

## Extension 4: Valence Bond Model and Hybridization

### 1. Prerequisites

The key ideas required to understand this section are:

Topic	Book page
VSEPR theory	67
More advanced ideas about electronic structure	43
Electron density map for hydrogen	57
Better model for bonding in alkenes	333

### 2. The Valence Bond model and hybridization of orbitals

So far, we have used Lewis structures and VSEPR theory to model covalent bonding between elements predict and the shapes of the molecules that result. These two theories are models and, although they are very useful, like all scientific models they are not perfect.

The Valence Bond model (developed by Linus Pauling; see page 63 of the book) describes bonding when we stop thinking of electrons as dots or crosses and start thinking of them as occupying orbitals.

Bond formation occurs when the electron clouds on two atoms overlap, and two electrons of opposite spin are paired up in the overlapping orbitals. The overlap increases the probability of finding the electrons between the two nuclei – ‘gluing the nuclei together’. A picture of this, for the  $H_2$  molecule, is shown on page 57 of the book. So far, so good, but with more complicated molecules, such as water, the theory needs to be expanded to explain molecular shapes.

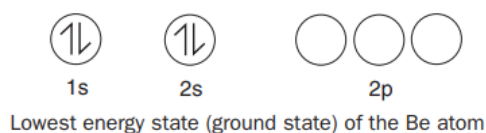
We know water is a bent molecule with a bond angle of  $105^\circ$ . Oxygen has two unpaired electrons (one in each of two p orbitals), and the hydrogens have one s electron each. What would you expect the bond angle of water to be from the simple overlap model? Think of the shapes of s and p orbitals – the bond angle would be expected to be  $90^\circ$ !

Quantum mechanical calculations can explain why the predicted bond angle is not the same as that measured. These calculations lead to the conclusion that the arrangement of the orbitals in the oxygen atom in the water molecule is not the same as the arrangement in the isolated atom.

The atomic orbitals in the oxygen atom **mix** to give a new set of atomic orbitals called hybrid orbitals. This process is called hybridization. Hybrid orbitals have shapes and orientations that are different from the atomic orbitals in isolated atoms. They arrange themselves as far apart as possible to minimise repulsion of the paired electrons within them.

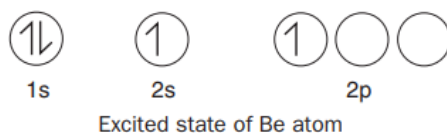
### 3. sp hybridization

For example, when Be bonds with Cl to make the molecule  $BeCl_2$ ; the electron arrangement in the isolated Be atom is as follows:

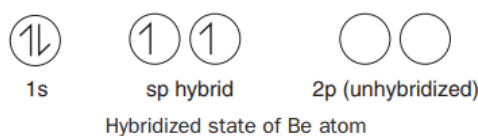


There are no unpaired electrons, and since covalent bonds are formed by the pairing of electrons with opposite spin, how does Be bond with Cl?

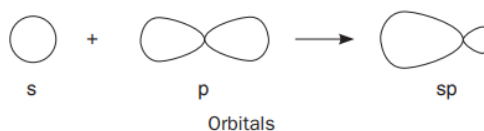
A 2s electron is transferred (or excited) to one of the 2p orbitals:



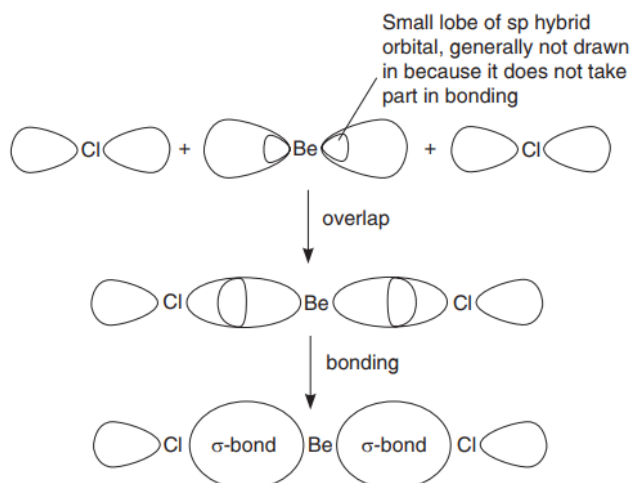
The Be atom now has two unpaired electrons to bond with two chlorine atoms, but we still need to explain why  $\text{BeCl}_2$  molecules are linear. On bonding the 2s and one 2p orbital 'mix' to form two new identical hybrid orbitals, each of which is occupied by one unpaired electron. Because the new orbitals are formed from one s and one p orbital, they are called **sp hybrid orbitals**. The Be atom now has an electron arrangement as follows:



The shapes of the new hybrid sp orbitals are shown below:



The two sp orbitals lie at an angle of  $180^\circ$ . Each overlaps with a 3p orbital from a chlorine atom and two electrons (one from Be, one from Cl), which are paired up in each region of overlap to form two identical covalent bonds.



Each bond between Be and Cl is a sigma ( $\sigma$ )-bond;  **$\sigma$ -bonds are formed when there is a high concentration of electron density between two nuclei**. The molecule is linear.

## 4. $sp^2$ hybridization

For example, when B bonds with F to make the molecule  $\text{BF}_3$  (a trigonal planar molecule) some of the atomic orbitals in B hybridize as shown in the following steps:



Lowest energy state (ground state) of the B atom

Now one of the paired 2s electrons gets promoted to the 2p orbital, so there are three unpaired electrons in all:



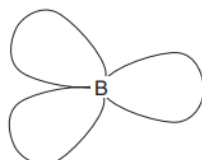
Excited state of B atom

On bonding, one s and two p orbitals mix to get three  $sp^2$  hybrid orbitals

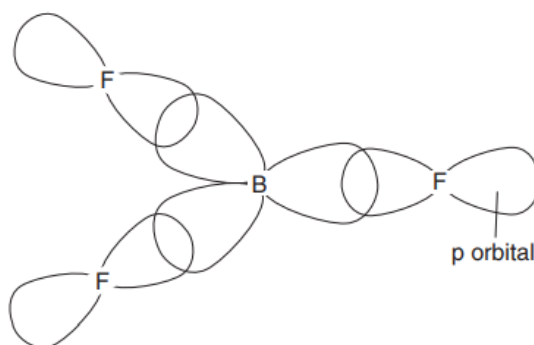


Hybridized state of B atom

**Notice that the number of hybrid orbitals formed is always the same as the number of atomic orbitals that are mixed together to make them (in this case three).** The three  $sp^2$  hybrid orbitals are arranged in one plane and  $120^\circ$  apart:


 $sp^2$  hybrid orbitals

Each overlaps with a 2p orbital on an F atom and the six valence electrons (three from B and one from each F) form three  $\sigma$ -bonds:



## 5. $sp^3$ hybridization

For example, when C bonds with H to make  $CH_4$  (a tetrahedral molecule), some of the atomic orbitals hybridize as follows:



Ground state of C atom

Now one of the paired 2s electrons gets promoted to the empty 2p orbital so there are four unpaired electrons in all:



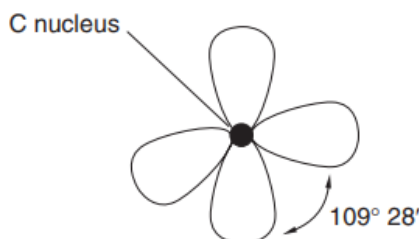
Excited state of C atom

On bonding, one s and three p orbitals mix to get four  $sp^3$  hybrid orbitals:

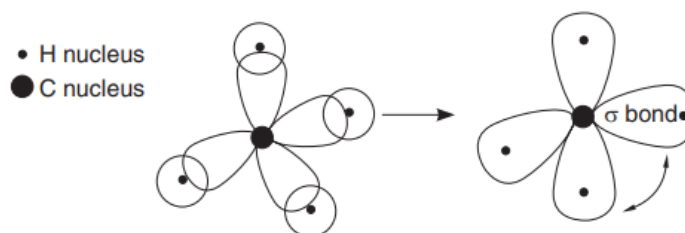


Hybridized state of C atom

The four  $sp^3$  hybrid orbitals are arranged in a tetrahedral shape:



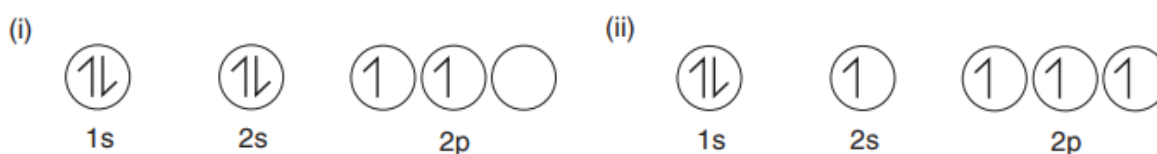
Each overlaps with 1s orbital on an H atom and the eight valence electrons (four from C and one from H) form four  $\sigma$ -bonds.



Note that it takes energy for boron or carbon to promote electrons to vacant orbitals, but more than enough energy is 'got back' by the formation of extra covalent bonds, making the process worthwhile.

## 6. The bonding in ethene

In ethene,  $C_2H_4$ , each carbon atom is  $sp^2$  hybridized:



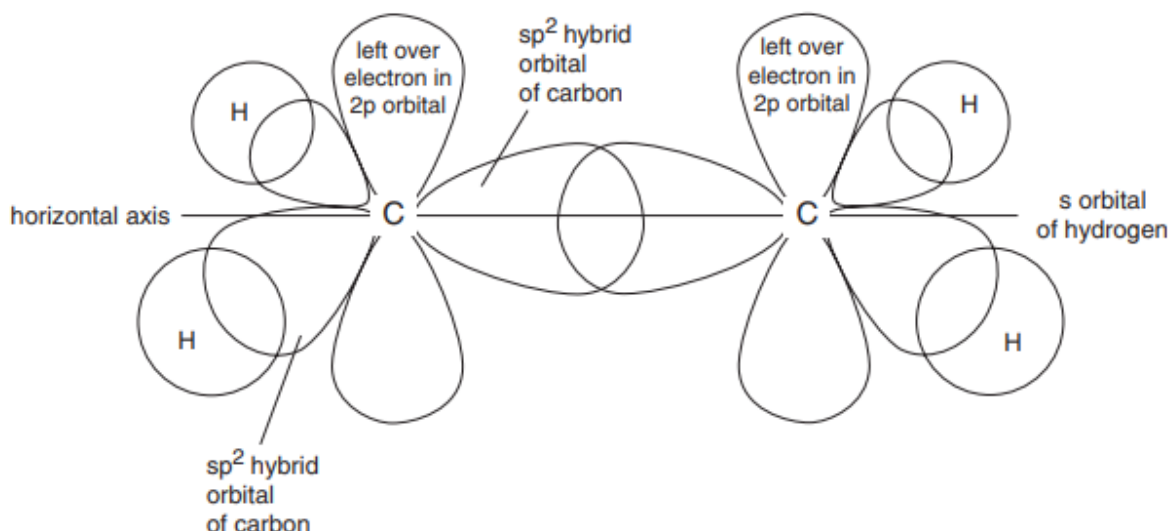
Ground state of C

Excited state of C

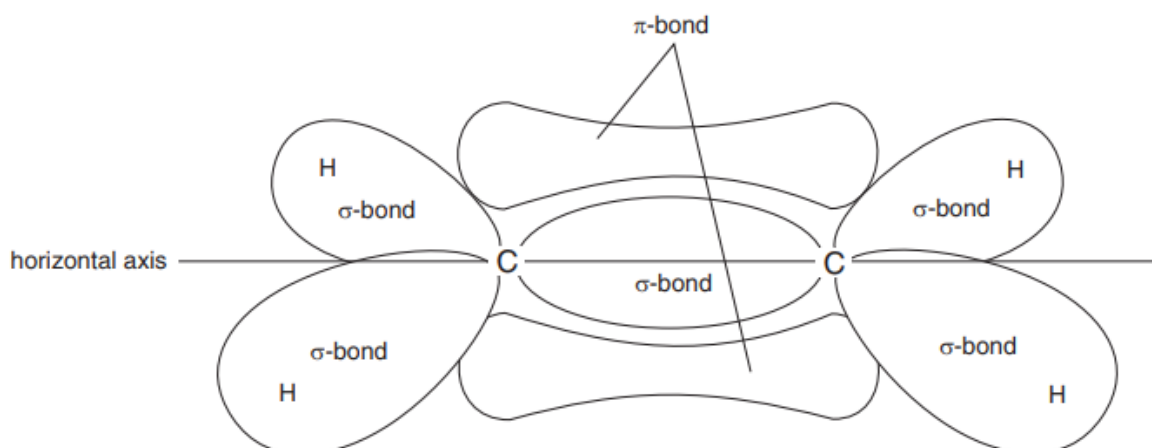


$sp^2$  hybridized state of C

A  $\sigma$ -bond framework arises from the  $sp^2$  orbitals on each carbon atom with each other and with the 1s orbitals on two hydrogen atoms.



Two unpaired electrons, each one in an unhybridized  $2p$  orbital on each carbon atom, are left over. These  $2p$  orbitals overlap sideways and the electron pair formed occupies a new orbital with electron density above and below the plane of the molecule. The bond now formed is a  $\pi$ -bond (see page 333 in the book).

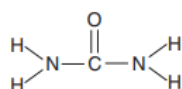


## EXERCISE 4A

Use the Valence Bond model and hybridization of orbitals theory to explain the shapes of (i) the ammonia molecule,  $\text{NH}_3$ ; (ii) the water molecule  $\text{H}_2\text{O}$ .

## Revision Questions

- Draw Lewis structures for the following molecules:
  - $\text{NF}_3$ .
  - $\text{N}_2\text{O}$  (O is the central atom).
  - $\text{GeH}_4$  (Ge has four electrons in the outer shell of its atoms).
  - $\text{HOBr}$  (O is the central atom and Br has seven electrons in the outer shell of its atoms).
- Draw a Lewis structure for the fertilizer urea. Its structural formula is:



3. Which of the following pairs forms the more polar bond?

- (i) C-H or Si-H?
- (ii) S-O or S-S?
- (iii) Br-Cl or Br-F?

4. Write a Lewis structure for the azide ion  $\text{N}_3^-$ . The actual structure of the ion is a resonance hybrid of two different structures – can you write its structural formula?

5. In terms of Valence Bond theory and hybridization of orbitals, describe the bonding in  $\text{C}_2\text{H}_2$ , (a linear molecule).

## Answers

### Exercises

#### Exercise 4A

(i) A nitrogen atom forms  $sp^3$  hybrid orbitals as follows:



(promotion of an electron from  $2s \rightarrow 2p$  would not bring an increase in the number of unpaired electrons). The three bonding electrons and lone pair electrons are in  $sp^3$  hybrid orbitals; the bonding electrons overlap with three electrons in  $1s$  orbitals from three hydrogen atoms and pair up to form three  $\sigma$ -bonds. The lone pair and three bonds are arranged in an *approximately* tetrahedral shape (remember that the lone pair of electrons push bonding pairs of electrons closer together than the tetrahedral angle of  $109.5^\circ$ ).

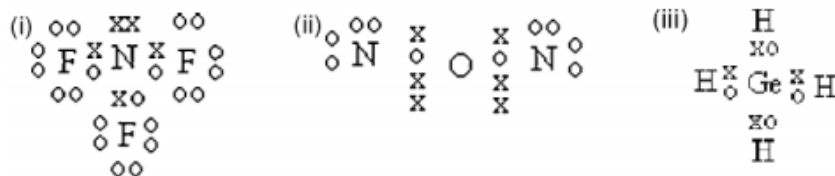
(ii) The bonding orbitals in an oxygen atom hybridize as follows:



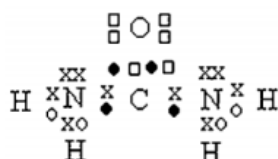
The two unpaired electrons in  $sp^3$  hybrid orbitals overlap with two hydrogen  $1s$  electrons in  $1s$  orbitals from two hydrogen atoms and pair up to form two  $\sigma$ -bonds. The lone pairs and two bonds are arranged in an *approximately* tetrahedral shape (remember that the two lone pairs of electrons push the two bonding pairs of electrons much closer together than the tetrahedral angle of  $109.5^\circ$ ).

### Revision Questions

1.



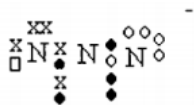
2.



3.

- (i) C-H.
- (ii) S-O.
- (iii) Br-F.

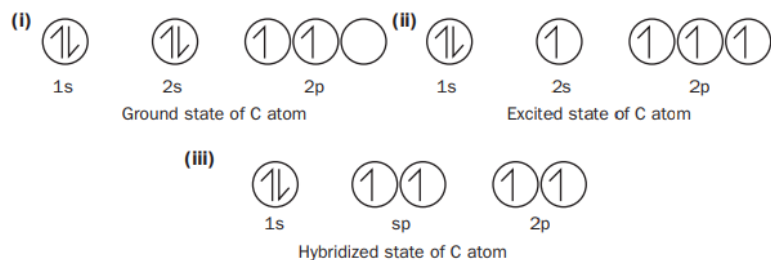
4.



x, o, ♦ = electrons from N's

♦ = electron from -ve charge

5. In ethyne,  $C_2H_2$ , each carbon atom is  $sp$  hybridized:



A linear  $\sigma$ -bond framework arises from overlap of the  $sp$  orbital on each C with the  $1s$  orbital of C and the  $sp$  orbital on the other C. This leaves two unpaired electrons in  $2p$  unhybridized orbitals on each C. They overlap to form two  $\pi$ -bonds, as shown in the diagram below.

