

## 1.3: Overview of Valence Bond Theory

Molecular bonding occurs due to an energy minimum that occurs as electrons are shared between 2 nuclei. The potential energy is approximated as a harmonic potential depending on the displacement,  $R$ , of the nuclei from their equilibrium positions.

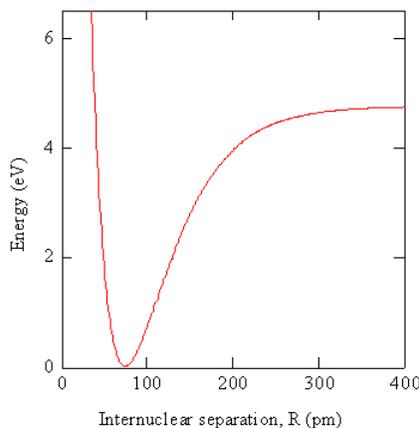


Figure 1.3.1 : The potential energy function for a diatomic molecule.

The graph in Figure 1.3.1 shows the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When  $R$  is very large there are two atoms that are weakly interacting. As  $R$  becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of  $R$ , the internuclear repulsion is very large so the energy is large and positive. This shows the energy advantage of chemical bonding but doesn't describe anything about molecular shapes or numbers of bonds that an atom will form.

Valence Bond (VB) Theory looks at the interaction between atoms to explain chemical bonds. It is one of the two common theories that helps describe the bonding between atoms. The other theory is Molecular Orbital Theory. Take note that these are theories and should be treated as such; they are not always perfect.

### Introduction

Valence Bond Theory has its roots in Gilbert Newton Lewis's paper *The Atom and The Molecule* in which he suggested that bonding results from sharing of electron pairs between two atoms. Walter Heitler and Fritz London brought a quantum mechanical foundation to explain this type of bonding and added the ideas that resonance and wavefunctions contributed to chemical bonds. Heitler and London's theory proved to be successful, providing Linus Pauling and John C. Slater with an opportunity to assemble a general chemical theory containing all of these ideas. Valence Bond Theory was the result, which included the ideas of atomic orbital overlap, hybridization, resonance, and covalent-ionic superposition to describe chemical bonds.

### Atomic Orbital Overlap

Valence bond theory describes that bonds are formed between atoms because the atomic orbitals overlap and the electrons in those orbitals are localized within the area of that overlap. They have a higher probability of being found within that bond; we will return to this statement when we talk about wavefunctions. Dihydrogen ( $H_2$ ) is a simple diatomic gas that has been used to illustrate this idea; however, let's look at  $Cl_2$  as a simple example. Chlorine has seven valence electrons. From its Lewis structure, one can see that Cl has a radical. That sole radical indicates that Cl can bond once. As a general rule, the number of unpaired electrons denotes how many bonds that atom can make. Since there is only one unpaired electron in each Cl, those electrons interact to bond. In this case, the 3p orbitals overlap. Lone pairs can be seen as the orbitals not interacting with each other. The idea of atomic orbitals overlapping works well for simple molecules, such as diatomic gases, but more complex molecules cannot be explained simply by the overlap of atomic orbitals, especially if they defy the octet rule when drawing out Lewis structures and if they bond beyond their predicted amount.

### Atomic Orbital Hybridization

Consider phosphorus pentafluoride ( $PF_5$ ). P, the central atom, has five valence electrons, with 2 electrons paired in the 3s orbital and three unpaired electrons in the 3p orbital. Thus, P should only be able to form three bonds based on its ground state atomic orbitals. However, since  $PF_5$  exists with phosphorus as the central atom, P must be able to bond five times. This requires [orbital](#)

**hybridization** which creates degenerate hybrid orbitals that allow atoms to bond well beyond their normal amount. Orbitals involved in hybridization are the s, p, and d atomic orbitals. There are certain principles for hybrid orbitals:

1. The number of orbitals mixed must match the number of resulting hybrid orbitals.
2. Hybrid orbitals are more directional than atomic orbitals and lead to greater overlap (which makes stronger bonds)

Hybrid orbitals consist of  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^2d$ ,  $sp^3d$ , and  $sp^3d^2$  (3). Returning back to  $PF_5$ , let's see how hybrid orbitals can describe its bonds. Remember that P can only bond three times, but we need it to bond five times. In order to bond five times, five orbitals must be singularly filled (one electron in each). Bonds occur when orbitals with only one electron are spin paired with the electron from another atom. The five orbitals can be acquired by  $sp^3d$  orbital hybridization. Starting off with a total of five atomic orbitals will result in five hybrid orbitals. Note that since P is in period 3, it has d orbitals in the same energy level. Thus, 3d orbitals can be used to hybridize, even though electrons do not occupy it in the ground state. The process is outlined in the figure below. Remember to follow the **aufbau principle**, **Hund's rule**, and the **Pauli exclusion principle** when assigning electrons to their orbitals. Note that only valence electrons are involved in hybridization and bonding.

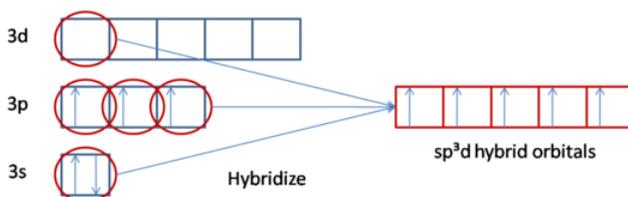


Figure1: Depiction of  $sp^3d$  hybridization.  
Author: Tony Chhom

Now, P has five hybrid orbitals. Remember that P has five valence electrons. Electrons too are not lost or gained, so those electrons transfer over to the hybrid orbitals. Fill them in accordingly, following Hund's rule and the Pauli exclusion principle. Note that the hybrid orbitals are now degenerate, so the aufbau principle doesn't apply for this case. From  $sp^3d$  hybridization, P has five unpaired electrons and can now bond with five fluorine atoms.

The number of hybrid orbitals ends up equal to the number of electron groups surrounding the atom. This includes lone pairs as well as bond pairs. In the example,  $PF_5$ , there are no lone pairs. The type of hybrid orbitals also corresponds to the molecular shape. In the case of  $PF_5$ , its shape as defined by **VSEPR** is trigonal bipyramidal. The shape can also be determined by the type of hybridization. With the following common shapes related to hybridization:

- $sp$  linear
- $sp^2$  trigonal planar
- $sp^3$  tetrahedral
- $sp^3d$  trigonal bipyramidal

## Wavefunctions in VB Theory

The wavefunction is a solution to the Schrödinger equation (a quantum mechanical solution for electrons) describes the state of an electron. From the name of the function, one can derive that the electron can behave like a wave. This wave-like behavior of the electrons defines the shapes of the orbitals. Thus, it makes sense that wavefunctions are related to Valence Bond Theory. If orbitals overlap to create bonds, and orbital shapes and the state of an electron is described by the wavefunction, then it makes sense that the overlap of orbitals (the bonds) can be described by wavefunctions as well. Thus, covalent and ionic bonds can be described by wavefunctions. Covalent and ionic representations of a bond represent the same bond, but they differ in how the electrons are placed. This is called resonance. Different intermolecular interactions give rise to different wavefunctions. Recall from Hund's Rule and the Pauli exclusion principle that electrons must be spin paired when the right conditions are met. Due to this, there are two separate ways to represent a covalent bond in terms of electron spin, which is related to the wavefunction. The figure shows the two different cases for two electrons in a bond. Thus, it is possible to write two different wavefunctions that describe each case, which can be superimposed to describe the overall covalent bond (2). The superposition of the covalent bond and ionic bond wavefunctions will result in an overall wavefunction that describes the state of the molecule. Due to this module being an overview of Valence Bond Theory, the full details will not be covered.



Figure 2: A) The electron from one undetermined atom to the left has an upward spin while the electron from another undetermined atom to the right has a downward spin. B) The spins are now reversed.  
Author: Tony Chhom

While the wavefunction doesn't have any direct physical significance, the wavefunction squared will result in a probability density of where the electrons are located relative to the nucleus. These give rise to the common shapes of s, p, d and f orbitals. Recall that when atomic orbitals overlap, the electrons are localized and more likely to be found within that overlap. In terms of electrostatic interactions, this bond will result in some form of equilibrium between all of the electrostatic forces (between the electrons and the electrons with each nucleus) (1). If the overlap is too far in, there is a net repulsion force; the electrons will also be forced apart. If the atomic orbital overlap is too small, the net attraction force is very small; the electron will have a smaller chance of remaining in the overlap since they will be more attracted to their own nucleus. If the overlap is just right, then the electrons are attracted to both nuclei and more likely to stay in the overlapped area. Thus, wavefunctions and electrostatic forces can both explain why electrons are localized within their bonds.

## Reliability of Valence Bond Theory and Uses

Valence Bond Theory can help describe how bonds are formed. However, there are some notable failures when it comes to Valence Bond Theory. One such failure is dioxygen. Valence Bond Theory fails to predict dioxygen's paramagnetism; it predicts that oxygen is diamagnetic. A species is paramagnetic if electrons are not spin paired and diamagnetic if the electrons are spin paired. Since Valence Bond theory begins with the basis that atomic orbitals overlap to create bonds and through that reasoning, one can see that electrons are spin paired when bonds overlap, dioxygen is indeed predicted to be diamagnetic if Valence Bond Theory is used. In reality, that is not the case. Also,  $sp^2d$  and  $sp^3$  both have a coordinate number of four. Thus, Valence Bond Theory cannot predict whether the molecule is a square planar or tetrahedral (3). One must correctly draw the Lewis structure and use VSEPR to determine the shape of some molecules.

## Problems

### ? Exercise 1.3.1

Draw the Lewis structures HF, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>. Which orbitals are involved with bonding for HF? Now, use hybridization to explain the bonds of CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>. Can you account for the single, double, and triple bonds via orbitals overlapping and hybridization? It is not required to draw the hybridization process, but it might help you in your thinking.

#### Answer

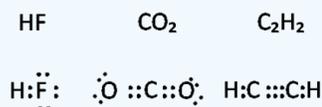


Figure 3: Lewis structures of HF, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>. Author: Tony Chhom

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HF: Hydrogen has one electron in the 1s orbital. Fluorine has two electrons in the 2s orbital, and five in the 2p orbitals. These can be derived from the electron configurations. We are only interested in the valence electrons, so the lower shell can be ignored. Remember to fill in the orbitals accordingly. The orbitals available to bond are Hydrogen's 1s orbital and one of Fluorine's 2p orbitals. Thus, the bond must take place between these two orbitals. This is a sigma bond. A bond of this type, or one of similar orientation, such as two s orbitals, are the bonds associated with hybrid orbitals when hybridization takes place.

CO<sub>2</sub>: C has four valence electrons; two are in 2s and two are in 2p. O has six valence electrons; two in 2s and four in 2p. Notice that there is a double bond. Now, hybridize to explain the bonds. When determining the coordinate number, double bonds and triple bonds count as one bond. Thus, the coordinate number of C is 2 and the corresponding hybridization is sp. The diagram below shows the sp hybridization process for C. Notice that two 2p orbital remains unhybridized. We fill in the hybrid orbitals with two of C's electrons so that C has space available to bond with the two O's. The hybrid orbitals describes two sigma bonds between C and the O's; one 2p orbital from each O is used in this process. Two electrons remain for C, which are allocated to the unhybridized orbitals. Now, C can form the other two bonds for a total of four which is what is expected due to the presence of two double bonds. The unhybridized orbitals overlap O's 2p orbitals and forms what is called a pi bond. There is one pi bond and one sigma bond between C and each O. The lone pairs of the O's are the filled 2s orbital and the final and filled 2p

orbital. Thus, a double bond is explained by one sigma bond associated with the hybrid orbitals and a pi bond associated with unhybridized p orbitals.

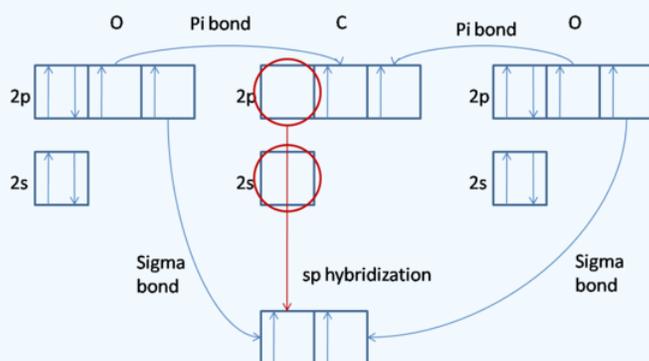


Figure 4:  $sp$  hybridization and types of bonds.  
Author: Tony Chhom

$C_2H_2$ : C has four valence electrons (two in 2s and two in 2p) and H has one (one in 1s). There is a total of ten valence electrons. From the Lewis structure, one can see that there is a triple bond between the two C's. For each C, one can explain the bonds through  $sp$  hybridization (a triple bond and one single bond). This process is similar to  $CO_2$ . However, in this case, C's available unhybridized 2p orbitals bond together with the unhybridized p orbitals of the other C. Now, there are two pi bonds and one sigma bond between the C's; there is one sigma bond between each C and H bond. Thus, a triple bond is explained by one sigma bond associated with the hybrid orbitals and two pi bonds associated with unhybridized p orbitals.

### ? Exercise 1.3.2

Using VSEPR, one can derive that  $IBr_5$  has an octahedral parent shape. Now, use Valence Bond Theory to account for all of the bonds and verify that the parent shape is indeed an octahedral. Why can you determine the parent shape of a molecule based on Valence Bond Theory? Show your work.

#### Answer

I is the central atom. Usually, the least electronegative atom is the central atom. Drawing the Lewis structure reveals that I can only form one bond. However, with the use of hybridization, I can form more bonds. Showing that is the goal. First, find out how many valence electrons  $IBr_5$  has. This is simply derived by adding all of the valence electrons from each atom; all have 7 valence electrons, so  $(6)(7)=42$ . Then, use Lewis structure and allocate all of the electrons into the correct places. You will find that the Lewis structure looks like the picture below.



Figure 5: Lewis dot structure of  $IBr_5$ . Author: Tony Chhom

Notice that there is a lone pair. Remember that the number of hybrid orbitals needed is the summation of lone pairs and bonds. This is a total of six; thus a  $sp^3d^2$  hybridization is needed. This process is shown below. Take note that the lone pair is the only spin paired electrons in the hybrid orbitals. Since the coordinate number is six, then the family shape of this molecule is an octahedral shape. Even the lone pairs are accounted for when hybridization takes place. It is because we used the coordinate number (determined by using Lewis dot structure first) to determine the type of hybridization that hybridization does indeed give the correct family shape. There are of course exceptions, such as  $sp^2d$  and  $sp^3$ . We cannot predict the shape based on hybridization alone for these.

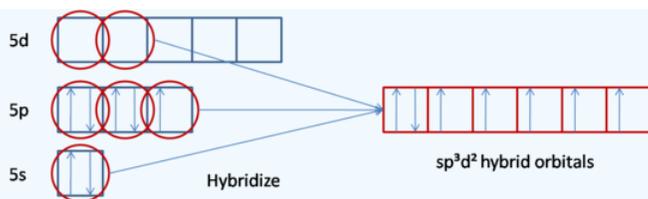


Figure 6: Original depiction of  $sp^3d^2$  hybridization.  
Author: Tony Chhom

### ? Exercise 1.3.3

Determine the family shapes correlated with the  $sp^3$ ,  $sp^3d$ , and  $sp^3d^2$  hybridization. Does this mean that all molecules with the respectable hybridization will have the same shape? Explain.

#### Answer

The shapes are tetrahedral, trigonal bipyramidal, and octahedral respectively. Not all molecules will have the shape associated with the hybridization type because lone pairs must be taken into account as well. For example, look at problem number two. The coordinate number is six. That tells you that the *parent shape* is an octahedral. However, the shape of  $IBr_5$  will only be that shape if the lone pair was another atom. The parent shape will not always match the actual shape of the molecule. It gives you a place to start and is only true if lone pairs do not exist. "Removing" one bond away from the octahedral shape will give the result of the square-base pyramidal shape.

### ? Exercise 1.3.4

Predict which of these atoms/molecules is diamagnetic using Valence Bond Theory: H,  $H_2$ , and NO.

#### Answer

One can solve this problem simply by counting the valence electrons. H has only one electron; it is not paired with any other electron and thus must be paramagnetic.  $H_2$  has two valence electrons; thus, those electrons are spin paired and  $H_2$  is diamagnetic. NO has eleven valence electrons; it is paramagnetic. In general, if an atom/molecule has an odd number of electrons, then that atom/molecule is paramagnetic. It is diamagnetic if it has an even number of electrons; however, like the case of  $O_2$ , this does not always work.

### ? Exercise 1.3.5

Briefly summarize Valence Bond Theory. Is it always reliable?

#### Answer

Valence Bond Theory looks at the interaction between orbitals to describe bonds. It can also be used to derive the shape of the molecule in question, as well as determining whether or not an atom/molecule is diamagnetic or paramagnetic; however Valence Bond Theory is not always reliable. It fails in some cases. One must always remember that this is a theory.

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