

# Molecular Orbital Analysis for the Hydrogen Molecule Ion Bond

Frank Rioux  
College of St. Benedict and St. John's University  
St. Joseph, MN 56374

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.

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

The molecular energy operator in atomic units:  $H = \frac{-1}{2} \cdot \left[ \frac{d}{dr} \left( r^2 \cdot \frac{d}{dr} \right) \right] - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$

The energy integral to be minimized by the variation method:  $E = \frac{\int (a + b) \cdot H \cdot (a + b) \, d\tau}{2 + 2 \cdot S} = \frac{H_{aa} + H_{ab}}{1 + S}$

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:  $\alpha := 1$        $R := .1$

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

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

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

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

HydrogenMoleculeIon = HydrogenAtom + HydrogenIon

Theory	-0.5865	-0.5000	0	BondEnergy = 0.0865
Experiment	-0.6029	-0.5000	0	BondEnergy = 0.1029

The experimental ground state energy is -0.6029  $E_h$ . 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.

$$E = \int \Psi_{\text{MO}} \cdot (T + V) \cdot \Psi_{\text{MO}} d\tau = T_{\text{aa}} + T_{\text{ab}} + V_{\text{aa}} + V_{\text{ab}}$$

$$T_{\text{aa}}(\alpha, R) := \frac{\frac{\alpha^2}{2 \cdot m}}{1 + \exp(-\alpha \cdot R) \cdot \left(1 + \alpha \cdot R + \frac{\alpha^2 \cdot R^2}{3}\right)}$$

$$T_{\text{ab}}(\alpha, R) := \frac{\frac{\alpha^2}{2 \cdot m} \cdot \exp(-\alpha \cdot R) \cdot \left(1 + \alpha \cdot R - \frac{\alpha^2 \cdot R^2}{3}\right)}{1 + \exp(-\alpha \cdot R) \cdot \left(1 + \alpha \cdot R + \frac{\alpha^2 \cdot R^2}{3}\right)}$$

$$V_{\text{aa}}(\alpha, R) := \frac{\left(\frac{1}{R} + \alpha\right) \cdot \exp(-2 \cdot \alpha \cdot R) - \alpha}{1 + \exp(-\alpha \cdot R) \cdot \left(1 + \alpha \cdot R + \frac{\alpha^2 \cdot R^2}{3}\right)}$$

$$V_{\text{ab}}(\alpha, R) := \frac{\frac{-1}{3} \cdot \exp(-\alpha \cdot R) \cdot \frac{3 \cdot \alpha \cdot R + 5 \cdot \alpha^2 \cdot R^2 - 3}{R}}{1 + \exp(-\alpha \cdot R) \cdot \left(1 + \alpha \cdot R + \frac{\alpha^2 \cdot R^2}{3}\right)}$$

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

$$T_{\text{aa}}(\alpha, R) + T_{\text{ab}}(\alpha, R) + V_{\text{aa}}(\alpha, R) + V_{\text{ab}}(\alpha, R) = -0.58651$$

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

$$T_{\text{aa}}(\alpha, R) + T_{\text{ab}}(\alpha, R) = 0.58651$$

#### Total Potential Energy

$$V_{\text{aa}}(\alpha, R) + V_{\text{ab}}(\alpha, R) = -1.17301$$

#### Virial Theorem Satisfied

$$\frac{|V_{\text{aa}}(\alpha, R) + V_{\text{ab}}(\alpha, R)|}{T_{\text{aa}}(\alpha, R) + T_{\text{ab}}(\alpha, R)} = 2$$

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

#### Electron Kinetic Energy

$$T := T_{\text{aa}}(\alpha, R) + T_{\text{ab}}(\alpha, R)$$

$$T = 0.58651$$

$$\frac{T}{T + |V_{\text{en}}| + V_{\text{nn}}} = 21.27 \%$$

#### Electron-Nucleus Potential Energy

$$V_{\text{en}} := V_{\text{aa}}(\alpha, R) + V_{\text{ab}}(\alpha, R) - \frac{1}{R}$$

$$V_{\text{en}} = -1.67219$$

$$\frac{|V_{\text{en}}|}{T + |V_{\text{en}}| + V_{\text{nn}}} = 60.63 \%$$

#### Nucleus-Nucleus potential energy

$$V_{\text{nn}} := \frac{1}{R}$$

$$V_{\text{nn}} = 0.49918$$

$$\frac{V_{\text{nn}}}{T + |V_{\text{en}}| + V_{\text{nn}}} = 18.10 \%$$

In light of these calculations the following comments on the covalent bond in the  $\text{H}_2^+$  are made.  $V_{\text{en}}$  is the largest and only negative term, and might be thought of as the glue holding the  $\text{H}_2^+$  molecule together. However, a ground state (stable molecule) requires "energetic" opposition to the attractive  $V_{\text{en}}$ , otherwise molecular collapse occurs. This opposition is provided by  $T$  and  $V_{\text{nn}}$ . 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.