

XIII. The Hydrogen molecule

We are now in a position to discuss the electronic structure of the simplest molecule: H₂. For the low-lying electronic states of H₂, the BO approximation is completely satisfactory, and so we will be interested in the electronic Hamiltonian

$$\hat{H}_{el} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{R_{AB}} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|} + \frac{1}{r_{12}}$$

where “1” and “2” label the two electrons and “A” and “B” label the two nuclei.

a. Minimal Atomic Orbital Basis

It is not possible to solve this problem analytically, and so we want to follow our standard prescription for solving this problem: we define a basis set and then crank through the linear algebra to solve the problem in that basis. Ideally, we would like a very compact basis that does not depend on the configuration of the molecule; that is, we want basis functions that do not depend on the distance between the two nuclei, R_{AB} . This will simplify the work of doing calculations for different bond lengths.

The most natural basis functions are the atomic orbitals of the individual Hydrogen atoms. If the bond length is very large, the system will approach the limit of two non-interacting Hydrogen atoms, in which case the electronic wavefunction can be well approximated by a product of an orbital on atom “A” and an orbital on atom “B” and these orbitals will be exactly the atomic orbitals (AOs) of the two atoms. Hence, the smallest basis that will give us a realistic picture of the ground state of this molecule must contain two functions: $|1s_A\rangle$ and $|1s_B\rangle$. These two orbitals make up the minimal AO basis for H₂. For finite bond lengths, it is advisable to allow the AOs to polarize and deform in response to the presence of the other electron (and the other nucleus). However, the functions we are denoting “ $|1s_A\rangle$ ” and

“ $|1s_B\rangle$ ” need not exactly be the Hydrogenic eigenfunctions; they should look similar to the 1s orbitals, but any atom-centered functions would serve the same purpose. Since the actual form of the orbitals will vary, in what follows, we will give all the expressions in abstract matrix form, leaving the messy integration to be done once the form of the orbitals is specified.

b. Molecular Orbital Picture

We are now in a position to discuss the basic principles of the molecular orbital (MO) method, which is the foundation of the electronic structure theory of real molecules. The first step in any MO approach requires one to define an effective one electron Hamiltonian, \hat{h}_{eff} . To this end, it is useful to split the Hamiltonian into pieces for electrons “1” and “2” separately and the interaction:

$$\hat{h}(1) \equiv -\frac{1}{2}\nabla_1^2 - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} \quad \hat{h}(2) \equiv -\frac{1}{2}\nabla_2^2 - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|}$$

$$\hat{V}_{12} \equiv \frac{1}{r_{12}}$$

The full Hamiltonian is then

$$\hat{H}_{el} = \hat{h}(1) + \hat{h}(2) + \hat{V}_{12} + \frac{1}{R_{AB}}$$

where it should be remembered that within the BO approximation, R_{AB} is just a number. For H_2 in a minimal basis, the simplest choice for \hat{h}_{eff} suffices: we will choose our one electron Hamiltonian to just be the one electron part of the full \hat{H} (\hat{h}). The matrix representation of \hat{h} in the minimal basis is:

$$\begin{pmatrix} \langle 1s_A | \hat{h} | 1s_A \rangle & \langle 1s_A | \hat{h} | 1s_B \rangle \\ \langle 1s_B | \hat{h} | 1s_A \rangle & \langle 1s_B | \hat{h} | 1s_B \rangle \end{pmatrix} \equiv \begin{pmatrix} \varepsilon & h_{AB} \\ h_{AB} & \varepsilon \end{pmatrix}.$$

where we made use of the average one electron energy:

$$\varepsilon \equiv \langle 1s_A | \hat{h} | 1s_A \rangle = \langle 1s_B | \hat{h} | 1s_B \rangle$$

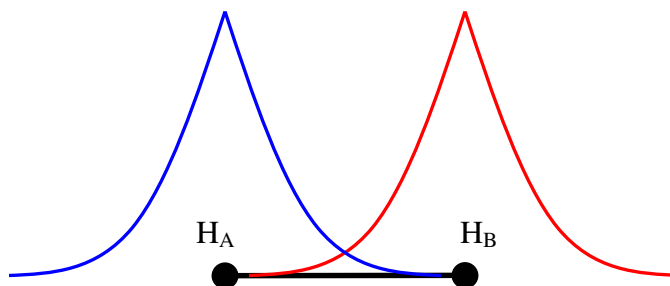
and the off-diagonal coupling (often called a “resonance” integral):

$$h_{AB} \equiv \langle 1s_A | \hat{h} | 1s_B \rangle = \langle 1s_B | \hat{h} | 1s_A \rangle.$$

We can immediately diagonalize this matrix; the eigenvalues are $\varepsilon_{\pm} = \varepsilon \pm h_{AB}$ and the eigenstates are:

$$|\phi_+\rangle \propto \frac{1}{\sqrt{2}}(|1s_A\rangle + |1s_B\rangle) \quad |\phi_-\rangle \propto \frac{1}{\sqrt{2}}(|1s_A\rangle - |1s_B\rangle)$$

The eigenstates of the effective one-electron Hamiltonian are called molecular orbitals (just as the basis functions are called atomic orbitals). They are one-electron functions that are typically delocalized over part (or all) of the molecule. As a first step, we need to normalize these MOs. This is more complicated than it might at first appear, because the AOs are **not orthogonal**. For example,



as the atoms approach each other, the two AOs might look like the picture at right. However, if we define the **overlap integral** by

$$S \equiv \langle 1s_A | 1s_B \rangle,$$

we can normalize the MOs:

$$\langle \phi_+ | \phi_+ \rangle = \frac{1}{2} (\langle 1s_A | 1s_A \rangle + \langle 1s_B | 1s_A \rangle + \langle 1s_A | 1s_B \rangle + \langle 1s_B | 1s_B \rangle) = 1 + S$$

$$\langle \phi_- | \phi_- \rangle = \frac{1}{2} (\langle 1s_A | 1s_A \rangle - \langle 1s_B | 1s_A \rangle - \langle 1s_A | 1s_B \rangle + \langle 1s_B | 1s_B \rangle) = 1 - S$$

which implies that the normalized wavefunctions are:

$$|\phi_+\rangle = \frac{1}{\sqrt{2(1+S)}}(|1s_A\rangle + |1s_B\rangle) \quad |\phi_-\rangle = \frac{1}{\sqrt{2(1-S)}}(|1s_A\rangle - |1s_B\rangle).$$

These eigenfunctions merely reflect the **symmetry** of the molecule; the two hydrogen atoms are equivalent and so the eigenorbitals must give equal weight to each 1s orbital. So our “choice” of the one electron Hamiltonian actually does not matter much in this case; any one-electron Hamiltonian that reflects the symmetry of the molecule will give the same molecular orbitals. For historical reasons, $|\phi_+\rangle$ is usually denoted $|\sigma\rangle$ while $|\phi_-\rangle$ is denoted $|\sigma^*\rangle$.

The second step in MO theory is to construct a single determinant out of the MOs that corresponds to the state we are interested in. For the purposes of illustration, let us look at the lowest singlet state built out of the molecular orbitals. First, note that $h_{AB} < 0$, so $|\sigma\rangle$ is lower in energy than $|\sigma^*\rangle$. Neglecting the interaction, then, the lowest singlet state is:

$$|\Phi_{MO}\rangle = ||\sigma\rangle|\bar{\sigma}\rangle|$$

and this is the MO ground state for H₂. How good an approximation is it? Well, we can compute the expectation value of the energy, $\langle \sigma | \langle \bar{\sigma} | \hat{H}_{el} | \sigma \rangle | \bar{\sigma} \rangle$ as follows. First, we decompose the wavefunction into spatial and spin parts and note that the spin part is normalized:

$$\begin{aligned} \langle \sigma | \langle \bar{\sigma} | \hat{H}_{el} | \sigma \rangle | \bar{\sigma} \rangle &= \langle \sigma(1) | \langle \sigma(2) | \hat{H}_{el} | \sigma(1) \rangle | \sigma(2) \rangle \langle \Phi_{spin} | \Phi_{spin} \rangle \\ &= \langle \sigma(1) | \langle \sigma(2) | \hat{H}_{el} | \sigma(1) \rangle | \sigma(2) \rangle \end{aligned}$$

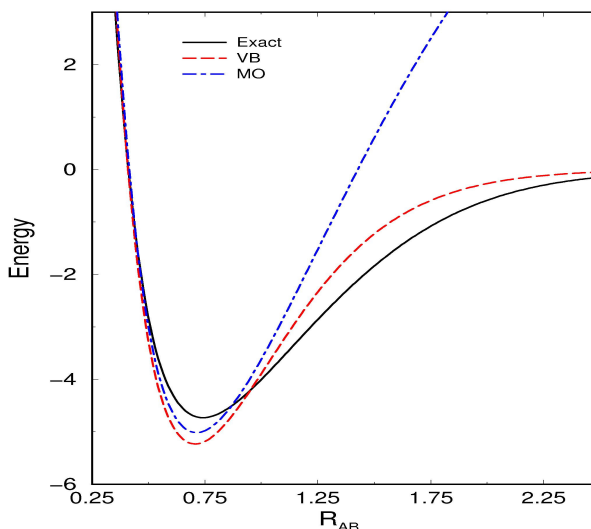
Then, we note that $\hat{H}_{el} = \hat{h}(1) + \hat{h}(2) + \hat{V}_{12} + 1/R_{AB}$ and

$$\begin{aligned} \langle \sigma(1) | \langle \sigma(2) | \hat{h}(1) | \sigma(1) \rangle | \sigma(2) \rangle &= \langle \sigma(1) | \hat{h}(1) | \sigma(1) \rangle \langle \sigma(2) | \sigma(2) \rangle \\ &= \langle \sigma(1) | \hat{h}(1) | \sigma(1) \rangle \equiv \varepsilon_{\sigma} \\ \langle \sigma(1) | \langle \sigma(2) | \hat{h}(2) | \sigma(1) \rangle | \sigma(2) \rangle &= \langle \sigma(2) | \hat{h}(2) | \sigma(2) \rangle \langle \sigma(1) | \sigma(1) \rangle \\ &= \langle \sigma(2) | \hat{h}(2) | \sigma(2) \rangle \equiv \varepsilon_{\sigma} \\ \langle \sigma(1) | \langle \sigma(2) | \hat{V}_{12} | \sigma(1) \rangle | \sigma(2) \rangle &\equiv J_{\sigma\sigma} \end{aligned}$$

Taken together, these facts allow us to write:

$$\begin{aligned} \langle \Psi_{MO} | \hat{h}_1 | \Psi_{MO} \rangle &= \langle \Psi_{MO} | \hat{h}_1 | \Psi_{MO} \rangle + \langle \Psi_{MO} | \hat{h}_2 | \Psi_{MO} \rangle + \langle \Psi_{MO} | \hat{V}_{12} | \Psi_{MO} \rangle + \frac{1}{R_{AB}} \\ &= 2\varepsilon_{\sigma} + J_{\sigma\sigma} + \frac{1}{R_{AB}} \end{aligned}$$

Each of the first two terms is energy of a single electron (either 1 or 2) in the field produced by the nuclei (\hat{h}) while the third is the *average repulsion* of the two electrons. Note that the second and third terms are both positive, so binding has to arise from the one-electron piece. This is the MO energy for the ground state of H₂. For a reasonable choice of the 1s-like basis functions – it turns out to be more convenient to fit the exponential decay of the hydrogenic orbitals to a sum of Gaussians- we can use a computer to compute the unknowns above (ε_{σ} and $J_{\sigma\sigma}$) and plot the total energy as a function of R_{AB}, we get the result pictured at right. The exact adiabatic energy



function (derived from experimental data) is shown in black, and the agreement is quite good at low energies. If we want to summarize the results with a few key numbers, we can note that MO theory predicts the bond distance to be .72 Å, compared with the correct answer of .74 Å. This is certainly not spectroscopic accuracy, but it is decent. We can also compare the binding energies:

$$D_e = E_{H_2}(R_e) - 2E_H.$$

MO theory predicts a binding energy of 5.0 eV, compared with the experimental value of 4.75 eV. Again, not excellent, but not too shabby for such a simple wavefunction, with no free parameters. The MO approximation we've used is clearly quite crude, but it **works**! There is no reason to expect this quality of agreement between such a simple theory and the real world, so this result is extremely encouraging. Unfortunately, far from equilibrium, we get a nasty surprise: the molecule does not dissociate into two Hydrogen atoms!

c. Valence Bond Picture

To get an ideal of what is going on near dissociation, we expand the MO ground state in terms of the AO configurations:

$$\begin{aligned} |\Phi_{MO}\rangle &\Rightarrow |\sigma(1)\rangle|\sigma(2)\rangle|\Phi_{spin}\rangle \\ &\Rightarrow \frac{1}{2(1+S)} (|1s_A(1)\rangle + |1s_B(1)\rangle)(|1s_A(2)\rangle + |1s_B(2)\rangle)|\Phi_{spin}\rangle \\ &\Rightarrow \frac{1}{2(1+S)} (|1s_A(1)\rangle|1s_A(2)\rangle + |1s_A(1)\rangle|1s_B(2)\rangle + |1s_B(1)\rangle|1s_A(2)\rangle + |1s_B(1)\rangle|1s_B(2)\rangle)|\Phi_{spin}\rangle \end{aligned}$$

The middle two terms on the last line (which are called “covalent” configurations) are exactly what we would expect at dissociation: one electron on each Hydrogen atom. However, the first and last terms (which are called “ionic” configurations) correspond to putting two electrons on one atom and none on the other – which gives us H⁺ and H⁻ at dissociation! Since the weight of these terms is fixed, we cannot help but get the wrong wavefunction (and hence wrong energy) when we try to dissociate this molecule. Near equilibrium, ionic terms contribute significantly to the true wavefunction. Hence MO theory is good there, but is always terrible at dissociation.

An alternative to the MO picture is valence bond (VB) theory. Here, one uses significantly more physical intuition and discards the ionic configurations from the MO wavefunction. Thus, the VB ground state wavefunction is:

$$|\Psi\rangle \propto \left(\frac{|1s_A(1)\rangle|1s_B(2)\rangle + |1s_B(1)\rangle|1s_A(2)\rangle}{\sqrt{2}} \right) \left(\frac{|\uparrow(1)\rangle|\downarrow(2)\rangle - |\downarrow(1)\rangle|\uparrow(2)\rangle}{\sqrt{2}} \right)$$

$$\equiv |\Psi_{space}\rangle |\Psi_{spin}\rangle$$

The VB picture presumes that this wavefunction is a good approximation to the true wavefunction for all bond distances (as opposed to just being accurate at large R_{AB}). To see if this is a good approximation, we can compute the average energy $\langle \hat{H} \rangle$ for this VB state. First, we normalize the VB wavefunction,

$$\langle \Psi | \Psi \rangle = \langle \Psi_{space} | \Psi_{space} \rangle \langle \Psi_{spin} | \Psi_{spin} \rangle$$

$$\Rightarrow \langle \Psi | \Psi \rangle = \langle \Psi_{space} | \Psi_{space} \rangle$$

$$\Rightarrow \frac{1}{2} (\langle 1s_A(1) | \langle 1s_B(2) | + \langle 1s_B(1) | \langle 1s_A(2) |) (| 1s_A(1)\rangle | 1s_B(2)\rangle + | 1s_B(1)\rangle | 1s_A(2)\rangle)$$

$$\Rightarrow \frac{1}{2} \left(\begin{array}{c} \begin{array}{c} \nearrow 1 \\ \langle 1s_A(1) | \langle 1s_B(2) | \langle 1s_A(1) | 1s_B(2) \rangle \\ \searrow S^2 \end{array} + \begin{array}{c} \nearrow S^2 \\ \langle 1s_A(1) | \langle 1s_B(2) | \langle 1s_B(1) | 1s_A(2) \rangle \\ \searrow 1 \end{array} + \\ \begin{array}{c} \nearrow 1 \\ \langle 1s_B(1) | \langle 1s_A(2) | \langle 1s_A(1) | 1s_B(2) \rangle \\ \searrow S^2 \end{array} + \begin{array}{c} \nearrow S^2 \\ \langle 1s_B(1) | \langle 1s_A(2) | \langle 1s_B(1) | 1s_A(2) \rangle \\ \searrow 1 \end{array} \end{array} \right)$$

$$\Rightarrow \langle \Psi | \Psi \rangle = 1 + S^2$$

Hence, the correctly normalized VB wavefunction is:

$$|\Psi_{VB}\rangle \equiv \frac{1}{2\sqrt{1+S^2}} (|1s_A(1)\rangle|1s_B(2)\rangle + |1s_B(1)\rangle|1s_A(2)\rangle) (|\uparrow(1)\rangle|\downarrow(2)\rangle - |\downarrow(1)\rangle|\uparrow(2)\rangle)$$

Now, we want to compute $\langle \hat{H}_{el} \rangle$ for this state. First, we note that the spin part doesn't matter, because the Hamiltonian is spin-independent:

$$\langle \Psi_{VB} | \hat{H}_{el} | \Psi_{VB} \rangle = \langle \Psi_{spin} | \langle \Psi_{space} | \hat{H}_{el} | \Psi_{space} \rangle | \Psi_{spin} \rangle = \langle \Psi_{space} | \hat{H}_{el} | \Psi_{space} \rangle \langle \Psi_{spin} | \Psi_{spin} \rangle$$

$$= \langle \Psi_{space} | \hat{H}_{el} | \Psi_{space} \rangle$$

The only remnant of the spin state is the fact that the spatial

wavefunction is symmetric, which is only possible if the spin part is antisymmetric. Treating each term in $\langle \hat{H}_{el} \rangle$ separately,

$$\begin{aligned} & \langle \Psi_{VB} | \hat{h}_1 | \Psi_{VB} \rangle \\ & \Rightarrow \frac{1}{2(1+S^2)} (\langle 1s_A(1) | \langle 1s_B(2) | + \langle 1s_B(1) | \langle 1s_A(2) |) \hat{h}_1 (| 1s_A(1) \rangle | 1s_B(2) \rangle + | 1s_B(1) \rangle | 1s_A(2) \rangle) \\ & \Rightarrow \frac{1}{2(1+S^2)} \left(\begin{array}{c} \begin{array}{c} \nearrow \varepsilon \\ \langle 1s_A(1) | \langle 1s_B(2) | \hat{h}_1 | 1s_A(1) \rangle | 1s_B(2) \rangle \\ \searrow \varepsilon \end{array} \\ + \\ \begin{array}{c} \nearrow S h_{AB} \\ \langle 1s_A(1) | \langle 1s_B(2) | \hat{h}_1 | 1s_B(1) \rangle | 1s_A(2) \rangle \\ \searrow S h_{AB} \end{array} \\ + \\ \begin{array}{c} \begin{array}{c} \nearrow \varepsilon \\ \langle 1s_B(1) | \langle 1s_A(2) | \hat{h}_1 | 1s_A(1) \rangle | 1s_B(2) \rangle \\ \searrow \varepsilon \end{array} \\ + \\ \begin{array}{c} \nearrow S h_{AB} \\ \langle 1s_B(1) | \langle 1s_A(2) | \hat{h}_1 | 1s_B(1) \rangle | 1s_A(2) \rangle \\ \searrow S h_{AB} \end{array} \end{array} \right) \\ & \Rightarrow \langle \Psi_{VB} | \hat{h}_1 | \Psi_{VB} \rangle = \frac{\varepsilon + S h_{AB}}{(1+S^2)} \end{aligned}$$

Because the two electrons are identical, the matrix elements of \hat{h}_2 are the same as for \hat{h}_1 . The only remaining term is the average value of the interaction:

$$\begin{aligned} & \langle \Psi_{VB} | \hat{V}_{12} | \Psi_{VB} \rangle \\ & \Rightarrow \frac{1}{2(1+S^2)} (\langle 1s_A(1) | \langle 1s_B(2) | + \langle 1s_B(1) | \langle 1s_A(2) |) \hat{V}_{12} (| 1s_A(1) \rangle | 1s_B(2) \rangle + | 1s_B(1) \rangle | 1s_A(2) \rangle) \\ & \Rightarrow \frac{1}{2(1+S^2)} \left(\begin{array}{c} \langle 1s_A(1) | \langle 1s_B(2) | \hat{V}_{12} | 1s_A(1) \rangle | 1s_B(2) \rangle \\ + \\ \langle 1s_A(1) | \langle 1s_B(2) | \hat{V}_{12} | 1s_B(1) \rangle | 1s_A(2) \rangle \\ + \\ \langle 1s_B(1) | \langle 1s_A(2) | \hat{V}_{12} | 1s_A(1) \rangle | 1s_B(2) \rangle \\ + \\ \langle 1s_B(1) | \langle 1s_A(2) | \hat{V}_{12} | 1s_B(1) \rangle | 1s_A(2) \rangle \end{array} \right) \end{aligned}$$

the second and third terms are the same, and are termed “exchange” integrals because the bra orbitals are in the opposite order as in the ket:

$$K \equiv \langle 1s_A(1) | \langle 1s_B(2) | \hat{V}_{12} | 1s_B(1) \rangle | 1s_A(2) \rangle = \langle 1s_B(1) | \langle 1s_A(2) | \hat{V}_{12} | 1s_A(1) \rangle | 1s_B(2) \rangle.$$

The second and third terms are also equal, and are termed “direct” or “Coulomb” integrals because the resulting integrals look like the Coulomb interaction between two charge densities:

$$J \equiv \langle 1s_B(1) | \langle 1s_A(2) | \hat{V}_{12} | 1s_A(1) \rangle | 1s_B(2) \rangle = \langle 1s_A(1) | \langle 1s_B(2) | \hat{V}_{12} | 1s_B(1) \rangle | 1s_A(2) \rangle$$

Thus, we have the result

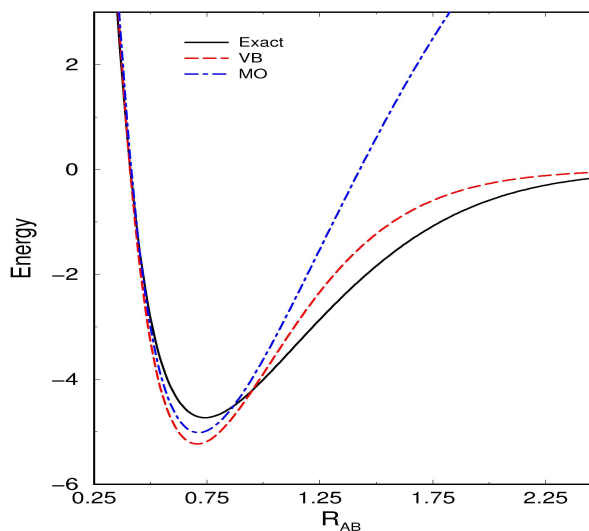
$$\langle \Psi_{VB} | \hat{V}_{12} | \Psi_{VB} \rangle = \frac{J + K}{(1+S^2)}$$

Adding all the terms together, we have:

$$\begin{aligned} \langle \Psi_{VB} | \hat{h}_1 | \Psi_{VB} \rangle &= \langle \Psi_{VB} | \hat{h}_1 | \Psi_{VB} \rangle + \langle \Psi_{VB} | \hat{h}_2 | \Psi_{VB} \rangle + \langle \Psi_{VB} | \hat{V}_{12} | \Psi_{VB} \rangle + \frac{1}{R_{AB}} \\ &= 2 \frac{\varepsilon + S h_{AB}}{(1 + S^2)} + \frac{J + K}{(1 + S^2)} + \frac{1}{R_{AB}} \end{aligned}$$

The Coulomb and exchange terms are positive. The nuclear repulsion is clearly positive. Hence the only terms that lead to binding of the molecule in this picture are the average one-electron energy ε and the resonance integral h_{AB} . If the former term is dominant, the binding is said to be due to **delocalization**, since an electron that is totally localized on one atom would just give the atomic value for ε , which implies no net binding. If h_{AB} is large the bond is said to involve some **resonance** character, which can be connected to the familiar concept of resonance between different Lewis dot structures.

If we again use a computer to evaluate all the integrals, we get the potential curve pictured below for VB theory. As expected, this simple VB wavefunction obtains the correct dissociation limit, where MO theory fails. Further, the agreement of the simple VB result is surprisingly good even near equilibrium: VB predicts the bond distance to be .71 Å (compared with the correct answer of .74 Å) and $D_e = 5.2$ eV (compared to 4.75 eV). Hence, the VB wavefunction also gives good agreement with no free parameters. But most importantly, it lets us know that we understand how to improve the wavefunction whenever we spot an obvious error: in this case, we saw that dissociation was poor and constructed the VB ansatz to cure the problem.



This VB approach is typically generalized as follows when dealing with polyatomic molecules. We can generally write the wavefunction as a product of a space and spin part:

$$|\Psi\rangle = |\Psi_{space}\rangle |\Psi_{spin}\rangle.$$

The major assumption in VB theory is that the space part can be well represented by a **product** of atomic-like functions. Thus, for water we would immediately write down a spatial part like this:

$$|\Psi_{space}\rangle \approx |1s_{H_A}\rangle |1s_{H_B}\rangle |1s_O\rangle |1s_O\rangle |2s_O\rangle |2s_O\rangle |2p_{xO}\rangle |2p_{xO}\rangle |2p_{yO}\rangle |2p_{zO}\rangle$$

however, there are two things wrong with this wavefunction. First, we all know that atomic orbitals **hybridize** in a molecule. Hence, we need to make appropriate linear combinations of the AOs (in this case sp^3 hybrids) to get the hybridized AOs. In this case the four sp^3 hybrids can be written symbolically as:

$$|sp_i^3\rangle = c_{s,i}|2s\rangle + c_{x,i}|2p_x\rangle + c_{y,i}|2p_y\rangle + c_{z,i}|2p_z\rangle$$

and so a more appropriate spatial configuration is:

$$|\Psi_{space}\rangle \approx |1s_{H_A}\rangle |1s_{H_B}\rangle |1s_O\rangle |1s_O\rangle |sp_{1O}^3\rangle |sp_{1O}^3\rangle |sp_{2O}^3\rangle |sp_{2O}^3\rangle |sp_{3O}^3\rangle |sp_{4O}^3\rangle.$$

The other problem with this state is that it lacks the proper symmetry for describing Fermions; the overall state needs to be antisymmetric. In the case of two electrons this was easy to enforce – singlets have symmetric spatial parts and triplets antisymmetric parts. However, in the case of many electrons the rules are not so simple; in fact, it turns out to be impossible to program a computer to do this without having the time required grow exponentially with the number of electrons!

Formally, we will just leave the derivation at this point by defining an operator \mathcal{A} that “antisymmetrizes” the wavefunction, in which case

$$|\Psi_{VB}\rangle = \mathcal{A}\left\{|1s_{H_A}\rangle |1s_{H_B}\rangle \dots |sp_{1O}^3\rangle |sp_{2O}^3\rangle |sp_{2O}^3\rangle |sp_{3O}^3\rangle |sp_{4O}^3\rangle |\Psi_{spin}\rangle\right\}$$

In general VB results are very accurate for the small systems where it can be applied. The bond lengths are a bit too short, and the binding energies tend to be too small, but the qualitative results are excellent. Further, the correct hybridized atomic orbitals fall directly out of the calculation, so there are nice qualitative insights to be gained here. Also, notice that the atomic configurations are expected to change very little or not at all as the geometry of the molecule changes (since the orbitals depend on the atom and not the molecular structure). Hence, these VB wavefunctions have a strong connection to the diabatic states discussed previously. However, despite the benefits

of a VB approach, the exponential amount of time one must invest to do these calculations means that they will never be practical for molecules most people are interested in.