

6.2: Valence Bond Theory: Orbital Overlap as a Chemical Bond

Key Concept Video Valence Bond Theory

In the Lewis model, a chemical bond is a shared electron pair. In **valence bond theory**, a chemical bond is the overlap between two half-filled **atomic orbitals (AOs)**. Unlike the Lewis model, which represents valence electrons as dots, valence bond theory treats valence electrons as residing in quantum-mechanical atomic orbitals. In some cases, these orbitals are simply the standard *s*, *p*, *d*, and *f* atomic orbitals that we learned about in **Chapter 2**. In other cases, these orbitals are *hybridized atomic orbitals*, a kind of blend or combination of two or more standard atomic orbitals.

Valence bond theory is an application of a general quantum-mechanical approximation method called *perturbation theory*. In perturbation theory, a complex system (such as a molecule) is viewed as a simpler system (such as two atoms) that is slightly altered or perturbed by some additional force.

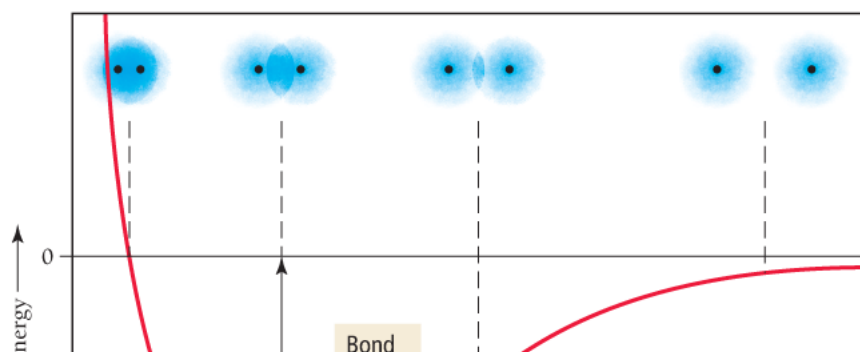
When two atoms approach each other, the electrons and nucleus of one atom interact with the electrons and nucleus of the other atom. In valence bond theory, we calculate the effect of these interactions on the energies of the valence electrons in the atomic orbitals. If the energy of the system is lowered because of the interactions, then a chemical bond forms. If the energy of the system is raised by the interactions, then a chemical bond does not form.

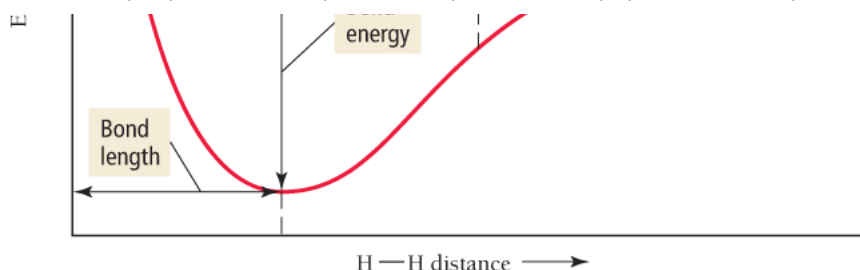
The interaction energy is usually calculated as a function of the distance between the nuclei of the two bonding atoms. **Figure 6.1** shows the calculated interaction energy between two hydrogen atoms as a function of the distance between their nuclei. The *y*-axis of the graph is the potential energy that results from the interactions between the charged particles in the two atoms. The *x*-axis is the separation (or internuclear distance) between the two atoms. As we can see from the graph, when the atoms are far apart (right side of the graph), the interaction energy is nearly zero because the two atoms do not interact to any significant extent. As the atoms get closer, the interaction energy becomes negative. This is a net stabilization that attracts one hydrogen atom to the other. If the atoms get too close, however, the interaction energy begins to rise, primarily because of the mutual repulsion of the two positively charged nuclei.

Figure 6.1 Interaction Energy Diagram for H_2

The potential energy of two hydrogen atoms is lowest when they are separated by a distance that allows their *1s* orbitals a substantial degree of overlap without too much repulsion between their nuclei. This distance, at which the system is most stable, is the bond length of the H_2 molecule.

Interaction Energy of Two Hydrogen Atoms





The most stable point on the curve occurs at the minimum of the interaction energy—this is the bond length. At this distance, the two atomic $1s$ orbitals have a significant amount of overlap, and the electrons spend time in the internuclear region where they interact with both nuclei. The value of the interaction energy at the equilibrium bond distance is the bond energy.

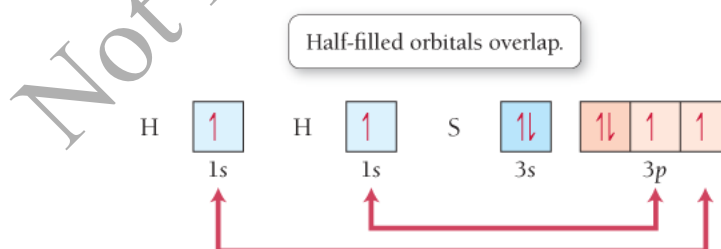
When we apply valence bond theory to calculate the interaction energies for a number of atoms and their corresponding molecules, we arrive at the following general observation: *The interaction energy is usually negative (or stabilizing) when the interacting atomic orbitals contain a total of two electrons that can spin-pair (orient with opposing spins).* Most commonly, the two electrons come from two half-filled orbitals, but in some cases, the two electrons come from one filled orbital overlapping with a completely empty orbital (this is called a coordinate covalent bond, and we will cover it in more detail in [Chapter 22](#)). In other words, when two atoms with half-filled orbitals approach each other, the half-filled orbitals *overlap*—parts of the orbitals occupy the same space—and the electrons occupying them align with opposite spins. This results in a net energy stabilization that constitutes a covalent chemical bond. The resulting geometry of the molecule emerges from the geometry of the overlapping orbitals.

When *completely filled* orbitals overlap, the interaction energy is positive (or destabilizing) and no bond forms.

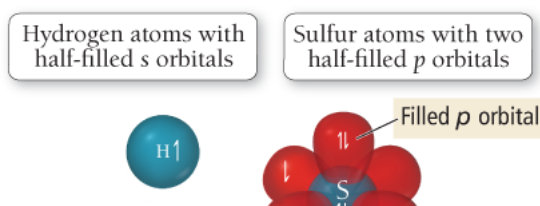
Summarizing Valence Bond Theory:

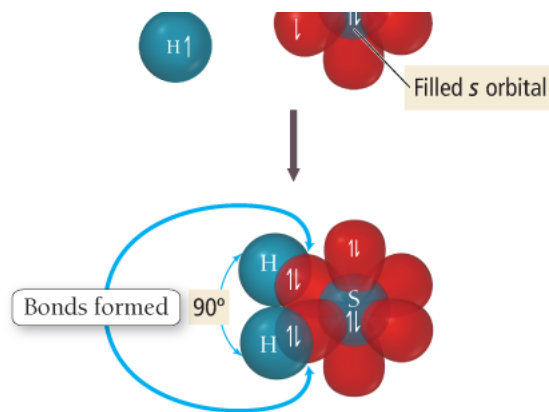
- The valence electrons of the atoms in a molecule reside in quantum-mechanical atomic orbitals. The orbitals can be the standard s , p , d , and f orbitals, or they may be hybrid combinations of these.
- A chemical bond results from the overlap of two half-filled orbitals and spin-pairing of the two valence electrons (or less commonly the overlap of a completely filled orbital with an empty orbital).
- The geometry of the overlapping orbitals determines the shape of the molecule.

We can apply the general concepts of valence bond theory to explain bonding in hydrogen sulfide, H_2S . The valence electron configurations of the atoms in the molecule are as follows:



The hydrogen atoms each have one half-filled orbital, and the sulfur atom has two half-filled orbitals. The half-filled orbitals on each hydrogen atom overlap with the two half-filled orbitals on the sulfur atom, forming two chemical bonds as illustrated in the following diagram:





To illustrate the spin-pairing of the electrons in the overlapping orbitals, we superimpose a half-arrow for each electron in each half-filled orbital and show that, within a bond, the electrons are spin-paired (one half-arrow is pointing up, and the other is pointing down). We also superimpose paired half-arrows in the filled sulfur s and p orbitals to represent the lone pair electrons in those orbitals. (Since those orbitals are full, they are not involved in bonding.)

A quantitative calculation of H_2S using valence bond theory yields bond energies, bond lengths, and bond angles. In the qualitative treatment here, we simply show how orbital overlap leads to bonding and make a rough sketch of the molecule based on the overlapping orbitals. Notice that, because the overlapping orbitals on the central atom (sulfur) are p orbitals and because p orbitals are oriented at 90° to one another, the predicted bond angle is 90° . The actual bond angle in H_2S is 92° . In the case of H_2S , a simple valence bond treatment matches well with the experimentally measured bond angle (in contrast to VSEPR theory, which predicts a bond angle of a bit less than 109.5°).

Conceptual Connection 6.1 What Is a Chemical Bond? Part I

Interactive

Not for Distribution