

Bond Potential of the Hydrogen Molecule

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Preface

Looking for the bond potential of a hydrogen molecule one would have to solve the Schrödinger-Equation with a Hamiltonian containing the kinetic energy of the protons as well as the electrons, the potential energy of the single electrons in the coulomb field of both protons and at last the repulsive potential of the electrons and protons. Written down as:

$$H = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{\hbar^2}{2m_p}(\nabla_A^2 + \nabla_B^2) - \frac{e^2}{4 * \pi * \epsilon_0 * r_{1A}} - \frac{e^2}{4 * \pi * \epsilon_0 * r_{1B}} - \frac{e^2}{4 * \pi * \epsilon_0 * r_{2A}} \\ - \frac{e^2}{4 * \pi * \epsilon_0 * r_{2B}} + \frac{e^2}{4 * \pi * \epsilon_0 * r_{AB}} + \frac{e^2}{4 * \pi * \epsilon_0 * r_{12}}$$

Where the indices 1 and 2 correspond to electron 1 and 2 and the indices A and B correspond to proton A and B. The Schrödinger-Equation with this Hamiltonian can't be solved purely analytically and therefore we had to apply valence bond theory, constructing a wave function from atomic hydrogen wave functions:

$$\Psi_b(\vec{r}_1, \vec{r}_2) = \varphi_A(\vec{r}_1)\varphi_B(\vec{r}_2) + \varphi_A(\vec{r}_2)\varphi_B(\vec{r}_1)$$

(neglecting the antibonding wave function). For this purpose the following ansatz was made:

$$\Psi_b(\vec{r}_1, \vec{r}_2) = \exp\left(\frac{r_{1A}}{a_0}\right)\exp\left(\frac{r_{2B}}{a_0}\right) + \exp\left(\frac{r_{2A}}{a_0}\right)\exp\left(\frac{r_{1B}}{a_0}\right)$$

Using the constructed wave function and a fixed distance between the nuclei (Born-Oppenheimer-Approximation) the aim was to calculate:

$$E_b = \langle \Psi_b | \hat{H} | \Psi_b \rangle / \langle \Psi_b | \Psi_b \rangle.$$

The first approach was made by converting the wave function and the Hamiltonian to spherical coordinates and evaluating parts of the resulting equation analytically in Mathematica. But it showed that the term with the repulsive potential could not be integrated by the standard integral function of Mathematica because of the distance between the two electrons r_{12} reaching zero when the two electrons were at the same spot in space.

Another effort was made trying to calculate the 6-dimensional integrals numerically in Matlab using FEM and Gaussian quadrature but with no satisfying results. Again the repulsive potential caused difficulties.

Finally the utilization of the Monte-Carlo-Integration method in Mathematica in combination with some bigger transformations and substitutions produced adequate results.

Calculations

The Hamiltonian was rearranged, so that the kinetic energy of electron 1 as well as the term for the potential energy of the electron in the coulomb field of proton A could be combined to the Hamiltonian of a single hydrogen atom. The same adjustment was made for electron 2 and proton B.

$$H_1 = -\frac{\hbar^2}{2m_e} (\nabla_1^2) - \frac{e^2}{4 * \pi * \epsilon_0 * r_{1A}}$$

$$H_2 = -\frac{\hbar^2}{2m_e} (\nabla_2^2) - \frac{e^2}{4 * \pi * \epsilon_0 * r_{2B}}$$

When calculating the norm of Ψ_b the following equation has to be solved:

$$\begin{aligned} \iint_{-\infty}^{+\infty} |\Psi_b(\vec{r}_1, \vec{r}_2)|^2 dV_1 dV_2 &= \int_{-\infty}^{+\infty} \varphi_A^2(r_1) dV_1 \int_{-\infty}^{+\infty} \varphi_B^2(r_2) dV_2 + \int_{-\infty}^{+\infty} \varphi_A^2(r_1) dV_1 \int_{-\infty}^{+\infty} \varphi_B^2(r_2) dV_2 \\ &+ \int_{-\infty}^{+\infty} \varphi_A(r_1) \varphi_B(r_1) dV_1 \int_{-\infty}^{+\infty} \varphi_A(r_2) \varphi_B(r_2) dV_2 \\ &+ \int_{-\infty}^{+\infty} \varphi_A(r_1) \varphi_B(r_1) dV_1 \int_{-\infty}^{+\infty} \varphi_A(r_2) \varphi_B(r_2) dV_2 \end{aligned}$$

Herein the integral over φ_A^2 or φ_B^2 has to be evaluated several times. For this reason the wave functions φ_A and φ_B were chosen to be normed:

$$\int_{-\infty}^{+\infty} \varphi_A^2(r_1) dV_1 = \int_{-\infty}^{+\infty} \varphi_B^2(r_2) dV_2 = 1$$

Which means, Ψ_b will be:

$$\Psi_b(\vec{r}_1, \vec{r}_2) = \frac{1}{\pi} * \left[\exp\left(\frac{r_{1A}}{a_0}\right) \exp\left(\frac{r_{2B}}{a_0}\right) + \exp\left(\frac{r_{2A}}{a_0}\right) \exp\left(\frac{r_{1B}}{a_0}\right) \right]$$

Furthermore the integrals over both wave functions were chosen to be

$$\int_{-\infty}^{+\infty} \varphi_A(r) \varphi_B(r) dV = S$$

so the norm becomes

$$\iint_{-\infty}^{+\infty} |\Psi_b(\vec{r}_1, \vec{r}_2)|^2 dV_1 dV_2 = 2 * (1 + S^2)$$

When evaluating $\langle \Psi | H | \Psi \rangle$ one gets two pairs of equal terms, the first being:

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \varphi_A(r_1) \varphi_B(r_2) \left\{ H_1 + H_2 - \frac{e^2}{4 * \pi * \epsilon_0 * r_{1B}} - \frac{e^2}{4 * \pi * \epsilon_0 * r_{2A}} + \frac{e^2}{4 * \pi * \epsilon_0 * r_{AB}} + \frac{e^2}{4 * \pi * \epsilon_0 * r_{12}} \right\} \varphi_A(r_1) \varphi_B(r_2) dV_1 dV_2$$

Because of

$$H_1 \varphi_A(r_1) \varphi_B(r_2) = E_0 \varphi_A(r_1) \varphi_B(r_2) \text{ and}$$

$$H_2 \varphi_B(r_2) \varphi_A(r_1) = E_0 \varphi_B(r_2) \varphi_A(r_1)$$

with E_0 being the bonding energy of one single hydrogen atom, the integral over the first two terms of the curly brackets can be easily calculated, amounting to $2 * E_0$, considering that φ_A and φ_B both are normed. The third and fourth term are the same because of the symmetry of the problem and were each named C in our calculations. The integral over the repulsive potential of the nuclei simply is

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \varphi_A(r_1)^2 \varphi_B(r_2)^2 \frac{e^2}{4 * \pi * \epsilon_0 * r_{AB}} dV_1 dV_2 = \frac{e^2}{4 * \pi * \epsilon_0 * r_{AB}}$$

taking into account that the distance r_{AB} is constant (Born-Oppenheimer). The fifth part plainly is the electron-electron interaction term and therefore called E_{WW} , so the entire integral amounts to:

$$\hat{E} = 2E_0 + 2C + \frac{e^2}{4 * \pi * \epsilon_0 * r_{AB}} + E_{WW}$$

Additionally the second pair of integrals looks as follows:

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \varphi_A(r_1) \varphi_B(r_2) \varphi_A(r_2) \varphi_B(r_1) \left\{ H_1 + H_2 - \frac{e^2}{4 * \pi * \epsilon_0 * r_{1B}} - \frac{e^2}{4 * \pi * \epsilon_0 * r_{2A}} + \frac{e^2}{4 * \pi * \epsilon_0 * r_{AB}} + \frac{e^2}{4 * \pi * \epsilon_0 * r_{12}} \right\} dV_1 dV_2$$

Herein we have to evaluate the integral

$$\int_{-\infty}^{+\infty} \varphi_A(r_2) \varphi_B(r_2) dV_2 \int_{-\infty}^{+\infty} \varphi_A(r_1) \left(-\frac{e^2}{4 * \pi * \epsilon_0 * r_{1B}} \right) \varphi_B(r_1) dV_1 = S * D$$

with S defined as above. We also get a slightly different electron-electron interaction term E_{AW} . This adds up to:

$$\tilde{E} = 2E_0 S^2 + 2DS + \frac{e^2}{4 * \pi * \epsilon_0 * r_{AB}} S^2 + E_{AW}$$

The final equation for the bonding energy of a hydrogen molecule becomes:

$$E_b = 2 \frac{\tilde{E} + \hat{E}}{\int_{-\infty}^{+\infty} |\Psi_b|^2 dV_1 dV_2}$$

Results

As mentioned above, using the Monte-Carlo-Integration method we managed to integrate this simplified formula for various bond lengths especially focusing on the anticipated bond length of about 0.074 nm. We then fitted a function similar to the Morse potential function to our resulting energy expectation values at the corresponding bond lengths (see Figure 1).

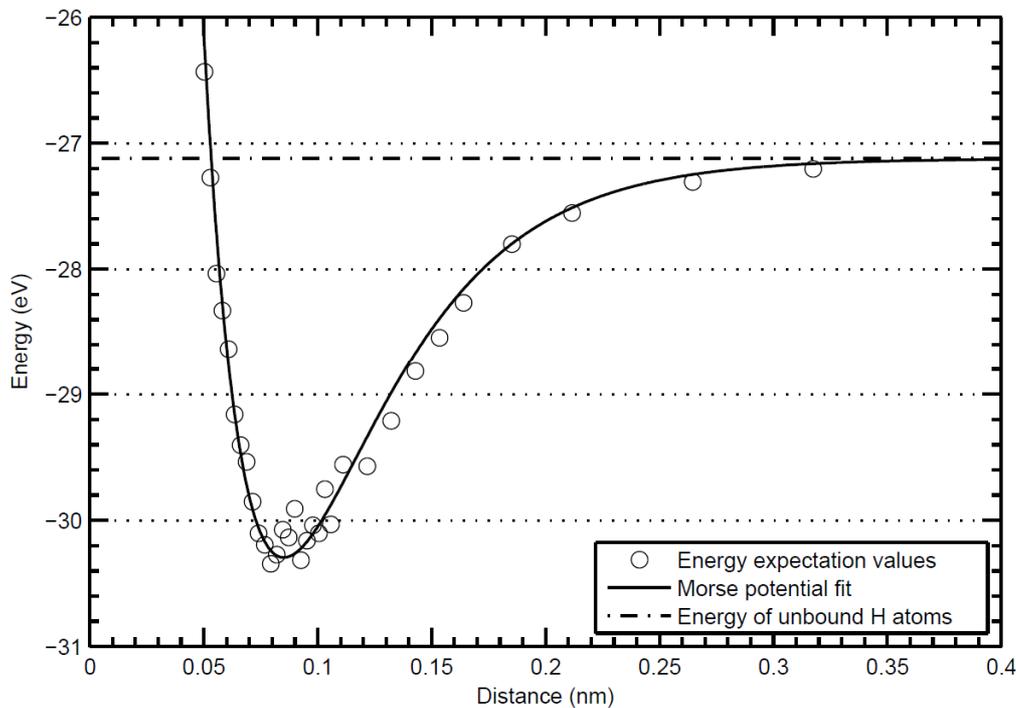


Figure 1: Calculated energy expectation values for predefined bond lengths.

The next step was to analyze the fit to find the bond length and energy. This was simply done by locating the minimum of the function, evaluating its energy expectation value and by calculating the energy for the bond length reaching infinity:

$$E_b = 3.63 \text{ eV}^1$$

$$r_{AB} = 0.085 \text{ nm}$$

Due to the rude simplifications made when assembling the wave function, these values still differ greatly from the actual values:

$$E_b = 4.52 \text{ eV}^2$$

$$r_{AB} = 0.074 \text{ nm}$$

¹ See h2_bond_data.nb

² See <http://lamp.tu-graz.ac.at/~hadley/ss1/lectures10/>

References

Hermann Haken, H. C. Wolf(2006). *Molekülphysik und Quantenchemie*. Springer.

Hadley, Peter. Bonds Abgerufen am 20. 11 2010 von Lectures: <http://lamp.tu-graz.ac.at/~hadley/ss1/lectures10/>