



Figure 1: Classical picture of the system investigated in this project: two hydrogen atoms, relatively far apart.

- Declaration: Oct 4, 2024
- Project supervisor: Krzysztof Pawłowski, pawlowski@cft.edu.pl
- Consultation: Oct 10, 2024 (Thursday!)
If needed – another meeting in the week
- Presentation: Jan, 31, 2025

How do neutral atoms interact and form molecules?

Do neutral atoms interact? While they may not form molecules unless they are very close, they experience forces even at larger distances. These forces arise from fluctuations in electron density, as explained by quantum mechanics.

In this project, you will explore the origin of interactions between neutral atoms. You will derive van der Waals interaction potential, and compute C_6 parameter. Additionally, you will explore the fundamental principles that govern the formation of molecules.

- a) Learn the origin of the van der Waals interaction
- b) Derive analytically the atomic parameter C_6
- c) How molecules are formed – on the case of hydrogen H_2 molecule.

Many ideas for this project are based on the lecture of Prof. J. Dalibard from the College de France.

Van der Waals interaction

In this part, you must derive the van der Waals interaction potential.

In what follows we will first assume that the positions of protons are fixed and classical, so that r_{AB} (see Fig. 1) is just a parameter. We will assume both atoms are in the electronic ground state:

$$\psi_A(\mathbf{r}) = \frac{e^{-r/a_0}}{\pi a_0^3}, \quad (1)$$

where a_0 is the Bohr radius.

1. Remind yourself the derivation of the interaction between two electric dipoles in the classical description:

$$U_{\text{dip}}(\mathbf{r}_{AB}) = \frac{1}{4\pi\epsilon_0} \frac{1}{r_{AB}^3} (\mathbf{d}_A \mathbf{d}_B - 3(\mathbf{u}_{AB} \mathbf{d}_A)(\mathbf{u}_{AB} \mathbf{d}_B)), \quad (2)$$

where r_{AB} is the length of the vector \mathbf{r}_{AB} between centers of masses of the dipoles, $\mathbf{u}_{AB} = \mathbf{r}_{AB}/r_{AB}$ and $\mathbf{d}_A = q(\mathbf{r} - \mathbf{r}_A)$, similarly \mathbf{d}_B .

- Assuming that both atoms are in the electronic ground state given by Eq. (1) compute the average dipole-dipole interaction energy between them.
- In quantum mechanics the wavefunction is a probability density amplitude. Let's use this interpretation to estimate numerically the dipole-dipole interaction.

- Assume that the first proton is in position $(0, 0, 0)$ and the second one $(0, 0, z_{p,B} = 5a_0)$. Draw 10 times the positions of both electrons, assuming they are in the electronic ground states given in Eq. (1) (centered at A and B). For every drawing, compute the value of the classical dipole-dipole interaction.
- Repeat the previous point, but for different positions $z_{p,B}$ of the second proton. Plot the results: the "interaction potentials" for the drawn positions of electrons, as a function of the position of the second proton.

- Use the second-order perturbation theory to compute the shift to the energy of the two hydrogen atoms:

$$\Delta E = - \sum_{n \neq 0} \frac{|\langle \psi_0 | U_{AB} | \psi_n \rangle|^2}{E_n - E_0}, \quad (3)$$

where $|\psi_0\rangle$ is the state studied so far – two atoms in the electronic ground states, at fixed distance r_{AB} .

- Compute numerically (3), for different position of the second proton $z_{p,B}$. Plot the results together with the results of the previous exercise.
- Compute analytically approximation to the sum (3):

$$\Delta E = - \sum_{m_A, m_B = -1, 0, 1} \frac{|\langle \psi_0 | U_{AB} | 2m_A, 2m_B \rangle|^2}{E_{2,2} - E_0}, \quad (4)$$

where $|2m_A, 2m_B\rangle$ is a state with both atoms in the first electronic excitation ($l = 1$, i.e. p-state) and different magnetic quantum numbers m .

- You should have found that the shift to the interaction energy is of the form:

$$\Delta E(r_{AB}) = - \frac{C_6}{r_{AB}^6} \quad (5)$$

What is the approximated form of the parameter C_6 ?

Do the atoms attract or repel each other? Justify your answer?

H_2 molecule

In the previous sections, we assumed that the atoms are far apart. This justified treating them as two dipoles, without bothering about electrons and protons.

Assume again that the positions of protons are fixed (the Born-Oppenheimer approximation), but the elementary particles interact via Coulomb forces. Our Hamiltonian will have the form:

$$H_{\text{el}}(\mathbf{d}_A, \mathbf{d}_B) = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} + V_{\text{Coulomb}}, \quad (6)$$

where

$$V_{\text{Coulomb}} = - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{q^2}{4\pi\epsilon_0 r_{1B}} - \frac{q^2}{4\pi\epsilon_0 r_{2A}} - \frac{q^2}{4\pi\epsilon_0 r_{2B}} + \frac{q^2}{4\pi\epsilon_0 r_{AB}} + \frac{q^2}{4\pi\epsilon_0 r_{12}}. \quad (7)$$

The indices 1 and 2 refer to electrons and A and B to protons. Here q is the charge of an electron.

- Assume first that the state of the atoms is such that each electron is in the electronic ground state. Draw the positions of electrons and find the interaction energy classically.

2. Let's consider two states:

$$\Psi_{I,\mathbf{r}_{AB}}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{0,A}(\mathbf{r}_1)\psi_{0,B}(\mathbf{r}_2) \quad \Psi_{II,\mathbf{r}_{AB}}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{0,B}(\mathbf{r}_1)\psi_{0,A}(\mathbf{r}_2), \quad (8)$$

where \mathbf{r}_1 is the position of the left electron, the one closer to the proton A (in Fig. 1) and \mathbf{r}_2 – the one closer to proton B. The orbitals are defined as follows:

$$\psi_{0,A}(\mathbf{r}) = \frac{e^{-|\mathbf{r}_1 - \mathbf{r}_A|/a_0}}{\pi a_0^3} \quad \psi_{0,B}(\mathbf{r}) = \frac{e^{-|\mathbf{r} - \mathbf{r}_B|/a_0}}{\pi a_0^3} \quad (9)$$

3. Assume such Ansatzes:

$$|\xi\rangle = \alpha\Psi_{I,\mathbf{r}_{AB}} + \beta\Psi_{II,\mathbf{r}_{AB}} \quad (10)$$

Compute numerically or deduce the optimal choice of α and β , for which the energy $\langle\xi|H_{\text{el}}|\xi\rangle$ is minimal.

Plot the resulting potential and discuss the optimal coefficient α and β for different \mathbf{r}_{AB} .

4. Try to show that the energy will have the form:

$$V_{\text{eff}}(r_{AB}) = \frac{\epsilon_{\text{dir}}(r_{AB}) + \epsilon_{\text{ex}}(r_{AB})}{1 + (\Delta(r_{AB}))^2}, \quad (11)$$

where

$$\epsilon_{\text{dir}}(r_{AB}) = \int d^3r_1 d^3r_2 \Psi_{I,\mathbf{r}_{AB}} H_{\text{el}} \Psi_{I,\mathbf{r}_{AB}} \quad (12)$$

$$\epsilon_{\text{ex}}(r_{AB}) = \int d^3r_1 d^3r_2 \Psi_{I,\mathbf{r}_{AB}} H_{\text{el}} \Psi_{II,\mathbf{r}_{AB}} \quad (13)$$

$$\Delta(r_{AB}) = \langle\psi_A|\psi_B\rangle \quad (14)$$

5. Take a look at the papers about Heitler-London method. Scan the literature to compare your results with a "true" potential.

6. How the calculation would change, once the spin of electron is accounted for?