Valence Bond Theory

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1 Introduction

The development of quantum mechanics (QM) (the Schrödinger Equation, $H\Psi = E\Psi$), placed a theoretical foundation under the experimental science of chemistry. One could argue (as did Dirac in a famous quote) that understanding chemistry is just a matter of solving these equations. In fact, this is not correct. Doing chemistry requires a qualitative understanding of how a reaction would change if the solvent, temperature, or pressure is changed or if the concentrations or ingredients are changed. Assuming that we could actually solve the Schrödinger Equation for any specified conditions would not necessarily provide any understanding of the chemistry. We require concepts based on QM, but which allow us to make *comparisons: atoms to molecules, ground to excited states, reactants to products, etc.*

The orbital description of atoms and molecules is probably the most powerful unifying concept to provide such understanding. At the foundation is the Aufbau principle for atoms serves as a semi-universal ordering of hydrogen-like orbitals that explains the periodic changes in the ground state character of the atoms and their excited states. Similarly, our most powerful concepts of molecular structures and properties are based on combining these atomic orbitals in ways appropriate for molecules. There are two major paradigms for doing this:

1. Molecular Orbital (MO) Theory. In MO theory one starts with a molecular framework and considers combinations of the atomic orbitals optimum for the molecule. These one-electron orbitals are ordered by energy, and the electrons are used to populate the lowest ones (retaining the Pauli principle—no more than 2 electrons per orbital). This approach is particularly useful for predicting excited states and is quite popular in spectroscopy. Also it is the framework used in rigorous QM calculations that go by such names as Hartree-Fock (HF), Self-Consistent Field (SCF), Density Functional Theory (DFT). Thus to describe N_2, we would take the 5 occupied atomic orbitals (denoted $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$) of each N atom and form 10 molecular orbitals (denoted $\sigma_g 1s$, $\sigma_u 1s$, etc) and occupy the lowest 7 with 2 electrons each (one with up-spin and one with down-spin).

2. Valence Bond (VB) Theory. In VB theory one starts with the occupied atomic orbitals of the atoms and constructs a many-electron wave function to describe bonding directly in terms of these atomic orbitals. This may sound similar to MO but the differences will become transparent below. VB theory is most useful for describing reactions and bond dissociations. This is because the many-electron states of the atoms are built into VB. However, VB is computationally much more complicated than MO and it is much less obvious how to describe excited states in terms of VB. Important chemical concepts such as resonance are based on VB concepts.

In this chapter we will illustrate the use of VB and MO concepts for the simplest molecules (H_2, He_2) and then apply these ideas to two simple problems that detail how to use them.

2 Bonding in H_2^+

We first consider the smallest possible molecule, H_2^+, consisting of one electron and two protons that are separated by a distance R. This system is sketched in Figure 1, where the two protons are denoted as a and b. The most important question is whether this system forms a bond (i.e. is the lowest energy for a finite value of R).

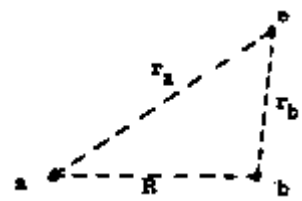

Figure 1: Coordinate system for H_2^+

2.1 Description Based Upon Linear Combination of Atomic Orbitals

Consider first the case with $R = \infty$. With the two protons infinitely far apart, the ground state is obtained by placing the electron in the $1s$ orbital of one or the other of the two protons. This leads to the two states, HH^+ and H^+H, which are described by the wave functions,

$$\chi_\ell = N \exp(-R_a) \tag{1}$$

and

$$\chi_r = N \exp(-R_b) \tag{2}$$

respectively, where χ_ℓ and χ_r denote hydrogen $1s$ orbitals centered on the left and right protons. N is a normalization factor – a scalar factor included to guarantee that the wave function contains only one electron.

For finite R, the exact wave functions no longer have the atomic form, but useful approximate wave functions are obtained by combining the atomic orbitals to form the wave function

$$\varphi = C_\ell \chi_\ell + C_r \chi_r. \tag{3}$$

This simple wave function is often referred to as linear combination of atomic orbitals (LCAO). The optimum linear combination of atomic orbitals wave function is the symmetric combination,

$$\varphi_g = \chi_\ell + \chi_r \tag{4}$$

where for simplicity we now ignore the normalization factor. The other combination of the orbitals is the antisymmetric combination,

$$\varphi_u = \chi_\ell - \chi_r \tag{5}$$

where again we ignore normalization.

The g and u labels denote the symmetry of the wave functions with respect to inversion, and stand for the German words *gerade* (even) and *ungerade* (uneven). Although symmetry arguments can be very powerful, we eschew them here, and the reader may assume that these labels represent *good* and *ungood*.

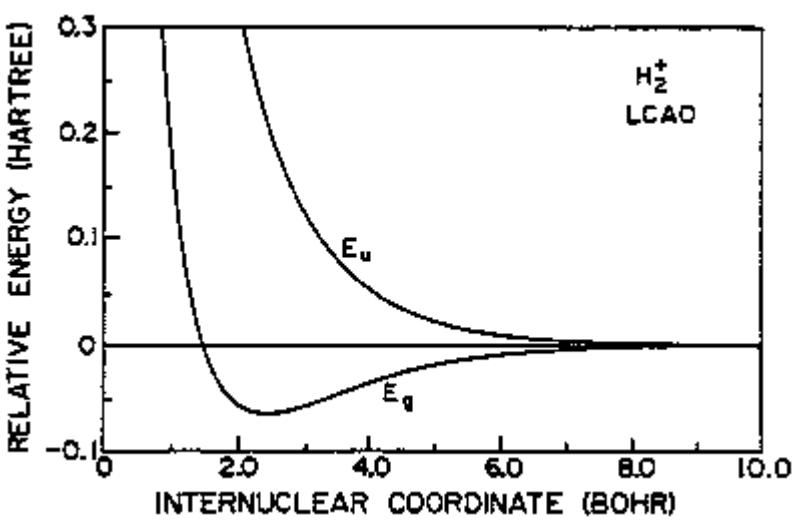

Figure 2: Bonding of the g and u states for H_2^+

The energies for the wave functions φ_g and φ_u in equations (4) and (5) are shown as a function of R in Figure 2. Here we see that the g state is strongly bonding (the energy drops as the nuclei are brought together), whereas the u state is strongly antibonding (the energy increases as the nuclei are brought together). Thus starting with two atoms at $R = 2$Å(4 bohr), the g state would experience forces pushing it toward smaller R, whereas the u state would hava a force pushing the atoms apart to $R = \infty$. The

objective of this section is to understand both the the φ_g and φ_u states bonding and antibonding character.

2.2 Contragradience and the Origin of Chemical Bonding

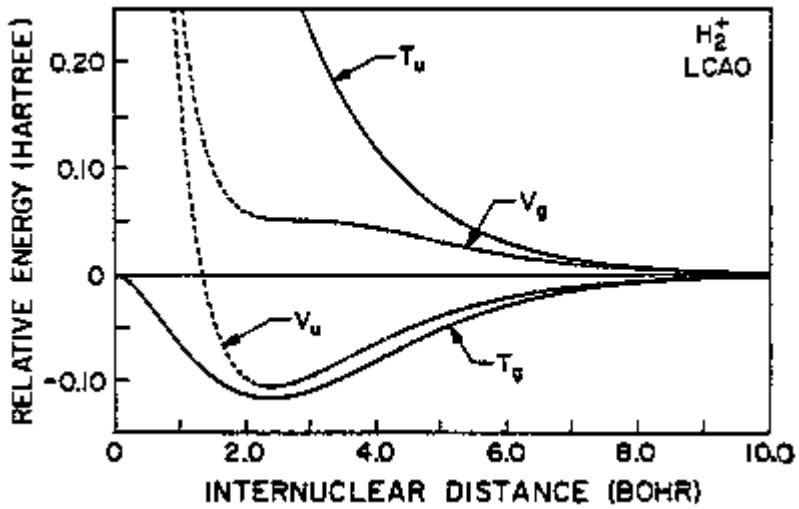

Figure 3: Kinetic, T, and Potential, V, energies of the bonding g and antibonding u orbitals for H_2^+. Note that even though V_g is unstable, the T_g effect compensates to create a bonding state.

Starting with the atomic orbitals and combining them to form MO's we find that g is bonding and u is antibonding. Now we want to understand what physics underlies the bonding and antibonding character. One common idea is that the g coherent superposition of atomic orbitals causes the electron density to increase in the bond region and that this increased charge attracts the two positive nuclei, leading to stabilization. The resulting change in the electrostatic energy (denoted V_g) is shown in Figure 3, where we see that it *increases* as the atoms are brought together. The problem is that the increase in the density in the bond region comes at the expense of a *decrease* in the nuclear region. As indicated in Figure 4 the potential is most negative near the nucleus so that the increase of the density in the bond region is antibonding in nature.

The only energy term in addition to electrostatics is kinetic energy. In QM, kinetic energy (denoted as T) has a dramatically different form than that of classical mechanics (CM).

$$T_{CM} = \frac{p^2}{2M}, \tag{6}$$

$$T_{QM} = \frac{<(\nabla\Phi)^2>}{2M}, \tag{7}$$

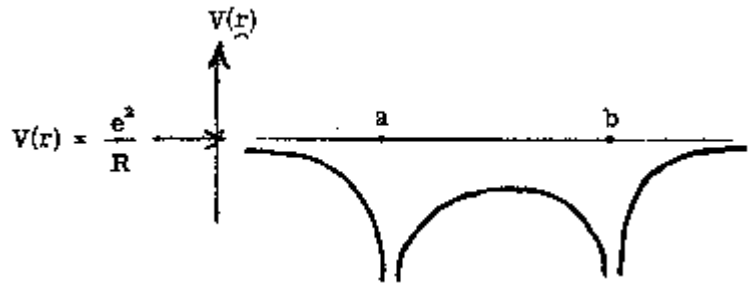

Figure 4: Potential energy for H_2^+. The potential is -∞ at the nuclei a and b, and is negative and finite at the midpoint.

where $\nabla\Phi$ is the gradient (derivative) of the wave function. Thus in CM the lowest T is for $p = 0$ (electron standing still) while in QM it is lowest for a very smooth wave function ($\nabla\Phi = 0$).

Indeed, as is clear from Figure 5, adding the two atomic orbitals to get g dramatically decreases the gradient in the bond region; for u the subtraction dramatically increases the gradient. These changes in T are much larger than the changes in V. The result is that bonding is dominated by the decrease in the kinetic energy resulting from the symmetric combination of atomic orbitals. The amount of the bonding depends on how much the gradient decreases. Thus, for the best bonding, we want the case in which both atomic orbitals have large gradients in opposite directions so that adding them leads to a big decrease in gradient. From Figure 3, we see that T_g has a minimum at 1Å. The reason is made clear in Figure 6. For large distances, the orbitals in the bond midpoint region have small slopes and hence do not change much in forming φ_u. For R near zero, the atomic orbitals have large gradients but the decrease is only for the very small region between the atoms, which is too small to be significant. Thus, the optimum bonding is created at a distance where both atomic orbitals are significant at the bond midpoint. This is approximately the sum of the atomic radii ($2 \times 0.53\text{Å} = 1.06\text{Å}$).

2.3 The Nodal Theorem

We saw in Section 2.2 that kinetic energy dominates bonding in H_2+. An analysis of kinetic energy allows us to make some general predictions about the shape of wave functions.

Consider a one dimensional potential $V(x)$ and consider the set of all eigenfunctions (all solutions of the Schrödinger Equation)

$$H\phi_j = E\phi_j \tag{8}$$

We can show quite generally that, except for very diabolical $V(x)$, the ground state is nodeless. It always positive except at the boundaries, where it goes to zero. A simple example is seen with H_2^+ where we found two orbitals g and u. The *nodal theorem*

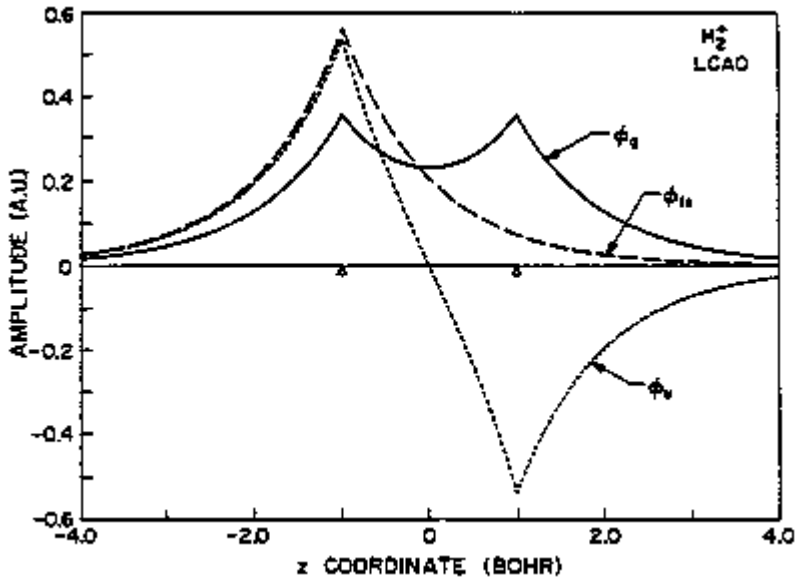

Figure 5: Bonding *g* orbital reduces the electron density at the nuclei.

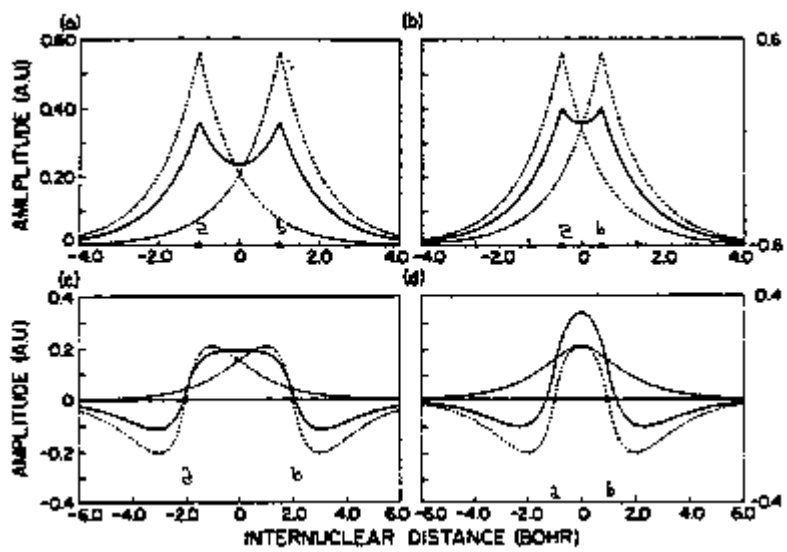

Figure 6: Overlap of 1*s* orbitals at bonding (a) and too-close (b) distances; overlap of 2*p* orbitals at bonding (c) and too-close (d) distances. Note that in both of the too-close examples, the contragradient region extends over a smaller region of space than in the bonding examples, leading to less stabilization.

tells us that the lowest state is g-like—nodeless. We will use this below to work out the bonding in H_2.

3 Bonding in H_2

Now that we understand the fundamental of bonding in H_2^+, we move our attention to H_2.

3.1 The Valence Bond Description of H_2

In the VB description of a molecule, we start with the full wave function for each atom at $R = \infty$ and combine the wave functions to form the wave function of the molecule, and then bring the atoms together to obtain optimal bonding. For H_2 at $R = \infty$ this consists of two hydrogen atoms infinitely far apart, say electron 1 on the left, and electron 2 on the right. The wave function for this configuration is

$$\Phi_a(\mathbf{r}_1, \mathbf{r}_2) = \chi_\ell(\mathbf{r}_1)\chi_r(\mathbf{r}_2). \tag{9}$$

This wave function Φ_a says that the probability of electron 1 being at a particular position is independent of where electron 2 is, and vice versa. Since the atoms are infinitely far apart, the electrons should not be influenced by each other.

There is a second wave function that is just as good, or as bad, as equation (37), namely,

$$\Phi_b(\mathbf{r}_1, \mathbf{r}_2) = \chi_r(\mathbf{r}_1)\chi_\ell(\mathbf{r}_2), \tag{10}$$

where the electrons have been interchanged. This wave function Φ_b is different from Φ_a since electron 1 is now on the opposite side of the universe. However, the energies of Φ_b and Φ_a must be the same, since electrons 1 and 2 have the same properties (they are indistinguishable particles).

We will find it useful to combine Φ_a and Φ_b into two new wave functions,

$$\Phi_g^{VB}(1,2) = \Phi_a(1,2) + \Phi_b(1,2) = \chi_\ell(1)\chi_r(2) + \chi_r(1)\chi_\ell(2) \tag{11}$$

$$\Phi_u^{VB}(1,2) = \Phi_a(1,2) - \Phi_b(1,2) = \chi_\ell(1)\chi_r(2) - \chi_r(1)\chi_\ell(2) \tag{12}$$

without normalization, because at finite R these are the optimum wave functions. Before examining the energies, we need to understand how to think about the relative locations of the electrons in these wave functions.

In Figure 7, we plot the four wave functions, Φ_a, Φ_b, Φ_g^{VB}, and Φ_u^{VB}. We see that Φ_u^{VB} has a nodal plane, corresponding to $z_1 = z_2$, whereas Φ_g does not. Indeed, along the line between the two peaks in Figure 7(c), we see that the gradient of the Φ_g^{VB} wave function is smaller than that of Φ_a or Φ_b, whereas the gradient of the Φ_u^{VB} wave function is larger. This decrease in the gradient of Φ_g^{VB}, and increase for Φ_u^{VB}, is inversely related to R. Thus, based on kinetic energy, we would expect that Φ_g^{VB} is bonding and Φ_u^{VB} is antibonding, and indeed this is the case, as shown in Figure 8. Here, the energies E_g and E_u for the valence bond wave functions of H_2 are shown.

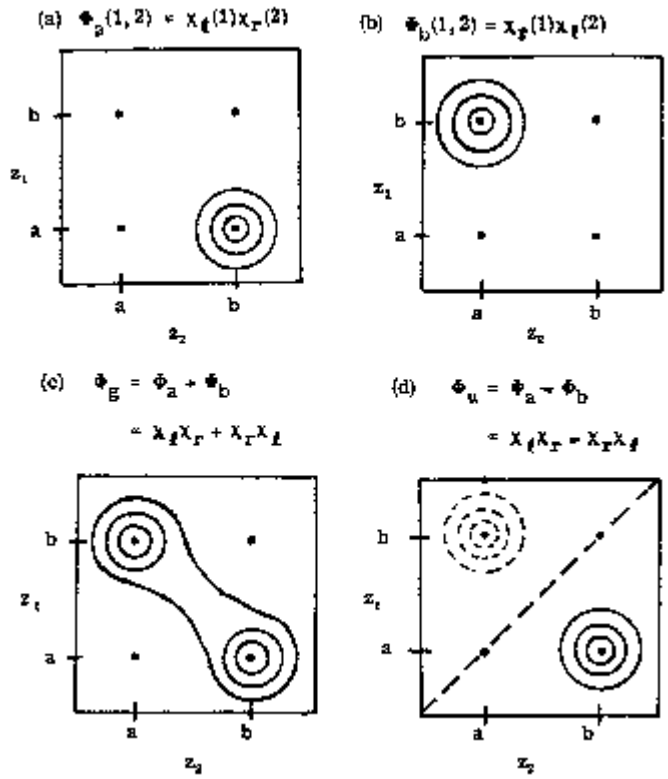

Figure 7: (a) $\Phi_a(1,2) = \chi_\ell(1)\chi_r(2)$; (b) $\Phi_b(1,2) = \chi_r(1)\chi_\ell(2)$; (c) $\Phi_g = \Phi_a + \Phi_b = \chi_\ell\chi_r + \chi_r\chi_\ell$; (d) $\Phi_u = \Phi_a + \Phi_b = \chi_\ell\chi_r - \chi_r\chi_\ell$

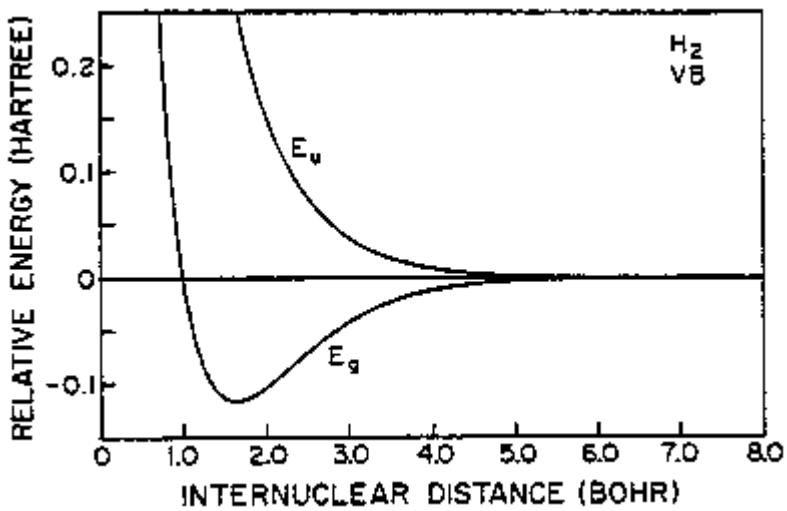

Figure 8: Energies of the g and u states of VB wave function.

3.2 The Molecular Orbital Description of H_2

The simplest wave function for H_2 is to start with an electron in the best molecular orbital of H_2^+, and to place a second electron in this φ_g orbital. This leads to the molecular orbital, MO, wave function for H_2,

$$\Phi_{gg}^{MO}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_g(\mathbf{r}_1)\varphi_g(\mathbf{r}_2). \tag{13}$$

First we will examine the meaning of the wave function (13). The total probability for electron 1 to be at some position $\mathbf{r}_1$, while electron 2 is simultaneously at some position $\mathbf{r}_2$ is

$$P(\mathbf{r}_1, \mathbf{r}_2) = |\Phi^{MO}(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\varphi_g(\mathbf{r}_1)|^2|\varphi_g(\mathbf{r}_2)|^2 = P_g(\mathbf{r}_1)P_g(\mathbf{r}_2). \tag{14}$$

This is just the product of the independent, probabilities for electron 1 to be at position $\mathbf{r}_1$, and electron 2 to be at position $\mathbf{r}_2$. Thus, the probability distribution for electron 1 is independent of electron 2. Consider the analogous case of a red die, electron 1, and a green die, electron 2. The probability of rolling a red 3 is 1/6 and the probability of rolling a green 5 is 1/6 so that the total probability of getting both a red 3 and a green 5 is 1/6 $\times$ 1/6 equal to 1/36. The dice are independent so that the probabilities multiply. Summarizing, a product wave function, as in equation (13), implies that the electrons move independently of each other, i.e. there is no correlation of their motions.

In addition to using the φ_g molecular orbital, we may construct wave functions of H_2 using the φ_u molecular orbital, leading to wave functions of the form

$$\Phi_{ug}^{MO}(1, 2) = \varphi_u(1)\varphi_g(2), \tag{15}$$

$$\Phi_{gu}^{MO}(1,2) = \varphi_g(1)\varphi_u(2), \tag{16}$$

and

$$\Phi_{uu}^{MO}(1,2) = \varphi_u(1)\varphi_u(2), \tag{17}$$

Since the φ_u orbital is antibonding, the above wave functions for H_2 lead to much higher energies than equation (13), except at large R; we expect an energy level diagram as in Figure 3.2.

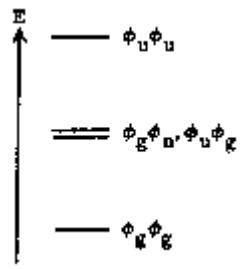

Figure 9: Simple energy diagram for molecular orbital wave functions of H_2.

So far we have discussed the molecular orbital wave function assuming that the bonding orbital φ_g is much better than the antibonding orbital φ_u. This is true for shorter internuclear distance R but does not remain true as the bond is stretched and broken. In general, molecular orbital wave functions lead to a good value for the bond length but a very poor description of the processes of dissociation.

The origin of this problem can be seen by substituting the atomic orbital description of the molecular orbital (4) into the molecular orbital wave function (13), leading to

$$\Phi_{gg}^{MO}(1,2) = \chi_\ell\chi_\ell + \chi_r\chi_r + \chi_\ell\chi_r + \chi_r\chi_\ell = \Phi_g^{VB} + \Phi_g^{ION}, \tag{18}$$

(again ignoring normalization) where

$$\Phi_g^{VB} = \chi_\ell\chi_r + \chi_r\chi_\ell \tag{19}$$

$$\Phi_g^{ION} = \chi_\ell\chi_\ell + \chi_r\chi_r \tag{20}$$

At very large R, the exact wave function will have one electron near the left proton and one at the right, as in equation (19), which we will refer to as the covalent part of the wave function. The other terms of (18) have both electrons near one proton and none near the other, thus creating an ionic wave function. At $R = \infty$, these ionic terms lead to the energy of H^- and H_2^+ rather than the energy of two hydrogen atoms. Since the molecular orbital wave function must have equal covalent and ionic contributions, it yields unfavorable energies for large R.

The basic problem with the molecular orbital wave function is that both electrons are in the same φ_g orbital, and hence, each electron has an equal probability of being on either center, regardless of the instantaneous location of the other electron. In the exact

wave function, the motions of the electrons tend to be correlated so that if one electron is on the left, the other tends to be on the right. This correlation is necessarily ignored in the molecular orbital wave function, and the resulting error is often referred to as the correlation error. For small R, the two centers are close to each other, and this neglect of correlation is not particularly important. At $R = \infty$, however, the correlation of electrons is of paramount importance and neglect of correlation leads to ludicrously poor wave functions.

In the next section, we will discuss a simple wave function, the valence bond wave function, that eliminates this problem of describing large R.

3.3 Comparison of VB and MO Wave Functions

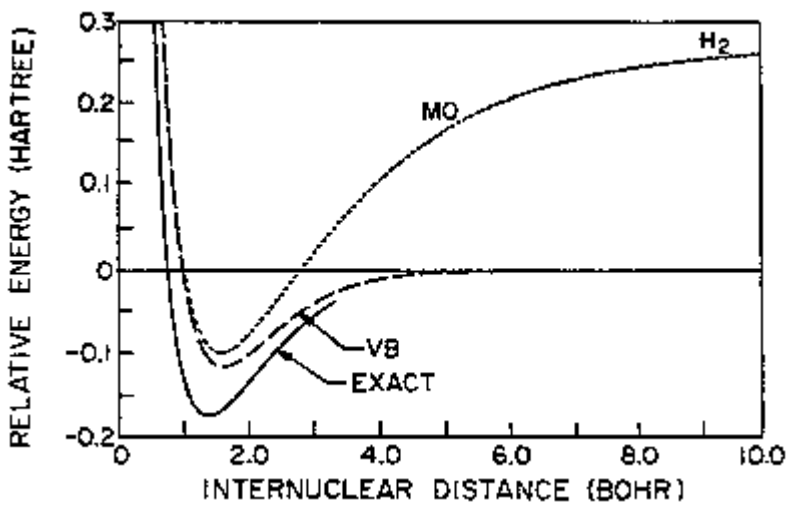

Figure 10: Energies of MO and VB wave functions.

The molecular orbital wave function is, ignoring normalization

$$\Phi_{gg}^{MO}(1,2) = \varphi_g(1)\varphi_g(2) = [\chi_\ell\chi_r + \chi_r\chi_\ell] + [\chi_\ell\chi_\ell + \chi_r\chi_r]\,, \tag{21}$$

whereas the valence bond wave function is

$$\Phi_g^{VB}(1,2) = [\chi_\ell\chi_r + \chi_r\chi_\ell]\,. \tag{22}$$

The energies for these wave functions are compared in Figure 10, where we see that the valence bond is always better, but that the difference becomes negligible for small R. Figure 10 illustrates the energy of the molecular orbital wave function for the ground state of H_2 with comparison to the valence bond and exact energies.

The wave functions are compared in Figure 11, showing graphically, how the valence bond wave function has smaller probability of having $z_1 = z_2$, leading to lower

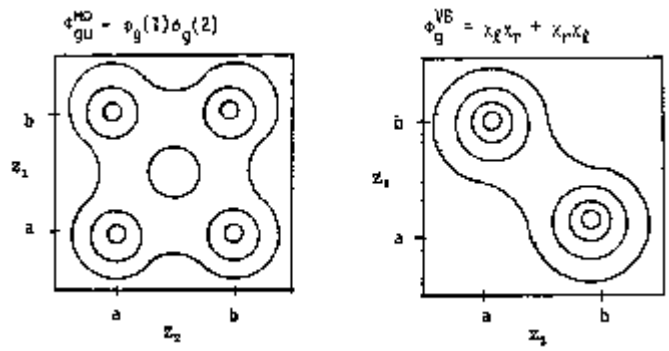

Figure 11: (a) $\Phi_{gu}^{MO} = \phi_g(1)\phi_g(2)$ (b) $\Phi_g^{VB} = \chi_\ell\chi_r + \chi_r\chi_\ell$.

electron repulsion energies. On the other hand, the molecular orbital wave function is smoother, leading to smaller kinetic energies. For normal bond distances, the electron repulsion effects dominate so that the valence bond wave function is better. However, for very short R, the kinetic energy becomes dominant, so the molecular orbital and valence bond wave functions lead to nearly identical total energies.

Expanding the molecular orbital description of the excited states in terms of atomic orbitals, ignoring normalization, leads to

$$\Phi_{gu}^{MO} = (\chi_\ell + \chi_r)(\chi_e ll - \chi_r) = \chi_\ell\chi_\ell + \chi_r\chi_\ell - \chi_\ell\chi_r - \chi_r\chi_r \tag{23}$$

and

$$\Phi_{ug}^{MO} = (\chi_\ell - \chi_r)(\chi_\ell + \chi_r) = \chi_\ell\chi_\ell - \chi_r\chi_\ell + \chi_\ell\chi_r - \chi_r\chi_r. \tag{24}$$

We may rewrite these equations as

$$\Phi_{gu}^{MO} = \Phi_u^{VB} + \Phi_u^{ION} \tag{25}$$

$$\Phi_{ug}^{MO} = \Phi_u^{VB} - \Phi_u^{ION} \tag{26}$$

(again ignoring normalization) where

$$\Phi_u^{VB} = \chi_r\chi_\ell - \chi_\ell\chi_r \tag{27}$$

$$\Phi_u^{ION} = \chi_\ell\chi_\ell - \chi_r\chi_r \tag{28}$$

That is, the first excited state of the molecular orbital description is identical to the first excited state in the valence bond description. Both describe a covalent repulsive state that separates to two free H atoms.

The molecular orbital description of the other excited state is

$$\Phi_{uu}^{MO} = (\chi_\ell - \chi_r)(\chi_\ell - \chi_r) = \chi_\ell\chi_\ell + \chi_r\chi_r - \chi_\ell\chi_r + \chi_r\chi_\ell. \tag{29}$$

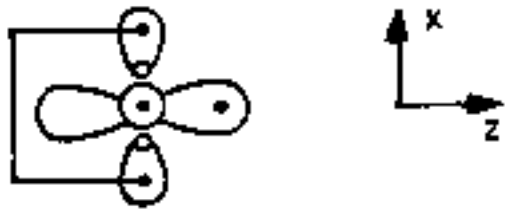

Figure 12: The ground state of C atom.

Recalling equation (21) we see that we may combine the gg and uu MO wave functions to form the VB description of the bond:

$$\Phi_g^{VB} = \Phi_{gg}^{MO} - \lambda \Phi_{uu}^{MO} \tag{30}$$

where λ is a scalar factor, and we again ignore normalization. Thus, we can fix up the molecular orbital wave function so that it behaves like the valence bond wave function, by mixing together the Φ_{gg}^{MO} and Φ_{uu}^{MO} wave functions.

4 Bonding Hydrogen to Carbon

The principles of bonding, discussed in simple examples above, apply also to chemical bonding in general. In this section, we will apply these simple valence bond ideas about chemical bonding to simple hydrocarbon examples.

4.1 Ground State of Carbon Atom

The ground state (^3P) of carbon has the electronic configuration $(1s)^2(2s)^2(2p)^2$. Here the $1s$ electrons are *core* electrons, and stay very close to the nucleus, and thus do not participate in chemical bonding. Thus, when we consider the chemical bonding of C atom, we normally only consider the behavior of the other, *valence* electrons.

Schematically, we represent the wave function for C atom in Figure 12. The ovals above and below the atom indicate a lobe orbital – the $2s$ pair of electrons that have hybridized with the $2p_x$ orbitals; the line connecting the lobe orbitals indicates singlet pairing of the electrons in the orbitals. The dots without lines connected to them indicate electrons that are not spin paired.

We now consider binding a H atom to the ground state of C.

4.2 Low-Lying States of CH$_n$

The lowest states of CH arise from bonding an H to either a carbon p orbital, forming the $^2\Pi$ ground state, as in Figure 13, or to a lobe orbital forming the $^4\Sigma^-$ state, shown in Figure 14.

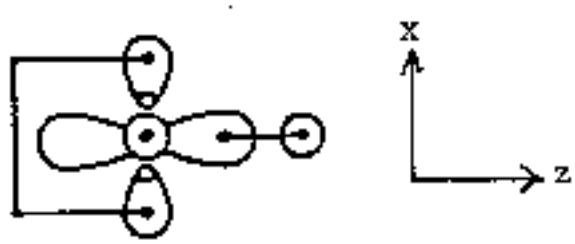

Figure 13: Bonding a H to a C p orbital, resulting in the $^2\Pi$ state.

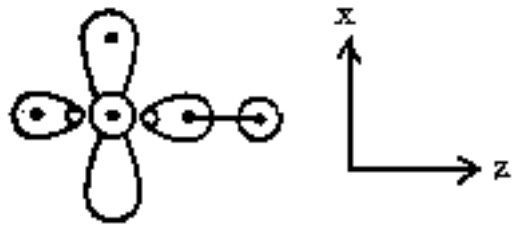

Figure 14: Bonding a H to a C lobe orbital, resulting in the $^4\Sigma^-$ state.

The major difference between the two states is that in order to bond to a lobe orbital, the two lobe orbitals must undo the spin pairing; such rearrangement costs energy and weakens the overall bond. Thus, bonding to the p orbital, forming the $^2\Pi$ state, is more favorable.

Now we take the $^2\Pi$ state of CH, and bond another H to it to form CH_2. The lowest states of CH_2 are obtained by bonding an H, either to a p orbital leading to a singlet state ($^1A_1$), shown in Figure 15, or a lobe orbital, leading to a triplet state ($^3B_1$), shown in Figure 16.

For CH_2, the $^3B_1$ state is favored by 9 kcal/mol. Interestingly, for SiH_2, the $^1A_1$ is more favorable, lying 18 kcal lower than the triplet state. Comparing CH_2 with SiH_2, there are two important factors favoring the $^3B_1$ state relative to the $^1A_1$. First, the bonds of the $^1A_1$ state involve perpendicular p orbitals, and hence, will favor small bond angles, approximately 90°. The bonds in the $^3B_1$ state, favor larger angles, approximately 128°, *vide supra*. For first row compounds, the importance of bond-bond repulsions, which are largest at small bond angles, leads to a significant increase in the energy of states involving small bond angles, relative to those with larger angles. This affect increases the energy of the $^1A_1$ state relative to the $^3B_1$ state. The second factor that account for the favoring of the $^3B_1$ state is that the lobe orbitals of first row atoms are closer in energy to p orbitals than in atoms in the Si row. The $^1A_1$ state involves two bonds to p orbitals, while the $^3B_1$ state involves one p bond and one lobe bond. Thus, this second effect also lowers the energy of the $^3B_1$ state relative to the $^1A_1$ state for CH_2. The net result is that the ordering of the first two states of CH_2 is inverted

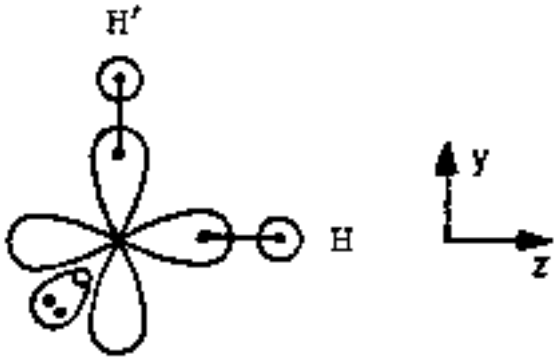

Figure 15: The $^1A_1$ state of CH_2.

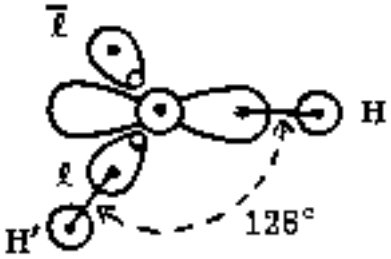

Figure 16: The $^3B_1$ state of CH_2.

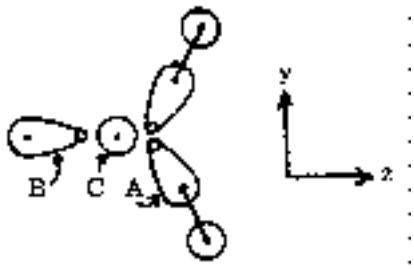

Figure 17: Options for bonding to the $^3B_1$ state of CH_2.

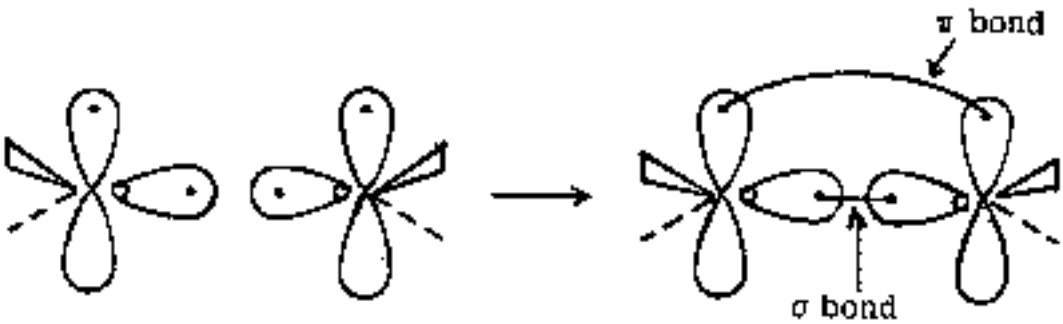

Figure 18: Two methylene $^3B_1$ molecules forming a σ and a π bond in ethylene.

with respect to the energies of SiH_2.

Starting with the $^3B_1$ ground state of CH_2 there are two possibilities for bonding a third hydrogen, the unpaired lobe orbital or the $p\pi$ orbital. These two options are shown as B and C, respectively, in Figure 17.

Again, due to the importance of bond-bond interactions, the lower configuration will be the one with larger bond angles. Bonding to the lobe leads to planar CH_3, with 120° bond angles, whereas bonding to the $p\pi$ orbital leads to two 90° bond angles. Thus, the lowest energy configuration of CH_3 is planar, whereas SiH_3 was found to be pyramidal. Because of the ability of $^3B_1$ CH_2 to bond an H to either the lobe or p orbital, the first constant for pyramidal distortion of CH_3 is quite small.

4.3 Ethylene

VB theory allows us to start with two methylene radicals, CH_2, in the ground state, and forming ethylene, $H_2C{=}CH_2$, we can form both a sigma bond and a pi bond, leading to the planar molecule ethylene molecule shown in Figure 18.

In the triplet state of CH_2, the HCH bond angle is 132.3°, but forming a bond to the carbon should decrease this angle, because of Pauli repulsion due to the new bond

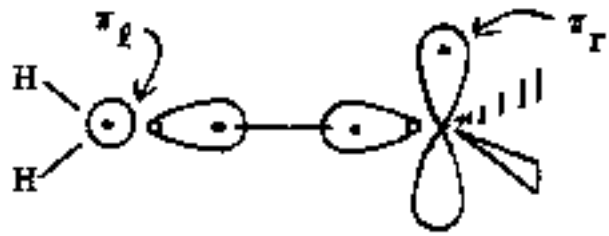

Figure 19: Twisted ethylene, where only a σ bond may be formed.

pair. Thus, in CH_3 the bond angle is decreased to 120° and in ethylene the HCH bond angle is decreased further to 117.6°.

Consider now the case where the plane of one methylene group is rotated about the CC axis by an angle of 90° with respect to the other. The structure of the resulting molecule is shown in Figure 19. Here only a sigma bond is formed. The nonbonding orbitals π_ℓ and π_r can be combined into singlet and triplet states. The singlet state is usually referred to as N, for normal or ground state, and the triplet state is referred to as T. Based solely on Hund's rule, we would expect the T state to be slightly lower than the N state for the twisted geometry. However, since these orbitals are localized on different centers, the energy splitting is quite small, approximately 1–2 kcal. In fact, other small effects lead to the N state at 90° being about 1 kcal below the T state.

Comparison of the energies of twisted and planar ethylene leads to the results in Figure 20. The singlet state prefers planar geometry since the overlap of the π_ℓ and π_r orbitals leads to a strong pi bond. However, for the triplet state, the π_ℓ and π_r orbitals must be orthogonalized to each other, and this state prefers the 90° twisted geometry.

According to Figure 20 the energy to twist the N state of ethylene by 90° is 65 kcal, breaking the pi bond. This barrier has been observed experimentally from studies of the kinetics for cis-trans isomerization di-deuterated ethylene. As the molecules is rotated, the strength of the pi bond is weakened, and the CC bond length increases. Thus, for the N state $R_{CC} = 1.34$Å at $\theta = 0°$, and $R_{CC} = 1.50$Å at $\theta = 90°$.

In the T state, the optimum geometry is twisted, $\theta = 90°$, since triplet pairing of the orbitals prefers the pi orbitals to not overlap. As the molecule is twisted toward the planar geometry the bond length increases from CC = 1.50 Å at $\theta = 90°$ to CC = 1.57 Å at $\theta = 0°$, and the energy barrier is 25 kcal. Note that in Figure 20 we show the T to N energy separation at $\theta = 0$, using the ground state geometry; the adiabatic excitation energy for $\theta = 0°$ is 91 kcal.

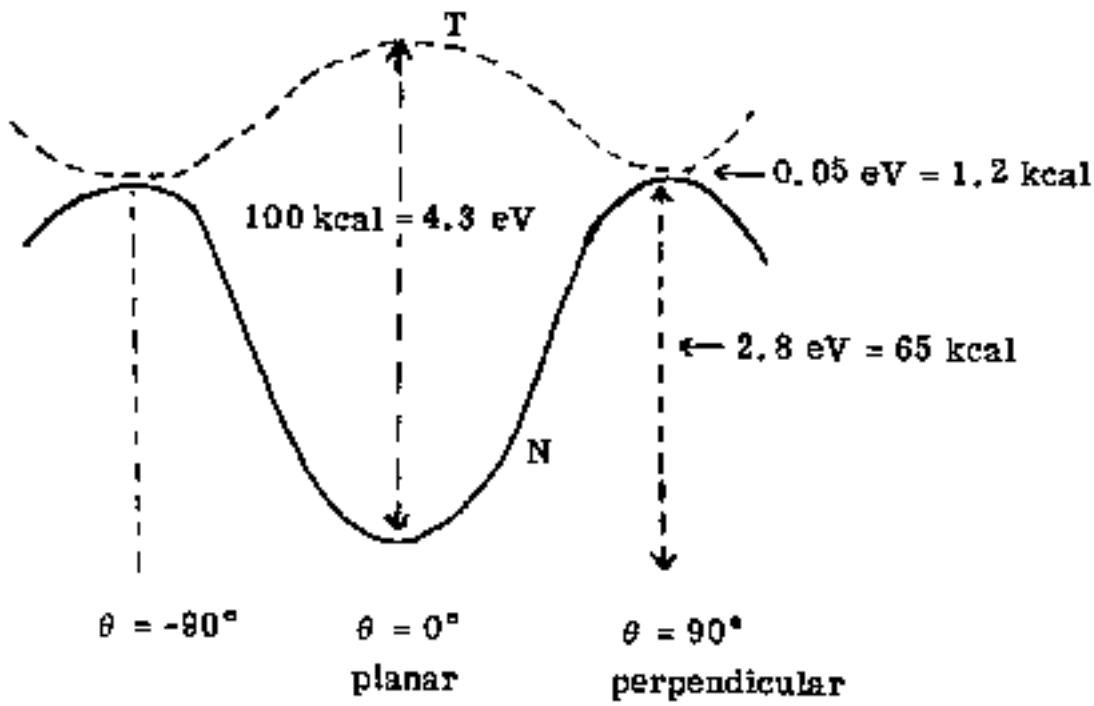

Figure 20: Energy profile for the singlet N state, and triplet T state, of ethylene, as the molecule is twisted about the C-C bond.