

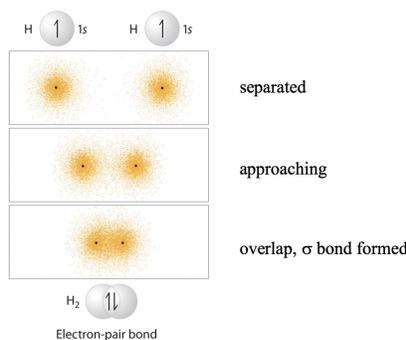
1.6: Valence Bond Theory and Hybridization

1.6.1 Valence Bond Theory

We have talked about how covalent bonds are formed through the sharing of a pair of electrons; here we will apply the **valence bond theory** to explain in more detail how the sharing happens. The valence bond theory describes the covalent bond formed from the overlap of two half-filled atomic orbitals on different atoms.

Let's start with the simple molecule H_2 . The atomic electron configuration of a hydrogen atom is $1s^1$, meaning that there is one electron (which is also the valence electron) in the sphere-shaped $1s$ orbital.

When two hydrogen atoms are approaching each other, the two $1s$ orbitals overlap, allowing the two electrons (each H donates 1 electron) to pair up for the bonding with the overlapping orbitals. The shared pair of electrons are under the attraction of both hydrogen nuclei simultaneously, resulting in them serving as a "glue" that holds the two nuclei together.



Formation of H-H σ bond

Figure 1.6a Formation of H-H bond

The overall energy changes of the system *versus* the distance between the two hydrogen nuclei can be summarized in the energy diagram below.

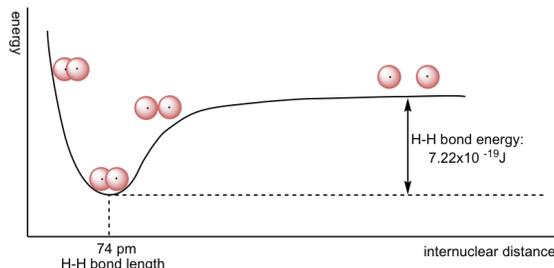


Figure 1.6b Potential energy of the hydrogen molecule as a function of internuclear distance

When the two atoms are separate, there is no overlap and no interaction. As they are getting closer, orbitals start to overlap, and there is attraction between the nucleus of one atom and the electron of the other atom, so the total energy of the system lowers. The energy lowers to its minimum level when the two atoms approach the optimal distance. The optimal distance is also defined as the **bond length**. H_2 molecules have a bond length of 74 pm (often referred to as 0.74 Å, $1\text{Å} = 10^{-10}\text{m}$). The energy difference between the most stable state (lowest energy state with optimum distance) and the state in which the two atoms are completely separated is called the **bond (dissociation) energy**. The bond energy is 7.22×10^{-19} J for one H-H bond, or 435kJ/mol.

When the two atoms get closer than the optimal distance, the repulsion between the two nuclei become predominant, and the energy of the system becomes even higher.

Another important character of the covalent bond in H_2 is that the two $1s$ orbitals overlap in a way that is referred to as head-to-head. The bond formed by head-to-head overlap is called **σ (sigma) bond**. σ bonds are cylindrically symmetrical, meaning if a cross-sectional plane is taken of the bond at any point, it would form a circle.

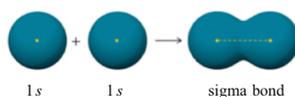


Figure 1.6c Cylindrical symmetry property of σ bond

The valence bond theory works well to explain the bonding in HF as well, with the 2p orbital of fluorine atom involved in the overlapping.

The fluorine atom has the valence electron configuration of $2s^2 2p^5$ as shown in the orbital diagram.

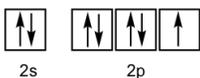


Figure 1.6d Orbital diagram of valence electrons in fluorine atom

For the three 2p orbitals, two of them are filled and the other one is half-filled with one single electron. The filled orbital cannot form bonds, so only the half-filled 2p is available for overlap. Therefore, the 1s orbital of the hydrogen atom overlaps head-to-head with the half-filled 2p orbital of the fluorine atom to form the H-F σ bond, as shown below.

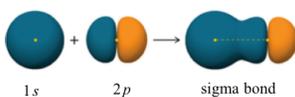


Figure 1.6e H-F σ bond

A σ bond can also be formed through the overlap of two p orbitals. The covalent bond in molecular fluorine, F_2 , is a σ bond formed by the overlap of two half-filled 2p orbitals, one from each fluorine atom as shown here.

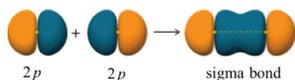


Figure 1.6f F_2 σ bond

However, when the valence bond theory is applied to organic molecules, for instance CH_4 , it does **not** work. The valence electron configuration of carbon atom is $2s^2 2p^2$ as shown in the orbital diagram.

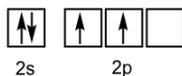


Figure 1.6g Orbital diagram of valence electrons in carbon atom

Based on the valence bond theory, with two half-filled orbitals available, the carbon atom should be able to form two bonds. However, carbon always has four bonds in any stable organic compound. To explain the bonding of carbon and other atoms that cannot fit into the simple valence bond theory, a new theory called orbital **hybridization** will be introduced as a supplement to the valence bond theory.

1.6.2 Hybridization and the Structure of CH_4

Simply speaking, hybridization means the mathematical combination of several orbitals to generate a set of new hybrid orbitals.

In the hybridization for CH_4 , the 2s and three 2p orbitals are combined to give a new set of four identical orbitals, that are called **sp^3 hybrid orbitals**. The symbol **sp^3** here identify the numbers and types of orbitals involved in the hybridization: **ones** and **three p** orbitals. For the hybridization process,

$$\text{number of hybrid orbitals} = \text{the total number of atomic orbitals that are combined}$$

It means that with total four orbitals combined, four new hybrid orbitals are generated, and they all named as **sp^3 hybrid orbitals**. These new hybrid orbitals are all in the same energy level that is between those of 2s and 2p orbitals, and are directed in a tetrahedral shape overall with the angle between any two orbitals as 109.5° . Each sp^3 hybrid orbital has two lobes that are very different in size. The lobe with the larger size is in the positive phase and is responsible for bonding.

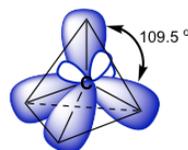
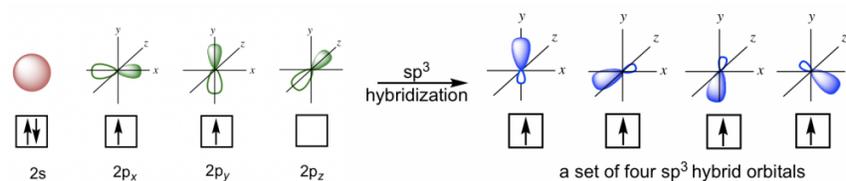


Figure 1.6h Four sp^3 hybrid orbitals oriented in tetrahedral shape

Since there are four sp^3 hybrid orbitals available, each of the four valence electrons occupies one of them, so there are four half-filled sp^3 orbitals in the carbon atom that are able to form four bonds. Therefore, the C-H bond of CH_4 is formed by the overlapping between the $1s$ orbital in the hydrogen atom and the sp^3 orbital in the carbon atom.

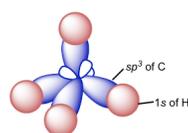


Figure 1.6i Orbital overlap of C-H bonds in methane

Because the arrangement of the four sp^3 hybrid orbitals is in a tetrahedral, the shape of the CH_4 molecule is also a tetrahedral, which is consistent with the shape predicted by VSEPR. The tetrahedral shape of the sp^3 carbon can usually be drawn using the solid and dashed wedges. Out of the four bonds, the two bonds that lie within the paper plane are shown as ordinary lines, the solid wedge represent a bond that point out of the paper plane, and the dashed wedge represent a bond that point behind the paper plane. These perspective drawings that show the 3D tetrahedral shape is particularly important in the discussion of stereochemistry in **Chapter 5**.

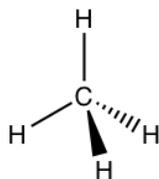


Figure 1.6j Tetrahedral shape of methane with solid and dashed wedges drawing

1.6.3 Hybridization and VSEPR

Other than sp^3 hybridization, there are also other types of hybridization that include sp , sp^2 , sp^3d and sp^3d^2 . Usually the hybridization on a certain atom can simply be determined by counting the total number of electron groups (bonding pairs and lone pairs). **The total number of electron groups just equals the total number of orbitals involved in the certain hybridization.** For example, in a CH_4 molecule, the central carbon atom has four 4 bonding pairs, so the hybridization of carbon is sp^3 (one s and three p orbitals, $1+3=4$). If a central atom has total five 5 electron groups (bonding pairs and lone pairs all together) around, then the hybridization is sp^3d (ones, three p and one d orbitals, $1+3+1=5$).

This correlation may remind you of VSEPR. Hybridization and VSEPR are two separate concepts, however they can be correlated together via the number of electron groups in common. The following table is very useful in correlating the hybridization and VSEPR shape/bond angles around the central atom and the total number of electron groups together.

Hybridization on central atom	Total number of electron pairs (BP and LP) around central atom	Geometry (Shape) of electron groups (electron pairs)

sp	2	linear
sp ²	3	trigonal planar
sp ³	4	tetrahedral
sp ³ d	5	trigonal bipyramidal
sp ³ d ²	6	octahedral

Table 1.3 Correlation between Hybridization and VSEPR

Exercises 1.8

1. What is the hybridization of the oxygen atom in H₂O molecule?
2. What is the hybridization of the xenon atom in XeF₄ molecule, and what is the shape of the whole molecule?

Answers to Practice Questions Chapter 1

1.6.4 The Hybridization and VSEPR in Organic Molecules

Organic molecules usually contain more than one central atom, so it is not practical to name the shape of the whole molecule; instead we can talk about the shape/bond angle about each central atom individually. For such purposes, make sure to include the lone pairs that are usually left out in the organic structures (refer to section 1.2.4). The different structural formulas of ethanol, acetic acid and ethanenitrile molecules are shown in the table below. The 3D molecular model for each compound is shown as well to help you visualize the spatial arrangement. We can see that the hybridization and VSEPR shapes need to be indicated for each internal atom separately. Taking the oxygen atom in the OH group of ethanol as an example, since there two pairs of lone pair electrons on the oxygen atom as well (omitted in the structures in the table though), the oxygen has sp³ hybridization and is in the tetrahedral shape.

	Kekulé structures	Perspective formula with hybridization and shape of central atoms	3D models
ethanol			
acetic acid			
ethanenitrile (acetonitrile)			

Table 1.4 Hybridization and VSEPR of organic molecule examples

Table 1.4 Hybridization and VSEPR of Organic molecule examples [\[Image Description\]](#)

1.6.5 Multiple Bonds in Organic Structure

Ethene (C₂H₄)

We will take Ethene (C₂H₄) as an example for understanding the structure of a double bond.

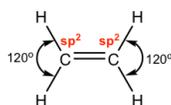


Figure 1.6k Ethene hybridization

According to the structure formula of C_2H_4 , there are three electron groups around each carbon. Through referring to **Table 1.3** it is determined that both carbons are in sp^2 hybridization, with the trigonal planar shape and a 120° bond angle. What does sp^2 hybridization mean to the carbon atom in this compound? It means that only three orbitals are involved in the hybridization (one $2s$ and two of $2p$ orbitals) out of the total four, and there is one $2p$ orbital left out, or not included in the hybridization, which is called the unhybridized $2p$.

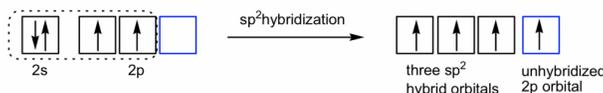
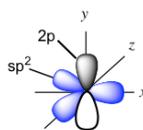


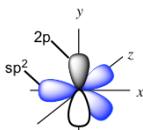
Figure 1.6l Orbital hybridization diagram of valence electrons in Ethene

The three new sp^2 hybrid orbitals and the unhybridized $2p$ are directed in the following arrangement: the three sp^2 hybrid orbitals are in the trigonal planar shape, and the unhybridized $2p$ is in the position that is perpendicular to the plane. Each orbital has one single electron, so all the orbitals are half-filled and are available for bonding. Both carbon atoms have the same set of orbitals (three sp^2 hybrid orbital and one unhybridized $2p$) as shown below.



the set of orbitals: $sp^2 + 2p$

Figure 1.6m The set of orbitals: $sp^2 + 2p$



the set of orbitals: $sp^2 + 2p$

Figure 1.6n The set of orbitals $sp^2 + 2p$

When the two carbons approach each other, the sp^2 on the x axis overlaps head-to-head to form the C-C σ sigma bond, and the “unhybridized” $2p$ overlaps side-by-side to form another new bond. **The side-by-side orbital overlapping forms the π (pi) bond.**

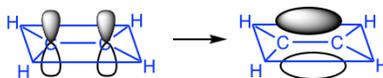


Figure 1.6o Side-by-side overlap of p orbitals leading to pi (π) bond

So now we understand that the C=C double bond contains two different bonds: σ (sigma) bond from sp^2-sp^2 orbital overlapping and π (pi) bond from $2p-2p$ overlapping. Because of the π bond, the overall shape of the whole C_2H_4 molecule is co-planar.

The other sp^2 hybrid orbitals on each carbon atom overlap with $1s$ orbital of H atoms and give total four C-H σ (sigma) bonds.

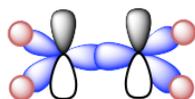


Figure 1.6p Sigma (σ) bond framework of C_2H_4

Ethyne (C_2H_2)

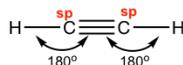


Figure 1.6q Ethyne hybridization

Ethyne C_2H_2 (common name is acetylene) has a $C\equiv C$ triple bond. Generally, triple bonds involve one σ sigma bond and two π (pi) bonds. Both carbon atom is in sp hybridization and in linear shape. With sp hybridization, each carbon has two sp hybrid orbitals and two unhybridized $2p$ orbitals. Each carbon uses one sp hybrid orbital to overlap head-to-head and gives the C-C the σ

sigma bond, meanwhile the 2p orbitals overlap side-by-side to give two π bonds as shown in the diagram below. The other sp orbitals are used for overlapping with 1s of hydrogen atoms to form C-H σ bonds.

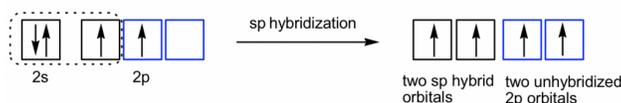
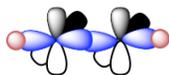
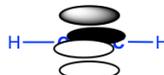


Figure 1.6r Orbital hybridization diagram of valence electrons in Ethyne



sigma (σ) bond framework of C_2H_2



two pi (π) bonds in C_2H_2

Figure 1.6s Sigma (σ) bond framework of Ethyne and two pi (π) binds of Ethyne

Image Descriptions

Table 1.4 image description: Ethanol's CH_3 , CH_2 , and OH are all in a sp^3 tetrahedral shape. Acetic acid's CH_3 , and OH are in a sp^3 tetrahedral shape and CO is in a sp^2 trigonal planar. Lastly, ethanenitrile's (acetonitrile) CH_3 in a sp^3 tetrahedral shape, and CN is in a sp linear shape. [\[Return to Table 1.4\]](#)

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