

**ATOMIC ORBITALS MIX BY QUANTUM MECHANICS THROUGH HYBRIDIZATION**

**Arpita Biswas, Priyanka Chandra, \*Prof. Dr. Dhrubo Jyoti Sen and Prof. Dr. Beduin Mahanti**

Department of Pharmaceutical Chemistry, School of Pharmacy, Techno India University, EM-4, Salt Lake City, Sector-V, Kolkata, West Bengal-700091.

**\*Corresponding Author: Prof. Dr. Dhrubo Jyoti Sen**

Department of Pharmaceutical Chemistry, School of Pharmacy, Techno India University, EM-4, Salt Lake City, Sector V, Kolkata, West Bengal-700091.

Article Received on 30/08/2019


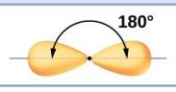

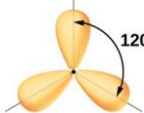
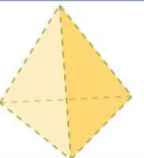
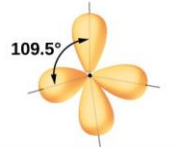

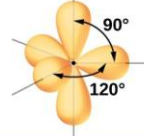

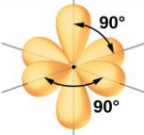
Article Revised on 21/09/2019

Article Accepted on 11/10/2019

**ABSTRACT**

Hybridization is defined as the concept of mixing two atomic orbitals with the same energy levels to give a degenerated new type of orbitals. This intermixing is based on quantum mechanics. The atomic orbitals of the same energy level can only take part in hybridization and both full filled and half-filled orbitals can also take part in this process provided they have equal energy. In chemistry, orbital hybridization (or hybridization) is the concept of mixing atomic orbitals into new hybrid orbitals (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds in valence bond theory. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties and are symmetrically disposed in space. Although sometimes taught together with the valence shell electron-pair repulsion (VSEPR) theory, valence bond and hybridization are in fact not related to the VSEPR model.

**KEYWORDS:** Atomic orbital, Molecular orbital, LCAO, VSEPR, s-orbital, p-orbital, d-orbital, f-orbital, Ionic Bonds, Covalent Bonds, Hydrogen Bonds, Polar Bonds.

Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp <sup>2</sup>	
4		tetrahedral	sp <sup>3</sup>	
5		trigonal bipyramidal	sp <sup>3</sup> d	
6		octahedral	sp <sup>3</sup> d <sup>2</sup>	

**Figure-1: Orbitals.**

**Overview:** During the process of hybridization, the atomic orbitals of similar energy are mixed together such as the mixing of two 's' orbitals (spherical) or two 'p' orbital's (dumb bell) or mixing of an 's' orbital with a 'p' orbital or 's' orbital with a 'd' orbital.

**What is Hybridization?** Redistribution of the energy of orbitals of individual atoms to give orbitals of equivalent energy happens when two atomic orbitals combine together to form hybrid orbital in a molecule. This process is called hybridization. The new orbitals thus formed are known as hybrid orbitals.<sup>[1]</sup>

**What is Chemical Bonding?** Chemical Bonding refers to the formation of a chemical bond between two or more atoms, molecules, or ions to give rise to a chemical compound. These chemical bonds are what keep the atoms together in the resulting compound. The attractive force which holds various constituents (atom, ions, etc.)

together and stabilizes them by the overall loss of energy is known as chemical bonding. Therefore, it can be understood that chemical compounds are reliant on the strength of the chemical bonds between its constituents. The stronger the bonding between the constituents, the more stable the resulting compound would be. The opposite also holds true; if the chemical bonding between the constituents is weak, the resulting compound would lack stability and would easily undergo another reaction to give a more stable chemical compound (containing stronger bonds). To find stability, the atoms try to lose their energy. Whenever matter interacts with another form of matter, a force is exerted on one by the other. When the forces are attractive in nature, the energy decreases. When the forces are repulsive in nature, the energy increases. The attractive force that binds two atoms together is known as the chemical bond.<sup>[2]</sup>

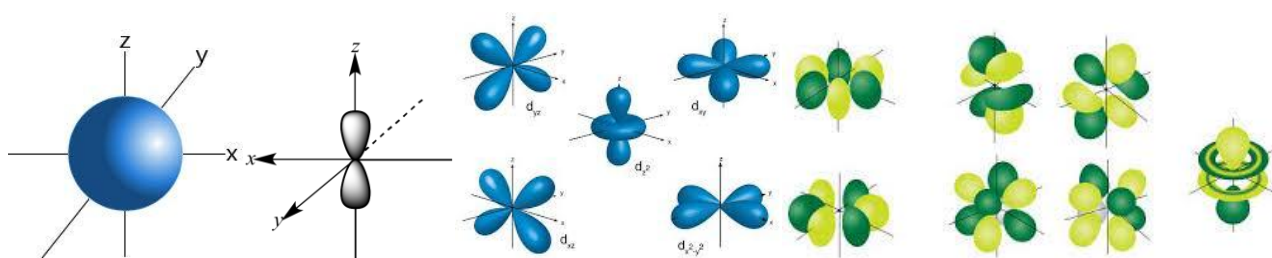


Figure-2: Shape of orbitals.

**Types of Chemical Bonds:** When substances participate in chemical bonding and yield compounds, the stability of the resulting compound can be gauged by the type of chemical bonds it contains. The type of chemical bonds formed varies in strength and properties. There are 4 primary types of chemical bonds which are formed by atoms or molecules to yield compounds. These types of chemical bonds include: **Ionic Bonds, Covalent Bonds, Hydrogen Bonds, Polar Bonds.** These types of bonds in chemical bonding are formed from the loss, gain, or sharing of electrons between two atoms/molecules.

**Ionic Bonding:** Ionic bonding is a type of chemical bonding which involves a transfer of electrons from one atom or molecule to another. Here, an atom loses an electron which is in turn gained by another atom. When such an electron transfer takes place, one of the atoms develops a negative charge (-ve) and is now called the anion<sup>(-)</sup>. The other atom develops a positive charge (+ve) and is called the cation<sup>(+)</sup>. The ionic bond gains strength from the difference in charge between the two atoms, i.e. the greater the charge disparity between the cation and the anion, the stronger the ionic bond.<sup>[3]</sup>

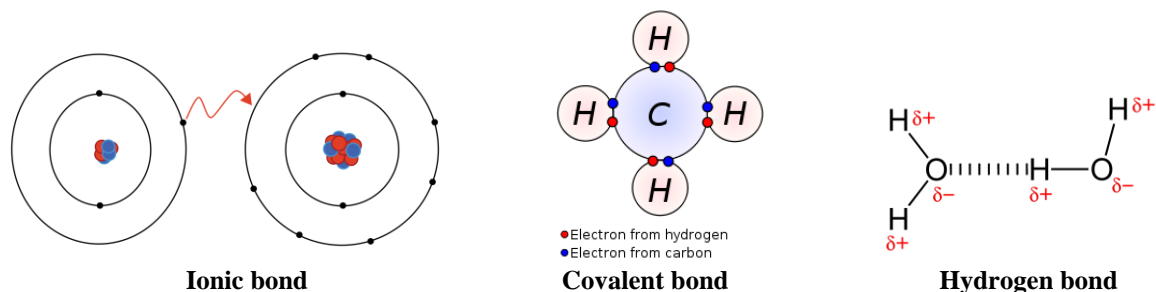


Figure-3: Bond formation.

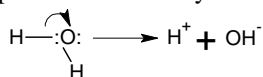
#### Covalent Bonding: Polar Covalent Bonding

Covalent bonds can be either be Polar or Non-Polar in nature. In Polar Covalent chemical bonding, electrons are shared unequally since the more electronegative atom pulls the electron pair closer to itself and away from the less electronegative atom. Water is an example of such a polar molecule. A difference in charge arises in different

areas of the atom due to the uneven spacing of the electrons between the atoms. One end of the molecule tends to be partially positively charged ( $\delta^+$ ) and the other end tends to be partially negatively charged ( $\delta^-$ ). A covalent bond indicates the sharing of electrons between atoms. Compounds that contain carbon (also called organic compounds) commonly exhibit this type of

chemical bonding. The pair of electrons which are shared by the two atoms now extend around the nuclei of atoms, leading to the creation of a molecule.

**Hydrogen Bonding:** Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen wherein the hydrogen develops a partial positive charge ( $\delta^+$ ). This implies that the electrons are pulled closer to the more electronegative oxygen atom. This creates a tendency for the hydrogen to be attracted towards the negative charges ( $\delta^-$ ) of any neighboring atom. This type of chemical bonding is called a hydrogen bond and is responsible for many of the properties exhibited by water.<sup>[4]</sup>



### What is Ionic Bond?

The bond formed as a result of strong electrostatic forces of attraction between a positively and negatively charged species is called an electrovalent or ionic bond. The positively and negatively charged ions are aggregated in an ordered arrangement called the crystal lattice which is stabilized by the energy called the Lattice enthalpy.

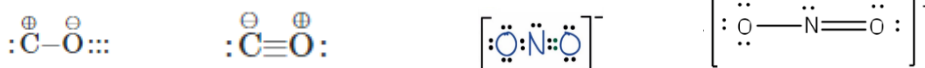


Figure-4: Ionic bond formation.

Step 4: The central position in the molecule is occupied by the least electronegative atom. Hydrogen and fluorine generally occupy the terminal positions.

Step 5: After distributing the shared pairs of electrons for single bonds, the remaining electron pairs are used for multiple bonds or they constitute lone pairs.<sup>[5]</sup>

The basic requirement is that each bonded atom gets an octet of electrons.

Example 1: Lewis formula for carbon monoxide, CO

Step 1: Counting the total number of valence electrons of carbon and oxygen atoms: C ( $2s^2 2p^2$ ) + O ( $2s^2 2p^4$ ):  $4 + 6 = 10$  that is,  $4(\text{C}) + 6(\text{O}) = 10$

Step 2: The skeletal structure of carbon monoxide is written as CO

Step 3: Drawing a single bond between C and O and completing octet on O, the remaining two electrons are lone pair on C.

Step 4: This does not complete the octet of carbon, and hence we have a triple bond.

Example 2: Lewis Structure of nitrite,  $\text{NO}_2^-$

Step 1: Counting the total number of valence electrons of one nitrogen atom, two oxygen atoms and the additional one negative charge (equal to one electron). Total Number of valence electrons is: N ( $2s^2 2p^3$ ) + 2O ( $2s^2 2p^4$ ) + 1 (negative charge)  $\Rightarrow 5 + 2(6) + 1 = 18e^-$

Step 2: The skeletal structure of nitrite ion is written as O-N-O

*Conditions for the formation of an Ionic Bond:* (1) The low ionization energy of the atom forming the cation. (2) High electron gain enthalpy of the atom forming the anion. (3) High negative lattice enthalpy of the crystal formed.

Generally, the ionic bond is formed between a metal cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  etc.) and non-metal anion ( $\text{Cl}^-$ ,  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^-$  etc.). The following steps are adopted for writing the Lewis dot structures or Lewis structures:

Step 1: Calculate the number of electrons required for drawing the structure by adding the valence electrons of the combining atoms. For Example, in methane,  $\text{CH}_4$  molecule, there are 8 valence electrons (in which 4 belongs to carbon while other 4 to H atoms).

Step 2: Each negative charge i.e. for anions, we add an electron to the valence electrons and for each positive charge i.e. for cations we subtract one electron from the valence electrons.

Step 3: Using the chemical symbols of the combining atoms and constructing a skeletal structure of the compound, divide the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

Step 3: Drawing a single bond between nitrogen and each oxygen atom: O-N-O

Step 4: Complete the octets of atoms.

This structure does not complete octet on N if the remaining two electrons constitute of a lone pair on it. Therefore, we have a double bond between one N and one of the two O atoms. The Lewis structure is in Figure-4.

### Bond Characteristics

**Bond Length:** During chemical bonding, when the atoms come closer to each other, the attraction takes place between them and the potential energy of the system keeps on decreasing till a particular distance at which the potential energy is minimum. If the atoms come more closer, repulsion starts and again the potential energy of the system begins to increase. At equilibrium distance, the atoms keep on vibrating about their mean position. The equilibrium distance between the centers of the nuclei of the two bonded atoms is called its **Bond length**. It is expressed in terms of an angstrom ( $\text{A}^\circ$ ) or picometer (pm). It is determined experimentally by x-ray diffraction or electron diffraction method or spectroscopic method. The bond length in chemical bonding is the sum of their **ionic radii**, in an ionic compound. In a covalent compound, it is the sum of their **covalent radii**. For a covalent molecule AB, the bond length is given by  $d = r_a + r_b$

### Factors Affecting the Bond length

*Size of the atoms:* The bond length increases with increase in the size of the atom.  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

*The multiplicity of Bond:* The bond length decreases with an increase in bond order.

*Type of hybridization:* A 's' orbital is smaller in size, greater the 's' character, shorter is the bond length.

### Bond Enthalpy

When atoms come close together the energy is released due to the chemical bonding between them. The amount of energy required to break one mole of bonds of a type so as to separate the molecule into individual gaseous atoms is called bond dissociation enthalpy or **Bond enthalpy**. Bond enthalpy is usually expressed in  $\text{KJ mol}^{-1}$ . Greater is the bond dissociation enthalpy, greater is the bond strength. For diatomic molecules like  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  the bond enthalpies are equal to their dissociation enthalpy. In the case of polyatomic molecules, bond enthalpies are usually the average

values, because the dissociation energy varies with each type of bond.<sup>[6]</sup>

In  $\text{H}_2\text{O}$ , first O–H bond enthalpy = 502 KJ/mol; Second bond enthalpy = 427 KJ/mol. Average bond enthalpy =  $(502 + 427) / 2 = 464.5 \text{ KJ/mol}$

### Factors Affecting Bond Enthalpy in Chemical Bonding

*Size of the atoms:* Greater the size of the atom, greater is the bond length and less is the bond dissociation enthalpy i.e. less is the bond strength during chemical bonding.

*Multiplicity of Bonds:* Greater is the multiplicity of the bond, greater is the bond dissociation enthalpy.

*Number of Lone Pair of Electrons Present:* More the number of lone pair of electrons present on the bonded atoms, greater is the repulsion between the atoms and thus less is the bond dissociation enthalpy of the chemical bond.

### Bond Angle:

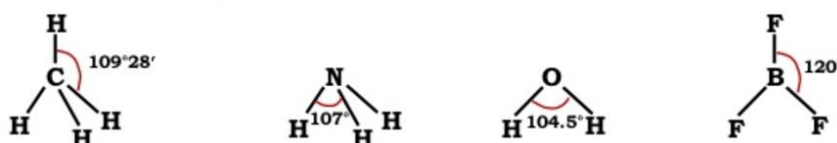


Figure-5: Bond angle.

A bond is formed by the overlap of atomic orbitals. The direction of overlap gives the direction of the bond. The angle between the lines representing the direction of the bond i.e. the orbitals containing the bonding electrons is called the **bond angle**.

**Bond Order:** In Lewis representation, the number of bonds present between two atoms is called the **bond order**. Greater the bond order, greater is the stability of

the bond during chemical bonding i.e. greater is the bond enthalpy. Greater the bond order, shorter is the bond length.

**Resonance in Chemical Bonding:** There are molecules and ions for which drawing a single Lewis structure is not possible. For example, we can write three structures of  $\text{O}_3$ .

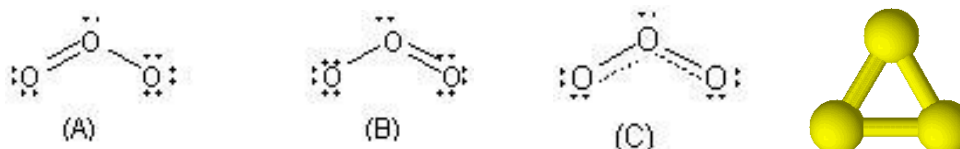


Figure-6: Ozone resonance and 3D structure.

In (A) the oxygen–oxygen bond on the left is a double bond and the oxygen–oxygen bond on the right is a single bond. In (B) the situation is just the opposite. The experiment shows, however, that the two bonds are identical. Therefore neither structure A nor B can be correct. One of the bonding pairs in ozone is spread over the region of all three atoms rather than localized on a particular oxygen–oxygen bond. This delocalized bonding is a type of chemical bonding in which bonding pair of electrons are spread over a number of atoms rather than localized between two. Structures (A) and (B)

are called resonating or canonical structures and (C) is the resonance hybrid. This phenomenon is called resonance, a situation in which more than one canonical structure can be written for a species. The chemical activity of an atom is determined by the number of electrons in its valence shell. With the help of the concept of chemical bonding, one can define the structure of a compound and is used in many industries for manufacturing products in which the true structure cannot be written at all.<sup>[7]</sup>

Some other examples:  
 $\text{CO}_3^{2-}$  ion

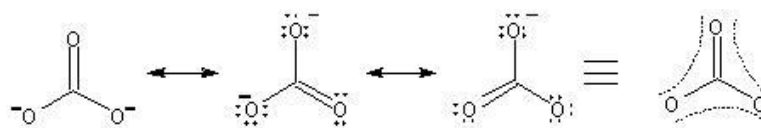


Figure-7: Resonance hybrid.

Carbon–oxygen bond lengths in carboxylate ion ( $-\text{COO}^-$ ) are equal due to resonance.

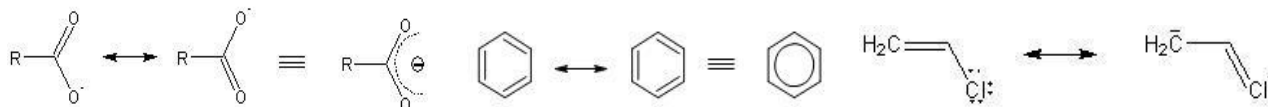


Figure-8: Resonance of Carboxylate ion, Benzene and Vinyl chloride.

The difference in the energies of the canonical forms and resonance hybrid is called resonance stabilization energy.

### London Dispersion Forces

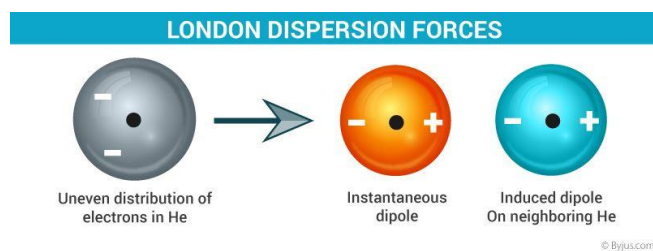


Figure-9: London Dispersion Forces.

Another form of chemical bonding is caused by **London dispersion forces**. These forces are weak in magnitude.

**Chemical Bonding – London Dispersion Forces:** These forces occur due to a temporary charge imbalance arising in an atom. This imbalance in the charge of the atom can induce dipoles on neighbouring atoms. For example, the temporary positive charge on one area of an atom can attract the neighbouring negative charge.<sup>[8]</sup>

### What is Molecular Orbital Theory?

The molecular orbital theory is a method developed at the beginning of the twentieth century by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. Molecular orbital theory approximates the molecular orbitals as linear combinations of atomic orbitals which can be illustrated as follows.

To better understand the molecular orbital theory, it is important to understand what atomic and molecular orbitals are?

**Linear Combination of Atomic Orbitals (LCAO):** Molecular orbitals can generally be expressed through a linear combination of atomic orbitals (LCAO). These LCAOs are useful in the estimation of the formation of these orbitals in the bonding between the atoms that make up a molecule. The Schrodinger equation used to describe the electron behaviour for molecular orbitals can be written in a method similar to that for atomic orbitals. It is an approximate method for representing molecular orbitals. It's more of a superimposition method where constructive interference of two atomic wave function produces a bonding molecular orbital whereas destructive interference produces non-bonding molecular orbital.<sup>[9]</sup>

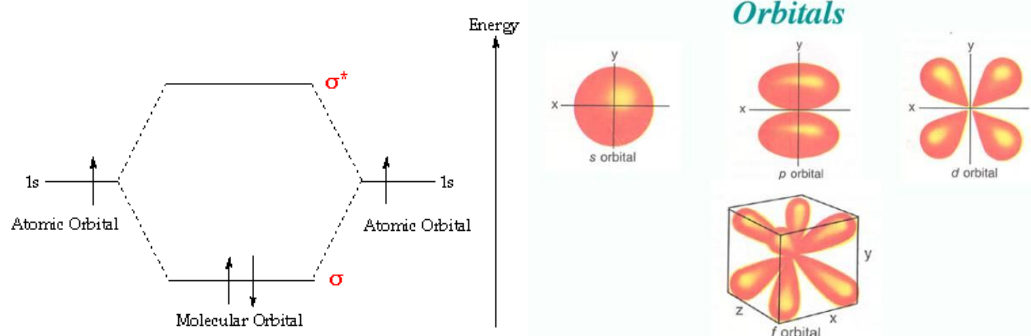


Figure-10: Molecular Orbital.



**Conditions for Linear Combination of Atomic Orbitals:** The conditions that are required for the linear combination of atomic orbitals are as follows:

**Same Energy of Combining Orbitals:** The atomic orbitals combining to form molecular orbitals should have comparable energy. This means that 2p orbital of an atom can combine with another 2p orbital of another atom but 1s and 2p cannot combine together as they have appreciable energy difference.

**Same Symmetry about Molecular Axis:** The combining atoms should have the same symmetry around the molecular axis for proper combination; otherwise, the electron density will be sparse. For e.g. all the sub-orbitals of 2p have same energy but still, 2pz orbital of an atom can only combine with a 2pz orbital of another atom but cannot combine with 2px and 2py orbital as they have a different axis of symmetry. In general, the z-axis is considered as the molecular axis of symmetry.<sup>[10]</sup>

**Proper Overlap between Atomic Orbitals:** The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms. The condition can be understood by two simple requirements. For the formation of proper molecular orbital, proper energy and orientation are required. For proper energy, the two atomic orbitals should have the same energy and for the proper orientation, the atomic orbitals should have proper overlap and the same molecular axis of symmetry.

**What are Molecular Orbitals?** The space in a molecule in which the probability of finding an electron is maximum can be calculated using the molecular orbital function. Molecular orbitals are basically mathematical functions that describe the wave nature of electrons in a given molecule. These orbitals can be constructed via the combination of hybridized orbitals or atomic orbitals from each atom belonging to the specific molecule. Molecular orbitals provide a great model via the molecular orbital theory to demonstrate the bonding of molecules.

**Types of Molecular Orbitals:** According to the molecular orbital theory, there exist three primary types of molecular orbitals that are formed from the linear combination of atomic orbitals (LCAO). These orbitals are detailed below.

Case 1: When the two waves are in phase so that they add up and amplitude of the wave is  $\Phi = \Psi_A + \Psi_B$

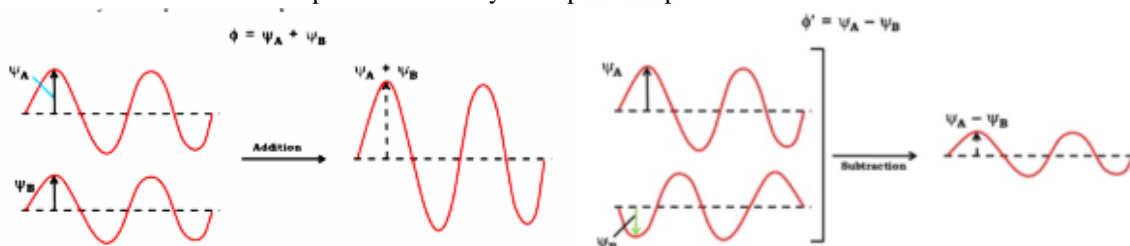


Figure-11: Schrodinger's wave equation.

**Anti Bonding Molecular Orbitals:** The electron density is concentrated behind the nuclei of the two bonding atoms in anti-bonding molecular orbitals. This results in the nuclei of the two atoms being pulled away from each other. These kinds of orbitals weaken the bond between two atoms.

**Non-Bonding Molecular Orbitals:** In the case of non-bonding molecular orbitals, due to a complete lack of symmetry in the compatibility of two bonding atomic orbitals, the molecular orbitals formed have no positive or negative interactions with each other. These types of orbitals do not affect the bond between the two atoms.<sup>[11]</sup>

**Features of Molecular Orbital Theory:** The atomic orbitals overlap to form new orbitals called molecular orbitals. When two atomic orbitals overlap they lose their identity and form new orbitals called molecular orbitals. The electrons in the molecules are filled in the new energy states called the **molecular orbitals** similar to the electrons in an atom being filled in an energy state called **atomic orbitals**. The probability of finding the electronic distribution in a molecule around its group of nuclei is given by the molecular orbital. The two combining atomic orbitals should possess energies of comparable value and similar orientation. For example, 1s can combine with 1s and not with 2s.

The number of molecular orbitals formed is equal to the number of atomic orbitals combining. The shape of molecular orbitals formed depends upon the shape of the combining atomic orbitals. According to the Molecular Orbital Theory, the filling of orbitals takes place according to the following rules:

**Aufbau's principle:** Molecular orbitals are filled in the increasing order of energy levels.

**Pauli's exclusion principle:** In an atom or a molecule, no two electrons can have the same set of four quantum numbers.

**Hund's rule:** It is of maximum multiplicity. Pairing of electrons doesn't take place until all the atomic or molecular orbitals are singly occupied.

**Formation of Molecular Orbitals:** An atomic orbital is an electron wave; the waves of the two atomic orbitals may be in phase or out of phase. Suppose  $\Psi_A$  and  $\Psi_B$  represent the amplitude of the electron wave of the atomic orbitals of the two atoms A and B.<sup>[12]</sup>

Case 2: When the two waves are out of phase, the waves are subtracted from each other so that the amplitude of the new wave is  $\Phi' = \Psi A - \Psi B$

#### Characteristics of Bonding Molecular Orbitals

The probability of finding the electron in the internuclear region of the bonding molecular orbital is greater than that of combining atomic orbitals. The electrons present in the bonding molecular orbital result in the attraction between the two atoms. The bonding molecular orbital has lower energy as a result of attraction and hence has greater stability than that of the combining atomic orbitals. They are formed by the additive effect of the atomic orbitals so that the amplitude of the new wave is given by  $\Phi = \Psi A + \Psi B$

They are represented by  $\sigma$ ,  $\pi$ , and  $\delta$ .

#### Characteristics of Anti-bonding Molecular Orbitals:

The probability of finding the electron in the internuclear region decreases in the anti-bonding molecular orbitals. The electrons present in the anti-bonding molecular orbital result in the repulsion between the two atoms. The anti-bonding molecular orbitals have higher energy because of the repulsive forces and lower stability. They

are formed by the subtractive effect of the atomic orbitals. The amplitude of the new wave is given by  $\Phi' = \Psi A - \Psi B$

They are represented by  $\sigma^*$ ,  $\pi^*$ ,  $\delta^*$

#### Why are Anti-bonding Orbitals Higher in Energy?

The energy levels of bonding molecular orbitals are always lower than those of anti-bonding molecular orbitals. This is because the electrons in the orbital are attracted by the nuclei in the case of bonding Molecular Orbitals whereas the nuclei repel each other in the case of the anti-bonding Molecular Orbitals.<sup>[13]</sup>

The lowering of the energy of bonding molecular orbital than the combining atomic orbital is called stabilization energy and similarly increase in energy of the anti-bonding molecular orbitals is called destabilization energy.

**Types of Hybridization:** Based on the types of orbitals involved in mixing, the hybridization can be classified as  $sp^3$ ,  $sp^2$ ,  $sp$ ,  $sp^3d$ ,  $sp^3d^2$ ,  $sp^3d^3$ . Let us now discuss the various types of hybridization along with their examples.

#### Difference between Bonding and Antibonding Molecular Orbitals

Molecular Orbital Theory	
Bonding Molecular Orbitals	Anti-Bonding Molecular Orbitals
Molecular orbitals formed by the additive effect of the atomic orbitals are called bonding molecular orbitals.	Molecular orbitals formed by the subtractive effect of atomic are called anti-bonding molecular orbitals.
Probability of finding the electrons is more in the case of bonding molecular orbitals.	Probability of finding electrons is less in antibonding molecular orbitals. There is also a node between the anti-bonding molecular orbital between two nuclei where the electron density is zero.
These are formed by the combination of + and + and - with - part of the electron waves.	These are formed by the overlap of + with - part.
The electron density, in the bonding molecular orbital in the internuclear region, is high. As a result, the nuclei are shielded from each other and hence the repulsion is very less.	The electron density in the antibonding molecular orbital in the internuclear region is very low and so the nuclei are directly exposed to each other. Therefore the nuclei are less shielded from each other.
The bonding molecular orbitals are represented by $\sigma$ , $\pi$ , $\delta$ .	The corresponding anti-bonding molecular orbitals are represented by $\sigma^*$ , $\pi^*$ , $\delta^*$ .

Table-1: Difference between Bonding Molecular Orbitals and Anti-Bonding Molecular Orbitals.

**sp Hybridization:** sp hybridization is observed when one s and one p orbital in the same main shell of an atom mix to form two new equivalent orbitals. The new

orbitals formed are called sp hybridized orbitals. It forms linear molecules with an angle of  $180^\circ$ .<sup>[14]</sup>

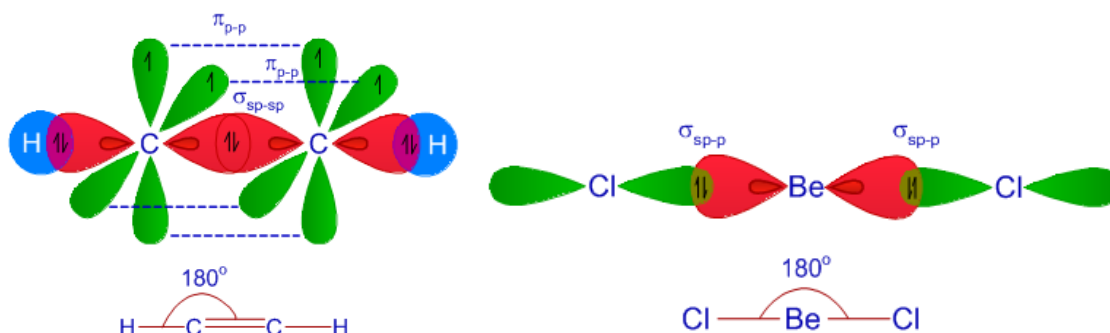


Figure-12: sp Hybridization.

This type of hybridization involves the mixing of one 's' orbital and one 'p' orbital of equal energy to give a new hybrid orbital known as an sp hybridized orbital. **sp hybridization is also called diagonal hybridization.** Each sp hybridized orbital has an equal amount of s and p character, i.e., 50% s and p character.

Examples of sp Hybridization: All compounds of beryllium like  $\text{BeF}_2$ ,  $\text{BeH}_2$ ,  $\text{BeCl}_2$ . All compounds of carbon-containing triple bond like  $\text{C}_2\text{H}_2$  ( $\text{H}-\text{C}\equiv\text{C}-\text{H}$ ).

**$\text{sp}^2$  Hybridization:**  $\text{sp}^2$  hybridization is observed when one 's' and two 'p' orbitals of the same shell of an atom mix to form 3 equivalent orbital. The new orbitals formed are called  $\text{sp}^2$  hybrid orbitals.  **$\text{sp}^2$  hybridization is also called trigonal hybridization.** It involves mixing

of one 's' orbital and two 'p' orbital's of equal energy to give a new hybrid orbital known as  $\text{sp}^2$ . A mixture of 's' and 'p' orbital formed in trigonal symmetry and is maintained at  $120^\circ$ .

All the three hybrid orbitals remain in one plane and make an angle of  $120^\circ$  with one another. Each of the hybrid orbitals formed has 33.33% 's' character and 66.66% 'p' character. The molecules in which the central atom is linked to 3 atoms and is  $\text{sp}^2$  hybridized have a triangular planar shape.

Examples of  $\text{sp}^2$  Hybridization: All the compounds of Boron i.e.  $\text{BF}_3$ ,  $\text{BH}_3$ . All the compounds of carbon containing a carbon-carbon double bond, Ethylene ( $\text{C}_2\text{H}_4$ )

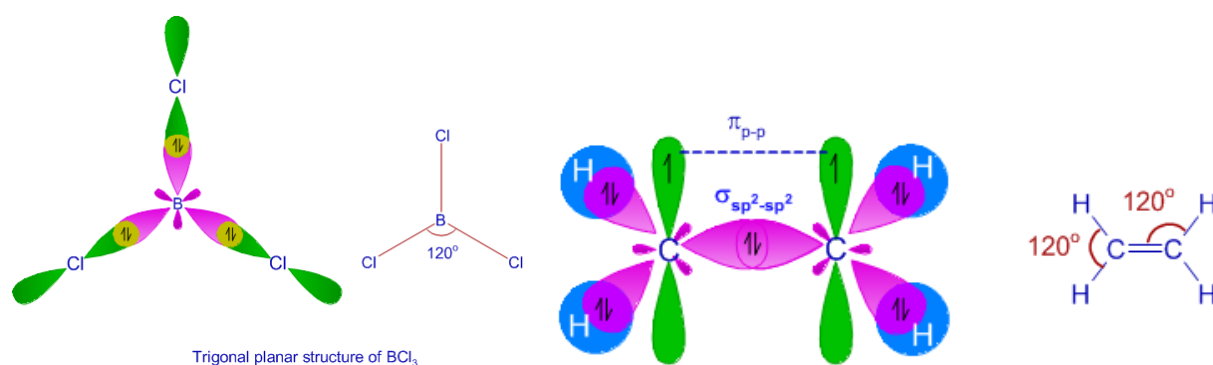


Figure-13:  $\text{sp}^2$  Hybridization.

**$\text{sp}^3$  Hybridization:** When one 's' orbital and 3 'p' orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, the type of hybridization is called a tetrahedral hybridization or  $\text{sp}^3$ . The new orbitals formed are called  $\text{sp}^3$  hybrid orbitals. These are directed towards the four corners of a **regular**

**tetrahedron** and make an angle of  $109^\circ 28'$  with one another. The angle between the  $\text{sp}^3$  hybrid orbitals is  $109.28^\circ$ . Each  $\text{sp}^3$  hybrid orbital has 25% 's' character and 75% 'p' character.

Example of  $\text{sp}^3$  hybridization: ethane ( $\text{C}_2\text{H}_6$ ), methane ( $\text{CH}_4$ ).

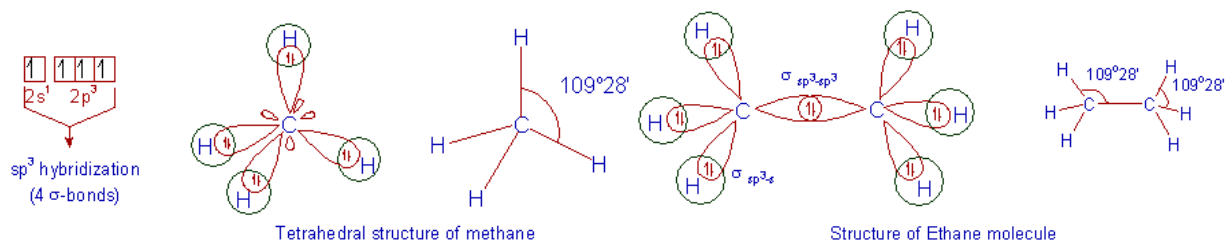


Figure-14:  $\text{sp}^3$  hybridization.

**$\text{sp}^3\text{d}$  Hybridization:**  $\text{sp}^3\text{d}$  hybridization involves the mixing of 3p orbitals and 1d orbital to form 5  $\text{sp}^3\text{d}$  hybridized orbitals of equal energy. They have **trigonal bipyramidal** geometry. The mixture of s, p and d orbital forms trigonal bipyramidal symmetry. Three hybrid orbitals lie in the horizontal plane inclined at an angle of  $120^\circ$  to each other known as the equatorial orbitals. The remaining two orbitals lie in the vertical plane at  $90^\circ$  plane of the equatorial orbitals known as axial orbitals. Example: Hybridization in Phosphorus pentachloride ( $\text{PCl}_5$ )

**$\text{sp}^3\text{d}^2$  Hybridization:**  $\text{sp}^3\text{d}^2$  hybridization has 1s, 3p and 2d orbitals, that undergo intermixing to form 6 identical  $\text{sp}^3\text{d}^2$  hybrid orbitals. These 6 orbitals are directed towards the corners of an **octahedron**. They are inclined at an angle of  $90^\circ$  to one another.

Example of  $\text{sp}^3\text{d}^2$  Hybridization: Sulfur hexafluoride ( $\text{SF}_6$ )

**$\text{sp}^3\text{d}^3$  Hybridization:**  $\text{sp}^3\text{d}^3$  hybridization has 1s, 3p and 3d orbitals, that undergo intermixing to form 7 identical  $\text{sp}^3\text{d}^3$  hybrid orbitals. These 7 orbitals are directed towards the corners of a pentagonal bipyramidal



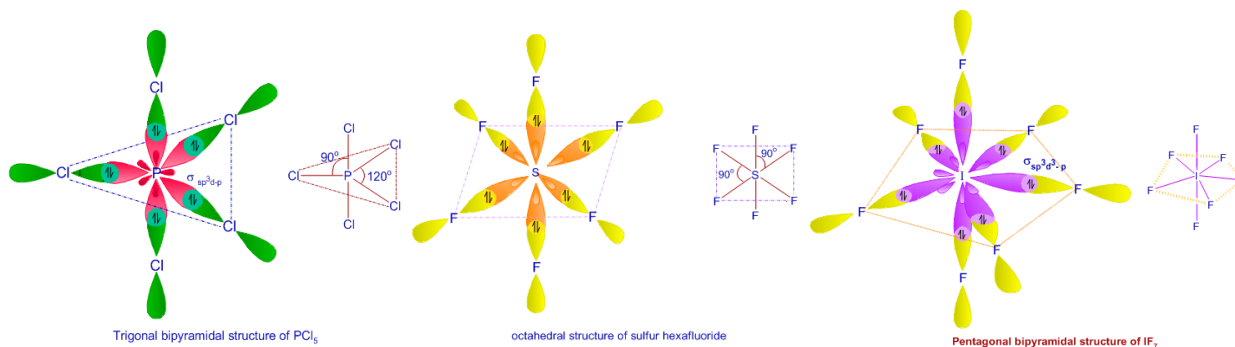
geometry. They are inclined at an angle of  $360^\circ$  to one another.

Example of  $sp^3d^3$  Hybridization: Iodine heptafluoride ( $IF_7$ )

**Key Features of Hybridization:** Atomic orbitals with equal energies undergo hybridization. The number of hybrid orbitals formed is equal to the number of atomic orbitals mixing. It is not necessary that all the half-filled orbitals must participate in hybridization. Even completely filled orbitals with slightly different energies can also participate. Hybridization happens only during the bond formation and not in an isolated gaseous atom.

The shape of the molecule can be predicted if hybridization of the molecule is known. The bigger lobe of the hybrid orbital always has a positive sign while the smaller lobe on the opposite side has a negative sign.<sup>[15]</sup>

*What are the different types of hybridization?* Based on the nature of the mixing orbitals, the hybridization can be classified as,  $sp$  hybridization (beryllium chloride, acetylene),  $sp^2$  hybridization (boron trichloride, ethylene),  $sp^3$  hybridization (methane, ethane),  $sp^3d$  hybridization (phosphorus pentachloride),  $sp^3d^2$  hybridization (sulfur hexafluoride),  $sp^3d^3$  hybridization (iodine heptafluoride).



**Figure-15:  $sp^3d$  Hybridization,  $sp^3d^2$  Hybridization and  $sp^3d^3$  Hybridization.**

Among  $sp$ ,  $sp^2$  and  $sp^3$ , which hybrid orbital is more electronegative? The percentage of  $s$  character in  $sp$ ,  $sp^2$ , and  $sp^3$  hybridized carbon is 50%, 33.33%, and 25% respectively.

Due to the spherical shape of  $s$  orbital, it is attracted evenly by the nucleus from all directions. Therefore, a hybrid orbital with more  $s$ -character will be closer to the nucleus and thus more electronegative. Hence, the  $sp$  hybridized carbon is more electronegative than  $sp^2$  and  $sp^3$ .

*Why the hybrid orbital during hybridization is better than their parent atoms?*

The reason why a hybrid orbital is better than their parents:

Parent  $s$ : because it is directional unlike the ' $s$ ' orbital.  
Parent  $p$ : because it has lower energy than ' $p$ ' orbital.

*What are hybrid orbitals?* The hybrid orbitals can be defined as the combination of standard atomic orbitals resulting in the formation of new atomic orbitals.

During hybridization, the hybrid orbitals possess different geometry of orbital arrangement and energies than the standard atomic orbitals. Also, the orbital overlap minimizes the energy of the molecule. The degenerate hybrid orbitals formed from the standard atomic orbitals:

1s and 1 p:  $sp$  orbitals; 1s and 2p:  $sp^2$  orbitals; 1s and 3p:  $sp^3$  orbitals; 1s, 3p, and 1d:  $sp^3d$  orbitals; 1s, 3p, and 2d:  $sp^3d^2$  orbitals.

*What is the difference between  $sp$ ,  $sp^2$  and  $sp^3$  hybridization?*  $sp$  hybridization occurs due to the mixing of one ' $s$ ' and one ' $p$ ' atomic orbital,  $sp^2$  hybridization is the mixing of one ' $s$ ' and two ' $p$ ' atomic orbitals and  $sp^3$  hybridization is the mixing of one ' $s$ ' and three ' $p$ ' atomic orbitals.<sup>[16]</sup>

*What is the percentage of  $s$  and  $p$  character in  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbital?* The percentage of  $s$  and  $p$  character in  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbital is:  $sp$ : ' $s$ ' characteristic 50% and ' $p$ ' characteristic 50%,  $sp^2$ : ' $s$ ' characteristic 33.33% and ' $p$ ' characteristic 66.66%,  $sp^3$ : ' $s$ ' characteristic 25% and ' $p$ ' characteristic 75%.

*Explain the five basic shapes of Hybridization?* The five basic shapes of hybridization are **linear**, **trigonal planar**, **tetrahedral**, **trigonal bipyramidal** and **octahedral**.

The geometry of the orbital arrangement:

**Linear:** Two electron groups involved resulting in  $sp$  hybridization, the angle between the orbitals is  $180^\circ$ .

**Trigonal planar:** Three electron groups involved resulting in  $sp^2$  hybridization, the angle between the orbitals is  $120^\circ$ .

**Tetrahedral:** Four electron groups involved resulting in  $sp^3$  hybridization, the angle between the orbitals is  $109.5^\circ$ .

**Trigonal bipyramidal:** Five electron groups involved resulting in  $sp^3d$  hybridization, the angle between the orbitals is  $90^\circ$ ,  $120^\circ$ .

**Octahedral:** Six electron groups involved resulting in  $sp^3d^2$  hybridization, the angle between the orbitals is  $90^\circ$ .

*Explain  $sp^3$  Hybridization in Methane?* The 2s and all the three (3p) orbitals of carbon hybridize to form four  $sp^3$  orbitals. These hybrid orbitals bond with four atoms of hydrogen through  $sp^3$ -s orbital overlap resulting in  $CH_4$  (methane). The geometry of orbital arrangement due to the minimum electron repulsion is tetrahedral.

*Amide molecule looks  $sp^3$  hybridized but it is  $sp^2$ , why?* The general process of hybridization will change if the atom is either enclosed by two or more 'p' orbitals or it has a lone pair to jump into a 'p' orbital. Therefore, in the case of amide molecule, the lone pair goes into a 'p' orbital to have 3 adjacent parallel 'p' orbitals (conjugation).

*What results in  $sp$ ,  $sp^2$  and  $sp^3$  hybridization?*  $sp$  and  $sp^2$  hybridization results in two and one unhybridized 'p' orbitals respectively whereas in  $sp^3$  hybridization there are no unhybridized 'p' orbitals.

*Explain the difference between molecular and hybrid orbitals?* The interactions between the atomic orbitals of two different atoms result in molecular orbitals whereas when the atomic orbitals of the same atom interact they form hybrid orbitals.<sup>[17-20]</sup>

## CONCLUSION

In chemistry, orbital hybridisation (or hybridization) is the concept of mixing atomic orbitals into new hybrid orbitals (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds in valence bond theory. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties and are symmetrically disposed in space. Although sometimes taught together with the valence shell electron-pair repulsion (VSEPR) theory, valence bond and hybridization are in fact not related to the VSEPR model.

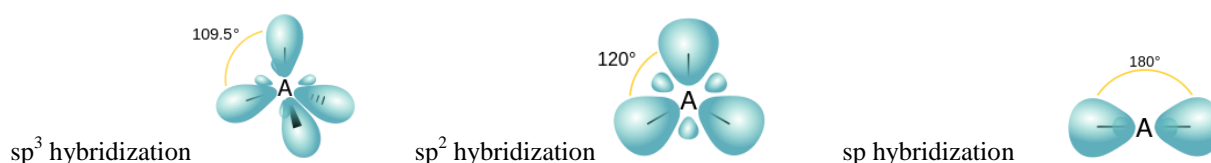
**History and uses:** Chemist Linus Pauling first developed the hybridisation theory in 1931 to explain the structure of simple molecules such as methane ( $CH_4$ ) using atomic orbitals. Pauling pointed out that a carbon atom forms four bonds by using one 's' and three 'p' orbitals, so that "it might be inferred" that a carbon atom would form three bonds at right angles (using 'p'

orbitals) and a fourth weaker bond using the 's' orbital in some arbitrary direction. In reality, methane has four bonds of equivalent strength separated by the tetrahedral bond angle of  $109.5^\circ$ . Pauling explained this by supposing that in the presence of four hydrogen atoms, the 's' and 'p' orbitals form four equivalent combinations or hybrid orbitals, each denoted by  $sp^3$  to indicate its composition, which is directed along the four C-H bonds. This concept was developed for such simple chemical systems, but the approach was later applied more widely, and today it is considered an effective heuristic for rationalizing the structures of organic compounds. It gives a simple orbital picture equivalent to Lewis structures.

Hybridization theory is an integral part of organic chemistry, one of the most compelling examples being Baldwin's rules. For drawing reaction mechanisms sometimes a classical bonding picture is needed with two atoms sharing two electrons. Hybridization theory explains bonding in alkenes and methane. The amount of 'p' character or 's' character, which is decided mainly by orbital hybridization, can be used to reliably predict molecular properties such as acidity or basicity.

**Overview:** Orbitals are a model representation of the behaviour of electrons within molecules. In the case of simple hybridization, this approximation is based on atomic orbitals, similar to those obtained for the hydrogen atom, the only neutral atom for which the Schrödinger equation can be solved exactly. In heavier atoms, such as carbon, nitrogen, and oxygen, the atomic orbitals used are the 2s and 2p orbitals, similar to excited state orbitals for hydrogen. Hybrid orbitals are assumed to be mixtures of atomic orbitals, superimposed on each other in various proportions. For example, in methane, the C hybrid orbital which forms each carbon-hydrogen bond consists of 25% 's' character and 75% 'p' character and is thus described as  $sp^3$  (read as s-p-three) hybridised.

Types of hybridization:  $sp^3$ : Four  $sp^3$  orbitals. Hybridization describes the bonding atoms from an atom's point of view. For a tetrahedrally coordinated carbon (e.g., methane  $CH_4$ ), the carbon should have 4 orbitals with the correct symmetry to bond to the 4 hydrogen atoms.



Carbon's ground state configuration is  $1s^2 2s^2 2p^2$  or more easily read:

	↑↓	↑↓	↑	↑	
C	1s	2s	2p	2p	2p

The carbon atom can use its two singly occupied p-type orbitals, to form two covalent bonds with two hydrogen

atoms, yielding the singlet methylene  $CH_2$ , the simplest carbene. The carbon atom can also bond to four

hydrogen atoms by an excitation (or promotion) of an electron from the doubly occupied 2s orbital to the empty

2p orbital, producing four singly occupied orbitals.

C*	↑↓	↑	↑	↑	↑
	1s	2s	2p	2p	2p

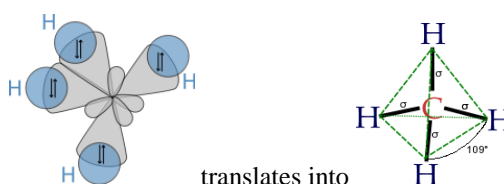
The energy released by formation of two additional bonds more than compensates for the excitation energy required, energetically favouring the formation of four C–H bonds. Quantum mechanically, the lowest energy is obtained if the four bonds are equivalent, which requires

that they are formed from equivalent orbitals on the carbon. A set of four equivalent orbitals can be obtained that are linear combinations of the valence-shell (core orbitals are almost never involved in bonding) 's' and 'p' wave functions, which are the four  $sp^3$  hybrids.

C*	↑↓	↑	↑	↑	↑
	1s	$sp^3$	$sp^3$	$sp^3$	$sp^3$

In  $CH_4$ , four  $sp^3$  hybrid orbitals are overlapped by hydrogen 1s orbitals, yielding four  $\sigma$  (sigma) bonds (that

is, four single covalent bonds) of equal length and strength.



$sp^2$ : Three  $sp^2$  orbitals. Ethene ( $C_2H_2$ ) structure

Other carbon compounds and other molecules may be explained in a similar way. For example, ethene ( $C_2H_4$ ) has a double bond between the carbons.

For this molecule, carbon  $sp^2$  hybridizes, because one  $\pi$  (pi) bond is required for the double bond between the carbons and only three  $\sigma$  bonds are formed per carbon atom. In  $sp^2$  hybridization the 2s orbital is mixed with only two of the three available 2p orbitals, forming a

total of three  $sp^2$  orbitals with one remaining 'p' orbital. In ethylene (ethene) the two carbon atoms form a  $\sigma$  bond by overlapping one  $sp^2$  orbital from each carbon atom. The  $\pi$  bond between the carbon atoms perpendicular to the molecular plane is formed by 2p–2p overlap. Each carbon atom forms covalent C–H bonds with two hydrogens by s– $sp^2$  overlap, all with  $120^\circ$  bond angles. The hydrogen–carbon bonds are all of equal strength and length, in agreement with experimental data.

C*	↑↓	↑	↑	↑	↑
	1s	$sp^2$	$sp^2$	$sp^2$	2p

$sp$ : The chemical bonding in compounds such as alkynes with triple bonds is explained by sp hybridisation. In this model, the 2s orbital is mixed with only one of the three 'p' orbitals, resulting in two sp orbitals and two remaining 'p' orbitals. The chemical bonding in

acetylene (ethyne) ( $C_2H_2$ ) consists of sp–sp overlap between the two carbon atoms forming a  $\sigma$  bond and two additional  $\pi$  bonds formed by p–p overlap. Each carbon also bonds to hydrogen in a  $\sigma$  s–sp overlap at  $180^\circ$  angles.

C*	↑↓	↑	↑	↑	↑
	1s	Sp	sp	2p	2p

## REFERENCES

- Gillespie, R.J. (2004), "Teaching molecular geometry with the VSEPR model", *Journal of Chemical Education*, 81(3): 298–304.
- Pauling, L. (1931), "The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules", *Journal of the American Chemical Society*, 53(4): 1367–1400.
- L. Pauling, *The Nature of the Chemical Bond* (3rd ed., Oxford University Press 1960) p.111–120.
- Clayden, Jonathan; Greeves, Nick; Warren, Stuart; Wothers, Peter (2001). *Organic Chemistry* (1st ed.). Oxford University Press. p. 105.
- Organic Chemistry, Third Edition* Marye Anne Fox James K. Whitesell, 2003.
- Fricke, Burkhard (1975). *Superheavy elements: a prediction of their chemical and physical properties. Recent Impact of Physics on Inorganic Chemistry. Structure and Bonding*, 21: pp. 89–144.

7. Weinhold, Frank; Landis, Clark R. (2005). Valency and bonding: A Natural Bond Orbital Donor–Acceptor Perspective. Cambridge: Cambridge University Press. pp. 367, 376, 381–383, 570–572.
8. Kaupp, Martin (2001). "Non–VSEPR" Structures and Bonding in d(0) Systems". *Angew Chem Int Ed Engl.*, 40(1): 3534–3565.
9. Jean, Yves (2005). *Molecular Orbitals of Transition Metal Complexes*. Oxford: Oxford University Press. pp. 37–76.
10. Angelo R. Rossi; Roald. Hoffmann (1975). "Transition metal pentacoordination". *Inorganic Chemistry*, 14(2): 365–374.
11. Roald. Hoffmann; Barbara F. Beier; Earl L. Muetterties; Angelo R. Rossi (1977). "Seven–coordination. A molecular orbital exploration of structure, stereochemistry, and reaction dynamics". *Inorganic Chemistry*, 16(3): 511–522.
12. E. Magnusson. Hypercoordinate molecules of second–row elements: d functions or d orbitals? *J. Am. Chem. Soc.*, 1990; 112: 7940–7951.
13. David L. Cooper; Terry P. Cunningham; Joseph Gerratt; Peter B. Karadakov; Mario Raimondi (1994). "Chemical Bonding to Hypercoordinate Second–Row Atoms: d Orbital Participation versus Democracy". *Journal of the American Chemical Society*, 116(10): 4414–4426.
14. Frenking, Gernot; Shaik, Sason, eds. (May 2014). "Chapter 7: Chemical bonding in Transition Metal Compounds". *The Chemical Bond: Chemical Bonding Across the Periodic Table*. Wiley–VCH.
15. C. R. Landis; F. Weinhold (2007). "Valence and extra–valence orbitals in main group and transition metal bonding". *Journal of Computational Chemistry*, 28(1): 198–203.
16. Richard D. Harcourt; Thomas M. Klapötke (2003). "Increased valence (qualitative valence bond) descriptions of the electronic structures of electron–rich fluorine–containing molecules". *Journal of Fluorine Chemistry*, 123(1): 5–20.
17. Frenking, Gernot; Shaik, Sason, eds. (2014). "Chapter 3: The NBO View of Chemical Bonding". *The Chemical Bond: Fundamental Aspects of Chemical Bonding*. John Wiley & Sons.
18. Kaupp, Martin (2007). "The role of radial nodes of atomic orbitals for chemical bonding and the periodic table". *Journal of Computational Chemistry*, 28(1): 320–325.
19. Kaupp, Martin (2014) [1st. Pub. 2014]. "Chapter 1: Chemical bonding of main group elements". In Frenking, Gernod & Shaik, Sason (eds.). *The Chemical Bond: Chemical Bonding Across the Periodic Table*. Wiley–VCH.
20. Kutzelnigg, W. (1988). "Orthogonal and non–orthogonal hybrids". *Journal of Molecular Structure: THEOCHEM*, 169: 403–419.