

## 1.10: The Chemical Bond

### The Hydrogen Molecule

This four-particle system, two nuclei plus two electrons, is described by the Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (1.10.1)$$

in terms of the coordinates shown in Figure 1.10.1. We note first that

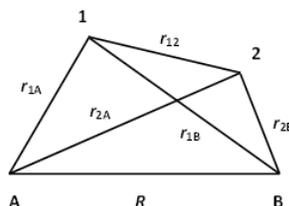


Figure 1.10.1: Coordinates used for hydrogen molecule.

the masses of the nuclei are much greater than those of the electrons,  $M_{\text{proton}} = 1836$  atomic units, compared to  $m_{\text{electron}} = 1$  atomic unit. Therefore nuclear kinetic energies will be negligibly small compared to those of the electrons. In accordance with the Born-Oppenheimer approximation, we can first consider the electronic Schrödinger equation

$$\hat{H}_{\text{elec}}\psi(r_1, r_2, R) = E_{\text{elec}}(R)\psi(r_1, r_2, R) \quad (1.10.2)$$

where

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (1.10.3)$$

The internuclear separation  $R$  occurs as a parameter in this equation so that the Schrödinger equation must, in concept, be solved for each value of the internuclear distance  $R$ . A typical result for the energy of a diatomic molecule as a function of  $R$  is shown in Figure 1.10.2. For a bound state, the energy minimum occurs at for  $R = R_e$ , known as the *equilibrium internuclear distance*. The depth of the potential well at  $R_e$  is called the *binding energy* or *dissociation energy*  $D_e$ . For the  $\text{H}_2$  molecule,  $D_e = 4.746$  eV and  $R_e = 1.400$  bohr =  $0.7406$  Å. Note that as  $R \rightarrow 0$ ,  $E(R) \rightarrow \infty$ , since the  $1/R$  nuclear repulsion will become dominant.

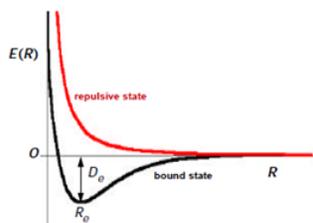


Figure 1.10.2. Energy curves for a diatomic molecule.

The more massive nuclei move much more slowly than the electrons. From the viewpoint of the nuclei, the electrons adjust almost instantaneously to any changes in the internuclear distance. The electronic energy  $E_{\text{elec}}(R)$  therefore plays the role of a *potential energy* in the Schrödinger equation for nuclear motion

$$\left\{ -\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 + V(R) \right\} \chi(r_A, r_B) = E\chi(r_A, r_B) \quad (1.10.4)$$

where

$$V(R) = E_{\text{elec}}(R) \quad (1.10.5)$$

from solution of Equation 1.10.2. Solutions of Equation 1.10.4 determine the vibrational and rotational energies of the molecule. These will be considered elsewhere. For the present, we are interested in the obtaining electronic energy from Equation 1.10.2 and 1.10.3. We will thus drop the subscript "elec" on  $\hat{H}$  and  $E(R)$  for the remainder this Chapter.

The first quantum-mechanical account of chemical bonding is due to Heitler and London in 1927, only one year after the Schrödinger equation was proposed. They reasoned that, since the hydrogen molecule  $H_2$  was formed from a combination of hydrogen atoms  $A$  and  $B$ , a first approximation to its electronic wavefunction might be

$$\psi(r_1, r_2) = \psi_{1s}(r_{1A})\psi_{1s}(r_{2B}) \quad (1.10.6)$$

Using this function into the variational integral

$$\tilde{E}(R) = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau} \quad (1.10.7)$$

the value  $R_e \approx 1.7$  bohr was obtained, indicating that the hydrogen atoms can indeed form a molecule. However, the calculated binding energy  $D_e \approx 0.25$  eV, is much too small to account for the strongly-bound  $H_2$  molecule. Heitler and London proposed that it was necessary to take into account the *exchange* of electrons, in which the electron labels in Equation 1.10.6 are reversed. The properly symmetrized function

$$\psi(r_1, r_2) = \psi_{1s}(r_{1A})\psi_{1s}(r_{2B}) + \psi_{1s}(r_{1B})\psi_{1s}(r_{2A}) \quad (1.10.8)$$

gave a much more realistic binding energy value of 3.20 eV, with  $R_e = 1.51$  bohr. We have already used exchange symmetry (and antisymmetry) in our treatment of the excited states of helium. The variational function (Equation 1.10.8) was improved (Wang, 1928) by replacing the hydrogen 1s functions  $e^{-r}$  by  $e^{-\zeta r}$ . The optimized value  $\zeta = 1.166$  gave a binding energy of 3.782 eV. The quantitative breakthrough was the computation of James and Coolidge (1933). Using a 13-parameter function of the form

$$\psi(r_1, r_2) = e^{-\alpha(\xi_1 + \xi_2)} \times \text{polynomial in } \{\xi_1, \xi_2, \eta_1, \eta_2, \rho\}, \xi_i \equiv \frac{r_{iA} + r_{iB}}{R}, \eta_i \equiv \frac{r_{iA} - r_{iB}}{R}, \rho \equiv \frac{r_{12}}{R} \quad (1.10.9)$$

they obtained  $R_e = 1.40$  bohr,  $D_e = 4.720$  eV. In a sense, this result provided a proof of the validity of quantum mechanics for molecules, in the same sense that Hylleraas' computation on helium was a proof for many-electron atoms.

## The Valence Bond Theory

The basic idea of the Heitler-London model for the hydrogen molecule can be extended to chemical bonds between any two atoms. The orbital function (8) must be associated with the singlet spin function  $\sigma_{0,0}(1, 2)$  in order that the overall wavefunction be antisymmetric. This is a quantum-mechanical realization of the concept of an electron-pair bond, first proposed by G. N. Lewis in 1916. It is also now explained why the electron spins must be paired, i.e., antiparallel. It is also permissible to combine an antisymmetric orbital function with a triplet spin function but this will, in most cases, give a repulsive state, as shown by the red curve in Figure 1.10.2

According to valence-bond theory, unpaired orbitals in the valence shells of two adjoining atoms can combine to form a chemical bond if they overlap significantly and are symmetry compatible. A  $\sigma$ -bond is cylindrically symmetrical about the axis joining the atoms. Two  $s$  AO's, two  $p_z$  AO's or an  $s$  and a  $p_z$  can contribute to a  $\sigma$ -bond, as shown in Figure 1.10.3 The  $z$ -axis is chosen along the internuclear axis. Two  $p_x$  or two  $p_y$  AO's can form a  $\pi$ -bond, which has a nodal plane containing the internuclear axis. Examples of symmetry-incompatible AO's would be an  $s$  with a  $p_x$  or a  $p_x$  with a  $p_y$ . In such cases the overlap integral would vanish because of cancelation of positive and negative contributions. Some possible combinations of AO's forming  $\sigma$  and  $\pi$  bonds are shown in Figure 1.10.3

Bonding in the HCl molecule can be attributed to a combination of a hydrogen 1s with an unpaired  $3p_z$  on chlorine. In  $Cl_2$ , a sigma bond is formed between the  $3p_z$  AO's on each chlorine. As a first approximation, the other doubly-occupied AO's on chlorine-the inner shells and the valence-shell lone pairs-are left undisturbed.

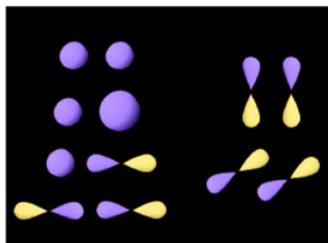


Figure 1.10.3. Formation of  $\sigma$  and  $\pi$  bonds.

The oxygen atom has two unpaired  $2p$ -electrons, say  $2p_x$  and  $2p_y$ . Each of these can form a  $\sigma$ -bond with a hydrogen  $1s$  to make a water molecule. It would appear from the geometry of the  $p$ -orbitals that the HOH bond angle would be  $90^\circ$ . It is actually around  $104.5^\circ$ . We will resolve this discrepancy shortly. The nitrogen atom, with three unpaired  $2p$  electrons can form three bonds. In  $\text{NH}_3$ , each  $2p$ -orbital forms a  $\sigma$ -bond with a hydrogen  $1s$ . Again  $90^\circ$  HNH bond angles are predicted, compared with the experimental  $107^\circ$ . The diatomic nitrogen molecule has a triple bond between the two atoms, one  $\sigma$  bond from combining  $2p_z$  AO's and two  $\pi$  bonds from the combinations of  $2p_x$ 's and  $2p_y$ 's, respectively.

## Hybrid Orbitals and Molecular Geometry

To understand the bonding of carbon atoms, we must introduce additional elaborations of valence-bond theory. We can write the valence shell configuration of carbon atom as  $2s^2 2p_x 2p_y$ , signifying that two of the  $2p$  orbitals are unpaired. It might appear that carbon would be divalent, and indeed the species  $\text{CH}_2$  (carbene or methylene radical) does have a transient existence. But the chemistry of carbon is dominated by tetravalence. Evidently it is a good investment for the atom to promote one of the  $2s$  electrons to the unoccupied  $2p_z$  orbital. The gain in stability attained by formation of four bonds more than compensates for the small excitation energy. It can thus be understood why the methane molecule  $\text{CH}_4$  exists. The molecule has the shape of a regular tetrahedron, which is the result of *hybridization*, mixing of the  $s$  and three  $p$  orbitals to form four  $sp^3$  hybrid atomic orbitals. Hybrid orbitals can overlap more strongly with neighboring atoms, thus producing stronger bonds. The result is four C-H  $\sigma$ -bonds, identical except for orientation in space, with  $109.5^\circ$  H-C-H bond angles.

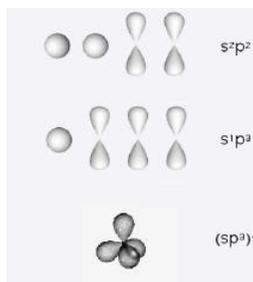
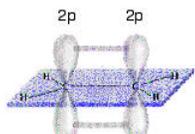
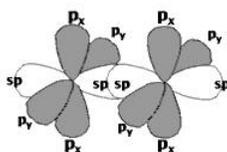


Figure 1.10.4. Promotion and hybridization of atomic orbitals in carbon atom.

Other carbon compounds make use of two alternative hybridization schemes. The  $s$  AO can form hybrids with *two* of the  $p$  AO's to give three  $sp^2$  hybrid orbitals, with one  $p$ -orbital remaining unhybridized. This accounts for the structure of ethylene (ethene):



The C-H and C-C  $\sigma$ -bonds are all trigonal  $sp^2$  hybrids, with  $120^\circ$  bond angles. The two unhybridized  $p$ -orbitals form a  $\pi$ -bond, which gives the molecule its rigid planar structure. The two carbon atoms are connected by a double bond, consisting of one  $\sigma$  and one  $\pi$ . The third canonical form of  $sp$ -hybridization occurs in C-C triple bonds, for example, acetylene (ethyne). Here, two of the  $p$  AO's in carbon remain unhybridized and can form two  $\pi$ -bonds, in addition to a  $\sigma$ -bond, with a neighboring carbon:



Acetylene  $\text{H-C}\equiv\text{C-H}$  is a linear molecule since  $sp$ -hybrids are oriented  $180^\circ$  apart.

The deviations of the bond angles in  $\text{H}_2\text{O}$  and  $\text{NH}_3$  from  $90^\circ$  can be attributed to fractional hybridization. The angle H-O-H in water is  $104.5^\circ$  while H-N-H in ammonia is  $107^\circ$ . It is rationalized that the  $p$ -orbitals of the central atom acquire some  $s$ -character and increase their angles towards the tetrahedral value of  $109.5^\circ$ . Correspondingly, the lone pair orbitals must also become hybrids. Apparently, for both water and ammonia, a model based on tetrahedral orbitals on the central atoms would be closer to the actual behavior than the original selection of  $s$ - and  $p$ -orbitals. The hybridization is driven by repulsions between the electron densities of neighboring bonds.

## Valence Shell Model

An elementary, but quite successful, model for determining the shapes of molecules is the *valence shell electron repulsion theory* (VSEPR), first proposed by Sidgwick and Powell and popularized by Gillespie. The local arrangement of atoms around each multivalent center in the molecule can be represented by  $AX_{n-k}E_k$ , where X is another atom and E is a lone pair of electrons. The geometry around the central atom is then determined by the arrangement of the  $n$  electron pairs (bonding plus nonbonding), which minimizes their mutual repulsion. The following geometric configurations satisfy this condition:

### $n$ shape

2 linear 5 trigonal bipyramid

3 trigonal planar 6 octahedral

4 tetrahedral 7 pentagonal bipyramid

The basic geometry will be distorted if the  $n$  surrounding pairs are not identical. The relative strength of repulsion between pairs follows the order  $E-E > E-X > X-X$ . In ammonia, for example, which is  $NH_3E$ , the shape will be tetrahedral to a first approximation. But the lone pair E will repel the N-H bonds more than they repel one another. Thus the E-N-H angle will increase from the tetrahedral value of  $109.5^\circ$ , causing the H-N-H angles to decrease slightly. The observed value of  $107^\circ$  is quite well accounted for. In water,  $OH_2E_2$ , the opening of the E-O-E angle will likewise cause a closing of H-O-H, and again,  $104.5^\circ$  seems like a reasonable value.

Valence-bond theory is about 90% successful in explaining much of the descriptive chemistry of ground states. VB theory fails to account for the triplet ground state of  $O_2$  or for the bonding in electron-deficient molecules such as diborane,  $B_2H_6$ . It is not very useful in consideration of excited states, hence for spectroscopy. Many of these deficiencies are remedied by molecular orbital theory, which we take up in the next Chapter.

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