

Lecture #15

Plan:

1. Review objective: explain bonding.
2. Strategy: use of variation principle and knowledge of atomic orbitals
3. Review: Born Oppenheimer approximations.
4. Review: The electronic Hamiltonian and variational principle.
5. choosing a trial wave function
6. The minimization process leads to an eigenvalues problem
7. Identification of coulomb, resonance and overlap integrals.
8. Approximate energy eigenvalues and functions
9. Adding the nuclear repulsion term.
10. Implications: bonding and anti-bonding states.

Questions you should be able to answer by the end of today's lecture:

1. Why does bonding occur?
2. How to calculate simple approximations to the molecular orbital in an ionized Hydrogen molecule.
3. How do the molecular orbitals change as the interatomic distance is decreased
4. What physical insight leads to the separation of the electronic and nuclear coordinates?
5. How to choose trial wave functions and use the variation principle.

Math Tools:

1. Variation method
2. Minimization of functionals

Review: Define the expectation value of an operator

$$\langle \hat{A} \rangle = \frac{\langle \mathbf{y} | \hat{A} | \mathbf{y} \rangle}{\langle \mathbf{y} | \mathbf{y} \rangle} = \frac{\int_{-\infty}^{\infty} \mathbf{y}^* \hat{A} \mathbf{y} dv}{\int_{-\infty}^{\infty} \mathbf{y}^* \mathbf{y} dv}$$

The physical interpretation is the average measurement value obtained by measuring physical quantity A on a system described by psi.

The variation method

Dealing with problems where H is known but not u_n and E_n so we do not know how to diagonalize H. The variation method allows one to find approximations to the eigenfunctions and eigenvalues of the Hamiltonian operator. The variation method is based on the idea that if we try to find a function that minimizes average E it will be close to the true ground state eigenfunction.

$$\bar{E} = \langle \hat{H} \rangle = \frac{\int_{-\infty}^{\infty} \mathbf{f}^* \hat{H} \mathbf{f} dv}{\int_{-\infty}^{\infty} \mathbf{f}^* \mathbf{f} dv} \geq E_{ground\ state}$$

Proof:

Because H is Hermitian its eigenfunctions are a complete set therefore any function can be expanded in terms of eigenfunctions:

$$\mathbf{f}(x) = \sum_{i=1}^n c_n u_n(x)$$

$$\langle \mathbf{f} | \hat{H} | \mathbf{f} \rangle = \sum_{i=1}^n |c_n|^2 E_n$$

and

$$\langle \mathbf{f} | \mathbf{f} \rangle = \sum_{i=1}^n |c_n|^2$$

For $\bar{E} = \langle \hat{H} \rangle = E_{ground}$ it is necessary and sufficient for all $c_n = 0$ except for $n=1$.

Eigenvalues other than the lowest one can be calculated using the variation method:

The Ritz Theorem: The expectation value of the Hamiltonian is stationary in the vicinity of its discrete eigenvalues.

All of the intelligence goes into choosing a “good” trial function, which already contains in it a large amount of the true eigenfunction. The trial function is chosen with the aid of physical insight. Hartree Fock method for calculating eigenfunctions of many electron Hamiltonians is also an example of the variation method.

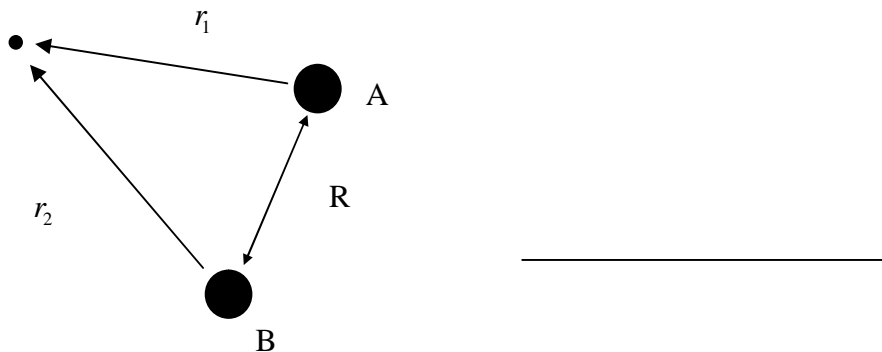
Understanding the chemical bond - Approximating the wave functions of molecules –LCAO linear combination of atomic orbitals

The problem:

How do we calculate the eigenfunctions of molecules?

The system – simple diatomic molecule

I] Draw the potential



II] Write the full Hamiltonian

$$\hat{H}(R_A, R_B, r) = \underbrace{-\frac{\hbar^2}{2m_e} \vec{\nabla}_r^2}_{\text{KE of electron}} - \frac{\hbar^2}{2m_p} \vec{\nabla}_A^2 + -\frac{\hbar^2}{2m_p} \vec{\nabla}_B^2 + \left(\underbrace{-\frac{e^2}{r_1} - \frac{e^2}{r_2}}_{\text{electron-nucleus attraction}} + \underbrace{\frac{e^2}{R}}_{\text{nuclear repulsion energy}} \right)$$

where,

$$\vec{r}_1 = \vec{r} - \vec{R}_A$$

$$\vec{r}_2 = \vec{r} - \vec{R}_B$$

In general the wave functions should contain all of the coordinates of the system
Because the protons are 1836 times heavier than the electrons they have much smaller velocity this means that at the time scales associated with the electronic movement the protons are stationary.

Review: The Born-Oppenheimer Approximation

- (1) The electronic wavefunctions depend only on the positions of the nuclei and not on their momentum
- (2) The positions of the protons are a parameter not a QM variable
- (3) Protons have a fixed separation R just add a constant to the energy.
- (4) Reduce the three body problem to an electron in a potential
- (5) The Hamiltonian is separable

Using the procedure we developed:

Write the Hamiltonian for the electron energy and nuclear repulsion energy.

$$\hat{H}_{el-nr} = \underbrace{-\frac{\hbar^2}{2m_e} \vec{\nabla}_r^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2}}_{\text{electronic energy } H_{el}} + \frac{e^2}{R}$$

$$\hat{H}_{elec} u_{elec}(r) = E_{elec} u_{elec}(r)$$

$$E_{elec} + E_{nuc\ nuc\ rep} = E_{elec} + 1/R$$

What we have is a functional dependence of the electronic energy on the nuclear separation $E_{elec}(R)$.

$$\hat{H}(R_A, R_B) = -\frac{\hbar^2}{2m_p} \vec{\nabla}_A^2 + -\frac{\hbar^2}{2m_p} \vec{\nabla}_B^2 + \left(E_{elec}(R) + \underbrace{\frac{e^2}{R}}_{\text{nuclear repulsion energy}} \right)$$

$$\hat{H}_{nuc}(R_A, R_B) u_{nuc}(R_A, R_B) = E_{nuc} u_{nuc}(R_A, R_B)$$

These eigenfunction represent the translation, rotation and vibration states of the crystal.

$$u_{Tot}(R_A, R_B, r) = u_{elec}(r) u_{nuc}(R_A, R_B)$$

We would like to find the exact energy eigenfunctions because this is difficult we will find approximate solutions

$$\hat{H}_e u = Eu$$

Assume that our solution can be written as a linear combination of atomic orbitals

$$\mathbf{f}(\vec{r}) = c_1 u_{100}(\vec{r}_1) + c_2 u_{100}(\vec{r}_2)$$

where

$$\vec{r}_1 = \vec{r} - \vec{R}_A$$

$$\vec{r}_2 = \vec{r} - \vec{R}_B$$

Since this wave function is not an energy eigenfunction we would like to minimize the average energy or the expectation value with respect to the coefficients,

$$E_{av} = \langle \hat{H} \rangle = \frac{\int_{-\infty}^{\infty} \mathbf{f} \hat{H} \mathbf{f} d\mathbf{v}}{\int_{-\infty}^{\infty} \mathbf{f} \mathbf{f} d\mathbf{v}}$$

Take a closer look at the integrals,

$$\bar{E}(c_1, c_2) = \frac{\int (c_1 u_{100}(\vec{r}_1) + c_2 u_{100}(\vec{r}_2)) \hat{H} (c_1 u_{100}(\vec{r}_1) + c_2 u_{100}(\vec{r}_2)) d\mathbf{v}}{\int (c_1 u_{100}(\vec{r}_1) + c_2 u_{100}(\vec{r}_2)) (c_1 u_{100}(\vec{r}_1) + c_2 u_{100}(\vec{r}_2)) d\mathbf{v}}$$

We are now going to apply the variation principle to allow us to find the function which minimizes E (Cauchy Reiman Theorem).

$$\frac{\partial \bar{E}}{\partial c_i} = 0$$

Get a number of integrals which we will label in the following way:

$$\begin{aligned}
 \int u_{100}(\vec{r}_1) \hat{H} u_{100}(\vec{r}_1) dr &\equiv H_{11} \\
 \int u_{100}(\vec{r}_2) \hat{H} u_{100}(\vec{r}_2) dr &\equiv H_{22} \\
 \int u_{100}(\vec{r}_1) \hat{H} u_{100}(\vec{r}_2) dr &\equiv H_{12} \\
 \int u_{100}(\vec{r}_2) \hat{H} u_{100}(\vec{r}_1) dr &\equiv H_{21} \\
 \left. \begin{aligned}
 \int u_{100}(\vec{r}_1) u_{100}(\vec{r}_1) dr &\equiv S_{11} = 1 \\
 \int u_{100}(\vec{r}_2) u_{100}(\vec{r}_2) dr &\equiv S_{22} = 1
 \end{aligned} \right\} \text{since } u_{100}(\vec{r}_i) \text{ is orthonormal} \\
 \left. \begin{aligned}
 \int u_{100}(\vec{r}_1) u_{100}(\vec{r}_2) dr &\equiv S_{12} \\
 \int u_{100}(\vec{r}_2) u_{100}(\vec{r}_1) dr &\equiv S_{21}
 \end{aligned} \right\} \neq 0 \text{ overlap integral } u_{100}(\vec{r}_i) u_{100}(\vec{r}_j) \text{ are non-orthogonal}
 \end{aligned}$$

The coulomb energy integral:

$$\begin{aligned}
 \int u_{100}(\vec{r}_1) \hat{H} u_{100}(\vec{r}_1) dr &\equiv H_{11} = H_{22} \\
 &= \underbrace{\int u_{100}(\vec{r}_1) \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_1} \right) u_{100}(\vec{r}_1) dr}_{E_1} - \underbrace{\int u_{100}(\vec{r}_1) \left(\frac{e^2}{r_2} \right) u_{100}(\vec{r}_1) dr}_{\text{coulomb integral}}
 \end{aligned}$$

The second term in the coulomb integral describes the attractive electrostatic interaction between the proton B and the electron around proton A tends to lower the energy.

The resonance energy contribution:

$$\begin{aligned}
 \int u_{100}(\vec{r}_1) \hat{H} u_{100}(\vec{r}_2) dr &\equiv H_{12} = H_{21} \\
 &= \underbrace{\int u_{100}(\vec{r}_1) \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_2} \right) u_{100}(\vec{r}_2) dr}_{E_1 S} - \underbrace{\int u_{100}(\vec{r}_1) \left(\frac{e^2}{r_1} \right) u_{100}(\vec{r}_2) dr}_{\text{resonant integral}}
 \end{aligned}$$

The interaction leads to the splitting and the creation of two energy levels

The overlap integral tends to destabilize the molecule.

Minimizing the energy expectation value with respect to the coefficients leads us to the determinant problem,

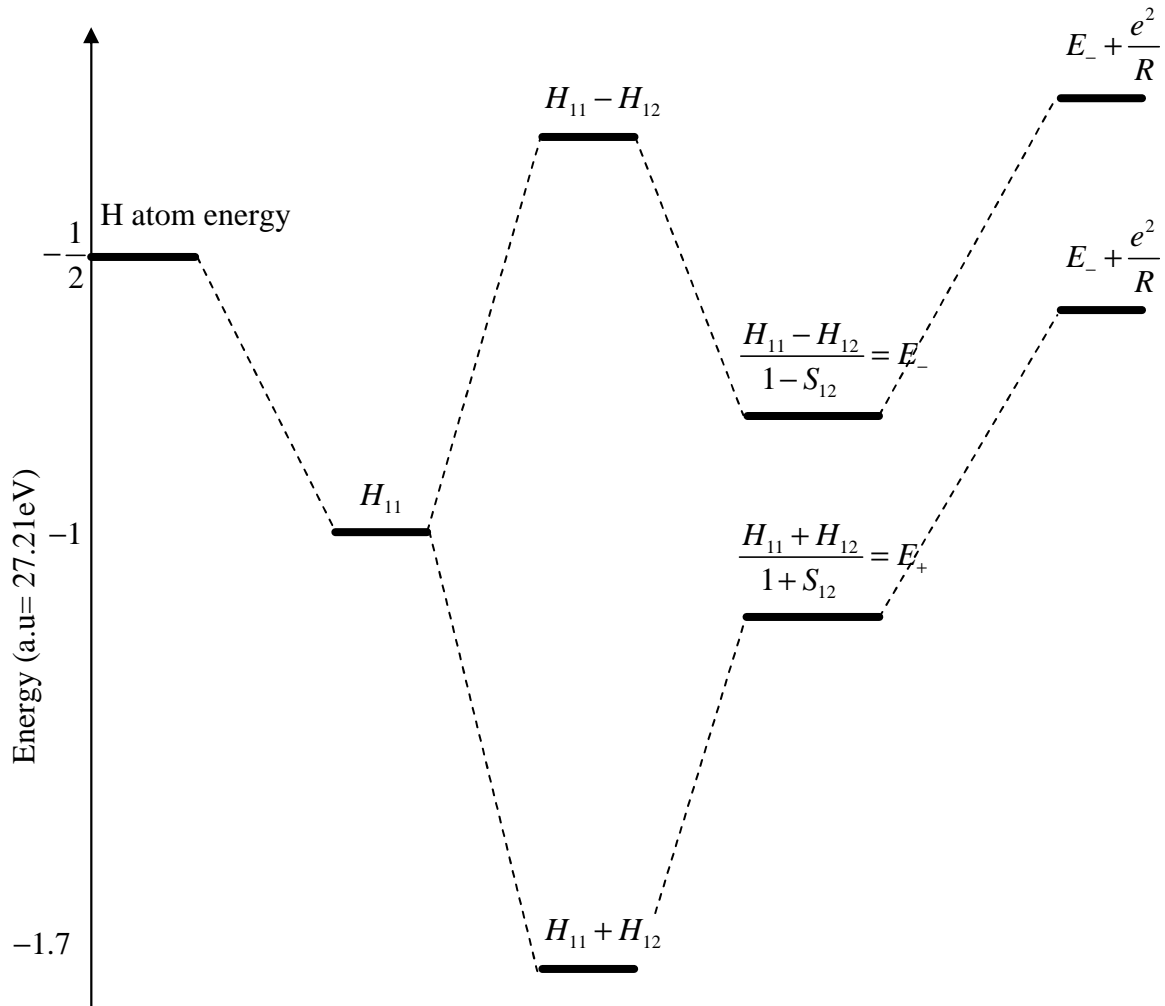
$$\begin{aligned}
 (H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 &= 0 \\
 (H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 &= 0
 \end{aligned}$$

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{pmatrix} 1 \\ 1 \end{pmatrix} \rightarrow E_+ = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

$$\begin{pmatrix} 1 \\ -1 \end{pmatrix} \rightarrow E_- = \frac{H_{11} - H_{12}}{1 - S_{12}}$$



We get two solutions for the approximate eigenfunctions,

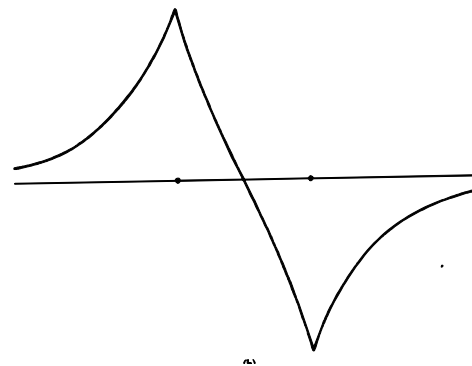
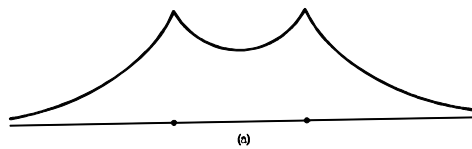
$$y_s(\vec{r}) = \frac{1}{\sqrt{2(1+S)}} (u_{100}(\vec{r}_1) + u_{100}(\vec{r}_2))$$

$$y_{s^*}(\vec{r}) = \frac{1}{\sqrt{2(1-S)}} (u_{100}(\vec{r}_1) - u_{100}(\vec{r}_2))$$

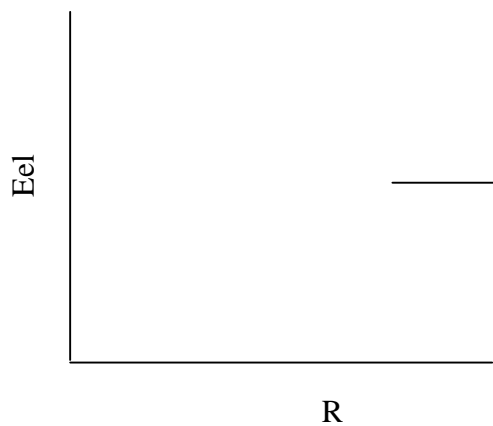
$$E_s < E_{s^*}$$

Consequences:

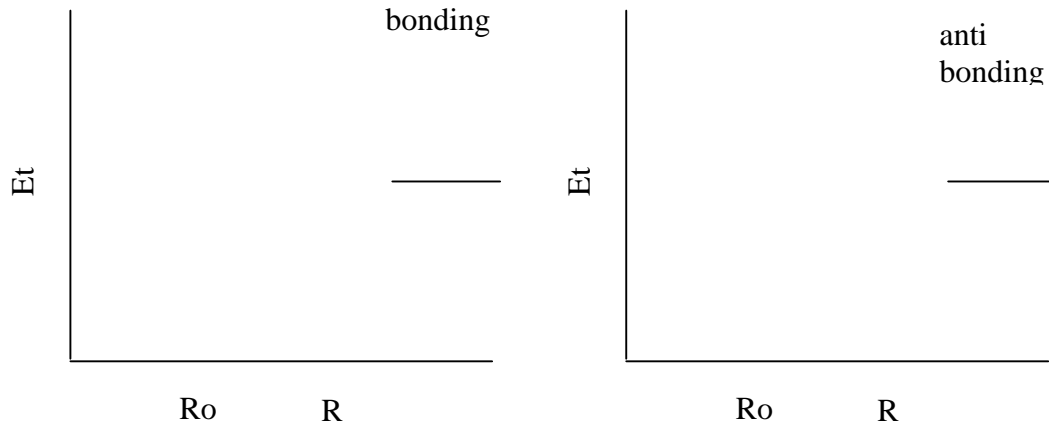
1. Odd and even wave functions the odd wavefunction has a node which is located between the two nuclei.
2. Draw the wavefunction evaluated along the internuclear separation line.



3. Splitting of the energy levels as the internuclear spacing decreases.



4. The total energy of the molecule (including the proton-proton) repulsion.



1. The lower electron eigenfunction or state has a corresponding minimum in the total energy while the higher energy electron states rise monotonically.
2. The internuclear distance at which the system achieves a minimum is the bond length which is $2 R_0$
3. The energy minimum in the lower curve indicates a stable molecule and the corresponding MO is called bonding MO. The other MO is called antibonding.
4. The electron in the bonding state will have a wavefunction that leads to a high probability of finding the electron in between the nuclei –this allows for the attractive e-p forces to offset the repulsive p-p interactions.

5. Near the minimum energy,

$$E \approx \frac{K}{2} (R - R_0)^2$$

K – is the bond stiffness.

6. In diatomic MO we distinguished between π and σ type bonds. What is the significance of this labeling scheme? Recall that the AO were labeled with s, p, d labels which were associated with the orbital angular momentum and the spherically symmetric potential. Since L^2 commuted with the Hamiltonian we could find a basis set which was common to \hat{L}^2 , \hat{L}_z and the Hamiltonian. In a linear molecule the rotational symmetry around the z axis is conserved hence there is a conservation of the \hat{L}_z component of the angular momentum that is why the MO are labeled according to their symmetries.