

# Lecture 20

## Many-electron Molecules

### Study Goal of This Lecture

- Born-Oppenheimer approximation
- LCAO approximation
- Hartree-Fock independent electron approximation

### 20.1 Preface

Now we have dealt with quantum states for many-electron atoms, it is time to move on to more complicated systems  $\Rightarrow$  many-electron models. What is the main additional difficulties?

- Molecules have additional nuclear motions (vibrations)
- Electron can delocalized, no spherical symmertry

### 20.2 Born-Oppenheimer Approximation

Consider a general molecular Hamiltonian:

$$\hat{H} = -\sum_{a=1}^M \frac{1}{2M_a} \nabla_a^2 + \sum_{a=1}^M \sum_{b>a}^M \frac{Z_a Z_b}{R_{ab}} - \underbrace{\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{a=1}^M \frac{Z_a}{r_{ia}} + \sum_{i=i}^N \sum_{j>i}^N \frac{1}{r_{ij}}}_{H_{electron}(R)}. \quad (20.1)$$

Since nuclei are much heavier than electrons, they move more slowly.  $\Rightarrow$  We consider electron moving in “fixed/static” nuclear coordinates: no momentum, position  $\{R\}$  fixed

$$\hat{H}_{elec}\{R_a\} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{a=1}^M \frac{Z_a}{r_{ia}} + \sum_{i=1}^N \sum_{j=1}^N \frac{1}{r_{ij}}. \quad (20.2)$$

Solution then can be solved from

$$\hat{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec}, \quad (20.3)$$

note  $\Psi_{elec} = \Psi_{elec}(\{R_a\})$ , also the electronic energy  $E_{elec}(\{R_a\})$  depends on nuclear coordinate  $\{R_a\}$ . Now if we consider the nuclear moving in the **averaged** electron influence:

$$\begin{aligned} \hat{H}_{nucl} &= \langle \Psi_{elec} | \hat{H} | \Psi_{elec} \rangle \\ &= -\sum_{a=1}^M \frac{1}{2M_a} \nabla_a^2 + \sum_{a=1}^M \sum_{b>a}^M \frac{Z_a Z_b}{R_{ab}} + \underbrace{\langle \Psi_{elec} | \hat{H}_{elec} | \Psi_{elec} \rangle}_{E_{elec}(\{R_a\})}. \end{aligned} \quad (20.4)$$

If we define total energy

$$E_{tot}(\{R_a\}) = E_{elec}(\{R_a\}) + \sum_{a=1}^M \sum_{b>a}^M \frac{Z_a Z_b}{R_{ab}}, \quad (20.5)$$

then

$$\hat{H}_{nucl} = -\sum_{a=1}^M \frac{1}{2M_a} \nabla_a^2 + \underbrace{E_{tot}(\{R_a\})}_{V(R), \text{ potential}}. \quad (20.6)$$

Therefore, nuclei moving in the potential  $E_{tot}(\{R_a\}) \rightarrow$  potential energy surface(PES).

If one solves

$$\hat{H}_{nucl} \Psi_{nucl} = \epsilon \Psi_{nucl}, \quad (20.7)$$

where  $\Psi_{nucl}$  is nuclear wave function and  $\epsilon$  is total energy. The total wavefunction will be

$$\Psi(\{r_i\}; \{R_A\}) = \Psi_{elec} \otimes \Psi_{nucl}. \quad (20.8)$$

We will focus on the electron part of the problem and neglect the nuclear Schrödinger equation throughout the course. Notice that for most nuclei (often than H & He), classical approximation is appropriate. It is reasonable to consider the nuclear problem as classical particle moving on the PES defined by  $E_{total} \rightarrow$  classical mechanics with PES provided by quantum mechanic.

## 20.3 Linear Combination of Atomic Orbitals

The next problem of going from atoms to molecules is the proper functional forms, i.e. basis sets, since molecules are not spherical. For the molecular system, atomic orbitals are good basis sets!! We will illustrate this by considering  $H_2^+$  molecular ion.

### 20.3.1 $H_2^+$ molecular ion

The Hamiltonian of  $H_2^+$

$$\hat{H}_e(R) = -\frac{\hbar}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{1A}} + \frac{1}{r_{1B}} \right) + \frac{e^2}{4\pi\epsilon_0 R}. \quad (20.9)$$

We hope to solve  $\hat{H}_e \psi_e = E_e \psi_e \implies$  approximate  $\psi_e$  as LCAO

$$\psi_e = \sum_i [C_{iA} \phi_{iA} + C_{iB} \phi_{iB}] = C_1 1s_A + C_2 1s_B. \quad (20.10)$$

We can then use the variational principle to determine  $C_1$  and  $C_2$  by minimizing  $\frac{\langle \psi_e | \hat{H}_e | \psi_e \rangle}{\langle \psi_e | \psi_e \rangle} = E$  via  $\frac{\partial E}{\partial C_i} = 0$ . For  $H_2^+$ , the minimal model is to use  $1s$  orbitals for the two H atoms. This is a minimal basis model. Also, in this particular problem, we know  $C_1 = C_2 = C$  by symmetry, but we will proceed as if  $C_1 \neq C_2$  to demonstrate more general scenario.  $\implies$  Determine  $C_1, C_2$  using variational principle.

The energy of  $H_2^+$  can be written as

$$\begin{aligned} E &= \frac{\int \psi^* \hat{H}_e \psi d\tau}{\int \psi^* \psi d\tau} \\ &= \frac{[C_1^* \langle 1s_A | + C_2^* \langle 1s_B |] \hat{H}_e [C_1 | 1s_A \rangle + C_2 | 1s_B \rangle]}{[C_1^* \langle 1s_A | + C_2^* \langle 1s_B |] [C_1 | 1s_A \rangle + C_2 | 1s_B \rangle]} \\ &= \frac{C_1^2 \langle 1s_A | \hat{H}_e | 1s_A \rangle + 2C_1 C_2 \langle 1s_A | \hat{H}_e | 1s_B \rangle + C_2^2 \langle 1s_B | \hat{H}_e | 1s_B \rangle}{|C_1|^2 + |C_2|^2 + 2C_1 C_2 \langle 1s_A | 1s_B \rangle}, \end{aligned} \quad (20.11)$$

now we define:

$$\begin{aligned} S &= \langle 1s_A | 1s_B \rangle, \text{ the } \mathbf{overlap\ integral} \\ H_{AA} &= \langle 1s_A | \hat{H}_e | 1s_A \rangle, \mathbf{coulomb\ integral} \\ H_{AB} &= \langle 1s_A | \hat{H}_e | 1s_B \rangle, \mathbf{resonance/transfer\ integral} \\ &\quad (\text{electron from } 1s_A \text{ to } 1s_B) \end{aligned}$$

Can you explain why this overlap integral is not zero? (Recall that the orbitals for the Hydrogen atoms are orthogonal.)

Therefore, we obtain:

$$E = \frac{C_1^2 H_{AA} + C_2^2 H_{BB} + 2C_1 C_2 H_{AB}}{C_1^2 + C_2^2 + 2C_1 C_2 S}. \quad (20.12)$$

To find the minimal  $E$  with respect to varying  $C_1, C_2$ , we first rewrite

$$(C_1^2 + C_2^2 + 2C_1 C_2 S)E = C_1 H_{AA} + 2C_1 C_2 H_{AB} + C_2 H_{BB}, \quad (20.13)$$

then

$$\frac{\partial}{\partial C_1} \Rightarrow (C_1^2 + C_2^2 + 2C_1 C_2) \frac{\partial E}{\partial C_1} + (2C_1 + 2C_2 S)E = 2C_1 H_{AA} + 2C_2 H_{AB}, \quad (20.14)$$

$$\frac{\partial}{\partial C_2} \Rightarrow (C_1^2 + C_2^2 + 2C_1 C_2) \frac{\partial E}{\partial C_2} + (2C_2 + 2C_1 S)E = 2C_2 H_{BB} + 2C_1 H_{AB}, \quad (20.15)$$

for the condition for minimal  $E$ :  $\frac{\partial E}{\partial C_1} = \frac{\partial E}{\partial C_2} = 0$ , we rearrange to yield:

$$\begin{aligned} C_1(H_{AA} - E) + C_2(H_{AB} - SE) &= 0, \\ C_1(H_{AB} - E) + C_2(H_{BB} - SE) &= 0. \end{aligned} \quad (20.16)$$

This is a system of homogeneous linear equations. There is a nontrivial solution only if the secular determinant of the coefficient is zero,

$$\begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{BB} - E \end{vmatrix} = 0. \quad (20.17)$$

This is the “secular equation”, which yields MOs and MO energy values. Note that the equation is a quadratic equation for  $E$ . So there are two solutions for  $E$ , with two corresponding sets of  $C_1, C_2$  (i.e. two MO wavefunctions.) In general, with  $N$  basis functions, there will be  $N$   $E_s$  and  $N$  MOs.  $\Rightarrow$  energy for molecular orbitals. In this case, one can show that  $H_{AA} = H_{BB} = E_{1s} + J$  and  $H_{AB} = E_{1s}S + K$ . The two solutions are

$$E_g = E_{1s} + \frac{J + K}{1 + S}, \quad (20.18)$$

$$E_u = E_{1s} + \frac{J - K}{1 - S}, \quad (20.19)$$

with

$$\Psi_g = \frac{1}{\sqrt{2(1 + S)}}(1s_A + 1s_B), \quad (20.20)$$

Recall the Cramer’s formula in senior high, for the equation to have more than one solution,  $\Delta = 0$ . Students with linear algebra background will recognize that this is equivalent to a matrix diagonalization.

$J$  is Coulomb’s integral

$$\Psi_u = \frac{1}{\sqrt{2(1-S)}}(1s_A + 1s_B). \quad (20.21)$$

$J, K, S$  are function of  $R$ , the explicit expression are:

$$\begin{aligned} J &= e^{2R}\left(1 + \frac{1}{R}\right), \\ K &= -\frac{S}{R}e^{-R}(1 + R), \\ S &= e^{-R}\left(1 + R + \frac{R^3}{3}\right), \end{aligned} \quad (20.22)$$

note that only  $K$  could be negative. Also, it is easy to verify that

$$\langle \Psi_g | \Psi_g \rangle = 1, \quad \langle \Psi_u | \Psi_u \rangle = 1, \quad \langle \Psi_g | \Psi_u \rangle = 0 \quad (20.23)$$

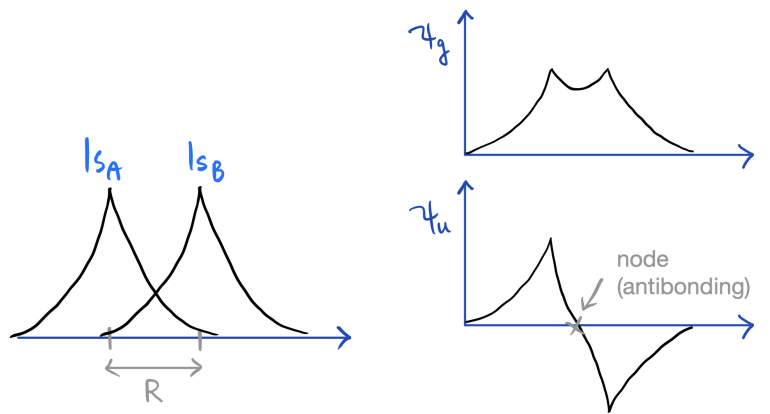
the  $u, g$  symbol is due to

$\Psi_g$ : even parity (symmetric combination), g: gerade,  
 $\Psi_u$ : odd parity (antisymmetric combination), u: ungerade.

gerade: German for even

ungerade: German for odd.

Now we can plot MOs:



(a) Two 1s orbitals.

(b) Bonding orbital and antibonding orbital

Figure 20.1: Molecular orbital for  $H_2^+$ .

and the potential energy surface  $E(R)$ :

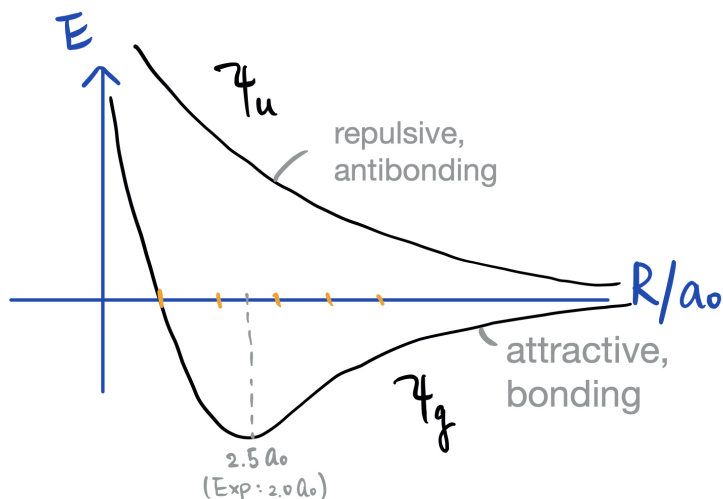


Figure 20.2: Potential energy surface for  $H_2^+$ .

The energy plot indicates:

1.  $\Psi_g$  is the ground state of the  $H_2^+$ , and  $\Psi_u$  is the excited state.
2. There is an energy minimum on  $\Psi_g \rightarrow$  stable  $H_2^+$  molecular ion at internuclear distance of  $2.5 \text{ \AA}$  (Exp:  $2.0 \text{ \AA}$ ).
3.  $E_u$  has minimum at  $R \rightarrow \infty$ . This show that in excited state, the force are all repulsive and there is no stable ion.
4.  $\Psi_g \rightarrow \Psi_u$  corresponds to excitation due to photons, therefore, absorption of photon could dissociate the molecular ion.

We thus say

$\Psi_g \leftarrow$  bonding orbital  
 $\Psi_u \leftarrow$  antibonding orbital.

The bonding/antibonding character also correspond to the existence of nodal plane between the nuclei, it can be shown rigorously using the virial theroem that whenever a MO has a nodel between two atoms, it will result in repulsive potential.

Very often, the bonding/antibonding orbital notation is used, we can plot the correlation diagram.

### 20.3.2 Correlation Diagram

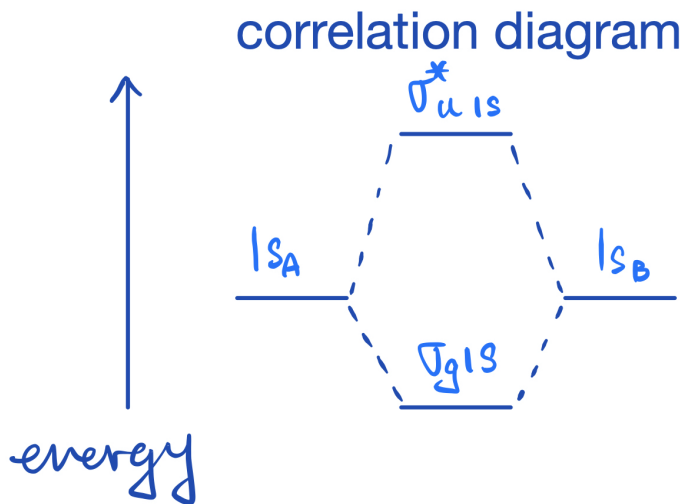


Figure 20.3: Correlation diagram for  $H_2^+$ .

**Type of bonding**

- $\sigma$ :  $\sigma$ -bond, 0 nodal plane across the two atoms.
- $\pi$ :  $\pi$ -bond, 1 nodal plane across the two atoms.
- $\delta$ :  $\delta$ -bond, 2 nodal plane across the two atoms.
- $\phi$ :  $\phi$ -bond, 3 nodal plane across the two atoms.

The number of nodal planes representing the total “axial” angular momentum, defined by the cylindrical symmetry. Note that the results using pure hydrogen  $1s$  orbital is not good.

For considering the  $2p$  orbital, it shows the power of choosing good basis set!

**Table of outcomes for different basis set**

	Exp.	Pure $1s$	Var. $1s + 2p$
De (eV)	2.79	1.76	2.73
Re ( $a_0$ )	2.0	2.5	2.01

To improve the result, consider improving the basis atomic functions. Recall that in the homework, we show that the ground state of hydrogen mixed with  $p_z$  orbitals when an external electric field is applied. Therefore, consider:

$$1s'_A = k^{\frac{3}{2}} \frac{1}{\sqrt{\pi}} e^{-kr_{1A}}, \tag{20.24}$$

$$(2p'_y)_A = \frac{\xi^{\frac{5}{2}}}{4(2\pi)^{\frac{1}{2}}} ye^{-\frac{\xi r_A}{2}}, \quad (20.25)$$

and

$$\psi \simeq [1s'_A + c(2p'_y)_A] + [1s'_B + c(2p'_y)_B]. \quad (20.26)$$

This yields a much improved result. The situation of bonding/antibonding orbitals can be generalized to general diatomic molecule.(See Silbey Figure 11.8 & 11.10)

## 20.4 Born-Oppenheimer Approximation-General Case

We consider a general molecular Hamiltonian:

$$\begin{aligned} \hat{H} = & \sum_{a=1}^M \frac{-\hbar^2}{2M_a} \nabla_a^2 + \sum_{a=1}^M \sum_{b=a+1}^M \frac{Z_a Z_b e^2}{R_{ab}} \\ & + \sum_{i=1}^N \frac{-\hbar^2}{2m_i} \nabla_i^2 - \sum_{a=1}^M \sum_{i=1}^N \frac{Z_a e^2}{r_{ia}} + \sum_{i=1}^N \sum_{i=j+1}^N \frac{e^2}{r_{ij}}. \end{aligned} \quad (20.27)$$

The full Schrödinger equation is

$$\hat{H}\Psi(\{r_i\}, \{R_a\}) = E\Psi(\{r_i\}, \{R_a\}). \quad (20.28)$$

In Born-Oppenheimer approximation, we assume nuclei and electron motions are fully decoupled, i.e. independent, thus:

$$\Psi(\{r_i\}, \{R_a\}) = \Psi_e(\{r_i\}) \times \Psi_n(\{R_a\}). \quad (20.29)$$

The Schrödinger equation becomes (using  $\hat{H} = \sum_{a=1}^M \frac{-\hbar^2}{2M_a} \nabla_a^2 + \hat{H}_e$ )

$$\left( \sum_{a=1}^M \frac{-\hbar^2}{2M_a} \nabla_a^2 + \hat{H}_e \right) \Psi_e \Psi_n = E \Psi_e \Psi_n. \quad (20.30)$$

If we solve the electronic part such that

$$\hat{H}_e \Psi_e = E_e(R) \Psi_e, \quad (20.31)$$

then we can multiply both sides of Equ.20.31 by  $\Psi_e^*$  and integrate all electronic degrees of freedom out:

$$\begin{aligned} \int \Psi_e^* \left( \sum_{a=1}^M \frac{-\hbar^2}{2M_a} \nabla_a^2 + \hat{H}_e \right) \Psi_e \Psi_n d\tau_e &= E \int \Psi_e^* \Psi_e \Psi_n d\tau_e \\ \Rightarrow \left( \sum_{a=1}^M \frac{-\hbar^2}{2M_a} \nabla_a^2 + H_e + \int \Psi_e^* \hat{H}_e \Psi_e d\tau_e \right) \Psi_n &= E \Psi_n, \end{aligned} \quad (20.32)$$



note that  $\int \Psi_e^* \hat{H}_e \Psi_e d\tau_e$  is potential energy surface( $E_e(R)$ ). Thus we can see that nuclei moving in the field due to averaged electron energy.