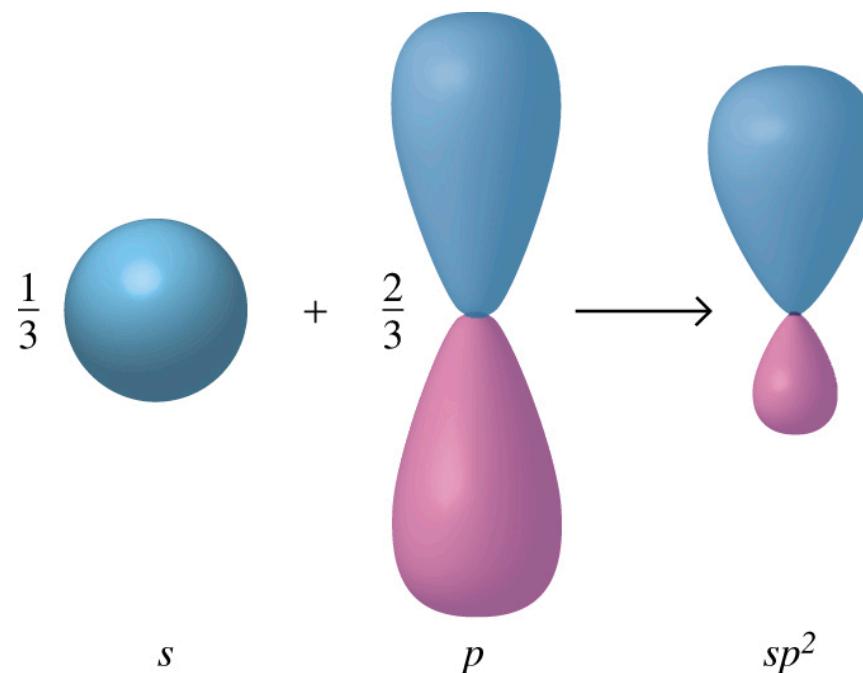
- but what if the  $s$  orbital mixes with only **two** of the three  $p$  orbitals to form  $3 \times sp^2$  hybrid orbitals, leaving the third  $p$  orbital unhybridised?
- three of the 4 valence electrons of C are re-distributed into equivalent  $sp^2$  orbitals, with the fourth remaining in the lone  $p$  orbital:



# hybridisation: $sp^2$

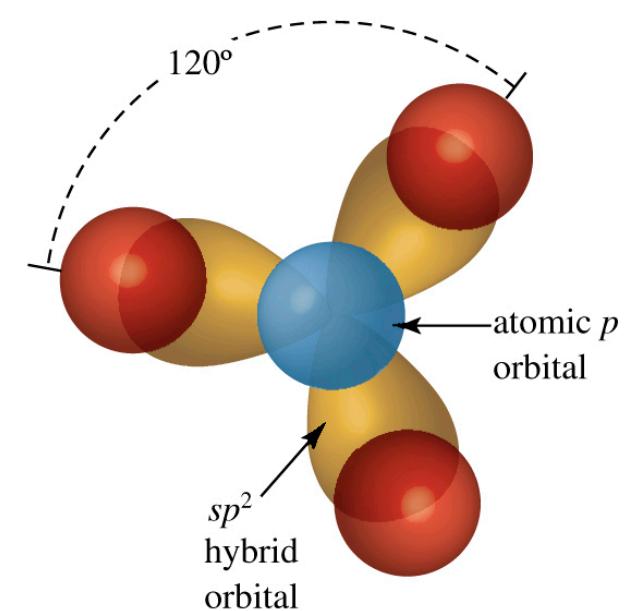
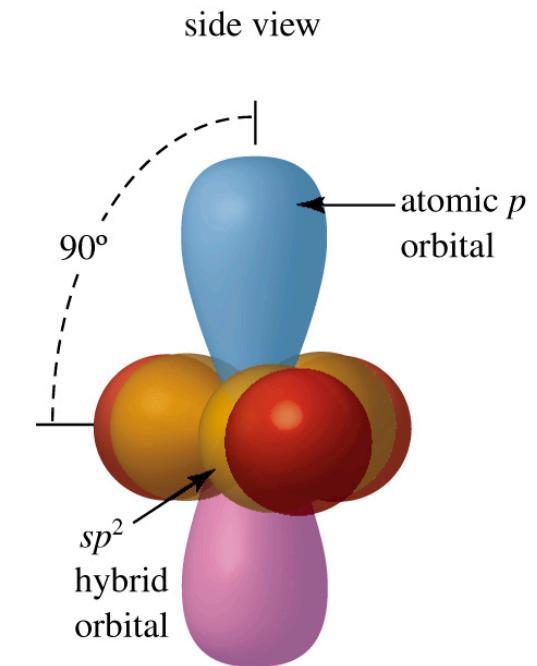
- $sp^2$  hybrid orbitals have a physical shape that reflects the constituent pure atomic orbitals:

$$3 \times sp^2 = (1 \times s) + (2 \times p)$$



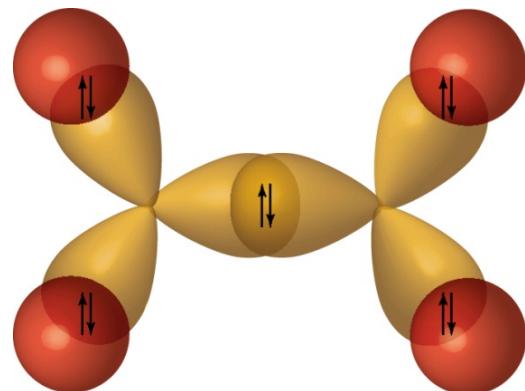
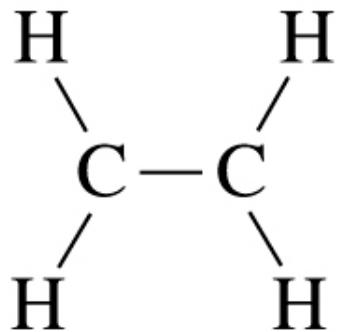
# hybridisation: $sp^2$

- $sp^2$  orbitals
  - mixing of  $1 \times s$  &  $2 \times p$  valence orbitals
  - three large lobes of hybridised orbitals
  - plus the residual  $p$  orbital
  - hybrid orbitals have ***trigonal planar*** geometry
  - each lobe of the hybrid presents only a **single sign** of the wavefunction



# hybridisation: $sp^2$

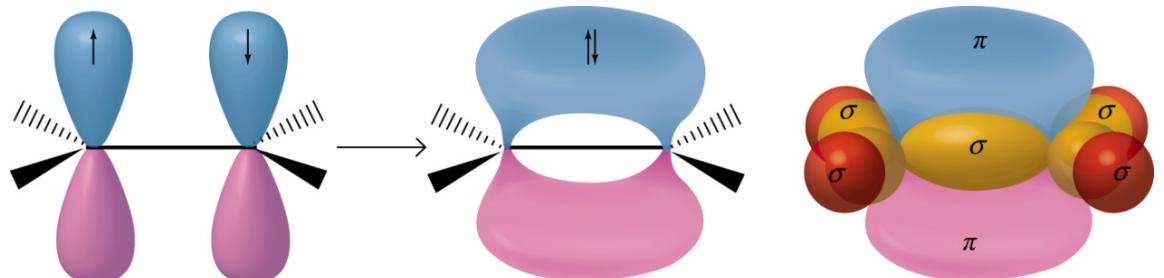
- Example: ethene:



- the  $sp^2$  orbitals form  $\sigma$  bonds with either the 1s orbitals of H or the corresponding  $sp^2$  orbital of the neighbouring C.

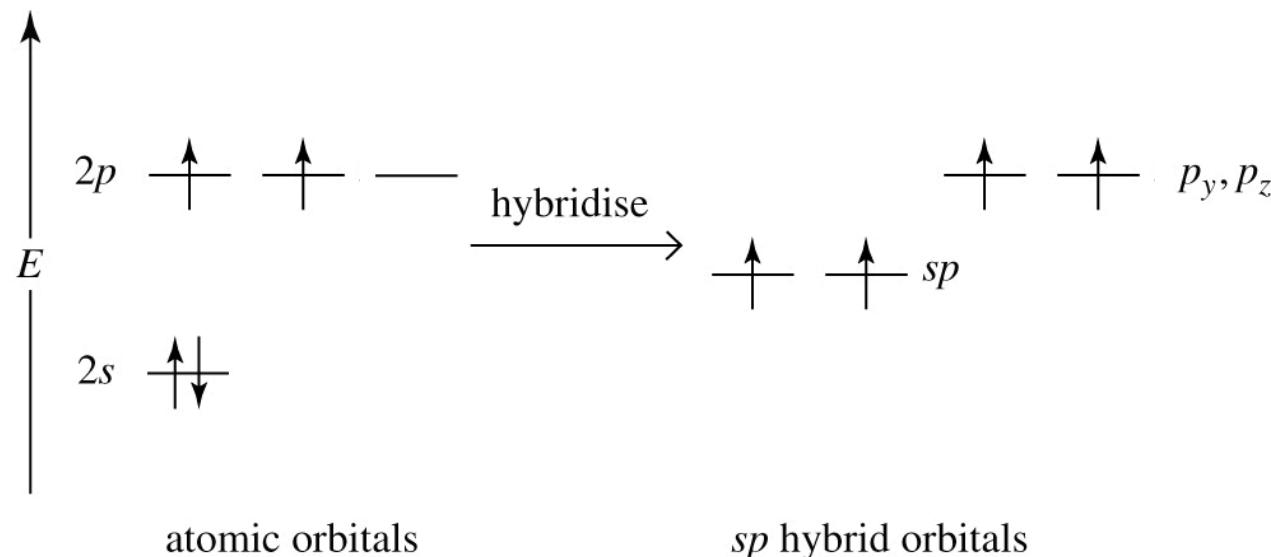
- the electrons in the atomic  $p$  orbitals of neighbouring C's can overlap to form a  $\pi$  bond.

## Double C=C bond



# hybridisation: $sp$

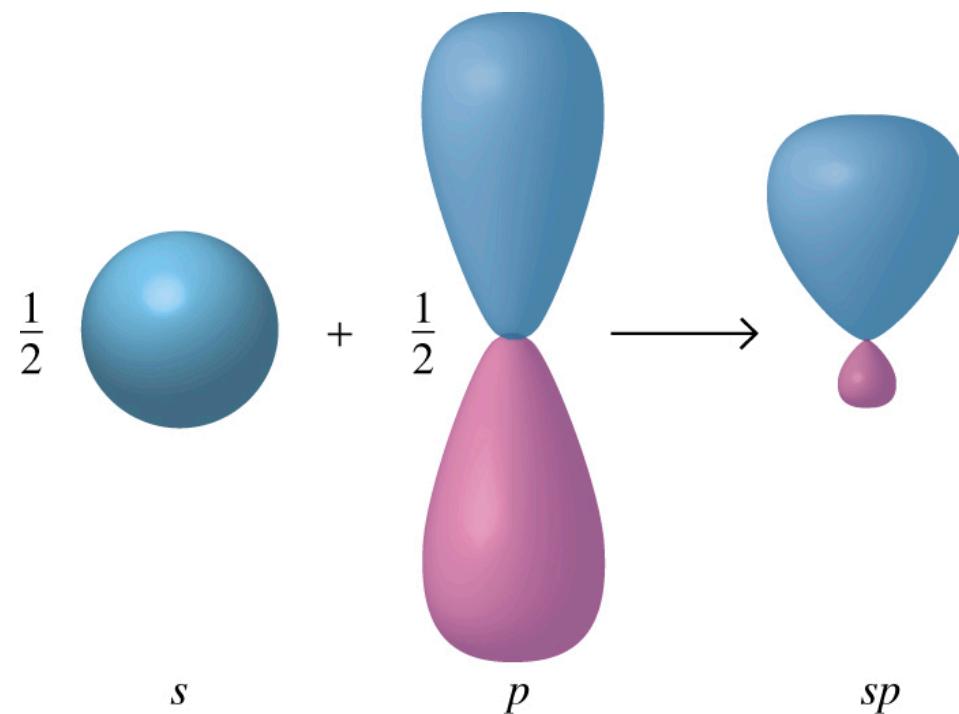
- in some cases, the  $s$  orbital mixes only with **one** of the three  $p$  orbitals to form  $2 \times sp$  hybrid orbitals, leaving the other two  $p$  orbitals unhybridised
- two of the 4 valence electrons of C are re-distributed into equivalent  $sp$  orbitals, with the remaining two residing in the atomic  $p$  orbitals:



# hybridisation: *sp*

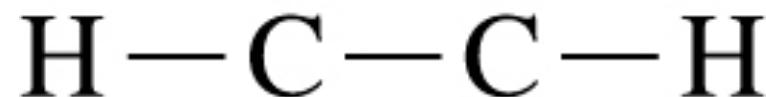
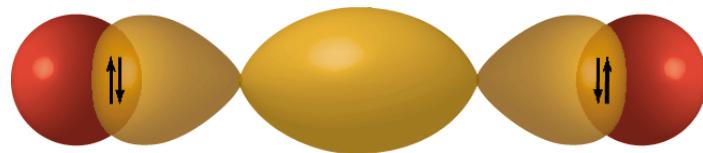
- *sp* hybrid orbitals have a physical shape that reflects the constituent pure atomic orbitals:

$$2 \times sp = (1 \times s) + (1 \times p)$$

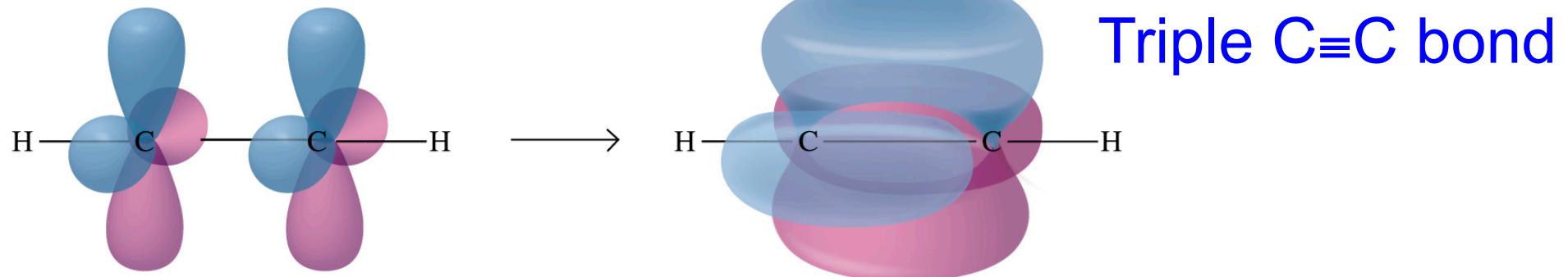


# hybridisation: $sp$

- Example: ethyne:

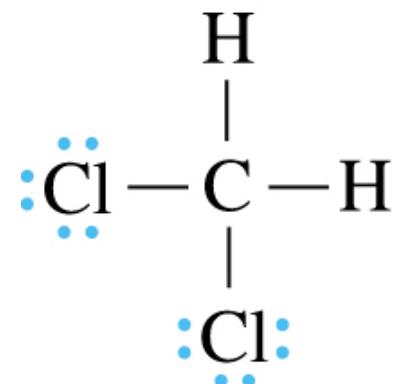


- the  $sp$  orbitals on the two carbon atoms form  $\sigma$  bonds with the  $1s$  orbitals of H and between each other.
- electrons in the two atomic  $p$  orbitals ( $p_x$  &  $p_y$ ) of neighbouring C's can overlap to form two  $\pi$  bonds.

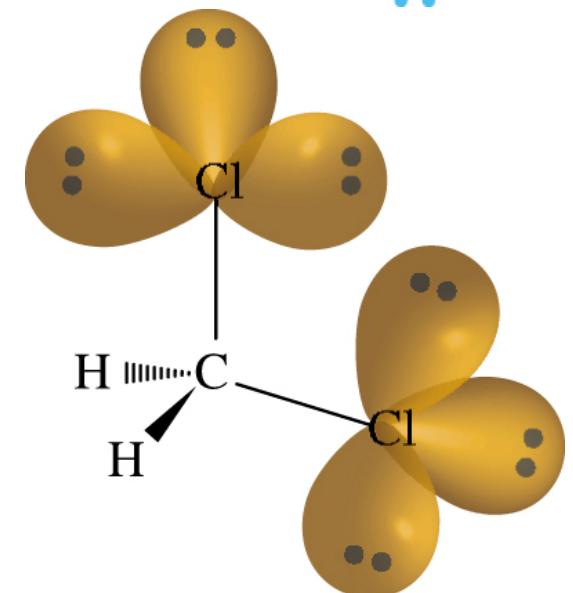
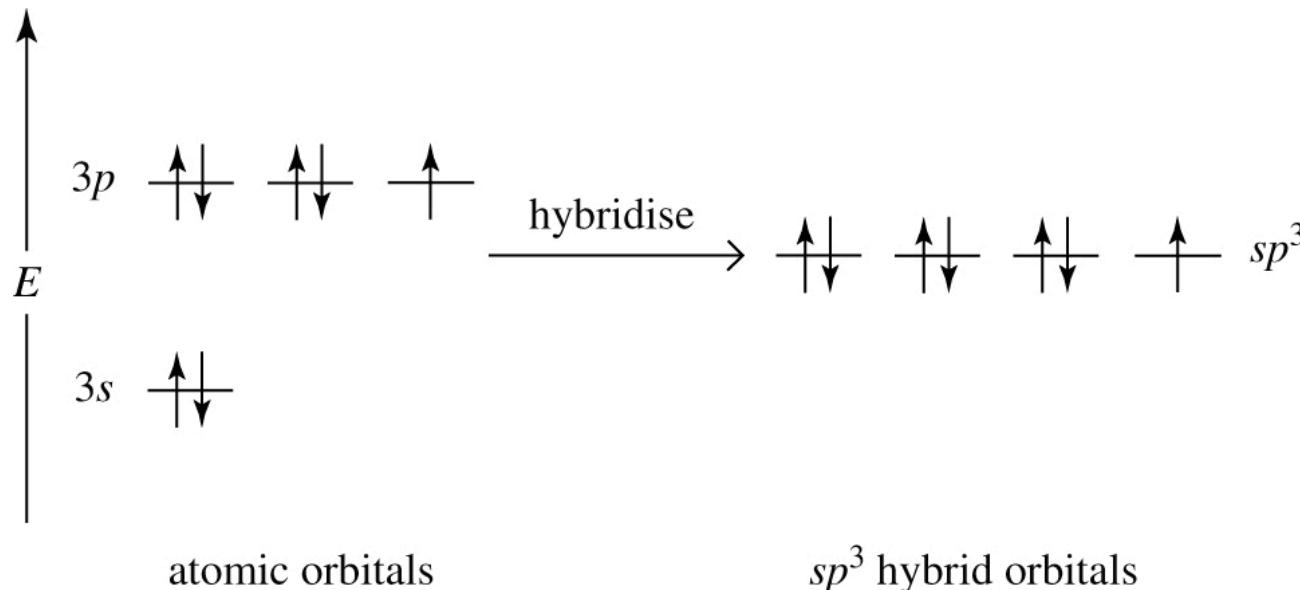


# hybridisation is not unique to C

- dichloromethane is  $\sim T_d$  about C ( $sp^3$ ) & has an  $AXE_3$  arrangement about Cl - distorted  $T_d$ .....?

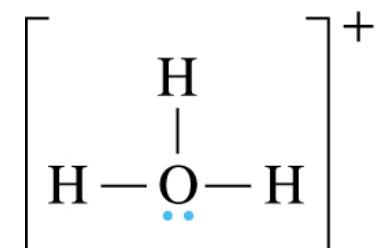


- Cl is **also**  $sp^3$  hybridised

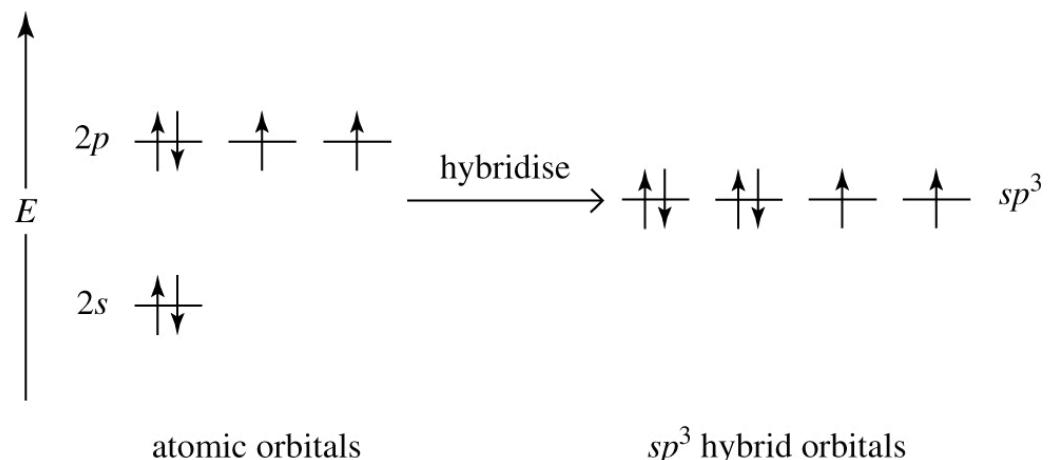
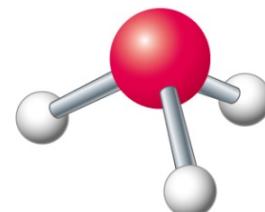
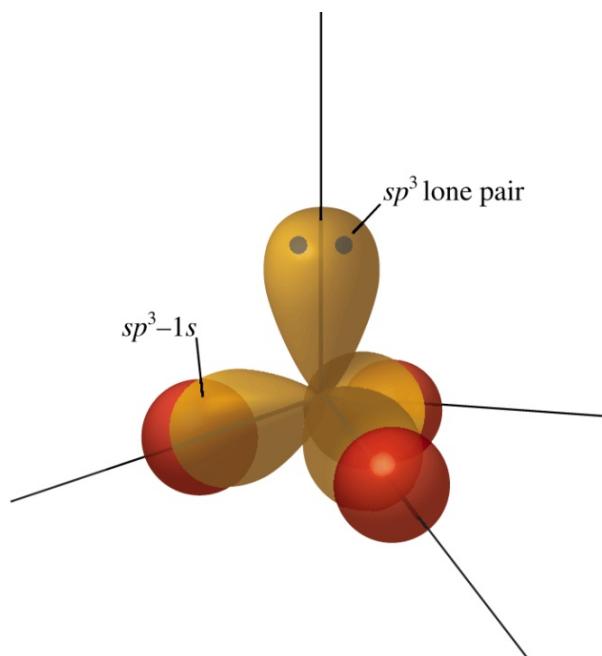


# hybridisation is not unique to C

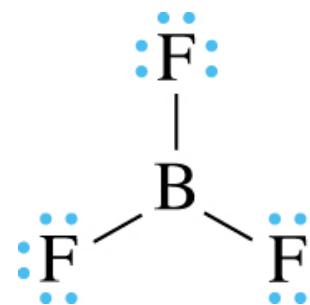
- the hydronium ion is ***trigonal pyramidal*** - what is the hybridisation about the O atom?



- O is  $sp^3$  hybridised:

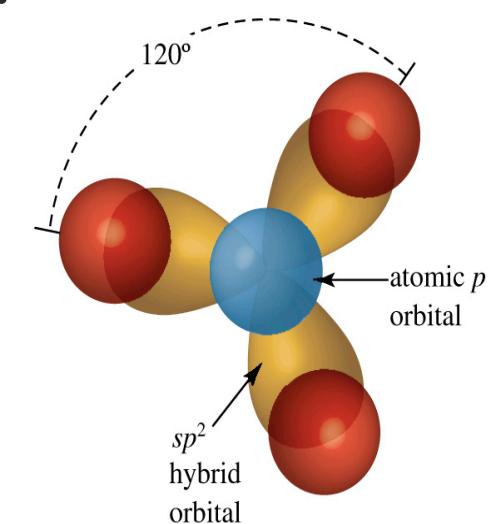
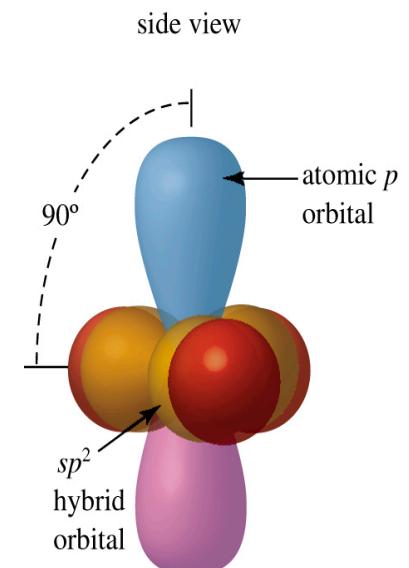
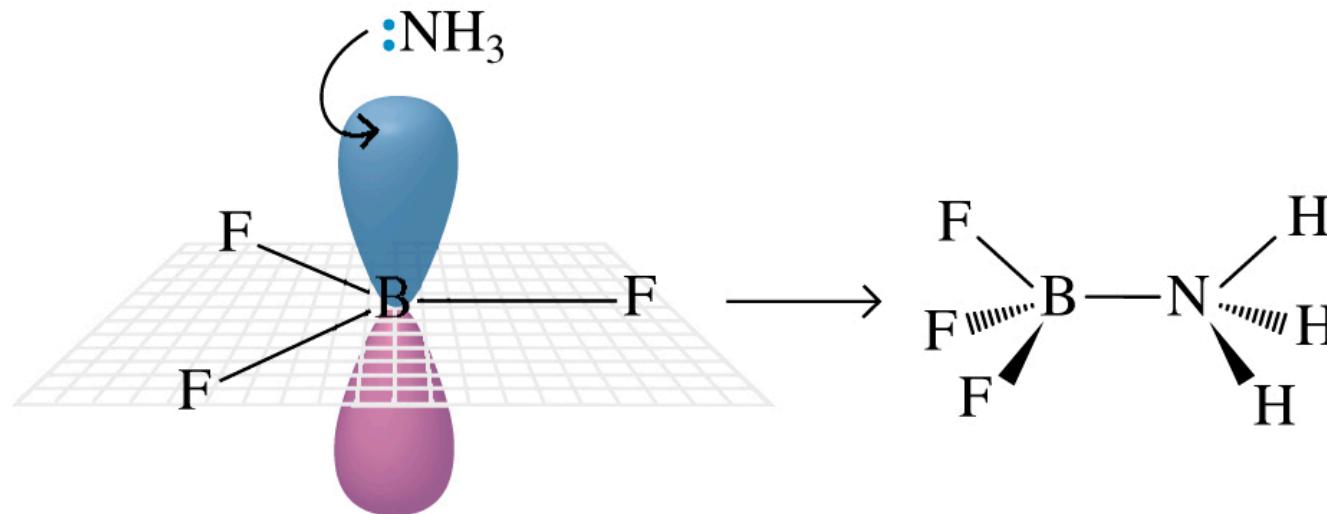


# remember electron-deficient $\text{BF}_3$ ?



- $\text{BF}_3$  is  $sp^2$  hybridised, sharing only 6 electrons
- one  $p$  orbital is vacant.

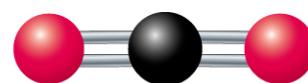
- $\text{BF}_3$  is susceptible to attack by electron-rich species to get an octet:



# VB hybridised schemes can account for the common geometries seen earlier

Linear

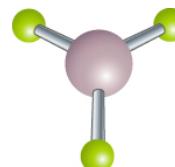
180°



$$s + p \rightarrow 2 sp$$

Trigonal planar

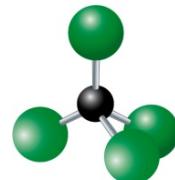
120°



$$s + 2 p \rightarrow 3 sp^2$$

Tetrahedral

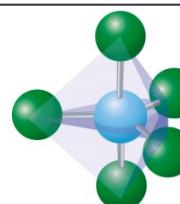
109.5°



$$s + 3 p \rightarrow 4 sp^3$$

Trigonal bipyramidal

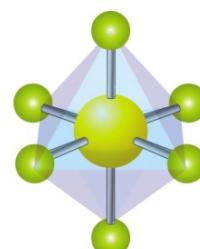
120° equatorial, 90° axial



$$s + 3 p + d \rightarrow 5 sp^3d$$

Octahedral

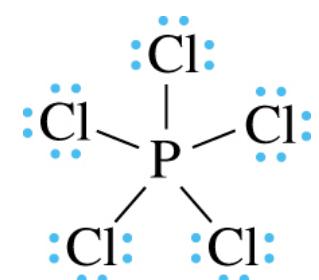
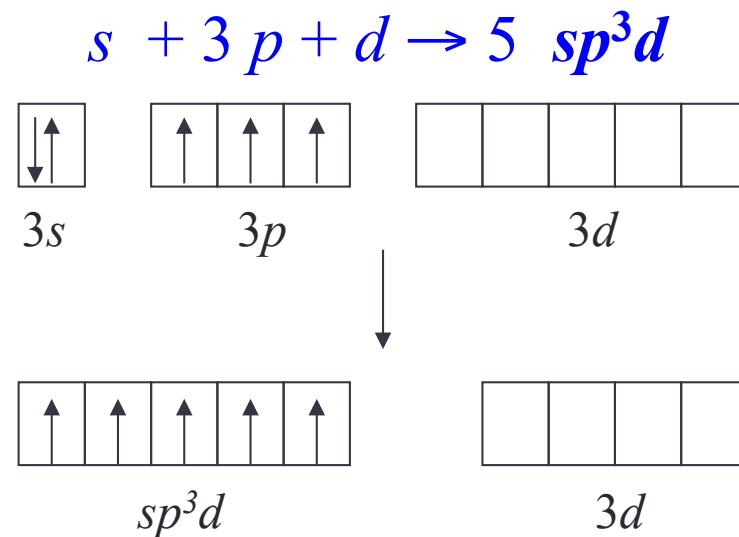
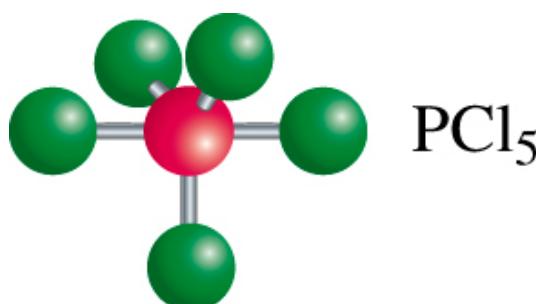
90°



$$s + 3 p + 2 d \rightarrow 6 sp^3d^2$$

# hybridisation with *d* orbitals

- in order for an atom to form more than four bonds around it, the *d* orbitals are needed for hybridisation.
- the lowest energy *d* orbitals are the  $3d$  orbitals; they can only hybridise with orbitals of similar energy and position, like the  $3s$  and  $3p$  orbitals.
- this explains why the 1st and second period elements **do not** exceed the **octet rule** (" $2d$ " orbitals do not exist!).



# Thank you