Module 3, Lecture 2

Structure and Reactions of Organic Molecules

Part 2 – Bonding, VSEPR and valence bond theory

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References to Brown *et al* text shown in BLUE

1

Learning Objectives:

- **to be able to use VSEPR theory to predict molecular shape**
- **to have an understanding of valence bond theory**
- **to have an understanding of why orbitals are hybridised.**

Textbook: **Chapter 9, sections 9.1-9.6, Chapter 22, section 24.3 Brown**

2

Molecular shape

Lewis structures can be a very helpful way to understand how electrons are arranged in molecules.

However, they do not tell us two important things.

1. What is the three-dimensional shape of the molecule.

2. What sorts of orbitals are the electrons in when the molecule is formed

We will now look at these two issues.

3

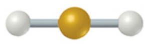
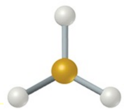
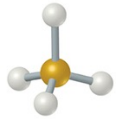
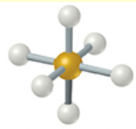
Valence Shell Electron Pair Repulsion (VSEPR) theory

VSEPR theory provides a way to work out the 3-D shape of a molecule.

It is based on the idea that pairs of electrons will be repelled from other pairs of electrons around an atom, so the shape the molecule adopts will be the one where these electron pair repulsions are best minimised.

In order to work out the shape of a molecule using VSEPR theory, we must first determine its Lewis Structure.

4

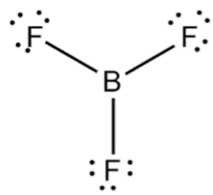
Number of sets of electron pairs *Electron domains*	Geometry of sets of electron pairs *Electron domains*		
2	Linear		180°
3	Trigonal planar		120°
4	Tetrahedral		109°
5	Trigonal bipyramidal		120° and 90°
6	Octahedral		90°

Textbook: Chapter 9

Three sets of electron pairs – Trigonal Planar Geometry

Consider the molecule boron trifluoride **BF_3**

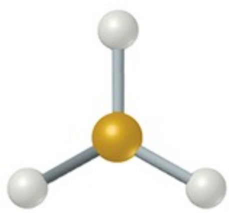
A Lewis structure for **BF_3** would look like this:



The central boron atom has three sets of electrons around it – one for each of the shared pairs forming the B-F bonds.

The lone pairs on the F atoms do not affect the overall shape.

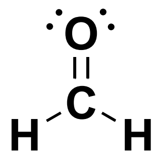
Thus the shape of the molecule is trigonal planar



Three sets of electron pairs – Trigonal Planar Geometry

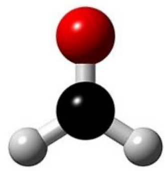
Consider the molecule **methanal** (formaldehyde) $\mathbf{CH_2O}$

A Lewis structure for methanal would look like this:



VSEPR makes no distinction between electron pairs in single, double or triple bonds

The central carbon atom has three sets of electrons around it – one for each of the shared pairs forming the C-H bonds, and one comprising the two pairs of shared electrons forming the two C-O bonds.

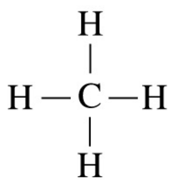


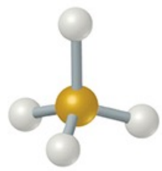
Thus the shape of the molecule is trigonal planar

7

Four sets of electron pairs – Tetrahedral Geometry

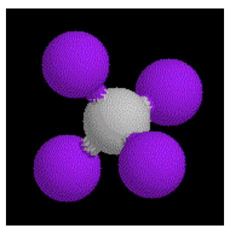
First, we consider methane, $\mathbf{CH_4}$





The Lewis structure for methane shows that there are four shared pairs of electrons around the central carbon atom.

VSEPR theory therefore indicates that the methane molecule has a tetrahedral structure.

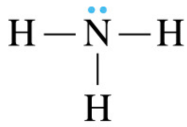


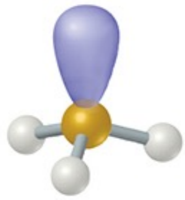
8

Four sets of electron pairs

Now, consider ammonia, **NH_3**

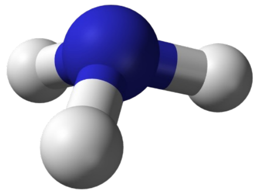
The Lewis structure is





The central nitrogen has four sets of electrons around it, so **the electron pairs** are arranged in a **tetrahedral** fashion.

However, only three of these are shared pairs and the shape of the molecule is **defined by the arrangement of the bonds.**



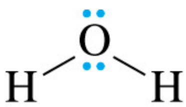
The ammonia molecule therefore has a **trigonal pyramidal** shape

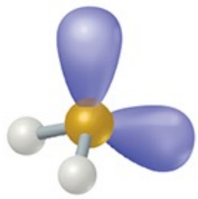
9

Four sets of electron pairs

Now consider water, **H_2O**

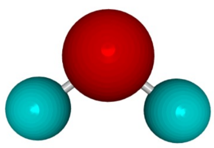
The Lewis structure is:





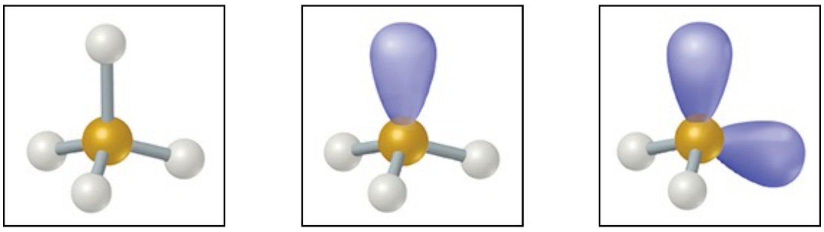
The central oxygen again has four sets of electrons around it, so **the electron pairs** will be **tetrahedrally** arranged.

However, only two of these are shared pairs, forming O-H bonds, so the shape is defined by these – **bent**



10

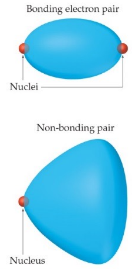
tetrahedral	trigonal pyramidal	bent



CH_4	NH_3	H_2O
4 Shared (bonding) pairs **0 Lone pairs**	**3 Shared (bonding) pairs** **1 Lone pair**	**2 Shared (bonding) pairs** **2 Lone pairs**

Note that lone pairs are actually more repelling than shared pairs.

This means that while the H-C-H bond angle in CH_4 is 109°, the H-N-H angle in NH_3 is actually 107° and the H-O-H bond angle in H_2O is 104.5°



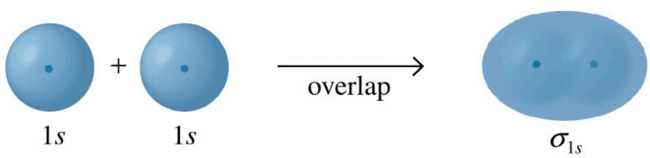
▲ FIGURE 9.7 Relative volumes occupied by bonding and non-bonding electron domains.

Valence Bond Theory

VSEPR helps us understand the shape of a molecule.

Need to consider the sorts of orbitals, bonding and lone pairs of electrons occupy.

Valence Bond Theory says in making a bond between two atoms, **half-filled atomic orbitals**, in which valence electrons from each atom lie, **overlap** to make a new orbital in which the pair of electrons exist.



1 electron in each atomic orbital

A pair of electrons in the new sigma (σ) orbital

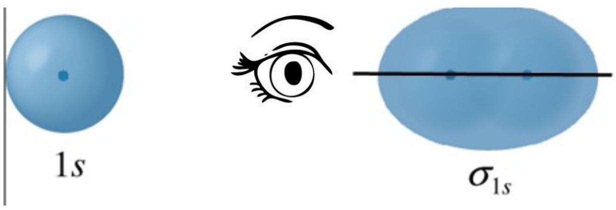
s orbitals and σ orbitals

A σ (sigma) orbital is spherically symmetrical about the internuclear axis.

End on a σ orbital "looks" like a s orbital

Arabic "s" in Greek is "σ"

So Arabic letters for atomic orbitals and Greek letters for molecular orbitals

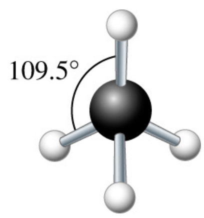


σ orbital
end on

13

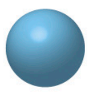
Bonding in methane

We have seen the Lewis structure and VSEPR theory suggest that methane should have a tetrahedral structure, with the H-C-H bonds at 109.5° to each other.

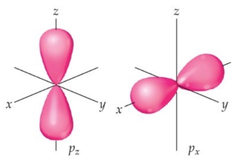


The electron configuration of carbon is $1s^2$ **$2s^2$ $2p^2$**.

So, the valence electrons on the carbon atom are in two different types of atomic orbitals.



2 are in a 2s orbital



2 are in 2p orbitals

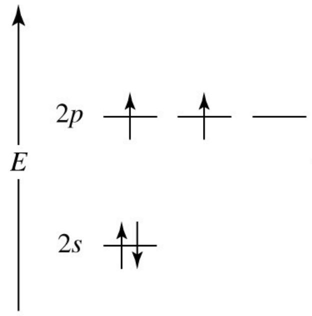
14

Bonding in methane

Overlapping the 1s orbitals on each of the hydrogens with the half filled orbitals on the carbon will only make two C-H bonds i.e. $:CH_2$.

The bonds will be at 90° to each other.

While a simple bonding theory, it does not account for experimental observation.



atomic orbitals
Carbon atom

15

Bonding in methane

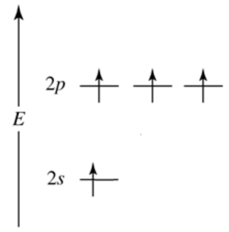
What we need is four half-fill orbitals.

Overlapping the 1s orbitals on each of the hydrogens with the half filled orbitals on the carbon will now make four C-H bonds.

One bond will be different from the other three.

Experimental evidence shows all four bonds are the same.

Still not a good model.



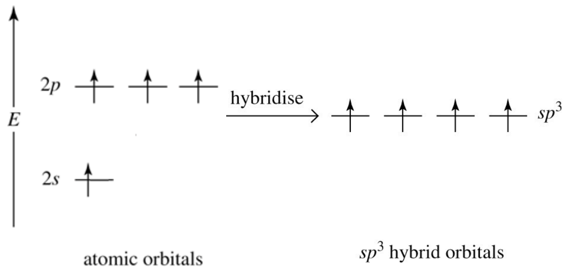
atomic orbitals

16

Bonding in methane

What we need is four half-fill orbitals, which are all the same, and so will lie at 109^o to each other.

This can be achieved by mixing the wavefunctions of the 2s and 2p orbitals together to make new types of orbitals – **hybrid orbitals**



four atomic orbitals

four hybrid orbitals

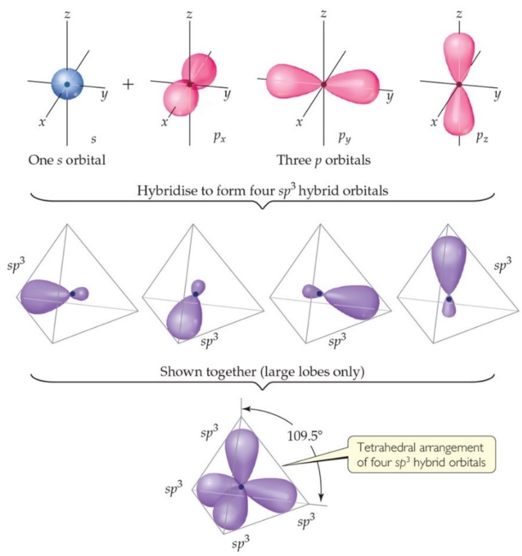
one s orbital three p orbitals

sp^3

Cannot create or destroy orbitals!

17

Bonding in methane

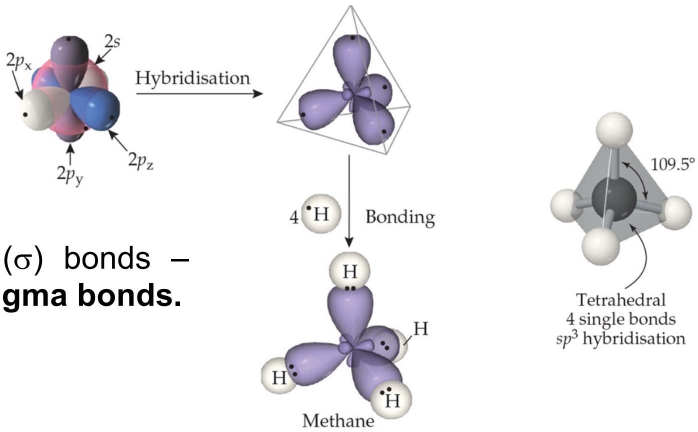


Textbook: **Chapter 24, section 24.3 Brown**

18

Bonding in methane

Now can overlap each of these sp^3 hybrid orbitals with a 1s orbital on the hydrogen atom to make the four bonds we need.



Note that these will be sigma (σ) bonds – **hybrid orbitals always lead to sigma bonds.**

Textbook: **Chapter 24, section 24.3 Brown**

19

✱ Homework ✱

Chemistry – the central science 15th Ed

Brown et al.

Problems 9.18, 9.22, 9.30

Answers on Blackboard

20