

Lecture 9: Molecular Orbital theory for hydrogen molecule ion

1 Molecular Orbital Theory for Hydrogen Molecule Ion

We have seen that the Schrödinger equation cannot be solved for many electron systems. The H_2^+ molecule ion is a molecule that has only one electron. However, there are 2 nuclei so it becomes a 3-particle problem. To solve this problem, we invoke an approximation that is known as the Born-Oppenheimer approximation wherein we assume that the electronic and nuclear degrees of freedom can be solved independently. Further, assuming that the kinetic energy of the nuclei are very small, we can solve the electronic problem at fixed internuclear separation as illustrated below.

$$\hat{H}(R_A, R_B, r) = -\frac{\hbar^2}{2m_p}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R}\right)$$

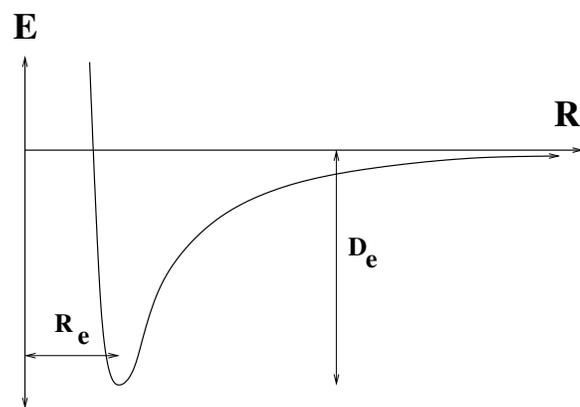
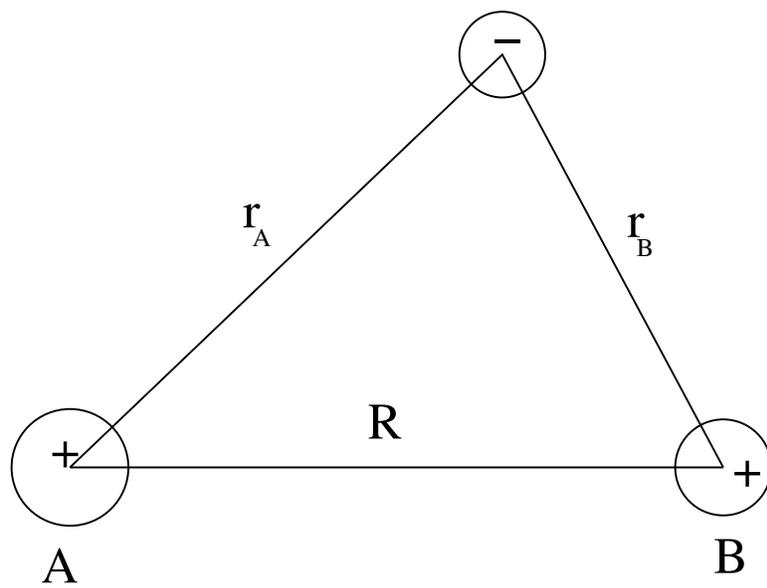
Under the BO approximation, we have

$$\hat{H}_{el}(r; R) = -\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R}\right)$$

The electronic wavefunction is to be treated as a function of the electronic coordinate r for fixed internuclear separation R . Thus the Schrödinger equation is given by

$$\hat{H}_{el}\psi(r; R) = E(R)\psi(r; R)$$

We can imagine solving this for different R . If there is a bond, then this energy should be minimum for some value of R as shown in the figure. This gives the equilibrium bond length R_e and the dissociation energy D_e of the



molecule. We will briefly describe this physical picture of the bond using Molecular Orbital theory.

According to MO theory, the electron in a molecule is located in orbitals (single-electron functions) called molecular orbitals. The molecular orbitals are different from the atomic orbitals since they are not centered at atomic nuclei. One way to construct the functions corresponding to molecular orbitals is to use linear combination of atomic orbitals (LCAO). For example, we can consider the linear combination of the 1s wavefunctions centered on both atoms.

$$\psi_{MO}(\vec{r}) = N(\psi_{1sA}(\vec{r}) \pm \psi_{1sB}(\vec{r}))$$

Note that ψ_{1sA} is a function centered at nucleus A. Thus we have

$$\psi_{1sA}(\vec{r}) = N_1 e^{-r_A/a_0}$$

and similarly for ψ_{1sB} . Assuming that the wavefunctions for ψ_{1sA} and ψ_{1sB} are normalized, we can calculate the value of N as follows

$$1 = \int \psi_{MO}^*(\vec{r})\psi_{MO}(\vec{r})d\vec{r} = N^2 \int \psi_{1sA}^*(\vec{r})\psi_{1sA}(\vec{r})d\vec{r} + 3\text{more terms}$$

We can easily show for real orbitals that the terms lead to

$$1 = N^2(2 \pm 2 \int \psi_{1sA}^*(\vec{r})\psi_{1sB}(\vec{r})d\vec{r})$$

The last term is denoted by S , so we can write

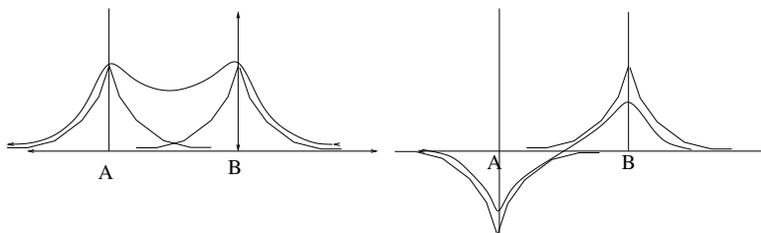
$$N = \frac{1}{\sqrt{2(1 \pm S)}}$$

where S denotes the overlap between the orbitals.

Of the two orbitals, the one with the positive sign turns out to have lower energy than the 1s orbital and is called the bonding MO and the one with negative sign has higher energy than 1s orbital and is called the antibonding MO.

$$\psi_{MO-Bonding} = \frac{1}{\sqrt{2(1+S)}}(\psi_{1sA}(\vec{r}) + \psi_{1sB}(\vec{r}))$$

Thus we can say that for a given R , the two 1s orbitals combine to give one bonding and one antibonding MO. The bonding MO turns out to have lower energy, but you could only know this if you could calculate the energies which



is difficult. The bonding MO has higher electron density in the internuclear axis, unlike in the case of the antibonding MO. The $1s$ bonding orbital is symmetric to inversion about the center and is referred to as *gerade* or simply *g* for short.

In fact we will write the previous equation in short form as

$$1\sigma_g \propto (1s_A + 1s_B)$$

The convention for naming this orbital is $1\sigma_g$. The antibonding orbital is labelled as $1\sigma_u^*$.

We could also combine the two $2s$ orbitals to form a $2\sigma_g$ and $2\sigma_u^*$ MOs. With p orbitals things get a little more complicated because the phase of the orbitals matters. Consider $2p_z$ orbital. This has opposite signs in the different halves. Now, when combining wavefunctions, we have to see the sign. For example, the bonding orbital is denoted as $3\sigma_u$ is given by

$$3\sigma_g \propto 2pz_A - 2pz_B$$

where we assume that the Z -axis is along the internuclear axis. The antibonding MO is given by

$$3\sigma_u^* \propto 2pz_A + 2pz_B$$

The sigma orbitals are spherically symmetric about the internuclear axis. We can also have orbitals which do not satisfy this condition. For example, if we take a linear combination of $2px$ orbitals located on the two atoms, we will see that

$$1\pi_u \propto 2px_A + 2px_B$$

and similarly for the $2py$ orbitals. These two MOs are degenerate. The antibonding MO is denoted by

$$1\pi_g^* \propto 2px_A - 2px_B$$

In the Hydrogen molecule ion, there is only one electron. The ground state corresponds to the electron in the $1\sigma_g$ orbital so this orbital is referred to as the Highest Occupied Molecular Orbital(HOMO). The lowest unoccupied MO(LUMO) is the $1\sigma_u^*$. These MOs were calculated at fixed internuclear separation. We can qualitatively see what happens when the internuclear separation is changed and define R_e and D_e as we had before for the $1\sigma_g$ MO. The antibonding MO does not show a minimum energy at some separation. This qualitative picture is borne out by numerical calculations.