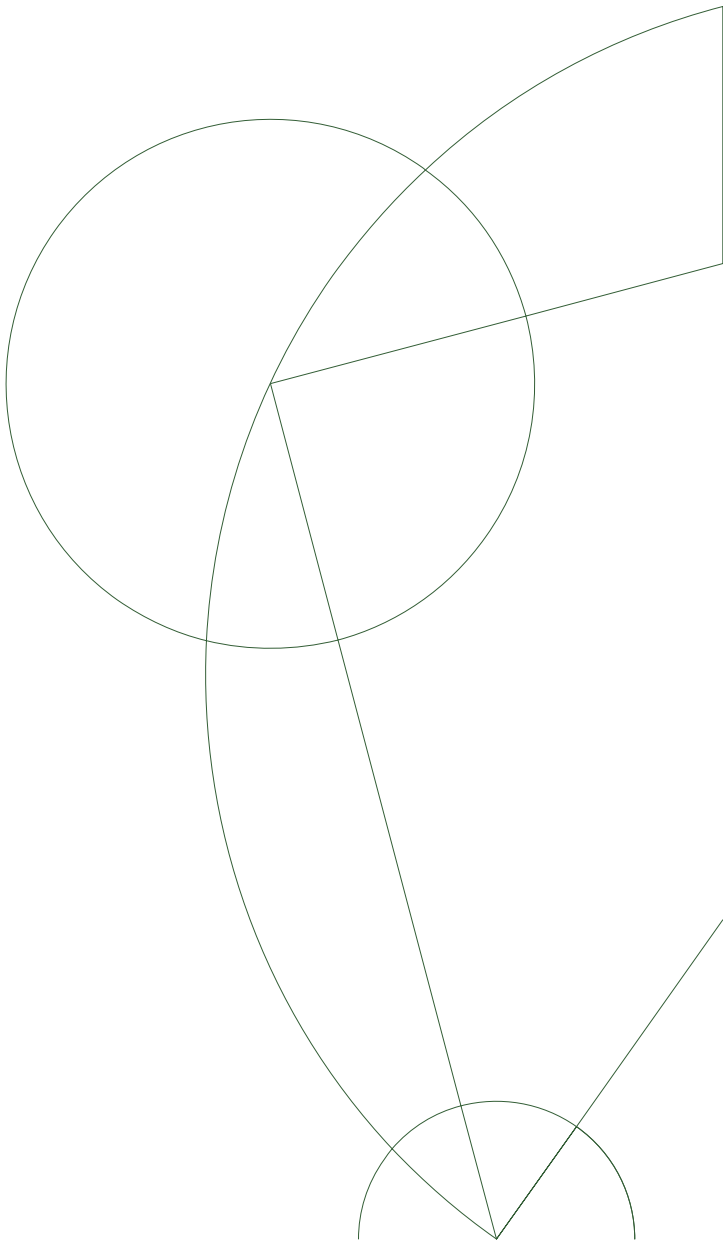
FACULTY OF SCIENCE
UNIVERSITY OF COPENHAGEN

Bacheloropgave

Simon Brink

Correlation effects in Molecules



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June 11, 2013

1 Reserving on an aggregated level

$$R = \sum_{i=2}^{n} R_i = \sum_{i=2}^{n} D_{i(n+1-i)} \left(\prod_{j=n+1-i}^{n-1} \hat{f}_j - 1 \right)$$

Contents

Abstract

In this thesis we will examine two different kind of approximations that describes correlation effects in molecules. In the first part we will look at the linear combination of atomic orbitals and how that leads to bonding/antibonding. We will then look at the description of a H_2 molecule that this approximation provides.

A new approximation will then be introduced, the Heitler-London approximation. We will again look at how it describes the correlation effects, and then lead on to the description of a H_2 molecule. The two approximations provided thus far will then be compared against each other, choosing the most appropriate to apply to a coupled quantum dot system in a quantum wire. Though LCAO has a slightly shorter bonding length, the bonding energy is much better in the Heitler-London approach.

The Heitler-London approximation is then applied to the coupled quantum dots and the ground and first exited state of the single particle coupled quantum dot states are examined.

Finally the approximation is applied to the two particle coupled quantum dots, providing us with the exchange coupling. It is then clear that the lowest energy state of the two particle quantum dots is the singlet state, though the difference decays as the distance between the two quantum dots increases.

Resume

I dette Bachelorprojekt vil vi undersøge to forskellige approksimationer der beskriver korrelations effekterne i molekyler. I den første del vil vi kigge på lineare kombinationer af atomare orbitaler og hvordan det leder os til bonding/antibonding. Vi vil derefter se på beskrivelsen af et H_2 molekyle som denne approksimation giver.

A ny approksimation vil så blive introduceret, Heitler-London approksimationen. Vi vil igen undersøge dens beskrivelse af korrelations effekter, og så føre videre til beskrivelsen af et H_2 molekyle. De to approksimationer vi har nu vil derefter blive sammenlignet for at vælge den bedst egnede til bruge på et koblet kvanteø system in en quantum wire. Selvom LCAO har en anelse kortere bindings længde så er bindings energien meget bedre i Heitler-London tilgangen.

Heitler-London approksimatinen bliver herefter brugt på de koblede kvanteøer og grundtilstanden samt den første ekciterede tilstand af enkelt partikel kvanteøen undersøges.

Til sidst bruges approksimationen på to partikel kvanteø systemet og giver os udvekslings koblingen. Det er herefter klart at den laveste energi tilstand a to partikel kvanteøerne er singlet tilstanden, selvom differensen falder som afstanden mellem de to kvanteøer øges.

Introduction

With the increase in the usage of quantum dots in nano electronics and the hope for their use in such areas as nano electronics and quantum computation eg. quantum gates[1], it becomes increasingly more important to understand and increase our knowledge of quantum dots. Through controlling electric gates along a nanowire it is possible to confine charges in all 3 dimension and obtain these artificial atoms. It is furthermore possible to obtain coupled quantum dots through this method[2], and it is this system that I will eventually look at.

A prerequisite for this study is an understanding of the correlation effects between two atoms, and two different approaches at describing a hetero molecule with two atoms will be examined. These two approximations are respectively the linear combination of atomic orbital (LCAO) and the Heitler-London approach. In the case with a two atomic hetero molecule the LCAO consists of two identical atomic orbitals in a linear combination. However, some of the correlation effects are left out and thus it might be a lesser approximation compared to the Heitler-London approach where more correlation effects are included.

A system of two coupled quantum dots are then treated to the Heitler-London approximation as it proves to be the best approximation. The Heitler-London approximation is then used to examine whether the singlet or triplet state is more energy favourable. Furthermore, the exchange coupling is examined to see how the coupling changes as the distance between the two quantum dots is varied.

Molecular orbital method & LCAO

There are several ways to approximate a two particle problem. The molecular orbital method is one way. In this method you first take the one-electron two-atom states and then add another electron. In this approximation the Hamiltonian is split into two parts[3]

$$H = H_1 + H_2$$

with

$$H_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_A|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_B|} + U_{eff}(\mathbf{r}_i), \quad i = 1, 2$$

This method includes the average potential caused by the other electron in the U_{eff} term.

The following eigenstate is then obtained for the two-atom, one-electron Schrödinger equation with the eigenfunction $\psi_i(r)$ and is called the molecular orbital.

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{|\mathbf{r} - \mathbf{R}_A|} - \frac{e^2}{|\mathbf{r} - \mathbf{R}_B|} + U_{eff}(\mathbf{r})\right]\psi_i(r) = \epsilon_i\psi_i(\mathbf{r})$$

If the molecular orbitals are known the wave function of the two-electron system can be written as a product of the wave functions of one-electron systems due to the separation of the Hamiltonian.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)$$

However, the Pauli exclusion principle has to be observed and the wave function needs to to be accompanied by a spin dependent part. If the same molecular orbital is chosen for both electrons the spin dependent part has to be antisymmetric. In the case with different molecular orbitals there are two possibilities. If a symmetric combination of r_1 and r_2 is chosen, the spin dependent part has to be chosen antisymmetric and the wave function is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) + \psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_1)]$$

with the singlet spin part

$$\chi_s(s_1, s_2) = \frac{1}{\sqrt{2}}[|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2.$$

If an antisymmetric combination of r_1 and r_2 is chosen, the spin dependant part is chosen to be symmetric, and the wave function is thus

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) - \psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_1)]$$

with the triplet spin part

$$\chi_t(s_1, s_2) = \begin{cases} |\uparrow\rangle_1|\uparrow\rangle_2 \\ \frac{1}{\sqrt{2}}[|\uparrow\rangle_1|\downarrow\rangle_2 + |\downarrow\rangle_1|\uparrow\rangle_2] \\ |\downarrow\rangle_1|\downarrow\rangle_2 \end{cases}$$

A form of this molecular orbital method is the LCAO (Linear Combinations of Atomic Orbitals), in which linear combinations of atomic wave functions are used. If the solutions to the Schrödinger equation are known, $\psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$, the molecular orbital can be constructed in the following way.

$$\psi_i(\mathbf{r}) = c_A\psi_A(\mathbf{r}) + c_B\psi_B(\mathbf{r})$$

If it's a diatomic molecule with the same two atoms, the atomic functions are expected to have the same probability. Thus $c_A = \pm c_B$ depending on whether the wave function is symmetric or antisymmetric. Furthermore, one has to take into account the overlap integral between the two atomic wave functions since they are not orthogonal to each other, $\langle\psi_A|\psi_B\rangle = \int \psi_A^*(\mathbf{r})\psi_B(\mathbf{r})d\mathbf{r} = S_{AB}$. We then obtain the normalized eigenfunctions of H

$$\psi_\pm(\mathbf{r}) = \frac{1}{\sqrt{2 \pm (S_{AB} + S_{AB}^*)}}[\psi_A(\mathbf{r}) \pm \psi_B(\mathbf{r})]$$

where ψ_+ is the bonding state and ψ_- is the antibonding state. When $\epsilon_A = \epsilon_B$ one obtain the corresponding energy given by $\langle\psi_\pm|H|\psi_\pm\rangle$ and the result

$$\epsilon_\pm = 2\epsilon_A + \frac{\pm(\epsilon_{AB} + \epsilon_{AB}^*)}{2 \pm (S_{AB} + S_{AB}^*)}$$

with

$$\epsilon_A = \int \psi_A^*(\mathbf{r})H_1\psi_A(\mathbf{r})d\mathbf{r}$$
$$\epsilon_{AB} = \int \psi_A^*(\mathbf{r})H_1\psi_B(\mathbf{r})d\mathbf{r}.$$

In the spatially symmetric configuration is called the bonding state since the electron density between the two atom cores is large. The exact opposite is the case for the antisymmetric configuration since it has a small electron density between the two cores and it is thus called the antibonding state, this is showed in figure 1.

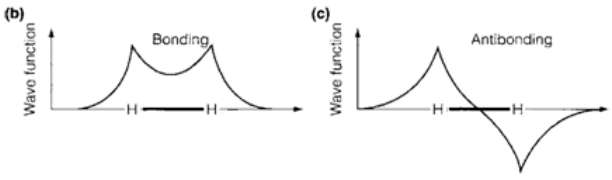

Figure 1: Sketch of a bonding state vs. an antibonding state[4]. It is clear that in the bonding state the electron density is large between the two atoms while it is smaller in the case of Antibonding.

Example: H_2

To illustrate the above mentioned approximation, it will be used on the hydrogen molecule. The chosen eigenstate for the singlet wave function is the hydrogen ground state

$$\psi_0(\overline{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\overline{r}/a_0} = \psi_A(\overline{r}) = \psi_B(\overline{r})$$

where a_0 is the Bohr radius. The bonding/antibonding wave function is then

$$\psi_\pm(\overline{r}_1, \overline{r}_2) = \frac{1}{\sqrt{2 \pm (S_{AB} + S_{AB}^*)}} [\psi_0(\overline{r}_1) \pm \psi_0(\overline{r}_2)]$$

where

$$\mathbf{r}_1 = |\mathbf{r} - \mathbf{R}_A|$$
$$\mathbf{r}_2 = |\mathbf{r} - \mathbf{R}_B|$$

The energy of the system is then

$$\begin{aligned}\langle \psi_\pm | H | \psi_\pm \rangle &= \frac{1}{2 \pm 2S_{AB}} \langle \psi_A^*(\overline{r}) \pm \psi_B^*(\overline{r}) | H | \psi_A(\overline{r}) \pm \psi_B(\overline{r}) \rangle \\ &= \frac{1}{2 + 2S_{AB}} \left(\langle \psi_A^*(\overline{r}) | H | \psi_A(\overline{r}) \rangle + \langle \psi_B^*(\overline{r}) | H | \psi_B(\overline{r}) \rangle \right. \\ &\qquad \left. \pm \langle \psi_A^*(\overline{r}) | H | \psi_B(\overline{r}) \rangle \pm \langle \psi_B^*(\overline{r}) | H | \psi_A(\overline{r}) \rangle \right).\end{aligned}$$

The first task is to calculate S_{AB} and thus the normalization factor. The position of the molecule is chosen so that R_A is at the origin and R_B is on the z-axis at a distance R (figure 2) and thus

$$\mathbf{r}_1 = \mathbf{r}$$
$$\mathbf{r}_2 = \sqrt{\mathbf{r}^2 + \mathbf{R}^2 - 2\mathbf{r}\mathbf{R}\cos\theta}.$$

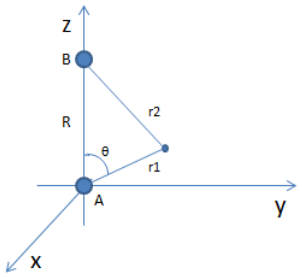

Figure 2: Sketch of the dihydrogen molecule in the LCAO approximation.

We then obtain[5]

$$\begin{aligned}S_{AB} = S_{AB}^* &= \frac{1}{\pi a_0^3} \int_0^{2\pi} \int_0^{\pi} \int_0^{R} e^{-r/a_0} e^{-\sqrt{r^2 + R^2 - 2rR\cos\Theta}/a_0} \overline{r}^2 \sin\theta \, d\overline{r} \, d\theta \, d\Phi \\ &= e^{-R/a_0} \left[1 + \left(\frac{R}{a_0} \right) + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right].\end{aligned}$$

We now have to evaluate the Hamiltonian and start off with exchange integral, ϵ_{AB}

$$\epsilon_{AB} = \int \psi_A^*(\overline{r}_1) H_1 \psi_B(\overline{r}_2) d\overline{r} = -\frac{1}{\pi a_0^3}\frac{e^2}{4\pi\epsilon_0}\int_0^{2\pi}\int_0^{\pi}\int_0^{R} e^{-r/a_0}\left|\frac{1}{\overline{r}_1}+\frac{1}{\overline{r}_2}\right| e^{-r_2/a_0}\overline{r}^2\sin\theta d\overline{r}d\theta d\phi$$
$$= \frac{-2}{a_0^3}\frac{e^2}{4\pi\epsilon_0}\int_0^{\pi}\int_0^{R} e^{-\overline{r}/a_0-\overline{r}_2/a_0}\overline{r}^2\left|\frac{1}{\overline{r}_1}+\frac{1}{\overline{r}_2}\right| dr d\phi$$

We then substitute $\mathbf{r}_2$ and do the θ integral

$$\int_0^{\pi} e^{-\sqrt{\overline{r}^2+R^2-2r\cos\theta}/a_0} = \frac{-a_0}{rR}\left[e^{-(r+R)/a_0}(r+R+a_0) - e^{-|r-R|/a_0}(|r-R|+a_0)\right]$$

Combining this we now get

$$\epsilon_{AB} = \frac{4}{a_0^2 R}\frac{e^2}{4\pi\epsilon_0}\left[-e^{-R/a_0}\int_0^{\infty}(r+R+a_0)e^{-2r/a_0}d\overline{r} + e^{-R/a_0}\int_0^{R}(R-r+a_0)d\overline{r}\right.$$
$$\left. + e^{R/a_0}\int_R^{\infty}(r-R+a_0)e^{-2r/a_0}\right]$$
$$= \frac{2e^2}{4\pi\epsilon_0}\frac{1}{a_0}\frac{a_0+R}{a_0}e^{-R/a_0}.$$

However, $\dfrac{e^2}{4\pi\epsilon_0}\dfrac{1}{a_0}$ is equal to the ground state energy of the hydrogen atom, $E_{1,h}$, and thus the result can be written as

$$\epsilon_{AB} = 2\left(\frac{a_0+R}{a_0}e^{-R/a_0}\right)E_{1,h}$$

Since the two atoms have identical wave functions we get another identical term for ϵ_{AB}^*. Furthermore, with the Hamiltonian being $\dfrac{1}{r_1}+\dfrac{1}{r_2}$ we twice the number, resulting in a total of 4 times this term.

Now all that remains is to evaluate ϵ_A and ϵ_B

$$\epsilon_A = \langle\psi_A^*(\overline{r})|H|\psi_A\rangle = \langle\psi_A^*(\overline{r})| - \frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{\overline{r}_1}+\frac{1}{\overline{r}_2}\right)|\psi_A(r)\rangle$$

However

$$\langle\psi_A^*(\overline{r}_1)| - \frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0\overline{r}_1}|\psi_A(\overline{r}_1)\rangle = E_{1,h}$$

is equal to the energy of a hydrogen atom in it's ground state, $e_{1,h}$. The last part of of ϵ_A is calculated in a similar way to how the normalization integral was done. After changing coordinates and doing the integrals one arrives at

$$\langle\psi_A^*(\overline{r})|\frac{e^2}{4\pi\epsilon_0 r_2}\psi_A(\overline{r})\rangle = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R}-\frac{a_0+R}{a_0^2}e^{-R/a_0}\right)$$
$$= \left(\frac{a_0}{R}-\frac{a_0+R}{a_0}e^{-R/a_0}\right)E_{1,h}$$

Combining this and the previous result we finally arrive at

$$\epsilon_A = \left(1 + \frac{a_0}{R} - \frac{a_0 + R}{a_0} e^{-R/a_0}\right) E_{1,h}$$

The same argument that was used to get ϵ^*_{AB} can be applied to ϵ_A and we thus get the same result for ϵ_B.

When we combine all of this we get the energy of the H_2 molecule to be

$$\epsilon_\pm = \frac{1}{\pm S_{AB}} \left(\epsilon_A + \epsilon_{AB}\right).$$

It is now quite clear when plotting the above function that the singlet state is the favourable one, furthermore, this approximation provides a binding energy of $2.6eV$ and a binding length of $0.85 \cdot 10^{-10}$ as seen in figure 3.

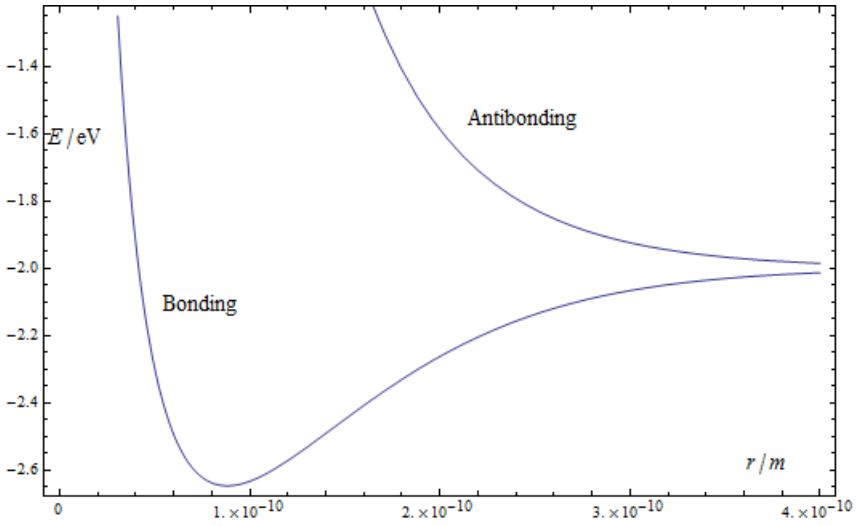

Figure 3: The bonding and antibonding energies as the distance between the two atom cores increases. The bonding state gives a binding energy of $2.6eV$ and a binding length of $0.85 \cdot 10^{-10}$

Heitler-London approximation

Whether the antiparallel spin alignment of two electrons is more favourable than the parallel spin alignment depends on the singlet-triplet energy splitting. This can be approximated through various methods, among those the Heitler-London approximation which is the second approximation we will be looking at, and the approximation the following section will be focused on.

In the tight-binding method the one-electron stationary-state wavefunction is a linear combination of atomic stationary-state wave functions centered at the lattice point r[6]. In the case of N = 2 the linear combinations become:

$$\psi_0(\overline{r}) = \psi_A(\overline{r}) + \psi_B(\overline{r}),$$
$$\psi_1(\overline{r}) = \psi_A(\overline{r}) - \psi_B(\overline{r}).$$

It then follows that the singlet and triplet states become:

$$\psi_s(\overline{r}_1, \overline{r}_2) = \psi_A(\overline{r}_1)\psi_B(\overline{r}_2) + \psi_A(\overline{r}_2)\psi_B(\overline{r}_1) + \psi_A(\overline{r}_1)\psi_A(\overline{r}_2) + \psi_B(\overline{r}_1)\psi_B(\overline{r}_2),$$

$$\psi_t(\overline{r}_1, \overline{r}_2) = 2[\psi_A(\overline{r}_1)\psi_B(\overline{r}_2) - \psi_A(\overline{r}_2)\psi_B(\overline{r}_1)].$$

These equations provide a good approximation for the ground state when electron-electron interactions are ignored, however, when they are not ignored the result is poor. The last two terms of the singlet state have both electrons localized around the same ion core and their interaction energy is not negligible. The triplet state doesn't suffer from this defect and thus provides a lower mean energy. The ground state, however, doesn't have to be a triplet state. A symmetric state is obtainable in the case where an electron is placed on each ion core and described by the first two terms of the singlet state above. This then gives us the following results that are proportional to the Heitler-London approximation:

$$\psi_s(\overline{r}_1, \overline{r}_2) = \psi_A(\overline{r}_1)\psi_B(\overline{r}_2) + \psi_A(\overline{r}_2)\psi_B(\overline{r}_1)$$

$$\psi_t(\overline{r}_1, \overline{r}_2) = [\psi_A(\overline{r}_1)\psi_B(\overline{r}_2) - \psi_A(\overline{r}_2)\psi_B(\overline{r}_1)]$$

Since the wave functions around the two ion cores are not orthogonal they overlap and the overlap integral $S_{AB} = \int \psi_A^*(\overline{r})\psi_B(\overline{r})d^3\overline{r}$ has to be taken into account. A normalization factor is then obtained:

$$N_\pm = \frac{1}{\sqrt{2(1 \pm |S_{12}|^2)}}$$

Thus we obtain the new wavefunctions:

$$\psi_s(\overline{r}_1, \overline{r}_2) = N_+[\psi_A(\overline{r}_1)\psi_B(\overline{r}_2) + \psi_A(\overline{r}_2)\psi_B(\overline{r}_1)]$$

$$\psi_t(\overline{r}_1, \overline{r}_2) = N_-[\psi_A(\overline{r}_1)\psi_B(\overline{r}_2) - \psi_A(\overline{r}_2)\psi_B(\overline{r}_1)]$$

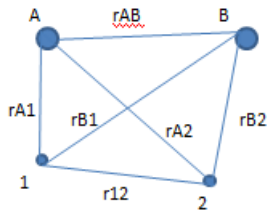

Figure 4: Schematic over the different interactions in the Heitler-London approximation. A and B are the atom cores while 1 and 2 are the electrons.

The Hamiltonian is then introduced

$$H = H + H_{int} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{\overline{r}_{A1}} + \frac{1}{\overline{r}_{B2}}\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{\overline{r}_{12}} + \frac{1}{\overline{R}} - \frac{1}{\overline{r}_{B1}} - \frac{1}{\overline{r}_{A2}}\right)$$

where all the interactions are shown in figure 41 and we get

$$\begin{aligned}\langle\psi_\pm|H|\psi_\pm\rangle &= N_\pm^2\langle\psi_A^*(\overline{r}_1)\psi_B^*(\overline{r}_2) \pm \psi_A^*(\overline{r}_2)\psi_B^*(\overline{r}_1)|H|\psi_A(\overline{r}_1)\psi_B(\overline{r}_2) \pm \psi_A(\overline{r}_2)\psi_B(\overline{r}_1)\rangle \\ &= 2N_\pm^2\left(\langle\psi_A^*(\overline{r}_1)\psi_B^*(\overline{r}_2)|H|\psi_A(\overline{r}_1)\psi_B(\overline{r}_2)\rangle \pm \langle\psi_A^*(\overline{r}_1)\psi_B^*(\overline{r}_2)|H|\psi_A(\overline{r}_2)\psi_B(\overline{r}_1)\rangle\right).\end{aligned}$$

This gives us exactly the energy of the singlet/triplet configuration

$$\epsilon_\pm = \epsilon_A + \epsilon_B + \frac{C \pm I}{1 \pm |S_{AB}|^2}.$$

where

$$C = \int \psi_A^*(\overline{r}_1)\psi_B^*(\overline{r}_2)H_{int}\psi_A(\overline{r}_1)\psi_B(\overline{r}_2)\ d^3\overline{r}$$
$$I = \int \psi_A^*(\overline{r}_1)\psi_B^*(\overline{r}_2)H_{int}\psi_B(\overline{r}_1)\psi_A(\overline{r}_2)\ d^3\overline{r}$$

Example: H_2

As was the case with LCAO the approximation will be tested on H_2. Once again the wavefunction being used for both atoms is the wavefunction of the hydrogen ground state, $\psi_0 = \psi_A = \psi_B$. The Heitler-London approximation then gives the singlet state as

$$\psi_{s,t}(\overline{r}_1, \overline{r}_2) = N_\pm[\psi_A(\overline{r}_1)\psi_B(\overline{r}_2) \pm \psi_A(\overline{r}_2)\psi_B(\overline{r}_1)].$$

Again we start by getting the normalization factor

$$\begin{aligned} N_\pm &= \frac{1}{\sqrt{2(1 \pm |S_{AB}|^2)}}, \\ S_{AB} &= \int \psi_A^*(\overline{r}_1)\psi_B(\overline{r}_2)\ d^3\overline{r} = \frac{1}{\pi a_0^3}\int e^{-\overline{r}/a_0}e^{-\overline{r}_2/a_0}\ d^3\overline{r} \\ &= e^{R/a_0}\left[1 + \left(\frac{R}{a_0}\right) + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right]. \end{aligned}$$

Next step is to calculate the first part of the Hamiltonian

$$\langle\psi_A^*(\overline{r}_1)\psi_B^*(\overline{r}_2)|H|\psi_A(\overline{r}_1)\psi_B(\overline{r}_2)\rangle.$$

This is equal to

$$\epsilon_1 = \frac{e^2}{4\pi\epsilon_0 a_0}\frac{a_0}{R}\left(1 + \frac{5}{8}\frac{R}{a_0} - \frac{3}{4}\frac{R^2}{a_0^2} - \frac{1}{6}\frac{R^3}{a_0^3}\right)e^{-2R/a_0}$$

The last part of the Hamiltonian is quite a bit more difficult due to the $\frac{1}{\overline{r}_1 - \overline{r}_2}$ part, however, according to Y. Sugiura[7] it becomes

$$\begin{aligned} X = \frac{e^2}{20\pi\epsilon_0 a_0}\Bigg[&-e^{-2R/a_0}\left(-\frac{25}{8} + \frac{23}{4}\frac{R}{a_0} + 3\frac{R^2}{a_0^2} + \frac{1}{3}\frac{R^3}{a_0^3}\right) + \frac{6a_0}{R}\left(s\left(\gamma + \log\left(\frac{R}{a_0}\right)\right)\right) \\ &+ s'e^{2R/a_0}Ei\left(-4\frac{R}{a_0}\right) - 2\sqrt{s\cdot s'}Ei\left(-2\frac{R}{a_0}\right)\Bigg]. \end{aligned}$$

where

$$\begin{aligned} s &= \left(1 + \frac{R}{a_0} + \frac{1}{3}\frac{R^2}{a_0^2}\right) \\ s' &= \left(1 - \frac{R}{a_0} + \frac{1}{3}\frac{R^2}{a_0^2}\right)^2 \end{aligned}$$

and Ei is the exponential integral while γ is Euler's constant. The rest of the integral gives

$$\epsilon_2 = X + \frac{e^2}{4\pi\epsilon_0 a_0}\frac{sa_0}{R} - \frac{2e^2}{4\pi\epsilon_0 a_0}\left(1 + 2\frac{R}{a_0} + \frac{4}{3}\frac{R^2}{a_0^2} + \frac{1}{3}\frac{R^3}{a_0^3}\right)e^{-2R/a_0}$$

When combining these results we get the singlet and triplet energies, which are plottet in figure 5.

With the Heitler-London approximation we obtain a binding length of $0.87\cdot 10^{-10}$m and a binding energy of 3.14eV. Comparing this result to the LCAO method we see that the binding length is slightly worse, while the binding energy is much improved.

There are, however, some limitations to the Heitler-London approximation. When the two atoms get too close and form a helium atom, the wavefunctions in the Heitler-London approximation are one-electron wavefunctions for a single charged atom while a much better description would be the one-electron wavefunctions for a double charged atom, such as the independent electron

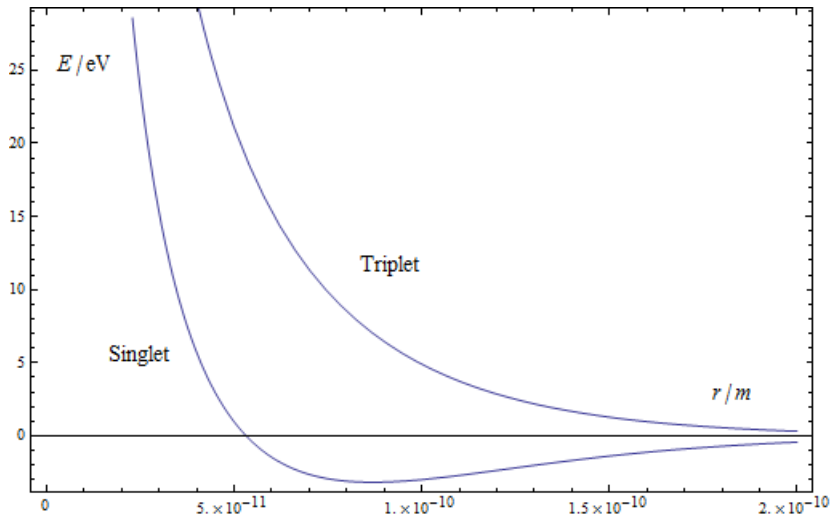

Figure 5: The singlet and triplet energies as the distance between the two cores increase. The singlet state gives a binding energy of 3.14 eV at a binding length of $0.87 * 10-10$m

approximation. Thus the Heitler-London approximation breaks when the two atoms are too close to each other, which is expected since the approximation was intended to describe situations where the atoms are further from each other. It is therefore unexpected that the approximation also breaks down when the atoms are too far from each other. In the case of hydrogen the approximation breaks when the distance between the two atoms exceeds 50 a_0. This happens in the limit of $R \to \infty$ where the energy difference between the singlet and triplet state becomes

$$\langle H \rangle_s - \langle H \rangle_t \to \left[-\frac{56}{45} + \frac{4}{15}\gamma + \frac{4}{15} \log\left(\frac{R}{a_0}\right) \right] \left(\frac{R}{a_0}\right)^3 \exp\left(-\frac{2R}{a_0}\right),$$

where γ is Euler's constant. Due to the log term that arises from the $\frac{1}{\overline{r}_1 - \overline{r}_2}$ part of the Hamiltonian the energy difference changes from being negative to positive for values of R higher than the mentioned 50 a_0. This is a problem since the singlet state should always be lower than the triplet state. Thus, as Yoshida[8] writes: "*The Heitler-London model does not give the correct asymptotic form in the limit* $R \to \infty$". This problem, however, has been described by Herring[9] and he notices that "*the Heitler-London approximation ignores (part of) the electron correlation effect and gives the unreasonable result in the limit* $R \to \infty$". We thus have to keep this in mind when utilizing the Heitler-London approximation.

Coupled Quantum Dots

In the previous sections two different approximation methods have been described and used on H_2 as an example. H_2, however, is not used as foundation for a lot of experiments these days. Artificial atoms such as quantum dots are used in abundance though. It is therefore interesting to test the Heitler-London approximation on two coupled quantum dots. The following calculations and approximations are based on the numbers supplied in the article by Zhang et al[10].

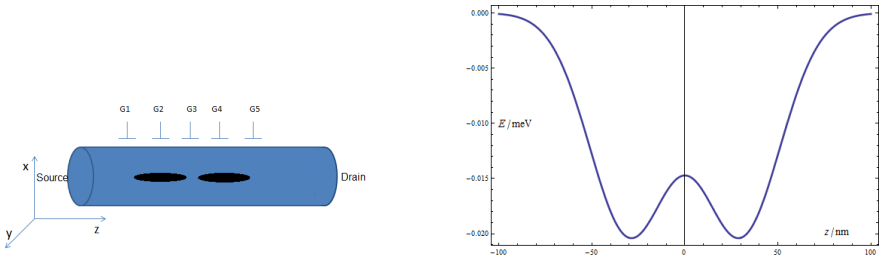

Figure 6: Left: Schematic of the quantum wire quantum dots. Gate 1 and 5 define the outer barrier, while gate 3 controls the interdot coupling. Gate 2 and 4 is used to tune the confinement in each quantum dot. Right: Potential of the QD's with a interdot distance of 60 nm, d = 30 nm

In this article, through manipulation of gates along the quantum wire, it is possible to confine electrons along the wire. As seen in figure 6 Gate 1 and 5 defines the outer barrier while Gate 2 and 4 controls the potential at the quantum dots. Gate 3 is not used treatment of the system, but it is possible to control the interdot coupling through that gate. Furthermore, the magnetic field is ignored since only a magnetic field along the z-axis is considered and this does nothing but increase the xy-plane confinement. The potential in the z direction is described as a linear combination of 2 Gaussians.

$$V(z) = -V_0 \left\{ \exp\left[-\frac{(z-d)^2}{l_z^2} \right] + \exp\left[-\frac{(z+d)^2}{l_z^2} \right] \right\}$$

where V_0 is set to 20 meV, 2d is the distance between the quantum dots, and l_z is the radius of the quantum dots. In the xy plane the system is described as a parabolic potential

$$V(\rho) = m\omega_\rho^2 \overline{\rho}^2/2$$

where

$$\omega_\rho = \hbar/m(D/2)^2$$

with D being the width of the nanowire. The Hamiltonian of the system

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{e^2}{4\pi\epsilon_0|\overline{r}_1 - \overline{r}_2|}$$
$$\hat{h}_i = \frac{\overline{p}_{\rho_i}^2}{2m} + V(\rho_i) + \frac{\overline{p}_{z_i}^2}{2m} + V(z_i).$$

In accordance with the Heitler-London approximation, the trial wavefunctions used are:

$$\chi_{\pm}(\overline{r}) = \frac{\phi_L(\overline{r}) \pm \phi_R(\overline{r})}{\sqrt{2(1 \pm S)}}$$

for the single particle ground and first excited state, while

$$\Psi_{\pm}(\overline{r}_1, \overline{r}_2) = \frac{\phi_L(\overline{r}_1)\phi_R(\overline{r}_2) \pm \phi_L(\overline{r}_2)\phi_R(\overline{r}_1)}{\sqrt{2(1 \pm S^2)}}$$

is used for the two particle singlet and triplet state. S denotes the overlap between the wavefunctions localized in the left and right quantum dots. There are no indexes since the two wavefunctions are identical and you end up with $2S$ and $2S^2$ respectively. The specific expressions for the wavefunctions are

$$\phi_{L/R}(\overline{r}) = \left(\frac{m\omega_\rho}{\pi\hbar}\right)^{1/2} \exp\left[-\frac{m\omega_\rho}{2\hbar}(x^2+y^2)\right] \left(\frac{m\omega_z}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega_z}{2\hbar}(z \pm a)^2\right].$$

where

$$\omega_z = \sqrt{2V_0/ml_z^2}$$

Single particle Quantum Dots

In the case of the single electron quantum dots scenario we have to get the normalization and thus the overlap integral.

$$\begin{aligned} S = \langle\phi_L|\phi_R\rangle &= \int \phi_L^*(\overline{r})\phi_R(\overline{r})\ d^3\overline{r} \\ &= 0.99 \exp^{-3.66*10^{15}d^2} \end{aligned}$$

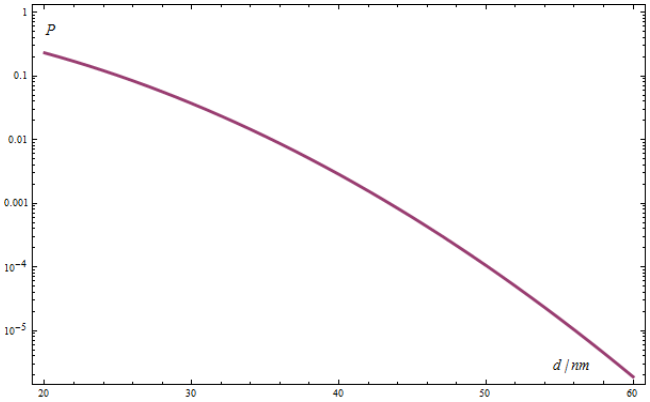

Figure 7: The overlap S as the distance between the two quantum dots is increased. It rapidly falls off as the distance d increases, furthermore it is worth noting that $S >> 1$

In the case of the single particle particle we have a ground state given by

$$\langle\chi_+|\hat{h}|\chi_+\rangle = \frac{1}{2+2S}\langle\phi_L(\overline{r}) + \phi_R(\overline{r})|\hat{h}|\phi_L(\overline{r}) + \phi_R(\overline{r})\rangle$$

and the first excited state given by

$$\langle \chi_- | \hat{h} | \chi_- \rangle = \frac{1}{2 - 2S} \langle \phi_L(\overline{r}) - \phi_R(\overline{r}) | \hat{h} | \phi_L(\overline{r}) - \phi_R(\overline{r}) \rangle.$$

Calculating these values with the only unknown quantity being the interdot distance of 2d we get the following plot in figure 9.

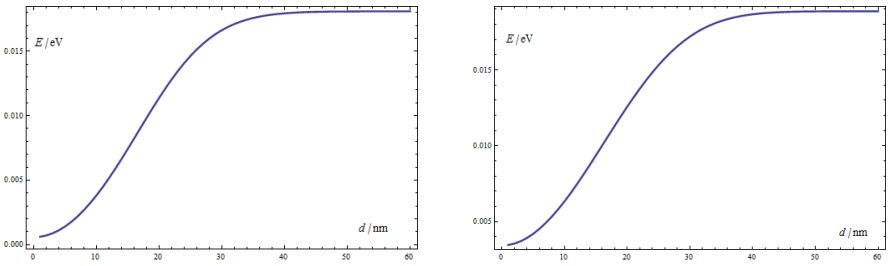

Figure 8: Left: Ground state energy of the single particle quantum dots scenario; Right: First excited energy state of the single particle quantum dots scenario.

Since $\langle \chi_+ | \hat{h} | \chi_+ \rangle$ is the ground state energy it is supposed to always have a lower energy than the first excited state, luckily, this is also the case as seen in figure 9.

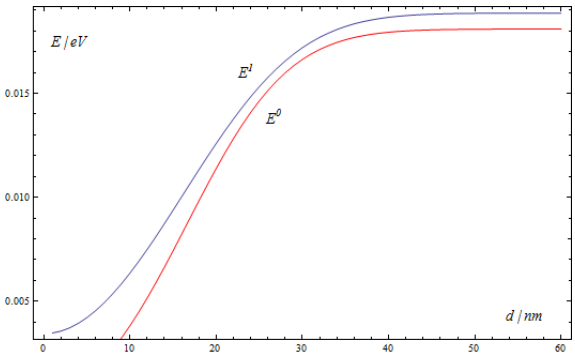

Figure 9: Single particle quantum dots ground state, E^0, and first excited state, E^1. It is clear that the ground state is the lowest energy state, even as d increases.

So far we've known whether the singlet state or the triplet state was the most energy favourable, however, this is no more the case. To get this information the singlet triplet splitting is the first thing to calculate.

Two-particle Quantum Dots

Once again we have to get the overlap integral, but in the case of the two-particle Quantum Dot the wave function consists of

$$\frac{\phi_L(\overline{r})\phi_R(\overline{r}) \pm \phi_L(\overline{r})\phi_R(\overline{r})}{N_\pm}$$

and we then get the normalization of $N_\pm = \frac{1}{\sqrt{2+2S^2}}$. If we wanted to calculate the singlet and triplet state energies we would have to calculate

$$\langle\Psi_+|\hat{H}|\Psi_+\rangle = \frac{1}{2+2S^2}\langle\phi_L(\overline{r}_1)\phi_R(\overline{r}_2)+\phi_L(\overline{r}_2)\phi_R(\overline{r}_1)|\hat{H}|\phi_L(\overline{r}_1)\phi_R(\overline{r}_2)+\phi_L(\overline{r}_2)\phi_R(\overline{r}_1)\rangle$$

for the singlet state energy and

$$\langle\Psi_-|\hat{H}|\Psi_-\rangle = \frac{1}{2-2S^2}\langle\phi_L(\overline{r}_1)\phi_R(\overline{r}_2)-\phi_L(\overline{r}_2)\phi_R(\overline{r}_1)|\hat{H}|\phi_L(\overline{r}_1)\phi_R(\overline{r}_2)-\phi_L(\overline{r}_2)\phi_R(\overline{r}_1)\rangle$$

for the triplet state energy. Fortunately that is not necessary since all we need to calculate is the exchange integral. According to the Heitler-London approximation we have

$$\epsilon_s > \epsilon_t = \frac{C+I}{1+S^2} > \frac{C-I}{1-S^2}$$

and in the case where $S \ll 1$, as it is in our case, the sign of I will determine whether the singlet or triplet energy state is the favourable one. To do this we do the following

$$I = \frac{1}{2}(E_- - E_+).$$

Where

$$\begin{aligned} E_\pm &= \langle\psi_\pm|\frac{e^2}{4\pi\epsilon_0|\overline{r}_1-\overline{r}_2|}|\psi_\pm\rangle \\ &= \frac{1}{1\pm S^2}(\langle\phi_L(\overline{r}_1)\phi_R(\overline{r}_2)|\frac{e^2}{4\pi\epsilon_0|\overline{r}_1-\overline{r}_2|}|\phi_L(\overline{r}_1)\phi_R(\overline{r}_2)\rangle \\ &\pm \langle\phi_L(\overline{r}_1)\phi_R(\overline{r}_2)|\frac{e^2}{4\pi\epsilon_0|\overline{r}_1-\overline{r}_2|}|\phi_R(\overline{r}_1)\phi_L(\overline{r}_1)\rangle \end{aligned}$$

This is plotted in figure 10, however, due to limited computational power, it is based on 40 data points with various degrees of convergence. The trend, however, is still clear in that it decays rapidly with increased interdot distance d, and furthermore the values are positive. From that it can be concluded that the most energy favourable state is the singlet and thus the electrons have opposite spin.

There is clearly a coupling between the two quantum dots, up to several meV at an interdot distance of 40 nm. It is, however, also clear that this coupling diminishes as the interdot distance increases, and once the quantum dots is at a distance of 120 nm the coupling is a factor of 10^6 lower than at 40 nm.

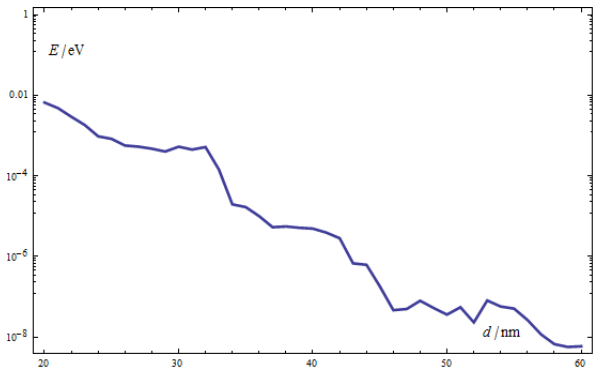

Figure 10: The exchange coupling, I, in the two particle quantum dots scenario. Due to limited computational power the graph is based on a limited number of data points (40), and slightly varied degrees of convergence.

Conclusion

To conclude we have seen how LCAO was used to successfully describe a H_2 molecule giving a good estimate for the binding length, however, the binding energy was far off. After performing similar calculations but utilizing the Heitler-London approximation a much improved binding energy was obtained. The binding length was slightly worse though, and the approximation falls short when the distance between the two atoms are too short, or, surprisingly, if the the distance is above 50 Bohr radii.

With this in mind it was used to describe two coupled quantum dots on a quantum wire. Successfully the one particle ground state and first exited state was calculated for the two couple quantum dots. Furthermore, in the case of the two particle coupled quantum dots, the exchange coupling was examined. Even though the data set could have been improved, had it not been for insufficient computational power, it showed clearly that the lowest energy state of the system was the singlet and the electron thus having opposite spin. In addition it was also clear that as the distance between the two coupled quantum dots increased, the exchange coupling decayed as would be expected. This method could be expanded and used on a triple coupled quantum dot to examine the possibilities of using such a system as a qubit.

References

[1] Guido Burkard, Daniel Loss and David P. DiVincenzo Coupled quantum dots as quantum gates, Physical Review B, **59**, 2070, 1999

[2] C. Fasth, A. fuhrer, M. T. Björk, and L. Samuelson, Nano Letters, **5**, 1487, 2005

[3] Jeno Solyom, Fundamentals of the Physics of Solids, Springer, 2007, p. 90-100

[4] http://www.expertsmind.com/?aspxerrorpath=/topic/molecular-orbitals:-homonuclear-diatomics/bonding-and-antibonding-orbitals-94385.aspx, 10/6-2013

[5] David J. Griffiths, Introduction to Quantum Mechanics, Pearson Education International, 2nd Edition, 2005 p. 305-307

[6] Neil W. Ashcroft and N. David Mermin, Solid state physics, Cengage Learning, 2012, p. 676-679

[7] Y. Sugiura, Über die Eigenschaften des Wasserstoffmoleküls im Grundzustande, The European physical journal, **45**, 484, 1927,

[8] Kei Yoshida, Theory of Magnetism, Springer, 1996, p. 60-62

[9] Conyers Herring, Critique of the heitler-london Method of Calculation Spin Couplings at large Distances, Review of Modern Physics, **34**, 631, 1962

[10] L.-X. Zhang, D. V. Melnikov, S. Agarwal, and J.-P. Leburton, Size effects in the exchange coupling between two electrons confined in quantum wire quantum dots, Physical Review B, **78**, 35418, 2008