

## Exp 2

### **Quantum Chemical calculation:**

The potential energy curves and the orbitals of  $H_2^+$

#### **1. Objectives**

A quantum chemistry solver is used to obtain the energy and orbitals of one of the simplest molecules,  $H_2^+$ , and the formation of chemical bonding is analyzed from a quantum-mechanical point of view.

(Refer to Sections 6.1 and 6.2 in Oxtoby 7<sup>th</sup> ed.)

#### **2. Introduction and Background information**

##### **2-1) Quantum picture of the chemical bond**

Chemical bond is the attraction to form molecules or solids and it represents the arrangement of atoms and indicates the geometries of molecules. From a classical point of view, chemical bonding has been represented by a model known as the Lewis concept. However, this model cannot explain the electrons hold the molecule together despite of repulsive force pushing nuclei apart. Also some molecular properties cannot be described by this classical argument. Depending on the distance between the atoms, the energy of the molecule varies, and chemical bonds are formed at distances that maintain the lowest energy. Let's consider the progress of forming bond on the simplest system  $H_2$ .

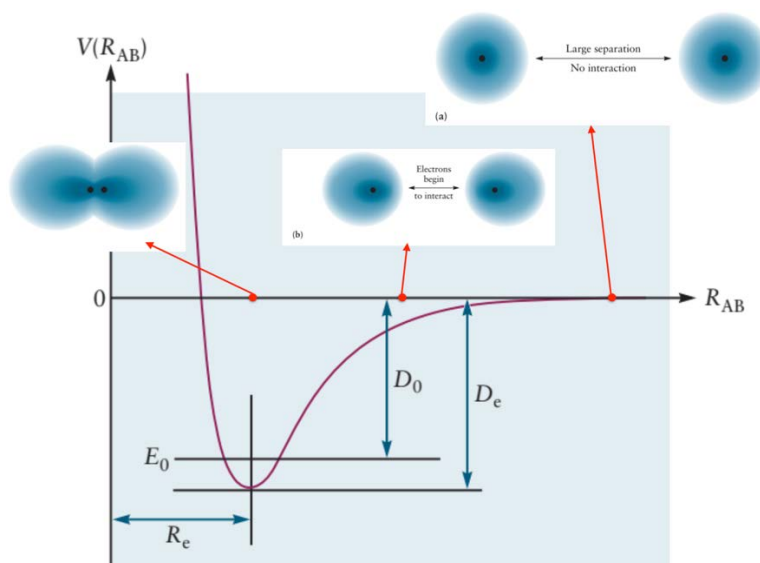


Figure 1

In this figure, at distance  $R_e$ ,  $H_2$  has minimum energy and it is called bond length and  $D_e$  is bond dissociation energy. However, according to the uncertainty principle, the minimum energy that can be experimentally measured is higher than this level, which has  $E_0$ . Then measured energy for bond dissociation is  $D_0$ . The point at  $R_e$  is useful for constructing model potentials and optimizing molecular geometry in calculations.

The effective potential energy can be divided into the following factors in order to explain how the negative charge existing between nuclei can overcome the Coulomb repulsion making the nuclei attract toward each other, which maintains the structure of the molecule; Coulomb repulsion between two protons, Coulomb repulsion between two electrons, Coulomb attraction between protons and electrons and kinetic energies of electrons. Then, we can express effective potential term as sum of average kinetic energy of electrons and average Coulomb interactions (electron-electron, nuclear-nuclear, electron-nuclear)

$$\bar{V}^{(eff)}(R_{AB}) = \bar{\mathcal{S}}(R_{AB}) + \bar{V}(R_{AB})$$

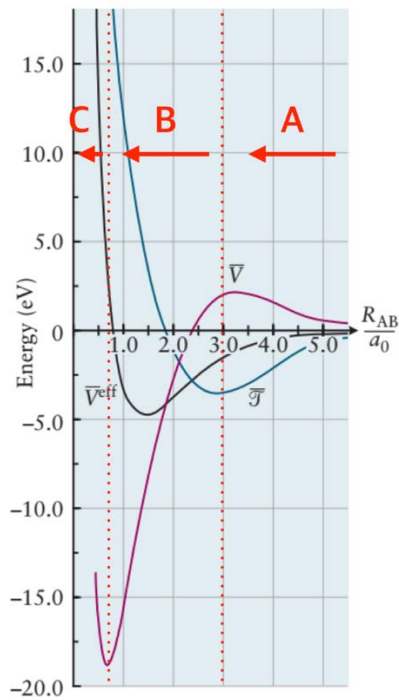


Figure 2

Above figure shows the contribution of average kinetic energy and average potential energy (Coulomb interactions) to effective potential energy. The change of the  $\bar{V}^{(\text{eff})}$  will be described in three intervals:

(Interval A)



Figure 4

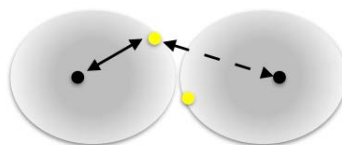


Figure 5

Black dots: protons, Yellow dots: electrons.

Solid line indicates interaction between the nucleus and the electron which belongs to same atom, while dashed line indicates interaction between the nucleus and the electron which was belongs to the other atom.

$\bar{V}$ : As the distance between atoms becomes closer, one electron begins to interact with a proton at another atom, and the amount of interaction with a proton at the same atom decreases. The average potential size increases.



Figure 6

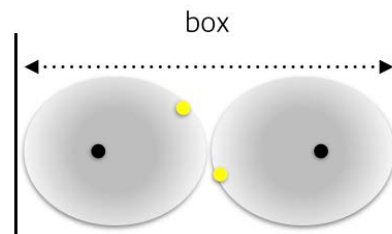


Figure 7

$\bar{S}$ : As discussed in Particle-in-a-box model, the electron's kinetic energy decreases as the size of the box is increased (eq 4.37 in Oxtoby 7<sup>th</sup> ed).

Since the degree of decrease in kinetic energy is greater than the degree of increase in potential energy, the effective potential energy decreases and chemical bonding begins to occur.

(Interval B)

$\bar{V}$ : As the distances between the electron and the nuclei are decrease, average potential energy decreases.

$\bar{S}$ : The confinement of the electron to the smaller volume yields the increase of the average kinetic energy.

(Interval C)

$\bar{V}$  : If distance between two nuclei is too small, their high repulsion energy increase the average potential energy.

$\bar{S}$  : The confinement of the electron to the smaller volume yields the increase of the average kinetic energy.

One of the purpose of this class is quantitative quantum chemical calculation of curves at the Figure 1 and Figure2. To do so, we need to solve the well-known equation, Schrodinger's equation. By solving this equation, we can obtain the wave functions of the electrons and their corresponding energies in a given system. In section 2-2) we will look at the basic quantum mechanical theories for quantitative computation of this curve.

## 2-2) Quantum chemical calculation

(\*This section has brief explanation of a quantum chemistry (or mechanics).

If you want to study more about this subject, refer to chapter 4, 5)

Several experiments have confirmed wave-particle duality, and it has been found that the motion of the particles is not explained by the classical mechanics. In classical mechanics, the motion of an object is described according to Newton's law of motion, while the Schrödinger equation plays a role in quantum mechanics. You can refer to chapter 4(p168~p169) of Oxtoby 7<sup>th</sup> ed for the origin of the Schrödinger equation and the validity of it.

Classical Mechanics

Quantum mechanics

$$F = ma \quad \longleftrightarrow \quad \hat{H}\psi = E\psi$$

How the physical system is organized determines the form of  $\hat{H}$  which is called *Hamiltonian operator*. Then, "solving the Schrödinger equation" means

that finding pair of  $\psi$  and corresponding  $E$  which satisfies this *differential equation* and they are the solutions of it. Generally, it has multiple solutions. Then we write as

$$\hat{H}\psi_i = E_i\psi_i \quad (i \text{ are integers})$$

$\psi$  indicates *wave function*, and it is the amplitude of the wave related to the motion of a particle. In particular, the wave function in one electron picture is called *orbital*. It can have positive, negative or zero values. The points or region with the zero amplitude of the wave function are called **nodes**. The wave function cannot be measured directly. Instead, we use  $\psi^2$  as a probability density of the particle and  $\psi(x,y,z)^2 dV$  is the probability that the particle exists in a small volume  $V$ . This probabilistic interpretation have shown consistent result of the motion on a microscopic scale.

$E$  is the *energy* associated with this wave function. Each wave function has corresponding energy value, which means the system has discrete values. It shows that the energy quantization is the consequence of Schrödinger equation. The wave function corresponds to the lowest energy value is called *ground state* and others are called *excited states*.

One of the example system called "Particle-in-a-box" can be described by the Schrödinger equation and it can be solved exactly (or analytically). You can practice solving the Schrödinger equation for this model (pp 172–4, Oxtoby 7<sup>th</sup> ed).

### 2-3) Using quantum chemical solver

The Schrodinger equation is a kind of differential equation and can be solved *analytically* for simple systems, such as the particle-in-a-box model, the hydrogen atom system or the  $H_2^+$  molecule system to be covered in the class. Solving the differential equation *analytically* means that the *exact solution* can be obtained by algebraic operations of the symbols in the equation, calculus, trigonometry, or other mathematical techniques. However, the Schrödinger equations of many other systems are complex to solve analytically, and

therefore requires a *numerical* analysis to obtain approximate solutions instead of exact solutions. Since, it takes too much time to get the solutions manually by numerical methods, some research institutes design algorithms of numerical analysis and obtain the solution with HPC (High performance computing). Many solvers have been developed which can calculate the various physical properties of molecules by devising numerical methods and algorithms. These solvers can expand the quantum mechanical theories and calculate the physical properties of the material. For example, the three-dimensional structures and the energies of the molecules which is in ground and excited state, IR frequencies, and the transition states and so on.

The solver we will use in this class is **ACE-Molecule**, which is being developed by the Prof. Woo Youn Kim's Laboratory in KAIST chemistry department.

To obtain the curves of Figure 1 and Figure 2 using quantum chemical calculations, we need an important assumption of the Born Oppenheimer approximation. The curves discussed in the previous section 2-1) also assumed the Born-Oppenheimer approximation.

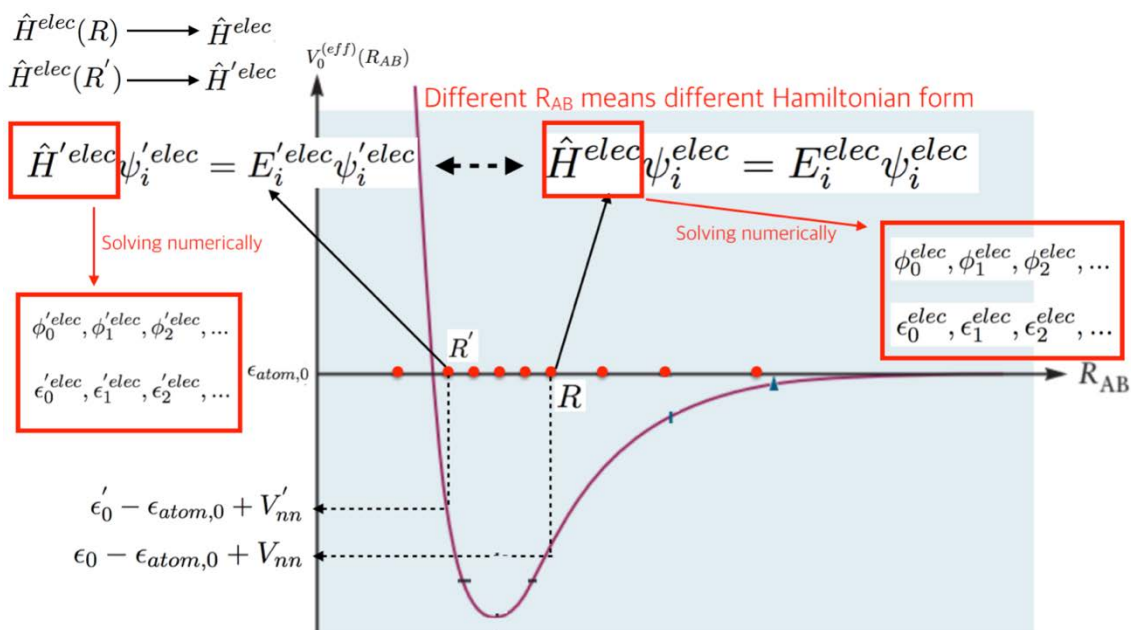
### ***Born-Oppenheimer approximation***

The mass of the nucleus is much larger than that of the electron. Thus, we can assume that the motion of electron is much faster than that of the electron, which means the positions of the nuclei can be fixed. Then, the kinetic energy of the nucleus is zero and the nucleus-nucleus Coulomb potential energy is constant. Based on this Born-Oppenheimer approximation, the energy of a molecule can be calculated as following two steps.

- 1) Solve the equation for electronic Hamiltonian first. Then we get the orbitals (single electron's wave function) and their energies
- 2) To get the total energy of the molecule, add the nucleus-nucleus Coulomb potential to the orbital energies.

Following is the schematic diagram to calculate the effective potential energy

curve of diatomic molecules.



### 3. Requisites

- 3-1) ACE-Molecule solver, installed in a remote server EDISON.
- 3-2) An orbital viewer program VESTA.

### 4. Procedure

(Refer to the PPT file for details)

- 1) Prepare input files:

**One input file and 10 structure files**

- 2) Sign in to EDISON (chem.edison.re.kr).  
Account information will be given by the TA.
- 3) Select the ACE-Molecule (KDFT ver2.0.3) solver
- 4) Submit your jobs.  
One input file and a structure file comprise one simulation job.
- 5) Download output files and analyze them.