

Student project

# **H<sub>2</sub> bond potential**

**with respect to the core distance**

Elias Henögl (0931157)  
Alexander Pranter (0931114)

February 2014

Molecular and Solid State Physics  
Univ.-Prof. Ph.D. Peter Hadley

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## 1 Preface

The goal of this student project is to calculate the H<sub>2</sub> bond potential in respect to the distance of the atom cores by the method of molecule orbital theory.

We will discuss the chosen wavefunctions and the Hamiltonian Operator as well as the geometry of the problem and the resulting integrals. Because of symmetry reasons the terms will be split up into symmetric, repeatedly appearing integrals. We will show the integrated functions graphically and discuss simplified numerical solution methods for electron electron interaction terms.

The result will contain the comparison of the bond potential for bonding and antibonding wavefunctions.

## 2 Calculation

### 2.1 Preconditions

First we will fix the positions of the cores (Born-Oppenheimer approximation) and use a Cartesian coordinate system with the origin between the two cores A and B to get symmetry in each, x,y and z-direction because we loose spherical symmetry by lining them up on the x-axis (figure 1).

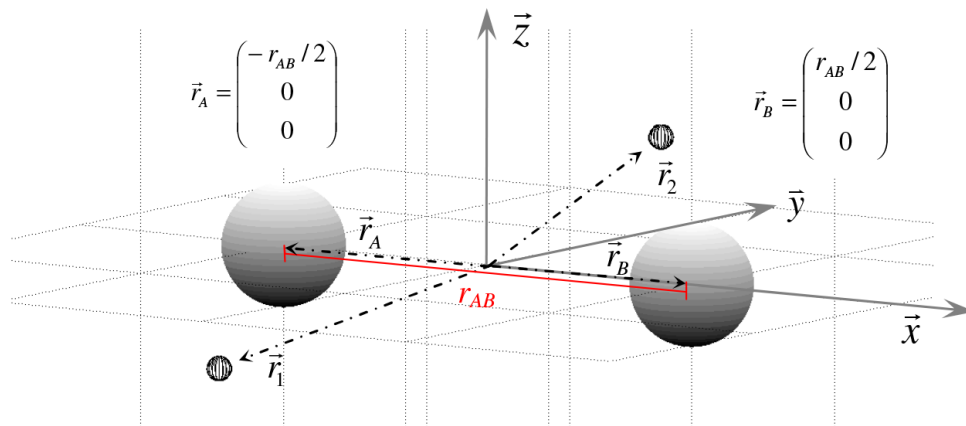


Figure 1: Cartesian coordinate system setup with the cores lined up on the x-axis

In order to evaluate the bonding energy in the H<sub>2</sub> molecule, we calculate the energy-eigenvalues of the Schrödinger-equation (1).

$$E = \frac{\iint \Psi H \Psi^* dV_1 dV_2}{\iint \Psi \Psi^* dV_1 dV_2} \quad (1)$$

The Hamiltonian for this two core (A,B), two electron (1,2) system contains the terms shown below.

$$\begin{aligned}
H = & \underbrace{-\frac{\hbar^2}{2m_A}\Delta_A - \frac{\hbar^2}{2m_B}\Delta_B}_{I} - \underbrace{\frac{\hbar^2}{2m_e}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2}_{II} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{B2}}}_{III} \\
& - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}}}_{IV} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{AB}}}_{V} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{VI} \quad (2)
\end{aligned}$$

Term I is cancelled due to the Born-Oppenheimer approximation (positions of the cores are fixed → no kinetic energy contribution of the cores).

- (I) Kinetic energy of the two cores A and B
- (II) Kinetic energy of the two electrons 1 and 2
- (III) Coulomb interaction of every electron with its original core
- (IV) Coulomb interaction of every electron with the opposite core
- (V) Coulomb interaction of the two cores
- (VI) Coulomb interaction of the two electrons

## 2.2 Molecular and atomic wavefunctions

As already mentioned in the preface, we will use the molecular orbital theory and construct the molecular wavefunction  $\Psi$  as a linear combination of the atomic 1s wavefunctions  $\varphi_A$  and  $\varphi_B$ . In further calculations we will use odd (3) and even (4) combinations and dismiss the corresponding invert symmetrical spinfunctions, as they give no input to the bond potential.

$$\Psi = \alpha(1)\alpha(2) \underbrace{[\varphi_A(\vec{r}_1)\varphi_B(\vec{r}_2) - \varphi_A(\vec{r}_2)\varphi_B(\vec{r}_1)]}_{\Psi_o} \quad (3)$$

$$\Psi = [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \underbrace{[\varphi_A(\vec{r}_1)\varphi_B(\vec{r}_2) + \varphi_A(\vec{r}_2)\varphi_B(\vec{r}_1)]}_{\Psi_e} \quad (4)$$

The **atomic** 1s wavefunction will be introduced normed to one, in reference to the probability density of one electron in a single H-atom over the whole space. The additional factors of the mixed term in order to norm the molecular wavefunction will be taken under consideration later.

$$\varphi_i(\vec{r}_j) = \frac{1}{\sqrt{N}} e^{-\frac{|\vec{r}_j|}{a_0}} \quad \text{with } i = A, B \quad ; \quad j = 1, 2 \quad \text{and} \quad N = \pi a_0^3 \quad (5)$$

To briefly illustrate the contribution of the electrons to the binding process, the radial probability in the xy-plane is shown in figure 3 on page 6, calculated with formula (6). Note that this simulation only displays a superposition of the radial probability function without taking the reshape of the single atom orbitals (caused by disturbance of the other atom) as well as electron-electron interaction into account.

$$P_r = r_{A1}^2 |\varphi(\vec{r}_{A1})|^2 + r_{B2}^2 |\varphi(\vec{r}_{B2})|^2 = \left( \left( x - \frac{r_{AB}}{2} \right)^2 + y^2 + z^2 \right) \exp \left( -\frac{2\sqrt{\left( x - \frac{r_{AB}}{2} \right)^2 + y^2 + z^2}}{a_0} \right) + \left( \left( x + \frac{r_{AB}}{2} \right)^2 + y^2 + z^2 \right) \exp \left( -\frac{2\sqrt{\left( x + \frac{r_{AB}}{2} \right)^2 + y^2 + z^2}}{a_0} \right) \quad (6)$$

### 2.3 Norm

Even though we use normed wavefunctions we have to limit our integration area ( $-5 \text{ \AA}$  to  $5 \text{ \AA}$ ) due to numerical integration and thereafter adjust the norm. This means we allow the electrons only to be in this specific volume. The difference of the numerical norm factor and the analytical can later be used to discuss this simplification.

The numerical norm integral

$$N = \int_{-5 \text{ \AA}}^{5 \text{ \AA}} |\varphi(x, y, z)|^2 dV \quad (7)$$

with the unnormalized probability density function

$$|\varphi(x, y, z)|^2 = \exp \left( -\frac{2\sqrt{x^2 + y^2 + z^2}}{a_0} \right) \quad (8)$$

results in  $N = 4.6554 \times 10^{-31}$

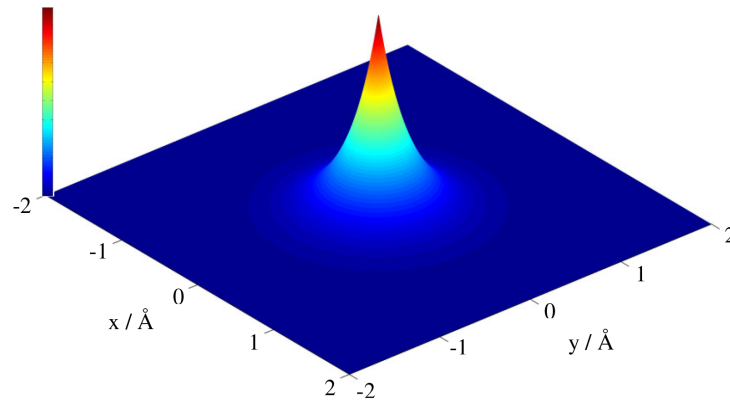


Figure 2: Probability density function (8) in the xy-plane.  
Blue: low values - Red: high values

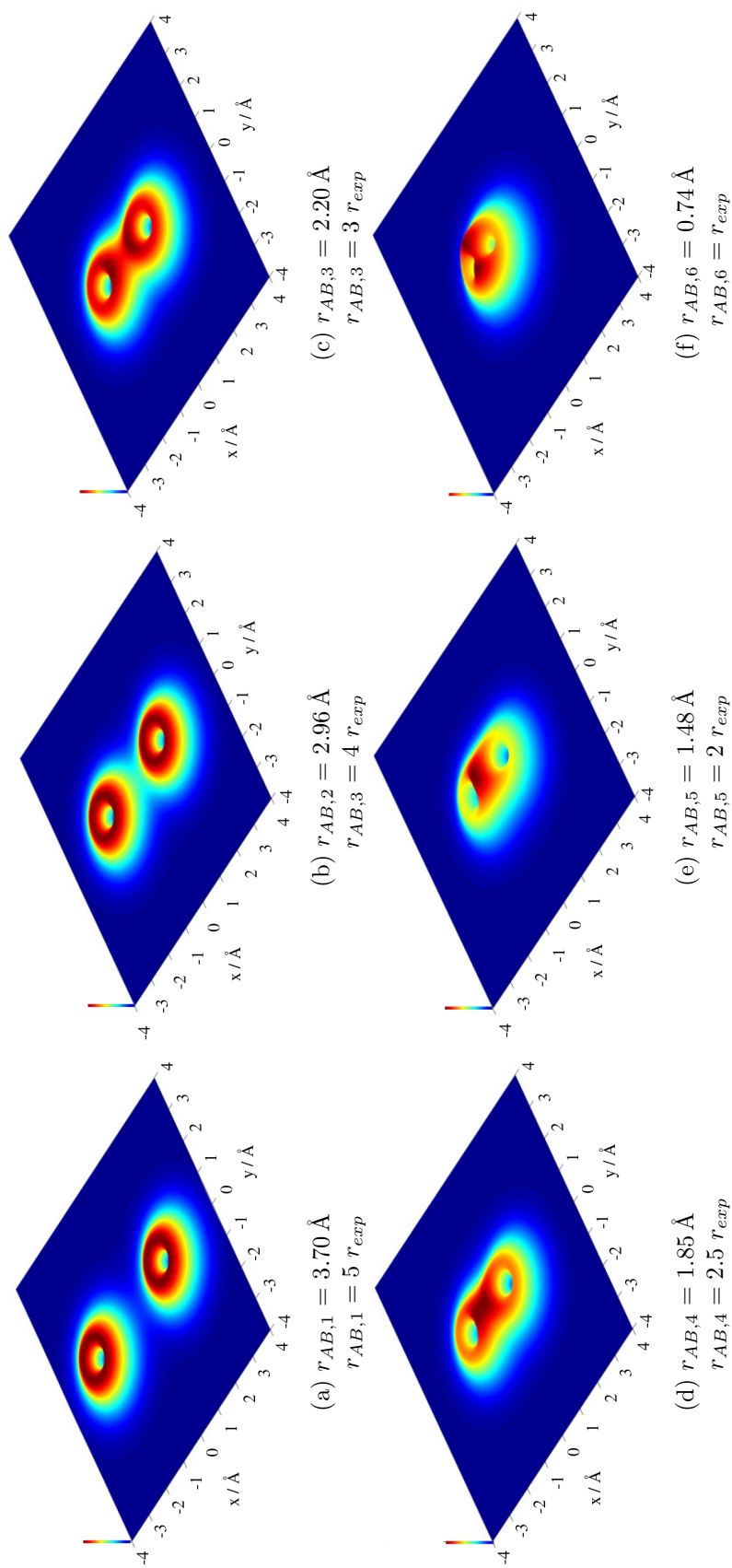


Figure 3: Superposition of the radial probability in the xy-plane for antisymmetric wavefunction with respect to  $r_{AB}$ .

$r_{exp}$  is the experimental determined core distance

Blue: low probability - Red: high probability

### 3 Integral calculation

First we concentrate on calculating the upper integral of equation (1) and split it into two identical integrals of the squared and two identical integrals of the mixed atomic wavefunctions.

Squared terms of  $\iint \Psi H \Psi^* dV_1 dV_2$ :

$$2 \iint \varphi_A(\vec{r}_1)^2 \varphi_B(\vec{r}_2)^2 \left( \underbrace{2E_0}_{II+III} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}}}_{IV} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{AB}}}_{V} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{VI} \right) dV_1 dV_2 \quad (9)$$

Mixed terms of  $\iint \Psi H \Psi^* dV_1 dV_2$ :

$$2 \iint \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_2) \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) \left( \underbrace{2E_0}_{II+III} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}}}_{IV} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{AB}}}_{V} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{VI} \right) dV_1 dV_2 \quad (10)$$

Because of symmetry reasons we can identify the following unique integrals which combine to the expressions (9) and (10). We identify the following integrals:

$$\begin{aligned} C &= \int \varphi_A(\vec{r}_1)^2 \left( -\frac{e^2}{4\pi\epsilon_0 r_{B1}} \right) dV_1 \\ S &= \int \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_1) dV_1 \\ D &= \int \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_1) \left( -\frac{e^2}{4\pi\epsilon_0 r_{B1}} \right) dV_1 \\ E_{ei} &= \iint \varphi_A(\vec{r}_1)^2 \varphi_B(\vec{r}_2)^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_1 dV_2 \\ E_{eei} &= \iint \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_2) \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_1 dV_2 \end{aligned}$$

With these unique integrals the squared terms evolve to:

(II+III):

$$\iint \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) \left[ -\frac{\hbar^2}{2m_e} \Delta_1 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{e^2}{4\pi\epsilon_0 r_{B2}} \right] \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) dV_1 dV_2 = 2E_0$$

(IV):

$$\iint \varphi_A(\vec{r}_1)^2 \varphi_B(\vec{r}_2)^2 \left[ -\frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} \right] dV_1 dV_2 = 2C$$

(V):

$$\underbrace{\iint \varphi_A(\vec{r}_1)^2 \varphi_B(\vec{r}_2)^2 dV_1 dV_2}_{=1} \frac{e^2}{4\pi\epsilon_0 r_{AB}} = \frac{e^2}{4\pi\epsilon_0 r_{AB}}$$

(VI):

$$\iint \varphi_A(\vec{r}_1)^2 \varphi_B(\vec{r}_2)^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_1 dV_2 = E_{ei}$$

Thereafter (9) is:

$$2 \left[ 2E_0 + 2C + \frac{e^2}{4\pi\epsilon_0 r_{AB}} + E_{ei} \right] \quad (11)$$

The mixed terms transform to:

(II+III):

$$\iint \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_2) \left[ -\frac{\hbar^2}{2m_e} \Delta_1 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{e^2}{4\pi\epsilon_0 r_{B2}} \right] \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) dV_1 dV_2 = 2E_0 S^2$$

(IV):

$$\iint \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_2) \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) \left[ -\frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} \right] dV_1 dV_2 = 2SD$$

(V):

$$\underbrace{\iint \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_2) \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) dV_1 dV_2}_{=S^2} \frac{e^2}{4\pi\epsilon_0 r_{AB}} = S^2 \frac{e^2}{4\pi\epsilon_0 r_{AB}}$$

(VI):

$$\iint \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_2) \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_1 dV_2 = E_{eei}$$

Thereafter (10) is:

$$2 \left[ 2E_0 S^2 + 2SD + S^2 \frac{e^2}{4\pi\epsilon_0 r_{AB}} + E_{eei} \right] \quad (12)$$

The Norm  $N_\Psi$  can be identified as:

$$\begin{aligned} N_\Psi &= \iint \Psi \Psi^* dV_1 dV_2 = \underbrace{\iint \varphi_A(\vec{r}_1)^2 \varphi_B(\vec{r}_2)^2 dV_1 dV_2}_{=1} \\ &+ 2 \underbrace{\iint \varphi_A(\vec{r}_1) \varphi_B(\vec{r}_1) \varphi_A(\vec{r}_2) \varphi_B(\vec{r}_2) dV_1 dV_2}_{=2S^2} + \underbrace{\iint \varphi_B(\vec{r}_2)^2 \varphi_A(\vec{r}_1)^2 dV_1 dV_2}_{=1} = 2 + 2S^2 \quad (13) \end{aligned}$$



All together, the bond potential results to

$$E = \frac{\iint \Psi H \Psi^* dV_1 dV_2}{\iint \Psi \Psi^* dV_1 dV_2} = 2E_0 + \frac{2C \pm 2DS + E_{ei} + E_{eei}}{1 \pm S^2} + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \quad (14)$$

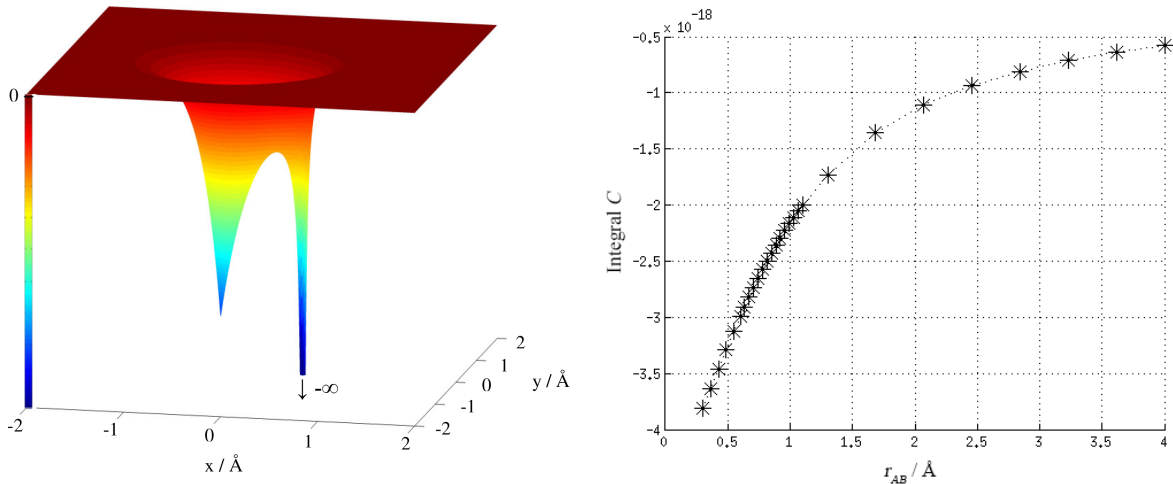
where the upper sign has to be chosen for even, the lower for odd molecular wavefunctions.

### 3.1 Coulomb interaction integral $C$

Integral  $C$  represents the Coulomb interaction of the electron 1 in a 1s state of core A with core B and is symmetric to the interaction of electron 2 in a 1s state of core B with core A:

$$C = \int \varphi_A(\vec{r}_1)^2 \left( -\frac{e^2}{4\pi\epsilon_0 r_{B1}} \right) dV_1 \quad (15)$$

To solve this three dimensional integral we used the Matlab routine "integral3" with an absolute tolerance  $AbsTol = 10^{-60}$  over an integrated volume from  $-5 \text{ \AA}$  to  $5 \text{ \AA}$ .



(a) Function  $f_C$  in the  $xy$ -plane for  $r_{AB} = 0.85 \text{ \AA}$  (b) Integral  $C$  with respect to the core distance  $r_{AB}$

Figure 4: Function  $f_C$  and Integral  $C(r_{AB})$

The  $xy$ -cut of the function  $f_C$  (figure 4a) clearly shows that the integral boundaries include all significant function values. Since  $f_C$  only produces negative function values the interaction between the electron and the core is, like physically expected, attractive. It shows that the electron 1 remains mostly around its own core A and contributes there the main part of the interaction energy, except it falls directly into the opposite core B producing the infinite singularity.

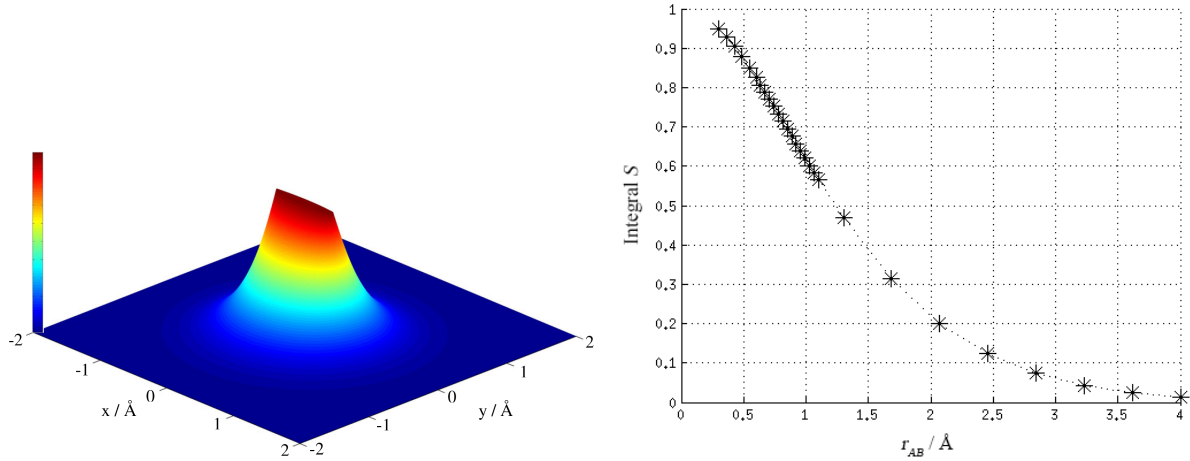
Figure 15 displays the increase of negative potential when the core distance decreases because the electron is more likely around the other core. If the core distance is infinite it is obvious that the electron doesn't interact with the other core. Then, this process contributes nothing to the overall potential.

### 3.2 Overlap integral $S$

The overlap integral  $S$  represents the probability of one electron located in between the cores not belonging to one specific atom. Like before it is symmetric for the two electrons.

$$S = \int \varphi_A(\vec{r}_1)\varphi_B(\vec{r}_1) dV_1 \quad (16)$$

The solving procedure is the same as for integral  $C$ .



(a) Function  $f_S$  in the  $xy$ -plane for  $r_{AB} = 0.85 \text{ \AA}$  (b) Integral  $S$  with respect to the core distance  $r_{AB}$

Figure 5: Function  $f_S$  and Integral  $S(r_{AB})$

If the core distance is approaching zero, the electron shells overlap completely and the integral sums up to one. Again the overlap region decreases when the core distance enlarges. As we can see, the function also decreases exponentially and contains no significant function values near the integral boundaries.

### 3.3 One electron exchange integral $D$

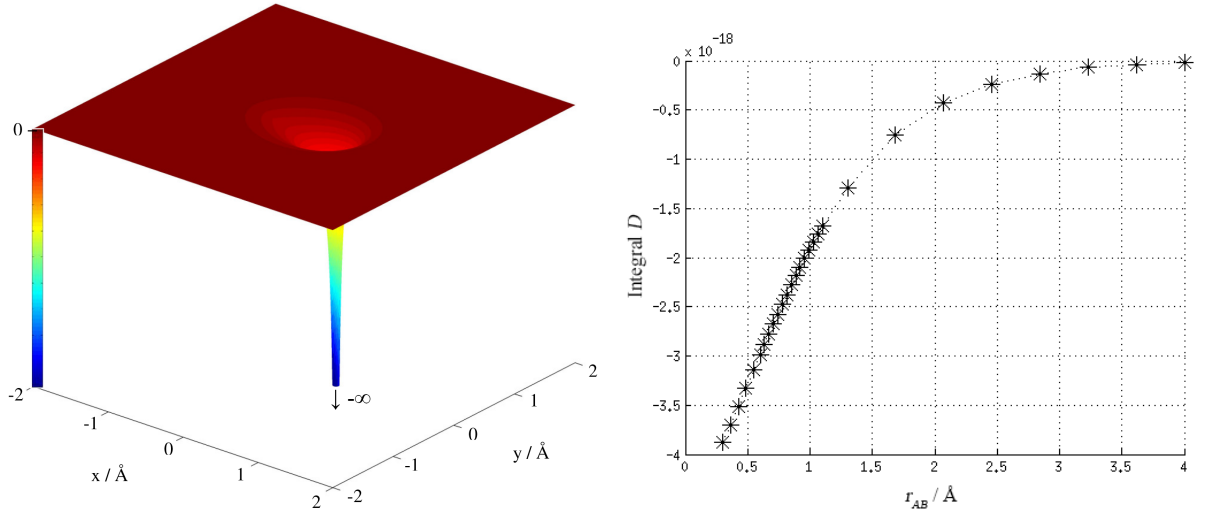
$D$  is the one electron exchange integral. It shows an electron which is in a state between the cores (like  $f_S$  (16)) interacting with one core.

$$D = \int \varphi_B(\vec{r}_1)\varphi_A(\vec{r}_1) \left( -\frac{e^2}{4\pi\epsilon_0 r_{B1}} \right) dV_1 \quad (17)$$

Again, the calculation is done with the Matlab routine "integral3".

Figure 6a displays that the integral boundaries are still valid, the electron now is mostly located between the two cores and contributes a singularity when falling into the interacting core. Once again, there is no difference when considering electron 1 and core B or electron 2 and core A.

If the core distance gets infinite, the overlap disappears and consequentially the integral contribution vanishes.



(a) Function  $f_D$  in the  $xy$ -plane for  $r_{AB} = 0.85 \text{ \AA}$  (b) Integral  $D$  with respect to the core distance  $r_{AB}$

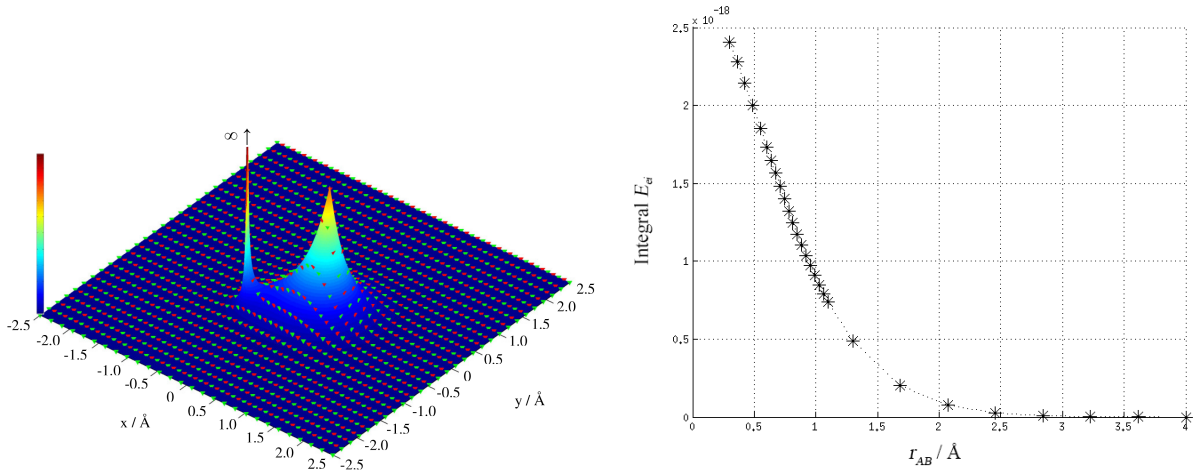
Figure 6: Function  $f_D$  and Integral  $D(r_{AB})$

### 3.4 Repulsive Coulomb electron interaction integral $E_{ei}$

$E_{ei}$  represents the repulsive Coulomb interaction of the electrons each being in a state around its original core.

$$E_{ei} = \iint \varphi_A(\vec{r}_1)^2 \varphi_B(\vec{r}_2)^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_1 dV_2 \quad (18)$$

This function unfolds in a six dimensional integral which has to be discretized to be solved. This is done by inserting a three dimensional grid with  $28^3$  supporting points per electron. While one electron position is fixed, the other is allowed to be at every lattice point. To avoid both electrons being at the same location one grid is shifted for a half grid spacing in the  $x$ -direction. All function values are then summed up and considered as constant for close proximity.



(a) Function  $f_{E_{ei}}$  in the  $xy$ -plane, one electron fixed (b) Integral  $E_{ei}$  with respect to the core distance  $r_{AB}$

Figure 7: Function  $f_{E_{ei}}$  and Integral  $E_{ei}(r_{AB})$

In figure 7a we see a xy-cut surface plot of the function  $f_{E_{ei}}$  where one electron is fixed and the other is **continuously** moved. The green triangles represent the fixed electron 1 while the red triangles represent the discrete locations of electron 2 for calculating the integral. In the shown case electron one is exactly at the infinite peak. Because of the shift of the red grid, the second electron is now not allowed to be at the same position, avoiding infinite rejection energy. With this approach the discretized function is now relatively well behaved and includes the base of the infinite peak by approximation.

### 3.5 Coulomb electron exchange interaction integral $E_{eei}$

$E_{eei}$  is the Coulomb electron exchange interaction integral where the exchange density is used to examine further repulsive Coulomb forces.

$$E_{eei} = \iint \varphi_B(\vec{r}_1)\varphi_A(\vec{r}_2)\varphi_A(\vec{r}_1)\varphi_B(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_1 dV_2 \quad (19)$$

The six dimensional integral is treated same as  $E_{ei}$  and also computed with  $28^6$  lattice points leading to 482 million function values for each core distance.

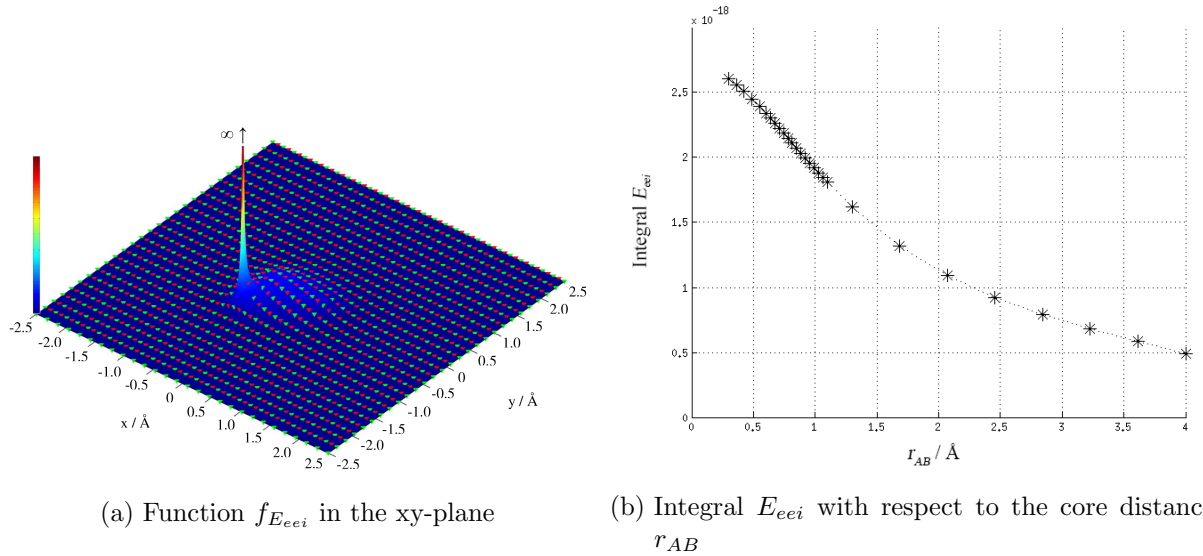
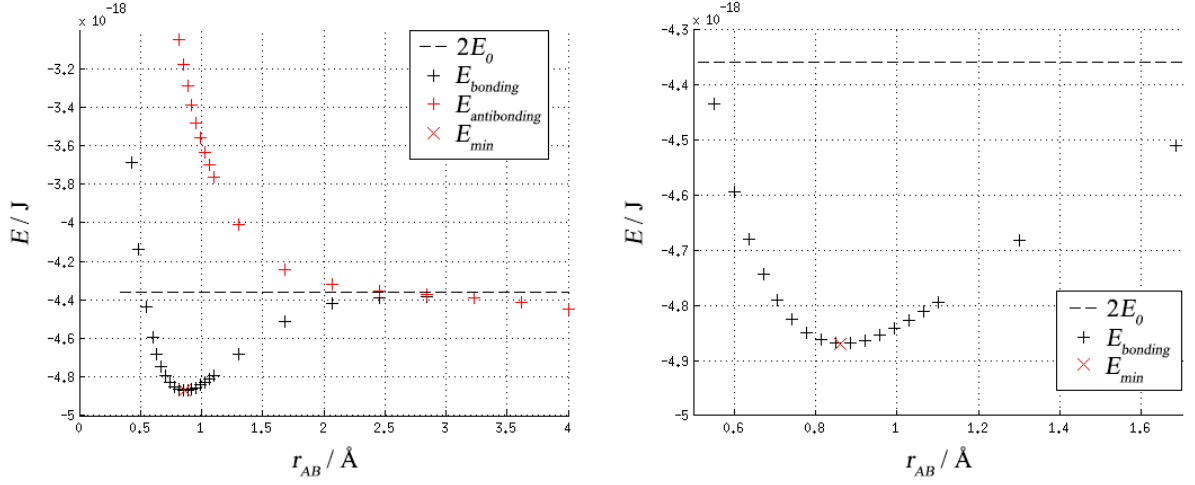


Figure 8: Function  $f_{E_{eei}}$  and Integral  $E_{eei}(r_{AB})$

Basically the schema is the same as in figure 7a, but now the exchange density is decisive for the electron location. Again the infinite peak represents the point of electron collision.

## 4 Result



(a) Bond potential with respect to  $r_{AB}$  for bonding and antibonding wavefunctions  
(b) Close-up of the bonding wavefunctions minimum  $E_{min}$

Figure 9: Bond potential for bonding ( $E_{bonding}$ ) and antibonding ( $E_{antibonding}$ ) wavefunctions with respect to the core distance  $r_{AB}$

To display the results we calculated all integrals for 28 different core distances. The first five equidistant points ranging from 0.30  $\text{\AA}$  to 0.55  $\text{\AA}$  were spaced 0.0625  $\text{\AA}$  apart. The next region containing the minimum held 15 points from 0.60  $\text{\AA}$  to 1.10  $\text{\AA}$  in a spacing of 0.036  $\text{\AA}$ . The last section included eight points 1.30  $\text{\AA}$  to 4.00  $\text{\AA}$  with a equidistant spacing of 0.386  $\text{\AA}$ . The range between the two lowest points was then investigated further with 15 points to find the minimum.

$$E_{min} = (-4.8686 \pm 0.0001) \times 10^{-18} \text{ J} \approx -30.4 \text{ eV} \quad (20)$$

at a bonding length of

$$r_{AB,min} = (0.869 \pm 0.001) \text{ \AA} \quad (21)$$

The bonding energy from the minimum  $E_{min}$  to  $2E_0 = -4.3588 \text{ J} \approx -27.2 \text{ eV}$  results to

$$E_{bond} = E_{min} - 2E_0 = (0.5098 \pm 0.0001) \times 10^{-18} \text{ J} \approx 3.18 \text{ eV} \quad (22)$$

## 5 Discussion

The calculated results differ from the experimental values<sup>1</sup> which are:

$$E_{min,exp} = 4.52 \text{ eV}$$
$$r_{AB,exp} = 0.74 \text{ \AA}$$

One of the reasons for this discrepancy is the chosen wavefunction  $\Psi$  which is constructed by spherical symmetric wavefunctions  $\varphi$ , while the H<sub>2</sub> molecule is not spherical symmetric. This means that the natural wavefunction for the H<sub>2</sub> potential is likely to be not spherical symmetric. To satisfy this circumstance, one might use p-orbitals or other non-spherical symmetric wavefunctions to improve the calculation.

Further trade-off is made by discretization of the six dimensional electron-electron interaction integrals (sections 3.4 and 3.5) in order to make them solvable. The results of these integrals could be improved by using more computation resources to decrease the grid spacing.

The constriction of the integral limits and the numerical calculated norm factor contribute no significant modification of the result due to exponential decreasing functions. The comparison of the numerical and analytical norm factor is shown below and differs only in the seventh decimal place.

$$N = 4.6554 \times 10^{-31}$$
$$N_{\text{analyt}} = \pi a_0^3 = 4.6554 \times 10^{-31}$$
$$N - N_{\text{analyt}} = 9.1341 \times 10^{-38}$$

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<sup>1</sup><http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/hmol.html>