Both the MO and VB theories are used to help determine the structure of a molecule. Unlike the VB theory, which is largely based off of valence electrons, the MO theory describes structure more in depth by taking into consideration, for example, the overlap and energies of the bonding and antibonding electrons residing in a particular molecular orbital. While MO theory is more involved and difficult, it results in a more complete picture of the structure of a chosen molecule. Despite various shortcomings, complete disregard of one theory and not the other would hinder our ability to describe the bonding in molecules.

Overview of MO and VB Theories

The theories have their own unique approach to determine bonding and thus the overall structure of a molecule. MO theory involves the production of molecular orbitals from the combination of atomic orbitals in a molecule. These molecular orbitals are delocalized over the molecule. The atomic orbitals are most effectively combined if they are of similar energy. A simple example is of a homogeneous diatomic gas. In this case, the orbitals of the same level and type (3s or 4p for example) are exactly the same energy and thus bond very well. More complex molecules involve the use of symmetry and group theory, but similar concepts apply. In order to bond, the atomic orbitals must be of similar energy and symmetry; as simple as that may sound, it becomes increasingly more difficult to create molecular orbital diagrams to describe the bonding of more complex molecules. A unique feature of MO theory is the creation of two types of molecular orbitals: bonding molecular orbitals and antibonding molecular orbitals. These form by adding the wavefunctions of the electron in such a way that constructive interference, thus increasing the probability that the electron will be in that bond as deemed by the name bonding molecular orbital, occurs and destructive interference, which reduces the probability that the electron will be in that bond as deemed by the name antibonding molecular orbital, occurs as well. A molecule is said to be stable or able to exist in some form if it has a bond order, or put more simply, more bonding molecular orbitals with filled electrons than antibonding molecular orbitals with filled electrons. Bond order can also be used to verify that the molecular orbital diagram is efficient and even gives us an insight into the bond distance. We want the same bond order from the molecular orbital diagram as the number of bonds in the molecule. Bonding molecular orbitals are lower in energy than antibonding molecular orbitals.

In contrast, VB theory utilizes the overlap of molecular orbitals. The overlaps are where the bonds are formed and these bonds are localized. The theory of orbital hybridization can be used for more complex molecules. In this case, hybrid orbitals are created from the mixing of atomic orbitals so that bonding can occur. In contrast to the molecular orbitals in MO theory, these hybrid orbitals are degenerate. Of course, the concept of the conservation of atomic orbitals applies for both theories. We cannot lose or gain orbitals when applying these theories; the number of atomic orbitals we start off with must be equal to the number of orbitals created by either theory. In VB theory, only the required number of hybrid orbitals are created. If, for example, we have a molecule with a central atom that requires five bonds, we create only five hybrid orbitals. The orbitals not involved in mixing can further bond to produce double or triple bonds in certain molecules; they overlap in such a way to create pi bonds. Hybrid orbitals only represent sigma bonding, and in some cases, the lone pairs of the atom in question. Double and triple bonds arrive from the interaction between the orbitals not involved in hybridization. It is often more convenient to start off with the Lewis structure of the molecule and from there, apply VB theory to describe why that molecule exists in such a form.
General Concepts and Uses

MO theory mainly uses symmetry and group theory, while VB theory utilizes Lewis structures and hybridization. They both have their own uses. MO theory can be difficult and tedious, but it provides a very good description of what is happening in the molecule; it also provides a more accurate bonding picture for molecules in which VB theory fails, such as O_2. VB theory can help describe why the molecule is in its particular shape; it gives an excellent overall picture of bonding and can be less confusing than MO theory, especially for more complex molecules for MO theory. The following links provide further information and examples of each theory:

- MO Theory: Orbital Interactions
- Valence Bond Theory: HCN

Which is the Superior Theory? Competition Between MO and VB Theories

Since the early to mid 1900’s, scientists have been contemplating which theory is the better approach to determine structure. Despite continued heated debate, many others view the MO and VB theories as teammates, strengthening one aspect that the other theory lacks explanation for. It is true that both theories are used for different purposes, and the failures of some cases for VB theory may look like a setback for this particular theory and a victory for MO theory, but the truth is, the use of both theories is equally important. One must keep in mind that these are theories and not always perfect; thus, having more than one theory is a blessing, especially if one theory fails. By taking into consideration the strengths, one can deduce a structure and analyze inherent characteristics about the structure more deeply than if one theory was simply disregarded. In the words of Roald Hoffmann: “Taken together, MO and VB theories constitute not an arsenal, but a tool kit... Insistence on a journey... equipped with one set of tools and not the other puts one at a disadvantage. Discarding any one of the two theories undermines the intellectual heritage of chemistry.”

References


Outside Links

- Valence Bond Theory:
  - www.youtube.com/watch?v=SrY6xdwv3o4&feature=related
Problems

1. What are the major differences between MO and VB theory?
2. Construct bonding in O₂ using both theories. What information does one theory give you that the other does not?
3. Construct bonding in BH₃ using both theories. Discuss how each theory uniquely describes the observation that all three B-F bonds are equal in length.
4. There has been much heated debate about what the ultimate view of molecular bonding is. In your opinion, what theory would you side with? For what reason(s)?

Answers

(1) The differences between MO theory and VB theory is how they look at how the atomic orbitals interact. MO theory combines atomic orbitals to create molecular orbitals while VB theory discusses the overlap of atomic orbitals.

(2) Upon constructing O₂ using VB theory, you will realize that O₂ has a Lewis structure with a double bond between the O’s with two lone pairs on each O atom. This molecule (or more specifically, each O) has a sp² hybridization; this means that an s and two p orbitals overlap in such a fashion that three hybrid orbitals are created. These orbitals contain one bond between the O’s (the sigma bond) and the lone pairs of the O. The unhybridized p overlaps to create a pi bond between the two O’s. Since all electrons are paired, this molecule will be repelled by a magnetic field. It is said to be diamagnetic.

Upon constructing an MO diagram for O₂, you will see that both the bonding and antibonding orbitals for the 1s molecular orbital is filled in (with two electrons each). The next to be filled in is the sigma bonding orbital between the p_z orbitals. This is followed by the pi bonding of the p_x and p_y orbitals. Finally, we fill in the pi antibonding orbitals; however, we must remember to apply Hund’s rule, so we have to singularly fill in each pi antibonding orbital. Overall, we used twelve valence electrons. Not all electrons are spin paired, so this molecule will be attracted to a magnetic field. It is said to be paramagnetic. This turns out to be true. The original picture below will help you.
(3) Using VB theory: Construction of the Lewis dot structure of BH$_3$ will result in B being in the center being singularly bonded and surrounded by all three H atoms. Since B is bonded to the same atom three times in exactly the same way, it makes sense that the bond lengths are all equal.

Using MO theory: Constructing BH$_3$ for MO theory requires the use of ligand group orbitals. Just treat H$_3$ as one "orbital" for the time being on the molecular orbital diagram. Upon construction of the MO diagram, one can use the bond order of each bond (which should all be the same) to determine that the bond lengths are the same. There is a general correlation between bond length and bond order: the higher the bond order, the smaller the bond length. If they have the same bond number and are all exactly the same, then they will have the same bond length. See *Inorganic Chemistry Third Edition* page 128 for the complete MO diagram.

(4) Answer depends on the reader.

**Contributors**

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