

### 3.13: Molecular Orbital Analysis for the Hydrogen Molecule Ion Bond

In this analysis the molecular orbital for the hydrogen molecule ion is formed as a linear combination of scaled hydrogenic 1s orbitals centered on the nuclei, a and b.

$$\Psi_{MO} = \frac{a+b}{\sqrt{2+2S}} \quad \text{where} \quad a = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha, r_a) \quad b = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha, r_b) \quad S = \int ab d\tau$$

The molecular energy operator in atomic units:

$$H = \frac{-1}{2} \left[ \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \right] - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

The energy integral to be minimized by the variation method:

$$E = \frac{\int (a+b)H(a+b)d\tau}{2+2S} = \frac{Haa+Hab}{1+S}$$

When this integral is evaluated a two-parameter variational expression for the energy (highlighted below) is obtained.

Electron mass:

$$m = 1$$

Seed values for the variational parameter and internuclear separation:

$$\alpha = 1 \quad R = .1$$

$$E(\alpha, R) = \frac{-\alpha^2}{2m} + \frac{\frac{\alpha^2}{m} - \alpha - \frac{1}{R} + \frac{1}{R}(1 + \alpha R)\exp(-2\alpha R) + \alpha \left(\frac{\alpha}{m} - 2\right)(1 + \alpha R)\exp(-\alpha R)}{1 + \exp(-\alpha R) \left(1 + \alpha R + \frac{\alpha^2 R^2}{3}\right)} + \frac{1}{R}$$

Minimization of the energy of the hydrogen molecule ion follows. There are two variational parameters, the orbital scale factor and the internuclear distance.

$$\text{Given} \quad \frac{d}{d\alpha} E(\alpha, R) = 0 \quad \frac{d}{dR} E(\alpha, R) = 0 \quad \left(\frac{\alpha}{R}\right) = \text{Find}(\alpha, R) \quad \left(\frac{\alpha}{R}\right) = \begin{pmatrix} 1.23803 \\ 2.0033 \end{pmatrix} \quad E(\alpha, R) = -0.58651$$

The calculation yields a stable molecule ion as is shown here.

	Hydrogen Molecule Ion	=	Hydrogen Atom	+	Hydrogen Ion	
Theory	-0.5865		-0.5000		0	Bond Energy = 0.0865
Experiment	-0.6029		-0.5000		0	Bond Energy = 0.1029

The experimental ground state energy is -0.6029 E<sub>h</sub>. The error in this calculation is calculate two ways: error in bond energy and error in total ground state energy.

$$\frac{.1029 - .0865}{.1029} = 15.9378\% \quad \left| \frac{E(\alpha, R) + .6029}{-.6029} \right| = 2.71911\%$$

It is instructive to calculate the kinetic and potential energy contributions to the total energy.

$$E = \int \Psi_{MO} (T + V) \Psi_{MO} d\tau = Taa + Tab + Vaa + Vab$$

$$Taa(\alpha, R) = \frac{\frac{\alpha^2}{2m}}{1 + \exp(-\alpha, R) \left(1 + \alpha R + \frac{\alpha^2 R^2}{3}\right)} \quad Tab(\alpha, R) = \frac{\frac{\alpha^2}{2m} \exp(-\alpha, R) \left(1 + \alpha R - \frac{\alpha^2 R^2}{3}\right)}{1 + \exp(-\alpha, R) \left(1 + \alpha R + \frac{\alpha^2 R^2}{3}\right)}$$

$$Vaa(\alpha, R) = \frac{\left(\frac{1}{R} + \alpha\right) \exp(-2\alpha R) - \alpha}{1 + \exp(-\alpha, R) \left(1 + \alpha R + \frac{\alpha^2 R^2}{3}\right)} \quad Taa(\alpha, R) = \frac{\frac{-1}{3} \exp(\alpha, R) \frac{3\alpha R + 5\alpha^2 R^2 - 3}{R}}{1 + \exp(-\alpha, R) \left(1 + \alpha R + \frac{\alpha^2 R^2}{3}\right)}$$

First we establish that these terms are correct by showing that they sum to the correct ground state energy calculated earlier.

$$Taa(\alpha, R) + Tab(\alpha, R) + Vaa(\alpha, R) + Vab(\alpha, R) = -0.58651$$

Next we establish that the virial theorem is obeyed. Quantum mechanical calculations that violate the appropriate virial theorem are not valid. For atomic and molecular systems the virial theorem is:  $\langle E \rangle = -\langle T \rangle = \langle V \rangle / 2$ .

Electron Kinetic Energy	Total Potential Energy	Virial Theorem Satisfied
$T_{aa}(\alpha, R) + T_{ab}(\alpha, R) = 0.58651$	$V_{aa}(\alpha, R) + V_{ab}(\alpha, R) = -1.17301$	$\frac{ V_{aa}(\alpha, R) + V_{ab}(\alpha, R) }{T_{aa}(\alpha, R) + T_{ab}(\alpha, R)} = 2$

Next we separate the nuclear potential energy into its two components: electron-nucleus and nucleus-nucleus.

Electron Kinetic Energy	Electron-Nucleus Potential Energy	Nucleus-Nucleus Potential Energy
$T = T_{aa}(\alpha, R) + T_{ab}(\alpha, R)$	$V_{en} = V_{aa}(\alpha, R) + V_{ab}(\alpha, R) - \frac{1}{R}$	$V_{nn} = \frac{1}{R}$
$T = 0.58651$	$V_{en} = -1.67219$	$V_{nn} = 0.49918$
$\frac{T}{T +  V_{en}  + V_{nn}} = 21.27\%$	$\frac{ V_{en} }{T +  V_{en}  + V_{nn}} = 60.63\%$	$\frac{V_{nn}}{T +  V_{en}  + V_{nn}} = 18.10\%$

In light of these calculations the following comments on the covalent bond in the  $H_2^+$  are made.  $V_{en}$  is the largest and only negative term, and might be thought of as the glue holding the  $H_2^+$  molecule together. However, a ground state (stable molecule) requires "energetic" opposition to the attractive  $V_{en}$ , otherwise molecular collapse occurs. This opposition is provided by  $T$  and  $V_{nn}$ . It might surprise those who think that chemical bonding is simply an electrostatic phenomenon, that nuclear repulsion makes a smaller contribution to molecular stability than electron kinetic energy.

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