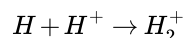


3.12: A Lite Version of Ruedenberg's Analysis of the Covalent Bond in the Hydrogen Molecule Ion

Appendix

This study of the nature of the H_2^+ covalent bond forms a molecular orbital as a linear combination of scaled hydrogenic orbitals, LCAO-MO. The quantum mechanical integrals necessary to carry out the required calculations are provided immediately below. Consult the first five sections of Chapter 23 of our textbook for an overview of the covalent bond in the hydrogen molecule ion. The reaction for its formation is,



For the hydrogen atom: $\langle E \rangle = -0.5$; $\langle T \rangle = 0.5$; $\langle V \rangle = -1.0$.

The Virial Theorem is expressed in a variety of ways:

$$\left| \frac{\Delta V}{\Delta T} \right| = 2 \quad \left| \frac{\Delta E}{\Delta T} \right| = 1 \quad \frac{\Delta E}{\Delta V} = \frac{1}{2}$$

The evaluated integrals required for this exercise are provided below:

Overlap integral:

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

Kinetic energy integrals:

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

Potential energy integrals:

$$Vaa(\alpha, R) = - \left[\alpha - \exp(-2\alpha R) \left(\frac{1}{R} + \alpha \right) \right]$$

Total energy integral:

$$E(\alpha, R) = \frac{Haa(\alpha, R) + Hab(\alpha, R)}{1 + S(\alpha, R)}$$

Bonding molecular orbital:

$$\Psi_{bmo}(\alpha, x, y, z, R) = \frac{\sqrt{\frac{\alpha^3}{\pi}} \left[\exp \left[-\alpha \sqrt{\left(x - \frac{R}{2}\right)^2 + y^2 + z^2} \right] + \exp \left[-\alpha \sqrt{\left(x + \frac{R}{2}\right)^2 + y^2 + z^2} \right] \right]}{\sqrt{2 + 2S(\alpha, R)}}$$

Demonstrate wavefunction is normalized:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi_{bmo}(1, x, y, z, 2)^2 dx dy dz = 1.0000$$

Anti-bonding molecular orbital:

$$\Psi_{amo}(\alpha, x, y, z, R) = \frac{\sqrt{\frac{\alpha^3}{\pi}} \left[\exp \left[-\alpha \sqrt{\left(x - \frac{R}{2}\right)^2 + y^2 + z^2} \right] - \exp \left[-\alpha \sqrt{\left(x + \frac{R}{2}\right)^2 + y^2 + z^2} \right] \right]}{\sqrt{2 - 2S(\alpha, R)}}$$

Demonstrate wavefunction is normalized:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi_{amo}(1, x, y, z, 2)^2 dx dy dz = 1.0000$$

Non-bonding molecular orbital:

$$\Psi_{nmo}(\alpha, x, y, z, R) = \frac{\sqrt{\frac{\alpha^3}{\pi}} \left[\exp \left[-\alpha \sqrt{\left(x - \frac{R}{2}\right)^2 + y^2 + z^2} \right] + i \exp \left[-\alpha \sqrt{\left(x + \frac{R}{2}\right)^2 + y^2 + z^2} \right] \right]}{\sqrt{2}}$$

Demonstrate wavefunction is normalized:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (|\Psi_{nmo}(1, x, y, z, 2)|^2) dx dy dz = 1.0000$$

The Covalent Bond in H_2^+

Variational Calculation of the Molecular Ground State and Bond Energy

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.

$$\Psi = \frac{a+b}{\sqrt{2+2S}}$$

where

$$a = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_a) \quad b = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_b) \quad S = \int a b d\tau$$

The energy operator:

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

The energy integral to be minimized by the variation method:

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

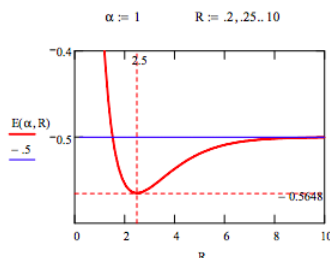
where

$$Haa = (a|T|a) + \left(a \left| \frac{-1}{r_a} \right| a\right) + \left(a \left| \frac{-1}{r_b} \right| a\right) + \left(a \left| \frac{1}{R} \right| a\right)$$

$$Hab = (a|T|b) + \left(a \left| \frac{-1}{r_a} \right| b\right) + \left(a \left| \frac{-1}{r_b} \right| b\right) + \left(a \left| \frac{1}{R} \right| b\right)$$

and $Haa = Taa + Vaa$ and $Hab = Tab + Vab$ and $Hba = Hab$. These integrals and the overlap integral S can be found in the appendix above.

1. Plot $E(\alpha, R)$ vs R, for $\alpha = 1$ for values of R ranging from 0.2 to 10 in increments of 0.05. You can make space by pressing . You can eliminate space by pressing . Use the markers for the x- and y-axis to find the optimum internuclear separation, R, and the ground-state energy.



Notice how shallow the energy minimum initially is. You can exaggerate the minimum by plotting from -0.6 to -0.4 on the y-axis.

2. Minimize the energy with respect to R with $\alpha = 1$. This will require a Given/Find solve block and seed values for α and R. Report the optimum R value (equilibrium bond distance) and the ground-state energy. Compare these calculated values to the literature values of 2.00 ao for R and -0.6029 Eh for the E.

$$\alpha = 1 \quad R = 2 \quad \text{Given } \frac{d}{dR} E(\alpha, R) = 0 \quad R = \text{Find}(R) \quad R = 2.4928 \quad E(\alpha, R) = -0.5648$$

$$\frac{R-2.00}{2.00} = 24.6415\% \quad \left| \frac{E(\alpha, R) + .6029}{-.6029} \right| = 6.3143\% \quad \frac{E(\alpha, R)}{-.6029} = 93.6875\%$$

Demonstrate that the calculated hydrogen molecule ion energy does not satisfy the Virial Theorem.

$$T = \frac{T_{aa}(\alpha, R) + T_{ab}(\alpha, R)}{1 + S(\alpha, R)} \quad T = 0.3827 \quad V = \frac{V_{aa}(\alpha, R) + V_{ab}(\alpha, R)}{1 + S(\alpha, R)} \quad V = -0.9475$$

$$\left| \frac{V}{T} \right| = 2.4759 \quad \left| \frac{E(\alpha, R)}{T} \right| = 1.4759 \quad \left| \frac{E(\alpha, R)}{V} \right| = 0.5961$$

3. Write the equation for breaking the H_2^+ bond. Then use the theoretical value of the ground state energy to calculate the bond energy of the hydrogen molecule ion and compare it to the experimental value, 0.1029 E_h . You may recall that the hydrogen atom ground state energy is -0.5 hartree.

$$\begin{array}{rclcl} \text{Hydrogen molecule ion} & = & \text{Hydrogen atom} & + & \text{Hydrogen ion} \\ -0.5648 & & -0.500 & & 0 \end{array} \quad \text{Bond energy} = 0.0648$$

4. The first three exercises refer to a variational calculation based on the hydrogen 1s orbital ($\alpha = 1$). Now treat both α and R as variational by minimizing the energy simultaneously with respect to α and R .

$$\text{Given } \frac{d}{dR} E(\alpha, R) = 0 \quad \left(\frac{\alpha}{R} \right) = \text{Find}(\alpha, R) \quad \left(\frac{\alpha}{R} \right) = \left(\frac{1.2380}{2.0033} \right) \quad E(\alpha, R) = -0.5865$$

Demonstrate that the calculated hydrogen molecule ion energy does satisfy the Virial Theorem.

$$T = \frac{T_{aa}(\alpha, R) + T_{ab}(\alpha, R)}{1 + S(\alpha, R)} \quad T = 0.5865 \quad V = \frac{V_{aa}(\alpha, R) + V_{ab}(\alpha, R)}{1 + S(\alpha, R)} \quad V = -1.1730$$

$$\left| \frac{V}{T} \right| = 2.0000 \quad \left| \frac{E(\alpha, R)}{T} \right| = 1.0000 \quad \left| \frac{E(\alpha, R)}{V} \right| = 0.5000$$

5. Compare E and R with the literature values. Recalculate the H_2^+ bond energy and compare it with the experimental value. Comment on the agreement between theory and experiment as compared with that found in part 3.

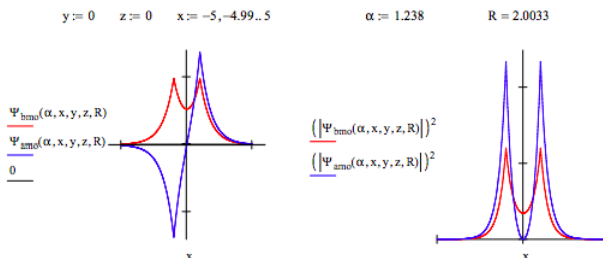
$$\begin{array}{rclcl} \text{Hydrogen Molecule Ion} & = & \text{Hydrogen Atom} & + & \text{Hydrogen Ion} \\ -0.5865 & & -0.5000 & & 0 \end{array} \quad \text{Bond Energy} = 0.0865$$

$$\frac{.1029 - .0865}{.1029} = 15.9378\% \quad \frac{.0865}{.1029} = 84.0622\% \quad \left| \frac{E(\alpha, R) + .6029}{-.6029} \right| = 2.7191\%$$

6. The vibrational force constant is the second derivative of the energy with respect to R evaluated at the energy minimum. Calculate the force constant and compare it to the experimental value of .103 in atomic units.

$$k = \frac{d^2}{dR^2} E(\alpha, R) \quad k = 0.1409 \quad \frac{k}{.103} = 136.8240\%$$

7. The appendix contains the bonding and antibonding orbitals for H_2^+ . On one graph plot Ψ for the bonding and antibonding orbitals along the bond axis (i.e. set y and z to zero). On another graph plot Ψ^2 for the bonding and antibonding orbitals. Compare these orbitals.



These figures show that the electron density is greatest at the nuclear centers, and that the bonding molecular orbital has significant electron density in the internuclear region. Just how much charge is transferred to the bond region will be calculated later. The antibonding molecular orbital has a node exactly between the two nuclei and thus removes charge from the internuclear region. This, of course, is why it called an anti-bonding molecular orbital.

A Mechanism for Covalent Bond Formation in H_2^+

The following two-step mechanism is proposed for covalent bond formation:

- The hydrogen atom and proton form an intermediate, nonbonding state at the equilibrium bond length ($R = 2.0033$) with the optimum value of the decay constant ($\alpha = 1.238$).
- The non-bonding state, $N_{nmo}(a + ib)$, morphs into the final molecular state, $N_{bmo}(a + b)$.

$$\left(\begin{array}{ccc} \frac{\text{Initial}}{\text{Atomic State}} & o & \frac{\text{Intermediate}}{\text{Non Bonding State}} & o & \frac{\text{Final}}{\text{Molecular State}} \\ H_{atom} + H_{ion} & o & \Psi_{nmo} = \frac{a+ib}{\sqrt{2}} & o & \Psi_{bmo} = \frac{a+b}{\sqrt{2+2S}} \end{array} \right)$$

8. We now calculate the kinetic (T), potential (V) and total energy (E) for each of the species involved in the mechanism.

In previous work we calculated the following values for the hydrogen atom. (The energy of the hydrogen ion by convention is 0).

$$E_h = -\frac{1}{2} \quad T_h = \frac{1}{2} \quad V_h = -1$$

The energy of the non-bonding intermediate state is calculated as follows.

$$E_{nb} = \int \frac{a-ib}{\sqrt{2}} H \frac{a+ib}{\sqrt{2}} d\tau = \frac{1}{2} \left(\int aH a d\tau + \int bH b d\tau \right) = H_{aa} = T_{aa} + V_{aa}$$

because

$$H_{bb} = H_{aa}$$

$$\begin{array}{lll} \text{Total: } H_{aa}(\alpha, R) = -0.4594 & \text{Kinetic: } T_{aa}(\alpha, R) = 0.7663 & \text{Potential: } V_{aa}(\alpha, R) = -1.2258 \\ \text{Nuclear potential energy: } & \frac{1}{R} = 0.4992 & \end{array}$$

In exercise 4 we calculated the energy contributions of the final molecular state of H_2^+ .

$$\begin{array}{lll} \text{Total:} & \text{Kinetic:} & \text{Potential:} \\ E(\alpha, R) = 0.5865 & \frac{T_{aa}(\alpha, R) + T_{ab}(\alpha, R)}{1+S(\alpha, R)} = 0.5865 & \frac{V_{aa}(\alpha, R) + V_{ab}(\alpha, R)}{1+S(\alpha, R)} = -1.1730 \end{array}$$

Nuclear potential energy:

$$\frac{1}{R} = 0.4992$$

We are now in a position to construct the following quantitative summary of the mechanism.

$$\left(\begin{array}{ccc} o & \frac{\text{Initial}}{\text{Atomic State}} & o & \frac{\text{Intermediate}}{\text{Non Bonding State}} & o & \frac{\text{Final}}{\text{Molecular State}} & o \\ o & H_{atom} + H_{ion} & o & \Psi_{nmo} = \frac{a+ib}{\sqrt{2}} & o & \Psi_{bmo} = \frac{a+b}{\sqrt{2+2S}} & \\ o & \alpha = 1 & \Delta & \frac{\alpha=1.238}{R=2.003} & \Delta & \frac{\alpha=1.238}{R=2.003} & \\ T & 0.50 & 0.2663 & 0.7663 & -0.1798 & 0.5865 & \\ V & -1.0 & -0.2258 & -1.2258 & 0.0528 & -1.1730 & \\ V_{ne} & -1.0 & -0.7250 & -1.7250 & 0.0528 & -1.6722 & \\ V_{nn} & 0 & 0.4992 & 0.4992 & 0 & 0.4992 & \\ E & -0.50 & 0.0407 & -0.4595 & -0.1270 & -0.5865 & \end{array} \right)$$

Interpretation of the Mechanism

The first step is atomic and endoergic. It is atomic because there is no constructive interference between the atomic orbitals. It is endoergic because kinetic energy increases more than potential energy decreases. The increase in kinetic energy and the decrease in potential energy are due predominantly to atomic orbital contraction from $\alpha = 1$ in the hydrogen atom to $\alpha = 1.238$ in the hydrogen molecule ion.

The second step is exoergic and molecular. The atomic orbitals form a molecular orbital leading to charge redistribution relative to the non-bonding intermediate state. This redistribution causes a decrease in kinetic energy because the electron is now more delocalized, and an increase in potential energy because the electron is drawn away from the nuclear centers into the high-potential energy internuclear region.

Overall the kinetic energy increases and potential energy decreases on bond formation, and the virial theorem is satisfied. This is the source of the conclusion that covalent bonding is a potential energy effect. However, as this analysis shows, both kinetic and potential energy play important roles in covalent bond formation.

This mechanism clarifies an important issue. It is commonly thought, and frequently taught, that from a potential energy point of view the internuclear region is the most favorable place for electron density because it is midway between to nuclei. However, this mechanism clearly shows that the redistribution of charge into the internuclear region due to the interference term in the bonding electron density occurs with an increase in potential energy ($0.0528 E_h$). From a purely electrostatic perspective the preferred location for an electron is in the nucleus.

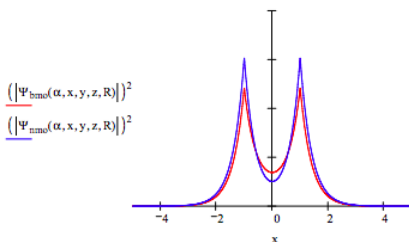
The Bonding Electron Density

9. How much of the total electron density, Ψ_{bmo}^2 , actually contributes to covalent bonding? This question can be answered by comparing the electron density in the intermediate non-bonding state with that of the final molecular state. First we will demonstrate that $\Psi_{nmo}^2 = (a^2 + b^2)/2$ and that this wave function is normalized because a and b are normalized.

$$\Psi_{nmo} = \frac{a+ib}{\sqrt{2}} \quad \left(\left| \frac{a+ib}{\sqrt{2}} \right| \right)^2 \rightarrow \frac{1}{2}a^2 + \frac{1}{2}b^2 \quad \int \frac{a-ib}{\sqrt{2}} \frac{a+ib}{\sqrt{2}} d\tau = \frac{1}{2} (\int a^2 d\tau + \int b^2 d\tau) = 1$$

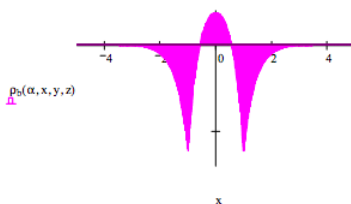
Ψ_{nmo}^2 shows the "atomic" electron density - the electron density that would exist in the absence of constructive interference between the two atomic orbitals, $1s_a$ and $1s_b$.

The non-bonding wave function is given in the appendix. Graph $|\Psi_{bmo}|^2$ and $|\Psi_{nmo}|^2$ along the bond axis and compare them.



10. The question posed in section 9 can now be answered. The bonding electron density can be defined as the charge redistribution that occurs in step 2 of the mechanism. Plot the difference between the total electron density and the non-bonding electron density along the bond axis. Interpret the plot. For example, where does the electron density in the internuclear region come from? What is the sign on the potential energy term for this transfer of electron density to the internuclear region? If this is an endoergic process, how is it funded?

$$\rho_b(\alpha, x, y) = (|\Psi_{bmo}(\alpha, x, y, z, R)|)^2 - (|\Psi_{nmo}(\alpha, x, y, z, R)|)^2$$



This graph shows that electron density is being transferred from the nuclear centers (low potential energy) to the internuclear region (high potential energy). This explains why potential energy increases during step 2. The kinetic energy decreases more because this redistribution of charge also involves charge delocalization, so it is the larger decrease in kinetic energy that funds the transfer of charge to the internuclear region.

11. The electron density in the internuclear region is equal to a polynomial in the overlap integral S and is given by $0.738S(1 - S)(1 - 0.577S^2)$. Use the value of S you calculated earlier to evaluate the amount of charge in the bonding region of H_2^+ . Comment on this value. For example, how does its value compare with a literal interpretation of the Lewis electron pair model of chemical bonding that says that chemical bonds are formed by sharing electrons between two nuclei.

$$0.738S(\alpha, R)(1 - S(\alpha, R))(1 - 0.577S(\alpha, R)^2) = 16.1\%$$

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