

The Heitler-London Model for the Hydrogen Molecule

Here we give some more details on the Heitler-London model for the hydrogen molecule. This is an important model for the understanding of magnetism since it introduces the concept of an exchange energy very nicely for a two-electron wave function in H_2 .

We assume that we have two hydrogen atoms A and B . We know the hamiltonian for these as

$$H_A = -\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{R}_A - \mathbf{r}_1|} \quad (1)$$

and

$$H_B = -\frac{\hbar^2 \nabla_2^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{R}_B - \mathbf{r}_2|}, \quad (2)$$

where $\mathbf{R}_{A,B}$ are the coordinates for the two nuclei, $\mathbf{r}_{1,2}$ are the coordinates for the electron belonging to atom A and atom B , respectively and $\nabla_{1,2}^2$ acts on electron 1 and 2, respectively. We also know the ground state solutions for the hydrogen atom hamiltonians. We call the ground state energy $E_A = E_B = E_0$ and the wave function $\Psi_A(\mathbf{r}_1)$ and $\Psi_B(\mathbf{r}_2)$.

It is straight forward to write down the hamiltonian for the molecule

$$H = -\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{\hbar^2 \nabla_2^2}{2m_e} + \frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{1}{|\mathbf{R}_A - \mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{R} \right\}, \quad (3)$$

where $R = |\mathbf{R}_A - \mathbf{R}_B|$ is the distance between the nuclei. We recognize that the new hamiltonian is simply the sum of the two individual atomic contributions plus the four last terms in the curly bracket: the interaction of the electrons with the "other" nucleus, the electron-electron interaction and the repulsion of the two positively charged nuclei. If we consider the problem for a fixed nuclear distance R the last term is just an energy offset and easy to treat but the other contributions cannot be handled in a simple way.

If we ignore the additional terms for the moment and write the hamiltonian simply as the superposition of the two atomic hamiltonians, the problem is easily solved by the product of the atomic wave functions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_A(\mathbf{r}_1)\Psi_B(\mathbf{r}_2) \quad (4)$$

because

$$\begin{aligned} H\Psi(\mathbf{r}_1, \mathbf{r}_2) &= (H_A + H_B)\Psi_A(\mathbf{r}_1)\Psi_B(\mathbf{r}_2) \\ &= E_A\Psi_A(\mathbf{r}_1)\Psi_B(\mathbf{r}_2) + \Psi_A(\mathbf{r}_1)E_B\Psi_B(\mathbf{r}_2) = (E_A + E_B)\Psi(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (5)$$

The resulting energy is just the sum of the two atomic ground state energies. This is hardly surprising since we removed all the interactions and the atoms do not “see” each other at all.

Apart from the fact that not much is gained by this, the choice of the wave function also has a more fundamental problem: In the molecule the two electrons cannot be distinguished anymore but our wave function does not reflect this. To see this, consider the probability densities for the first atom’s electron at \mathbf{r}_1 and the second atom’s electron at \mathbf{r}_2 . This is

$$P_{12} = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = |\phi_A(\mathbf{r}_1)|^2 |\phi_B(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2. \quad (6)$$

Since we cannot distinguish the electrons, this must be the same as the probability density for the first atom’s electron at \mathbf{r}_2 and the second atom’s electron at \mathbf{r}_1 which is

$$P_{21} = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2 d\mathbf{r}_2 d\mathbf{r}_1 = |\phi_A(\mathbf{r}_2)|^2 |\phi_B(\mathbf{r}_1)|^2 d\mathbf{r}_2 d\mathbf{r}_1. \quad (7)$$

It is easy to see that these probabilities are not the same. Consider for example a situation where \mathbf{r}_1 is very close to the first atom and \mathbf{r}_2 very close to the second. In this case, $|\phi_A(\mathbf{r}_1)|^2$ and $|\phi_B(\mathbf{r}_2)|^2$ are fairly high but, since the atoms are still separated, $|\phi_A(\mathbf{r}_2)|^2$ and $|\phi_B(\mathbf{r}_1)|^2$ are small. It is therefore clear that $P_{12} \neq P_{21}$.

To solve this problem, we need a wave function fulfilling

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2.$$

This means that the wave function must have the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = u\Psi(\mathbf{r}_2, \mathbf{r}_1),$$

where u is a complex number $u = e^{i\phi}$ and $u^2 = 1$. We could thus require that $u = 1$ or $u = -1$, giving symmetric and anti-symmetric solutions for particle exchange. For fermions, we have to require that the total wave function is anti-symmetric with respect to particle exchange and it is here where the spin of the electrons enters: The total wave function is the product of spatial and spin wave function. In order to achieve an anti-symmetric situation, we either have to have a symmetric spatial wave function and an anti-symmetric spin wave function or vice versa. This is achieved by the two wave functions

$$\Psi_{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\Psi_A(\mathbf{r}_1)\Psi_B(\mathbf{r}_2) + \Psi_A(\mathbf{r}_2)\Psi_B(\mathbf{r}_1)) \quad (8)$$

and

$$\Psi_{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\Psi_A(\mathbf{r}_1)\Psi_B(\mathbf{r}_2) - \Psi_A(\mathbf{r}_2)\Psi_B(\mathbf{r}_1)), \quad (9)$$

where the arrows denote the relative spin directions of the electrons, parallel or anti-parallel. The first has a total spin of 0 and is called the singlet state (because there is only one possible state for this). The second has a total spin of 1 and is called the triplet state (because there are three possibilities of realizing this).

The idea of the Heitler-London model is now to use these wave functions as a starting point for calculating the ground state energies of the hydrogen molecule. Without even performing the calculation, we can see that this will have some remarkable consequences. Since we have two different wave functions, depending on the electrons' spin, we will also obtain two non-equal energies as a solution. The resulting energy of the system does therefore depend on the spin of the electrons. This happens despite of the fact that the spin does not actually enter the calculation directly. Still, we shall see that it has a major effect on the result.

A practical calculations proceeds using the variational principle of quantum mechanics. This tells us that the energy calculated by

$$E = \frac{\int \Psi(\mathbf{r}_1, \mathbf{r}_2) H \Psi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}{\int \Psi(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}$$

using a trial wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is always greater or equal than the ground state energy of the system. For a $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ that closely approximates the true ground wave wave function, we can hope to get an accurate solution for the energy. In the present case, using the atomic wave function for the construction of $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ might not be entirely correct because the presence of the second atom can be expected to affect these. The simple approach might, however, still be a good guess.

The resulting energies from the explicit calculation can be written as

$$E = 2E_0 + \Delta E, \quad (10)$$

where E_0 is the ground state energy of a hydrogen atom and the second term is the energy change due the interaction between the two atoms. We get two possibilities for ΔE which depend on the electron spin directions. For the triplet state the energy is

$$\Delta E_{\uparrow\uparrow} = \frac{C(R) - X(R)}{1 - S(R)} \quad (11)$$

and for the singlet state it is

$$\Delta E_{\uparrow\downarrow} = \frac{C(R) + X(R)}{1 + S(R)}, \quad (12)$$

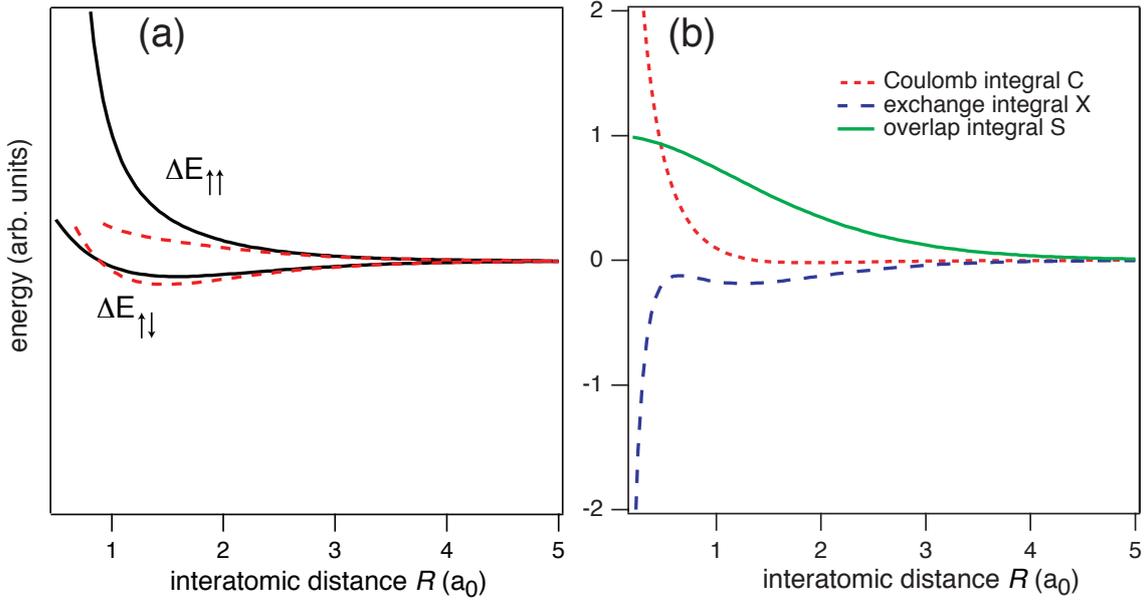


Figure 1: (a) Singlet and triplet ground state energies for the hydrogen molecule as a function of internuclear distance. The dashed lines are the approximation for a vanishing overlap integral. (b) The three integrals used in the calculation of the energies (12) and (11). Note that the vertical axis unit is energy for X and C . It is dimensionless for S .

where S , C and X are integrals called the overlap integral, the Coulomb integral and the exchange integral, respectively. They are given by the following expressions:

$$S = \int \Psi_A^*(\mathbf{r}_1)\Psi_B^*(\mathbf{r}_2)\Psi_A(\mathbf{r}_2)\Psi_B(\mathbf{r}_1)d\mathbf{r}_1d\mathbf{r}_2, \quad (13)$$

$$C = \int \Psi_A^*(\mathbf{r}_1)\Psi_B^*(\mathbf{r}_2)U\Psi_A(\mathbf{r}_1)\Psi_B(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2, \quad (14)$$

$$X = \int \Psi_A^*(\mathbf{r}_1)\Psi_B^*(\mathbf{r}_2)U\Psi_A(\mathbf{r}_2)\Psi_B(\mathbf{r}_1)d\mathbf{r}_1d\mathbf{r}_2, \quad (15)$$

with

$$U = \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{1}{R} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|} \right\}. \quad (16)$$

The energies are shown in Fig. 1(a) and the three integrals in Fig. 1(b). The integrals have a simple interpretation: S is just the overlap of the two wave functions. The Coulomb integral C is the electrostatic interaction energy between the two atoms, assuming that electron 1 is coupled to nucleus A and electron 2 to nucleus B. The exchange integral X measures the Coulomb interaction upon electron exchange between the two atoms.

Upon closer inspection of Fig. 1(b), we note that $S = 1$ for $R = 0$ and then decays (as the overlap is diminishing). We can therefore make the (a bit quick a dirty)

“long distance” approximation for the denominator in (12) and (11) that $S = 0$. This results in

$$E = (2E_0 + C) \pm X \quad (17)$$

with the “magnetic” interpretation presented in the book.

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