

# Lecture 21

## Valence Bond Theory

### Study Goal of This Lecture

- Configuration interaction
- Generalized valence bond theory

### 21.1 Configuration Interaction

Following the prescription we use for many electron atoms, we construct many-electron molecular wavefunction from Slater determinant of single electron wavefunctions. (This single electron wavefunction is molecular orbital.) Recall, an electron configuration correspond to a Slater determinant, then for Hydrogen molecule:

Recall that the orbital is single electron wavefunction.

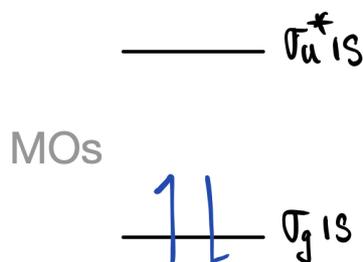


Figure 21.1: Electron configuration of  $H_2$ .

$$\begin{aligned}\Psi_{(1\sigma_g)^2} &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [1\sigma_g(1)\alpha(1)1\sigma_g(2)\beta(2) - 1\sigma_g(1)\beta(1)1\sigma_g(2)\alpha(2)].\end{aligned}\tag{21.1}$$

Expand it in atomic orbital:

$$\Psi_{(1\sigma_g)^2} = \frac{1}{2(1+S)} \times [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)].\tag{21.2}$$

The calculation yields the energy:  $D_e = 2.65eV (255kJ/mol)$  and bond length  $0.84\text{\AA}$ . The experimental value is  $D_e = 4.75eV$  and  $R_e = 0.74\text{\AA}$ . Results can be improved by considered a “screened”  $1s$  orbital, that is  $\phi_{1s} = k^{3/2}\pi^{-1/2}e^{-k\cdot r}$  and use the Hartree-Fock SCF approach to find optimal M.O. or further, consider many more basis functions( $p, d, \dots$ ).

These yield better results but the final “Hartree-Fock” result still does not yield the exact result, this cannot be improved by using bigger basis. Such results is intrinsic in the “single Slater determinant” approach. The reason is illustrated by considering the form of  $\Psi_{(1\sigma_g)^2}$ :

We call this as Hartree-Fock limit.

$$\Psi_{(1\sigma_g)^2} \sim \underbrace{1s_A(1)1s_A(2) + 1s_B(2)1s_B(1)}_{\substack{H_A^- H_B^+ + H_A^+ H_B^- \\ \text{ionic part}}} + \underbrace{1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)}_{\substack{\text{H-H} \\ \text{covalent part}}}.\tag{21.3}$$

This wavefunction describes a state with equal ionic and covalent characters even at  $R \rightarrow \infty$ , which we know it should be purely covalent when  $R \rightarrow \infty$ . This is a consequence of Slater determinant being uniform combination of all possible electron arrangements. To avoid this limitation, we need to consider interactions between different Slater determinant. For instance, consider the configuration of excited state.

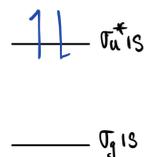


Figure 21.2: Electron configuration of excited state  $H_2$ .

$$\begin{aligned}\Psi_{(1\sigma_u)^2} &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_u(1)\alpha(1) & \sigma_u(1)\beta(1) \\ 1\sigma_u(2)\alpha(2) & \sigma_u(2)\beta(2) \end{vmatrix} \\ &= \frac{1}{2(1-S)} [1s_A(1) - 1s_B(1)] \times [1s_A(2) - 1s_B(2)] \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)],\end{aligned}\tag{21.4}$$

$$\Psi_{(1\sigma_u)^2} \sim 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) - 1s_A(1)1s_B(2) - 1s_A(2)1s_B(1),\tag{21.5}$$

then we assume the exact wavefunction is the combination of  $\Psi_{(1\sigma_g)^2}$  and  $\Psi_{(1\sigma_u)^2}$ :

$$\Psi = C_1\Psi_{(1\sigma_g)^2} + C_2\Psi_{(1\sigma_u)^2}.\tag{21.6}$$

Superposition of these two states will allow the balance between ionic and covalent contributions. This method is called “Configuration Interaction”, abbreviated as “CI”. Using this simple CI approach yields much better results, if a big basis sets and more configuration determinant are used, the result will approach the exact value.

This simple (actually the “simplest”) MO treatment illustrate the essential part of the MO theory, and apply the same procedure to more complex, polyatomic molecule are straightforward. Steps which have to take can be summarized as:

1. Find a set of functions centered on atoms or the “basis” AOs.
2. Represent MOs as LCAO, use HF-SCF to find a set of MOs that minimizes the energy of the N electron system.
3. Use CI to further improve the results.

The different between the exact energy and the Hartree-Fock limit is called the “correlation energy”.

Note that MO theory states from fully delocalized MOs, that do not assign electrons to individual atoms. This is quite different from the Lewis “bond” picture of molecules.

## 21.2 Valence Bond Theory

Another approach is to use the valence bond theory which begins by consider the neutral electron configuration of atoms. For example, for the  $H_2$  molecule, the

valence bond treatment considers

$$\begin{aligned} f_1 &= 1s_A(1)1s_B(2), \\ f_2 &= 1s_A(2)1s_B(1), \end{aligned} \quad (21.7)$$

$$\Psi_{covalent} = C_1 f_1 + C_2 f_2. \quad (21.8)$$

In this case, no need for variation, we know

$$\Psi_{\pm} = \frac{f_1 \pm f_2}{\sqrt{2(1 \pm S^2)}}. \quad (21.9)$$

The result yields  $D_e = 3.15eV$  and  $R_e = 0.87\text{\AA}$ . To further improve the result, one need to add the ionic contribution, that is

$$\Psi_{ionic} \sim 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2), \quad (21.10)$$

and then use

$$\Psi = C_1 \Psi_{covalent} + C_2 \Psi_{ionic}. \quad (21.11)$$

This is called the Generalized Valance Bond method, and it is basically the same with the simple CI approach!! For polyatomic molecules, localized ‘‘hybrid orbitals’’ need to be constructed first as the basis of the VB theory. For example,  $H_2O$  has eight valence electron and the oxygen atom is  $sp^3$  hybridized. Then the basis of constructing molecular wavefunction of water would be:

$$\begin{aligned} \phi_{sp^3(i)} &= \frac{1}{\sqrt{4}}(2s + 2p_x + 2p_y + 2p_z), \\ \phi_{sp^3(ii)} &= \frac{1}{\sqrt{4}}(2s - 2p_x - 2p_y + 2p_z), \\ \phi_{sp^3(iii)} &= \frac{1}{\sqrt{4}}(2s + 2p_x - 2p_y - 2p_z), \\ \phi_{sp^3(iv)} &= \frac{1}{\sqrt{4}}(2s - 2p_x + 2p_y - 2p_z), \\ \phi_{H_A} &= 1s_A, \phi_{H_B} = 1s_B. \end{aligned} \quad (21.12)$$

Note that in the VB picture, the ‘‘resonance structure’’ is considered in the GVB approach: The valence bond wavefunction is

$$\begin{aligned} \Psi_{VB} &\sim 1s_O(1)1\bar{s}_O(2)\phi_{sp^3(i)}(3)\bar{\phi}_{sp^3(i)}(4)\phi_{sp^3(ii)}(5)\bar{\phi}_{sp^3(ii)}(6) \\ &\times \left[ \phi_{sp^3(iii)}(7)1s_A(8) + \phi_{sp^3(iii)}(8)1s_A(7) \right] \\ &\times \left[ \phi_{sp^3(iv)}(9)1s_B(10) + \phi_{sp^3(iv)}(10)1s_B(9) \right] \\ &+ \text{all other electron permutations.} \end{aligned} \quad (21.13)$$

Only consider covalent configurations which share the electrons.

Construting the many-electrons wavefunction directly, no MO step.

Note that the VB wavefunction matches the idea of Lewis structure. (Check by yourself!)

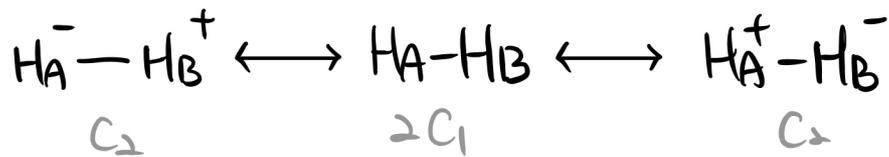


Figure 21.3: Resonance structure of  $H_2$ .

The VB method is mostly used in qualitative pictures. Quantitative calculations are also possible, in fact, if additional resonance wavefunctions are considered. i.e. the GVB approach, the GVB method is often better than HF method. However the calculation are often much complicated (especially the programming part) so it is difficult to apply. That's why the world of computation chemistry is dominant by MO approaches.