Valence Bond Theory 1

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Schrodinger's equation brought along with it the world of quantum mechanics. Now when we talk about bonding and electrons in particular, we must be able to describe what is happening in terms of wave functions and probability densities. Before, it was fine to say that when a covalent bond is formed, two atoms share a pair of electrons. But now the valence bond theory describes exactly what it means for two atoms to share electrons.

**INTRODUCTION**

What the valence bond theory introduces is the notion that orbitals with one electron overlap other orbitals also containing one electron of opposite spin to create an area of increased electron probability density, or a chemical bond.
If we recall when we learned about wavefunctions, waves can either have constructive or destructive interference. Every orbital has a corresponding wave function which represents the probability that an electron can be found within it. Constructive interference of these wavefunctions occur when the two waves that come together are "in-phase;" destructive interference occurs when the two waves are out of phase. The two wave functions have constructive interfere in a chemical bond which creates a new wavefunction for the area of orbital overlap. The valence bond theory is a localized electron theory. Electrons are constrained to the same orbital locations that they were in the individual atoms, and orbital themselves keep the same location.

I. This figure shows what does NOT happen in atomic orbital overlap.
II. This figure correctly identifies the type of constructive interference that takes place in covalent atomic orbital overlap. The wavefunctions of the two separate orbitals are in phase and increase the electron probability density in the orbital overlap. The two wavefunctions are out of phase and destructive interference takes place.

**WHY DO THE ATOMIC ORBITALS OVERLAP?**

As mentioned before, when two atomic orbitals come together, they form an area of increased electron probability. This overlap area is attracted to the nucleus much more than the two individual orbitals were. The electrons in the overlap are thus in a lower energy state which is the cause for the chemical bond. If this concept is hard to grasp, think back to the Bohr Atom representation of electron orbitals. The Bohr model says that the electron orbitals that come closer to the nucleus are attracted greatly to the nucleus and are thus in a lower energy state than orbitals further from the nucleus. If we apply this concept to the valence bond theory, we can say that areas of increased electron density probability are also much more attracted to the nucleus than areas of lesser electron density probability so are in a lower, more stable energy state.

**WHAT ARE PI AND SIGMA BONDS?**

*Sigma Bonds*
Among the covalent bonds, the bond with the most strength is considered the sigma bond because of its high stabilization between bonding orbitals. Sigma bonds are formed on the internuclear axis, are able to rotate and are considered symmetrical. Sigma bonds typically involve s-orbitals due to the single dimensional restraints of the s-orbitals. However, sigma bonds can also arise for an internuclear bond between two p-orbitals.

\[ \text{σ-Bindungen} \]

\[ \text{s-s} \quad \text{s-p}_z \quad \text{sp}^n \text{- sp}^n \quad \text{sp}^n \text{- s} \quad \text{p}_z \text{- p}_z \]

\[ \text{p}_z \text{- d}_z^2 \quad \text{d}_z^2 \text{- d}_z^2 \quad \text{d}_{x^2-y^2} \quad \text{d}_{x^2-y^2} \]

**Pi Bonds**

In contrast to sigma bonds, pi bonds involve p-orbitals and are not symmetrical around the axis and therefore cannot be rotated. Pi bonds are in most cases bonded along with sigma bonds. Pi bonds also have less strength than sigma bonds because the atomic orbitals have smaller overlaps.

\[ \text{Pi Bond formed from the overlap of two P orbitals.} \]

Single Bonds - Single bonds involve one sigma bond.

Double Bonds - Double bonds have one sigma bond and one pi bond. Although it may seem like a pi bond includes two bonds in itself, that is not true because the two overlaps occur within a single pi orbital. The reason for the two overlaps is that fact the p-orbitals include two phases separated by a nodal plane.
Triple Bonds - Triple bonds include one sigma bond and two pi bonds. The two pi bonds are perpendicular to each other so if you were to rotate the internuclear axis by 90°, the two pi bonds would seemingly switch places.

**Limitations of the Valence Bond Theory**

When the bonding scheme of certain polyatomic molecules is discussed, our simple valence bond theory fails to accurately describe what is going on. Methane is one of these molecules where we must expand upon our valence bond theory. The 2s orbital is filled with two electrons and the 2p\textsubscript{y} orbital has no electrons for use in bonding. This leaves only the 2p\textsubscript{x} and the 2p\textsubscript{z} orbitals as the orbitals that can participate in bonding. We know however, that in CH\textsubscript{4}, four hydrogen atoms must make four bonds with the central carbon atom.

What happens is that the carbon atom promotes one of its 2s electrons to the 2p\textsubscript{y} orbital. This leaves one electron in the 2s orbital and one electron in the 2p\textsubscript{y} orbital. All together, the central carbon now has four unpaired valence electrons to bond to each of the four hydrogen atoms. This is called hybridization.

To learn more about hybridization, [click here](#).

Another one of the shortcomings of the Valence Bond Theory is the inability to predict molecular geometries. If we take a look at the bonding orbitals of H\textsubscript{2}S, only two of the p orbitals of sulfur bond with a 1s orbital from H. The molecular geometry predicted by these two bonding orbitals is 90°. This is obviously incorrect because the valence bond theory does not take into account the lone pair electrons on the central S atom. The two lone pair electrons create a angle of 104.5° between the two hydrogen atoms. To learn more about electron geometries, [click here](#).
The following video is might help you to better understand the valence bond theory.

**IMPLICATIONS OF THE VALENCE BOND THEORY**

The valence bond theory can provide some essential insight into many of the chemical properties we observe. For example, the H-H bond strength in H2 is one of the strongest bonds because of the sigma bond between the hydrogen molecules. As we learned before sigma bonds are significantly stronger than pi bonds. Additionally, the involvement of only s-orbitals and increased overlap increases the bond strength. The F-F bond in F2 is significantly weaker due to the nature of the p-orbital bonds. There are many chemical properties such as bond strength and bond length that we can derive from analysis of the valence bonds that we would not be able to get from just lewis structures.

**Bond Dissociation Energy**

\[
\begin{align*}
\text{H}_2 & \quad 104.2 \text{ kcal/mol} \\
\text{F}_2 & \quad 36.6 \text{ kcal/mol}
\end{align*}
\]

*Figure showing the s-orbital overlap of the H₂ molecule. Figure by Parmveer Hansra.*
OUTSIDE LINKS

http://www.youtube.com/watch?v=SrY6xdwv3o4[1]
http://ocw.mit.edu/courses/chemistry...es/lecture-15/
http://www.youtube.com/watch?v=AzF8w...eature=related

REFERENCES


Drennan, Catherine, and Elizabeth Vogel Taylor. 5.111 Principles of Chemical Science, Fall 2008. (Massachusetts Institute of Technology: MIT OpenCourseWare), http://ocw.mit.edu (Accessed 21 Nov, 2010). License: Creative Commons BY-NC-SA

http://commons.wikimedia.org/wiki/Fi...a-bonds-2D.svg
http://keyhole.web.cern.ch/keyhole/t...y/hydrogen.jpg

PROBLEMS

1. How does a chemical bond form in terms of a valence bond method?
   a) Two electrons with the same spin overlap and the corresponding wavelengths constructively interfere.
   b) Electrons join together to create an area of high electron density probability.
   c) Two electrons of opposing spin overlap and the corresponding wavelengths constructively interfere.
   d) The internuclear forces share protons to form a chemical bond.
   e) Electron orbitals destructively interfere to form a chemical bond.

2. Describe the molecular geometry of H2O suggested by each of the following methods:
   (a) Lewis theory
   (b) valence-bond method using simple atomic orbitals (not hybridized);

3. What is the difference between a sigma bond and a pi bond? Compare and contrast the two.

4. Represent bonding in the CO2 molecule by
   a) Lewis structure
   b) The valence bond method
c) The orbital overlap

5. How many pi and sigma bonds does O2 have? What kind of a bond is this?

**Solutions**

1. C is correct
   - A is incorrect because of Pauli's exclusion principal.
   - B is incorrect because electrons don't join together.
   - D is incorrect because protons aren't involved in bonds.
   - E is incorrect because chemical bonds are formed with constructive interference.

2. a. There is a single bond between each hydrogen atom and the oxygen atom.
   - There are two lone pairs attached to the Oxygen atom because its electron configuration is [He] 2s22p4 creating a 104.5o bond angle.
   - The bond results from the overlapping of 1s orbital with a 2p orbital on O creating a 90o bond angle.

3. Sigma bonds are formed on the internuclear axis and are symmetrical if rotated. Pi bonds are not symmetrical. Typically sigma bonds are stronger than pi bonds due to the greater orbital overlap and resistance to rotation.

4. a. Lewis dot structure of CO2
   - Molecule is linear, and is a straight line with 180 degree angle. C is the central atom.
   - sp2 orbitals overlap each other.

5. O2 consists of 1 sigma bond and 1 pi bond. This is a double bond.

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