Problem 3 The Bohr's molecule
Deadline April, 30 2012

In 1913 Niels Bohr published his famous model of the hydrogen atom explaining for the first time the Rydberg's formula for the emission spectrum of atomic hydrogen. According to the Bohr's model, the electron in the hydrogen atom revolves around the positively charged nucleus along one of the allowed 'stationary' orbits satisfying the condition:

$$L = n\frac{h}{2\pi}, \tag{1}$$

where L is the electron's angular momentum, $n = 1, 2, ...$ is a positive integer number, and $h = 6.626 \times 10^{-34}$ J.s is the Planck's constant. For the sake of simplicity we will use also the 'reduced' Planck's constanth $\hbar = 1.055 \times 10^{-34}$ J.s . Thus, the quantization condition (1) could be rewritten in the form:

$$L = n\hbar. \tag{2}$$

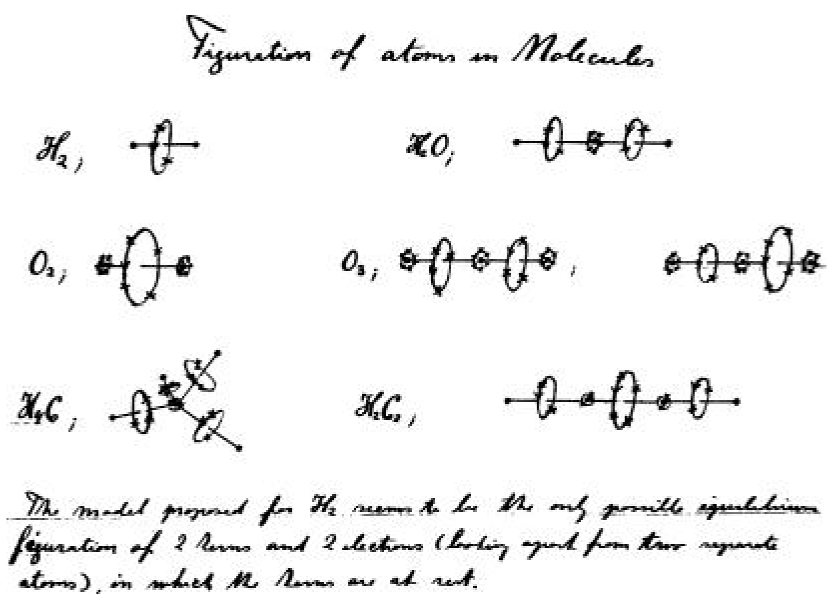

Figure 1: Stationary electronic orbits for different molecules as suggested by Niels Bohr in 1913.

Inspired by the agreement between the theoretical predictions of his model and the experimental data for the hydrogen atom, Niels Bohr has made an attempt to apply the concept of stationary orbit to more complicated systems like many-electron atoms and molecules. Figure 1 represents an original sketch by Niels Bohr of possible stationary electron orbits in a number of molecules. For the suggested molecular models, however, Bohr did not observed precise agreement with the experimental data concerning the distances between atomic protons and the molecular bonding energies.

The interest to the Bohr's molecular model, however, has revived after a number of recent publications showing that there is a larger variety of stationary orbits in the hydrogen molecule than originally suggested by Niels Bohr. It was demonstrated that by using different sets of orbits the Bohr's model provides a computationally non-demanding method for an approximate calculation of the molecular properties. In this problem you are going to investigate some physical characteristics of the hydrogen molecule as predicted by the original model of Bohr.

Description of the Bohr's model for H_2 molecule

Shown in Figure 2 is a detailed sketch of the model of the hydrogen molecule proposed by Niels Bohr. The two protons (p^+) are separated by a distance R. The two electrons (e^-) revolve with the same angular velocity around the same circular orbit, which is perpendicular to and bisects the line connecting the two protons. The electron-proton distances are denoted by r, and the radius of the circular orbit by ρ.

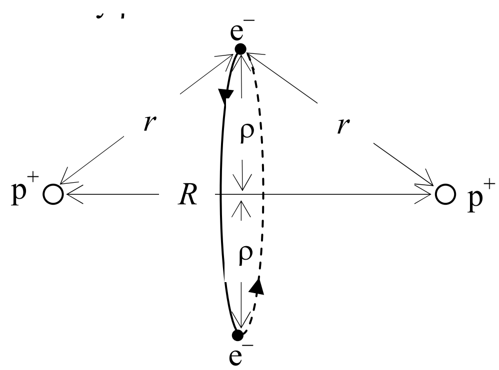

Figure 2: A schematic representation of the Bohr's model for the hydrogen molecule. Shown are all the relevant distances:

It is assumed that:

- The electrons move according to the Newton's laws of dynamics.
- The quantization condition (2) is satisfied by each of the electrons.
- The electrons lie on a same diameter of the circular orbit.

List of available physical constants

- Elementary electric charge: $e = 1.602 \times 10^{-19}\,\mathrm{C}$
- Coulomb's constant: $k = \frac{1}{4\pi\epsilon_0} = 8.988 \times 10^9\,\mathrm{N.m^2/C^2}$
- electric permittivity of vacuum: $\epsilon_0 = 8.854 \times 10^{-12}\,\mathrm{F/m}$
- Reduced Plank's constant: $\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34}\,\mathrm{J.s}$
- Mass of the electron: $m_e = 9.109 \times 10^{-31}\,\mathrm{kg}$
- Mass of the proton: $m_p = 1.673 \times 10^{-27}\,\mathrm{kg}$
- Speed of light: $c = 2.998 \times 10^8\,\mathrm{m/s}$

Part 1. H_2 **molecule in equilibrium**

In this task we assume that the two protons are at rest in their equilibrium positions.

1.A. Calculate the ratios r/R and ρ/R for a molecule with protons in equilibrium.

1.B. Derive an expression for the electric potential energy E_p of the molecule in terms of the internuclear distance R and the available physical constants.

1.C. Calculate the ratio E_k/E_p of the total kinetic energy of electrons to the potential energy of the molecule provided that the protons are in equilibrium positions.

1.D. Derive an expression for the minimum distance R_0 between protons in equilibrium in terms of the provided constants. Calculate the numerical value of R_0 .

The bonding energy E_b of a molecule is defined as the minimum energy required to dissociate the molecule into electrically neutral atoms separated by an infinite distances from each other.

1.E. Calculate the bonding energy E_b of the hydrogen molecule as predicted by the Bohr's model. You can use the ionization energy of the hydrogen atom, $E_I = 13.606\,\mathrm{eV}$.

Part 2. Vibrating H_2 molecule

In practice atomic nuclei in a molecule are not at rest but vibrate around their equilibrium positions. These vibrations persist even at temperatures close to 0 K due to the quantum nature of atomic motion. Therefore, as the temperature tends to 0 K, the energy and the amplitude of atomic vibrations tend to specific minimum values.

Since the protons are much heavier than the electrons, the velocities of the electrons in a molecule are several orders of magnitude higher than the nuclear velocities. For that reason, it is assumed in molecular physics that in each moment of time the electrons move along stationary orbits corresponding to the instantaneous positions of the protons as if the later were at rest. According to this approximation the effective potential energy E of the hydrogen molecule (does not include the kinetic energy of the protons) is a function of the instantaneous distance R between protons. The effective potential energy of the molecule when the atoms are at an infinite distance is taken to be zero. It is not possible to derive an exact expression for the function $E(R)$ even in the frame of the Bohr's model. Instead, this function can be approximated by several expressions, whose applicability is justified on an experimental basis. In this task we will adopt the so called Morse function:

$$E(R) = D(e^{2\alpha(1-R/R_0)} - 2e^{\alpha(1-R/R_0)}) \qquad (3)$$

where D and α are positive constants.

Remark: If you did not calculated R_0 and E_b in points (1D) and (1E), use in this task the following values instead: $R_0 = 0.6\,\text{Å}$ and $E_b = 3.0\,\text{eV}$.

2.A. Sketch qualitatively a graph of the Morse function. Indicate on the graph the equilibrium distance R_0 between protons and the bonding energy E_b of the molecule.

2.B. Write down a relation between the constant D and the bonding energy E_b.

We will consider the vibrations of the protons in the H_2 molecule in a reference frame where the molecular center–of–mass is at rest. Assume that the displacements of the protons from their equilibrium positions are much smaller than the distance R_0.

2.C. Derive an expression for the linear frequency v_{vib} of vibration of the hydrogen molecule in terms of α, R_0, E_b , and the proton mass m_p.

One of the experimental techniques used to measure the frequency of molecular oscillations is known as Raman spectroscopy. According to quantum mechanics, each system vibrating with a frequency v_{vib} can exchange energy only in discrete quanta hv_{vib} . Raman scattering is a process in which an incident photon of a specific wavelength λ_i interacts with a molecule and transfers to it one quantum of vibrational energy. As a result, the photon scatters away with a wavelength λ_s larger than the initial wavelength λ_i. In the Raman process the energy transformed into translational and rotational motion of the molecule is several orders of magnitude smaller than the energy transferred to vibration.

In a particular experiment an ampoule containing molecular hydrogen is illuminated with a monochromatic light of wavelength $\lambda_i = 514\,\text{nm}$.It has been established that there is a weak scattered light from the ampoule with a wavelength $\lambda_s = 664\,\text{nm}$.

2.D. Calculate numerically v_{vib} and determine the value of the constant α in the Morse function.

2.E. Make an order of magnitude estimate of the minimum possible amplitude A_{min} of the vibrations of protons in the hydrogen molecule.