Lecture 12 02/13/12

A. Introduction

- For problems where Schroediner's equation cannot be solved exactly, a form for the wave function is proposed. A common starting point is a linear combination of atomic orbitals (LCAO).

- Then the Viral Theorem of Quantum Mechanics states that the best we can do with an approximate wave function of this nature is obtain an upper bound to the true energy. The energy is calculated with the trial wave function Ψ using $E = \langle E \rangle = \dfrac{\int \Psi * H \Psi d\tau}{\int \Psi * \Psi d\tau}$

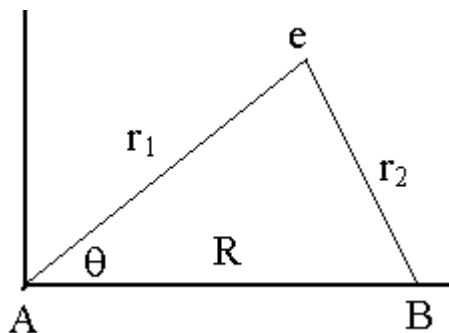- We applied this approach to the hydrogen molecule ion H_2^+ with Hamiltonian:

$$H \approx -\frac{h^2}{8\pi^2 m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R} - \frac{1}{r_1} - \frac{1}{r_2}\right)$$

and referring to the coordinate system at the right.

- We approximate the ground state wave function as the LCAO

$$\Psi \approx c_A \psi_{1s}^A + c_B \psi_{1s}^B$$

where $\psi_{1s}^A = \dfrac{1}{\sqrt{\pi}}e^{-r_1/a_0}$ and $\psi_{1s}^B = \dfrac{1}{\sqrt{\pi}}e^{-r_2/a_0}$

- With this wave function we obtain the energy expression:

$$\langle E \rangle \approx \frac{c_A^2 H_{AA} + 2c_A c_B H_{AB} + c_B^2 H_{BB}}{c_A^2 + 2c_A c_B S_{AB} + c_B^2}$$

- $H_{AA}=H_{BB}$, H_{AB} and S_{AB} are integrals. We examined the easiest one which is S_{AB}.

$$S_{AB} = \int \psi_{1s}^A \psi_{1s}^B d\tau = \int \psi_{1s}^B \psi_{1s}^A d\tau = e^{-R/a_0}\left[1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right]$$

- $S_{AB} = 1$ if R=0 and $S_{AB}=0$ if R approaches infinity. S_{AB} is called the overlap integral. It measures the degree to which the two atomic wave functions overlap in the molecule.

B. Variational Principle: Bonding and Anti-bonding Orbitals…

- Applying the variational principle, the energy of the electron in H^{2+} can be obtained by minimizing the variational energy with respect to the constants c_A and c_B…
- We obtain two secular equations:

$$\frac{\partial \langle E \rangle}{\partial c_A} = 0 = c_A (H_{AA} - E) + c_B (H_{AB} - S_{AB} E)$$

$$\frac{\partial \langle E \rangle}{\partial c_B} = 0 = c_A (H_{AB} - S_{AB} E) + c_B (H_{BB} - E)$$

- Solving these two equations for the energy we get two solutions… $\langle E \rangle_{\pm} = \dfrac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}}$

  where we have used the fact that $H_{AA} = H_{BB}$.

- Substituting each of these energies back into the secular equations we obtain two solutions $c_{A\pm} = \pm c_{B\pm}$. This yields two orbitals…each with a different energy…

$$\Psi_{\pm} = c_{\pm} \left(\psi_{1s}^A \pm \psi_{1s}^B \right)$$

  - We require that both orbitals be normalized: $\int \Psi_{\pm}^{*} \Psi_{\pm} d\tau = c_A^2 \int \left(\psi_{1s}^A \pm \psi_{1s}^B \right)^2 d\tau = 1$,

    from which we obtain… $c_{\pm} = \dfrac{1}{\sqrt{2 \pm 2S_{AB}}}$

- <u>Bonding Orbital</u>: $\Psi_{+} = \dfrac{1}{\sqrt{2 + 2S_{AB}}} \left(\psi_{1s}^A + \psi_{1s}^B \right)$ is called the bonding orbital and is

  given the shorthand σ_{1s}. The bonding orbital σ as an energy $\langle E \rangle_{+} = \dfrac{H_{AA} + H_{AB}}{1 + S_{AB}}$

  - The Coulomb integral H_{AA} has the form…

    - $H_{AA} = E_{1s} - \dfrac{e^2}{4\pi\varepsilon_0} \left(\int \dfrac{\left(\psi_{1s}^A \right)^2}{r_2} d\tau - \dfrac{1}{R} \int \psi_{1s}^2 d\tau \right) = E_{1s} - \dfrac{e^2}{4\pi\varepsilon_0} \left(\int \dfrac{\left(\psi_{1s}^A \right)^2}{r_2} d\tau - \dfrac{1}{R} \right)$

  - $E_{1s} = -\dfrac{\Re}{1^2} = -2.18 \times 10^{-18} J$. The second term $D = a_0 \int \dfrac{\left(\psi_{1s}^A \right)^2}{r_2} d\tau$ is called the

    direct integral. Evaluation of the direct integral yields: $D = \dfrac{a_0}{R} - \left(1 + \dfrac{a_0}{R} \right) e^{-2R/a_0}$.

    The Coulomb integral is therefore:

    $$H_{AA} = -\Re - \frac{e^2}{4\pi\varepsilon_0 a_0} \left(D - \frac{1}{R} \right) = -\Re - \frac{e^2}{4\pi\varepsilon_0 a_0} \left(\frac{a_0}{R} - \left(1 + \frac{a_0}{R} \right) e^{-2R/a_0} \right) + \frac{e^2}{4\pi\varepsilon_0 R}$$

- Because $R > a_0$, $D > 0$. The first two terms in the Coulomb integral are negative and reflect the stabilization of the molecule as a result of the attraction of the electron for the second nucleus, and would be expected to result in a more stable orbital energy than the isolated hydrogen atom. But as the atoms approach the nuclear

repulsion term $\dfrac{e^2}{4\pi\varepsilon_0 R}$ grows larger and hence the net contribution of H_{AA} to stabilization is small.

- The stabilization of the H^{2+} ion derives from the so-called resonance integral:

$$H_{AB} = \int \left(\psi_{1s}^A\right)^* H_0 \psi_{1s}^B d\tau - \frac{e^2}{4\pi\varepsilon_0}\left(\int \frac{\left(\psi_{1s}^A\right)^* \psi_{1s}^B}{r_2} d\tau - \frac{1}{R}\int \left(\psi_{1s}^A\right)^* \psi_{1s}^B d\tau\right)$$

$$= E_{1s} S_{AB} - \frac{e^2}{4\pi\varepsilon_0 a_0} X + \frac{e^2}{4\pi\varepsilon_0}\frac{S_{AB}}{R}$$

- $X = a_0 \int \dfrac{\left(\psi_{1s}^A\right)^* \psi_{1s}^B}{r_2} d\tau$ is called the exchange integral. $X = \left(1+\dfrac{R}{a_0}\right)e^{-R/a_0}$

- Physically H_{AB} is the stabilization deriving from the fact that the electron can shift from the ψ_{1s}^B orbital to the ψ_{1s}^A orbital. It is called the resonance integral because of the resemblance to the coupling or resonance of two classical oscillators. As a result of the negative resonance integral, the energy of an electron in the bonding orbital of H_2^+ is less than the energy of the electron in the 1s atomic orbital of a hydrogen atom.

- Combining our expressions for HAB and HAA we get

$$\langle E \rangle_+ = E_{1s} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} - \frac{e^2}{4\pi\varepsilon_0 a_0}\frac{D+X}{1+S_{AB}}$$

where $D + X = \frac{1}{x} - \left(1+\frac{1}{x}\right)e^{-2x} + (1+x)e^{-x} \Rightarrow x = R/a_0$
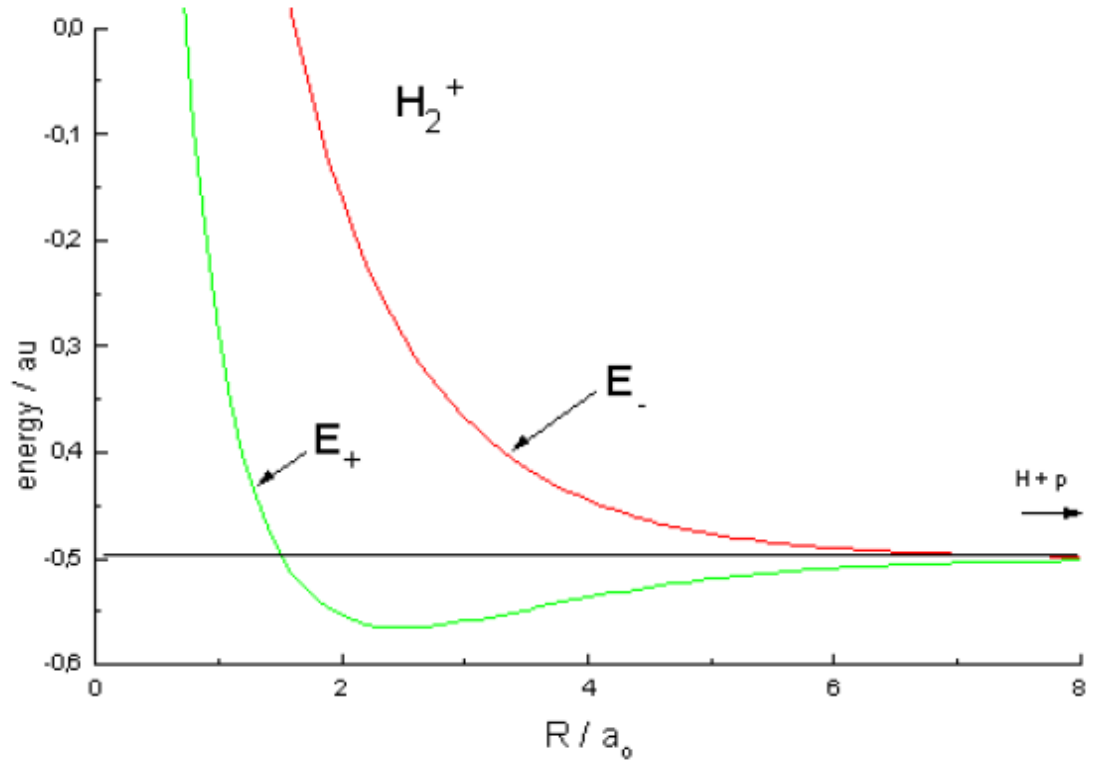
- The <u>Anti-bonding Orbital</u>: $\Psi_- = \dfrac{\psi_{1s}^A - \psi_{1s}^B}{\sqrt{2-2S_{AB}}}$ is called the anti-bonding orbital and is given the shorthand σ*$_{1s}$. The anti bonding orbital has an energy

$$\langle E \rangle_- = \frac{H_{AA} - H_{AB}}{1 - S_{AB}} = E_{1s} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} - \frac{e^2}{4\pi\varepsilon_0 a_0}\frac{D-X}{1-S_{AB}}$$

- This energy will be higher than the energy of an isolated hydrogen atom. This means that if the electron were in the σ*$_{1s}$ orbital of H_2^+, the molecule would be less stable than the separated hydrogen atom and ion.

- A plot of $\langle E \rangle_+$ and $\langle E \rangle_-$, the energies of the σ$_{1s}$ molecular bonding orbital and anibonding orbitals as functions of the internuclear distance R/a$_0$ are shown below, right.