Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is not infallible. It predicts, for example, that H₂S and PH₃ should have structures similar to those of H₂O and NH₃, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H₂O and NH₃. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX₂), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF₂ and BaF₂, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms.

Valence Bond Theory: A Localized Bonding Approach

Valence Bond Theory has its roots in Gilbert Newton Lewis's paper *The Atom and The Molecule*. Possibly unaware that Lewis’s model existed, Walter Heitler and Fritz London came up with the idea that resonance and wavefunctions contributed to chemical bonds, in which they used dihydrogen as an example. Their theory was equivalent to Lewis’s theory, with the difference of quantum mechanics being developed. Nonetheless, 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 resonance, covalent-ionic superposition, atomic orbital overlap, and hybridization to describe chemical bonds.

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm. According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a maximum of two electrons with opposite spin, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1s atomic orbital of one hydrogen atom overlaps with the singly occupied 1s atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a localized electron-pair bond (Figure \(\PageIndex{1}\)).
The formation of $\text{H}_2$ from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an $\text{H}_2$ molecule increases the electron density in the region between the two positively charged nuclei.

Although both Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure \(\PageIndex{2}\) shows an electron-pair bond formed by the overlap of two $ns$ atomic orbitals, two $np$ atomic orbitals, and an $ns$ and an $np$ orbital where $n = 2$. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.
An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where \( n = 2 \). The positive lobe is indicated in yellow, and the negative lobe is in blue.

An important aspect of Valence Bond theory is the concept of maximum overlap to form the strongest possible covalent bonds.

Let’s examine the bonds in BeH\(_2\), for example. According to the VSEPR model, BeH\(_2\) is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a \( 1s^22s^2 \) electron configuration, and each H atom has a \( 1s^1 \) electron configuration. Because the Be atom has a filled \( 2s \) subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied \( 1s \) orbitals on the H atoms. If a singly occupied \( 1s \) orbital on hydrogen were to overlap with a filled \( 2s \) orbital on beryllium, the resulting bonding orbital would contain three electrons, but the maximum allowed by quantum mechanics is two. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its \( 2s \) electrons into an empty \( 2p \) orbital and reverse its spin, in a process called promotion:

In this excited state, the Be atom would have two singly occupied atomic orbitals (the \( 2s \) and one of the \( 2p \) orbitals), each of which could overlap with a singly occupied \( 1s \) orbital of an H atom to form an electron-pair bond. Although this would produce BeH\(_2\), the two Be–H bonds would not be equivalent: the \( 1s \) orbital of one hydrogen atom would overlap
with a Be 2s orbital, and the 1s orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2p orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH₂ form, scientists developed the concept of hybridization.

**Reliability of Valence Bond Theory and Uses**

As one can see, 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, sp²d and sp³ both have a coordinate number of four. Thus, Valence Bond Theory cannot predict whether the molecule is a square planar or the other shape (3). One must correctly draw the Lewis structure and use VSEPR to determine the shape.

**Contributors and Attributions**

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