XIII. The Hydrogen molecule

We are now in a position to discuss the electronic structure of the simplest molecule: H_2. For the low-lying electronic states of H_2, the BO approximation is completely satisfactory, and so we will be interested in the electronic Hamiltonian

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

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: $\left|1s_A\right\rangle$ and $\left|1s_B\right\rangle$. These two orbitals make up the minimal AO basis for H_2. 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 “$\left|1s_A\right\rangle$” 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. Valence Bond Picture

As already touched on, we know what the spatial part of the electronic wavefunction looks like for large R_{AB}: it is just a product of the atomic orbitals:

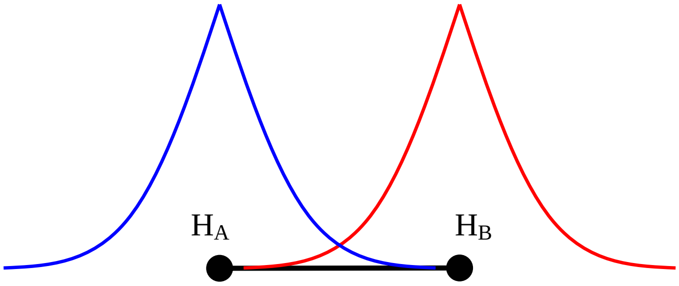
$$|\Psi\rangle \propto |1s_A\rangle|1s_B\rangle$$

But this description is incomplete, since it is not antisymmetric and it does not specify the ***spins*** of the electrons. There are, of course, two possible spin states (singlet and triplet), and we will primarily be interested in the singlet state. By analogy with the excited states of a two-electron atom, we can immediately write down the correct antisymmetric singlet state with the above spatial configuration:

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

The Valence Bond (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}) This may seem like an extreme approximation, but it works because the gap between the valence orbital (1s) and all the other orbitals (2s, 2p,…) is large in absolute terms (ca. 10 eV).

The first thing we need to do is normalize the VB state. This is more complicated than it might 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 VB wavefunction, since

$$\langle \Psi | \Psi \rangle = \langle \Psi_{space} | \Psi_{space} \rangle \overbrace{\langle \Psi_{spin} | \Psi_{spin} \rangle}^{1}$$

$$\Rightarrow \langle \Psi | \Psi \rangle = \langle \Psi_{space} | \Psi_{space} \rangle = \tfrac{1}{2}\left(\langle 1s_A | \langle 1s_B | + \langle 1s_B | \langle 1s_A | \right)\left(|1s_A\rangle |1s_B\rangle + |1s_B\rangle |1s_A\rangle \right)$$

$$= \tfrac{1}{2}\begin{pmatrix} \overbrace{\langle 1s_A | 1s_A \rangle \langle 1s_B | 1s_B \rangle}^{1} + \overbrace{\langle 1s_A | 1s_B \rangle \langle 1s_B | 1s_A \rangle}^{S^2} + \\ \underbrace{\langle 1s_B | 1s_B \rangle \langle 1s_A | 1s_A \rangle}_{S^2} + \underbrace{\langle 1s_B | 1s_A \rangle \langle 1s_A | 1s_B \rangle}_{1} \end{pmatrix}$$

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

Hence, the correctly normalized VB wavefunction is:

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

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. To get any further, it is useful to split the Hamiltonian into pieces for electrons "1" and "2" separately and the interaction:

$$\hat{h}_1 \equiv -\tfrac{1}{2}\nabla_1^{\,2} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} \qquad \hat{h}_2 \equiv -\tfrac{1}{2}\nabla_2^{\,2} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|}$$

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

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. Treating each term separately,

$$\langle\Psi_{VB}|\hat{h}_1|\Psi_{VB}\rangle=\frac{1}{2\left(1+S^2\right)}\left(\langle 1s_A|\langle 1s_B|+\langle 1s_B|\langle 1s_A|\right)\hat{h}_1\left(|1s_A\rangle|1s_B\rangle+|1s_B\rangle|1s_A\rangle\right)$$

$$=\frac{1}{2\left(1+S^2\right)}\begin{pmatrix}\overbrace{\langle 1s_A|\hat{h}_1|1s_A\rangle\langle 1s_B|1s_B\rangle}^{\varepsilon}+\overbrace{\langle 1s_A|\hat{h}_1|1s_B\rangle\langle 1s_B|1s_A\rangle}^{S\ h_{AB}}+\\ \underbrace{\langle 1s_B|\hat{h}_1|1s_A\rangle\langle 1s_A|1s_B\rangle}_{\varepsilon}+\underbrace{\langle 1s_B|\hat{h}_1|1s_B\rangle\langle 1s_A|1s_A\rangle}_{S\ h_{AB}}\end{pmatrix}$$

$$\Rightarrow\langle\Psi_{VB}|\hat{h}_1|\Psi_{VB}\rangle=\frac{\varepsilon+S\ h_{AB}}{\left(1+S^2\right)}$$

where we have defined the average one electron energy:

$$\varepsilon\equiv\langle 1s_A|\hat{h}_1|1s_A\rangle=\langle 1s_B|\hat{h}_1|1s_B\rangle$$

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

$$h_{AB}\equiv\langle 1s_A|\hat{h}_1|1s_B\rangle=\langle 1s_B|\hat{h}_1|1s_A\rangle$$

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:

$$\langle\Psi_{VB}|\hat{V}_{12}|\Psi_{VB}\rangle=\frac{1}{2\left(1+S^2\right)}\left(\langle 1s_A|\langle 1s_B|+\langle 1s_B|\langle 1s_A|\right)\hat{V}_{12}\left(|1s_A\rangle|1s_B\rangle+|1s_B\rangle|1s_A\rangle\right)$$

$$=\frac{1}{2\left(1+S^2\right)}\begin{pmatrix}\langle 1s_A|\langle 1s_B|\hat{V}_{12}|1s_A\rangle|1s_B\rangle+\langle 1s_A|\langle 1s_B|\hat{V}_{12}|1s_B\rangle|1s_A\rangle+\\ \langle 1s_B|\langle 1s_A|\hat{V}_{12}|1s_A\rangle|1s_B\rangle+\langle 1s_B|\langle 1s_A|\hat{V}_{12}|1s_B\rangle|1s_A\rangle\end{pmatrix}$$

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

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

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:

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

Thus, we have the result

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

Adding all the terms together, we have:

$$\left\langle \Psi_{VB} \middle| \hat{h}_1 \middle| \Psi_{VB} \right\rangle = \left\langle \Psi_{VB} \middle| \hat{h}_1 \middle| \Psi_{VB} \right\rangle + \left\langle \Psi_{VB} \middle| \hat{h}_2 \middle| \Psi_{VB} \right\rangle + \left\langle \Psi_{VB} \middle| \hat{V}_{12} \middle| \Psi_{VB} \right\rangle + \frac{1}{R_{AB}}$$

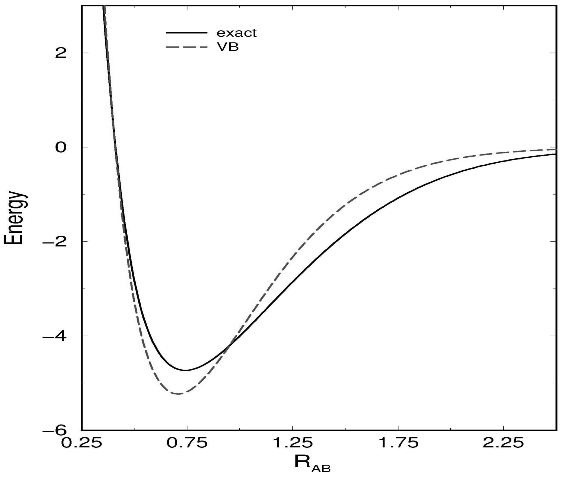
$$= 2\frac{\varepsilon + S\ h_{AB}}{\left(1+S^2\right)} + \frac{J+K}{\left(1+S^2\right)} + \frac{1}{R_{AB}}$$

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.

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 get the potential curve pictured. We can compare this to the “experimental” result, which can be gotten by one of two means: 1) taking the vibrational spectrum of H_2 and converting it to a potential or 2) choosing a large, essentially complete, basis of orbitals (atomic or otherwise), building the matrix

$$H_{ij;kl} = \left\langle \phi_i \middle| \left\langle \phi_j \middle| \hat{H}_{el} \middle| \phi_k \right\rangle \middle| \phi_l \right\rangle$$

and finding its lowest eigenvalue. These two approaches give precisely the same answer, and the result is shown in the figure. The agreement with our simple VB result is surprisingly good. If we want to summarize the results with a few key numbers, we can note that VB predicts the bond distance to be .71 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:

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

VB predicts a binding energy of 5.2 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.

This 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

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

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.

c. Molecular Orbital Picture

The molecular orbital (MO) picture is the other major tentpole of electronic structure. Instead of restricting the orbitals to be atomic-like functions (as in the VB picture), one allows them to delocalize over the whole molecule. This is done by defining an effective one electron Hamiltonian, $\hat{h}_{eff}$, and then finding its eigenfunctions. These eigenfunctions are the “molecular orbitals”.

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:

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

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

$$|\phi_+\rangle \propto \tfrac{1}{\sqrt{2}}\left(|1s_A\rangle + |1s_B\rangle\right) \qquad |\phi_-\rangle \propto \tfrac{1}{\sqrt{2}}\left(|1s_A\rangle - |1s_B\rangle\right)$$

We can normalize these:

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

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

which implies that the normalized wavefunctions are:

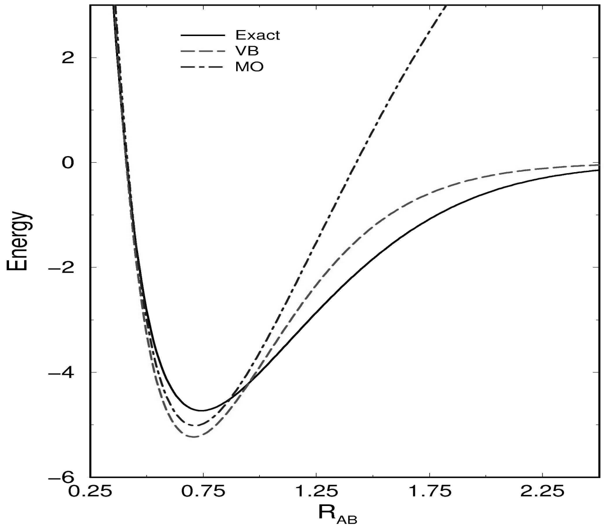
$$|\phi_+\rangle = \tfrac{1}{\sqrt{2(1+S)}}\left(|1s_A\rangle + |1s_B\rangle\right) \qquad |\phi_-\rangle = \tfrac{1}{\sqrt{2(1-S)}}\left(|1s_A\rangle - |1s_B\rangle\right).$$

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.

To compare with the VB results we already have, let us consider the lowest singlet state built out of the molecular orbitals. First, note that $h_{AB} < 0$, so $\left|\phi_+\right\rangle$ is lower in energy than $\left|\phi_-\right\rangle$. Neglecting the interaction, then, the lowest singlet state is:

$$\left|\Phi_{MO}\right\rangle = \left|\left|\phi_+\bar{\phi}_+\right|\right\rangle$$

and this is the MO ground state for H_2. How good an approximation is it? Well, we can compute the expectation value of the energy, $\left\langle\left|\phi_+\bar{\phi}_+\right|\middle|\hat{H}\middle|\left|\phi_+\bar{\phi}_+\right|\right\rangle$, as we did for the VB wavefunction and we get the result pictured at right. Near equilibrium, the results are very good (D_e=5.0 eV, R_e=.72 Å), but far from equilibrium, we get a nasty surprise: the molecule does not dissociate into two Hydrogen atoms!



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

$$
\begin{aligned}
\left|\Phi_{MO}\right\rangle &= \left|\phi_+\right\rangle\left|\phi_+\right\rangle\left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right) \\
&= \left(\frac{\left|1s_A\right\rangle + \left|1s_B\right\rangle}{\sqrt{2(1+S)}}\right)^2 \left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right) \\
&= \frac{1}{2(1+S)}\left(\left|1s_A\right\rangle\left|1s_A\right\rangle + \left|1s_A\right\rangle\left|1s_B\right\rangle + \left|1s_B\right\rangle\left|1s_A\right\rangle + \left|1s_B\right\rangle\left|1s_B\right\rangle\right)\left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right)
\end{aligned}
$$

The middle two terms (which are called “covalent” configurations) are exactly the terms that were present in the VB wavefunction, which gave the proper dissociation energy. 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 answer when we try to dissociate this molecule. Near equilibrium, ionic terms contribute about 25% to the true wavefunction. Hence MO theory is good there, but is always terrible at dissociation.

Despite the fact that MO theory does not give as good an answer for this simple model, it still ends up being the method of choice for chemistry for three primary reasons:

1) For polar bonds, ionic configurations are much more important than for a covalent bond like the H-H bond. Hence, VB theory (which only includes covalent configurations) will typically be somewhat worse than what we have seen here.
2) For many electrons, it is easy to program a computer to solve for the MOs and compute $\left\langle \hat{H}_{el} \right\rangle$ for the best single determinant built out of the MOs.
3) There many methods that have been designed to correct the failings of MO theory, so that even the glaring errors we noted in the dissociation of H_2 can be routinely corrected.

For a many electron molecule, there are three key steps to applying MO theory. The first step is defining the basis in which the Hamiltonian will be diagonalized. Typically, this is done by choosing a set of atomic-like functions and then writing each MO as a linear combination of AOs (LCAOs):

$$\left|\phi_i^{MO}\right\rangle = \sum_\alpha c_{i\alpha}\left|\phi_\alpha^{AO}\right\rangle$$

In principle, this AO basis should be chosen to be numerically complete, but, as we have already seen, one can get reasonable answers with a basis that is ***grossly*** undercomplete. Many semi-empirical theories work in the latter limit and ***define*** their one electron Hamiltonian with reference to a particular set of minimal basis functions. However, the best methods work with any basis.

The second element of the calculation is the definition of the effective one electron Hamiltonian $\hat{h}_{eff}$. Once this operator has been defined, the MOs are always given by

$$\hat{h}_{eff}\left|\phi_i^{MO}\right\rangle = \sum_\alpha c_{i\alpha}\hat{h}_{eff}\left|\phi_\alpha^{AO}\right\rangle = \varepsilon_i\sum_\alpha c_{i\alpha}\left|\phi_\alpha^{AO}\right\rangle = \varepsilon_i\left|\phi_i^{MO}\right\rangle$$

That is, they are the eigenstates of $\hat{h}_{eff}$ in the basis of AOs that we have chosen. There are a number of different choices one can make for this effective one particle Hamiltonian, and we have investigated two such choices already. For H_2 we used the pure one particle Hamiltonian and solved

$$\hat{h}\left|\phi_i^{MO}\right\rangle = \varepsilon_i\left|\phi_i^{MO}\right\rangle.$$

Another choice for the effective one electron Hamiltonian is to choose the one electron Hamiltonian ***plus*** the average field for a given electron interacting with the ***mean field*** of all the other electrons

$$\hat{F}\left(\phi^{MO}\right)\left|\phi_i^{MO}\right\rangle = \varepsilon_i\left|\phi_i^{MO}\right\rangle.$$

This is just the Hartree-Fock (HF) approach we encountered in treating the Helium atom. There are also other physical approximations one can make to define the one-electron Hamiltonian that are more or less accurate than these two methods, but in all MO theories there is ***some*** effective one electron Hamiltonian that defines the orbitals. Generally, the best theories are those (like HF) that have some condition of self-consistency between the orbitals.

The final step in an MO calculation is the calculation of the total energy. In all cases, one constructs the wavefunction by filling up the MOs starting with the lowest energy orbital and moving upward until all the electrons have been used up (the molecular aufbau principle). The wavefunction is then just the determinant constructed from these orbitals. For example, if we have $2N$ electrons the MO state will be:

$$\left|\Psi_{MO}\right\rangle = \left|\left|\phi_1\phi_{\bar{1}}\phi_2\phi_{\bar{2}}\phi_3....\phi_N\phi_{\bar{N}}\right|\right\rangle$$

In the Hartree-Fock approach, one assigns an energy to this determinant by computing the expectation value of the energy

$$\left\langle\Psi_{MO}\left|\hat{H}\right|\Psi_{MO}\right\rangle.$$

However, in some cases other forms are used. For example, in density functional theory (which is another MO approach) the energy is written as a functional of the electron density predicted by the MOs. The reason for this is that under certain assumptions, one can construct functionals of the density that are more accurate than the expectation value of the single determinant.