

Chemical Bonding Premaster 2021-2022

Course Pre-master Chemistry (joint degree)

Exam

Date: 28 October 2021

Time: 9:00-12:00

Pages: 7 (front page included)

Questions: 6

At every questions it is mentioned how many points can be earned with a total number of 100 points

Before you start:

- Check whether your version of the exam is complete.
 - Write your name and student number on each answer sheet and indicate the number of pages.
 - Your mobile phone should be turned off and it should be in you jacket and bag. Your jacket and bag should be on the ground.
 - Allowed tools/aids: the periodic table (awarded), (graphing) calculator and list of physical constants (awarded).
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Household notices

- You are not allowed to leave the room during the first 30 minutes and the last 15 minutes, not even for visiting the restroom.
 - 15 minutes before the end you will be warned that the submission time is approaching.
 - You are obliged to identify yourself at the request of the examiner (or his representative) with proof of registration and a valid proof of identity.
 - You are not allowed to use the toilet during the exam, unless the invigilator gives permission for this.
 - You can take this exam with you afterwards.
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Important constants

$$h = 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 2.998 \cdot 10^8 \text{ m/s}$$

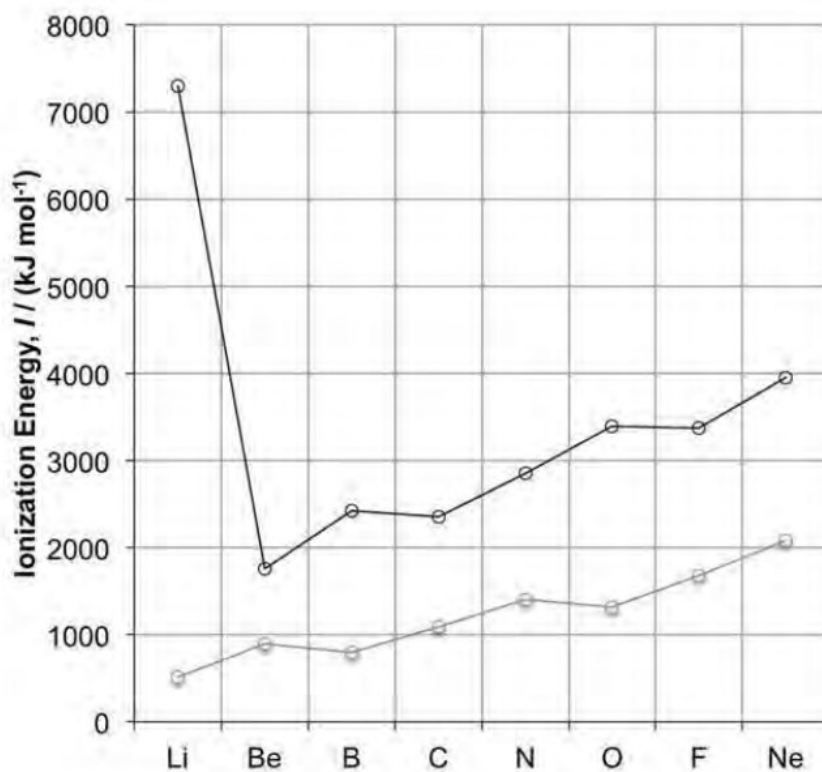
$$1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$$

$$m_e = 9.109 \cdot 10^{-31} \text{ kg}$$

Good luck!

Problem 1 (Ionisation trends and Rydberg) (19 points)

Consider the following trends in the first and second ionisation energies of the elements Li to Ne from the second period of the periodic table. The first ionisation energy is given by the grey line and the second by the black line.



a) (4pt) Give an explanation for why the first ionisation energy of Li is smaller than for the other elements and why the second ionisation energy of Li is much larger than for the other elements.

b) (4pt) Explain why the general trend of the first ionisation energy is to increase from Be to Ne.

Even though there are clearly trends visible in the figure, there are also some exceptions.

c) (3pt) Explain why the first ionisation energy from Be to B decreases instead of increases.

d) (3pt) Explain why the first ionisation energy from N to O again decreases instead of increases.

e) (5pt) During an experiment with an excited H atom a photon with wavelength 433.935 nm is measured. It has been determined that the transition belongs to the Balmer series ($n_1 = 2$). Give the value of n_2 .

$$\nu = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

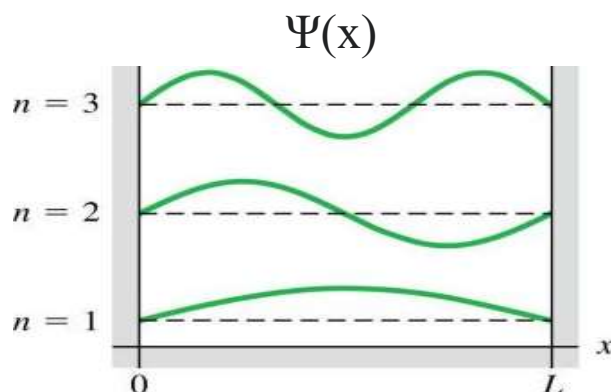
ν : frequency in s^{-1}

R : Rydberg constant = $3.28994 \times 10^{15} s^{-1}$

Z : atomic number

Problem 2 (Particle in a box) (15 points)

Below are a few solutions given for the particle in a box model ($\Psi(x)$). The box is one dimensional with length L .



a) (4pt) Explain what the interpretation is of $\Psi(x)$ and of the square of the wavefunction $\Psi(x)^2$.

From solving the particle in a box the following expression is obtained for the energy of the particle:

$$E_n = \frac{n^2 h^2}{8m_e L^2}$$

$n = 1, 2, 3, \dots$ h : Planck's constant; m_e : electron mass; L : length of the box

b) (3 pt) We consider a one dimensional box with an electron. It is given that the energy of the electron is 0.34 eV and that $n=2$. Calculate the length of the box L .

For now we assume that the box has $L = 3.00$ nm.

c) (4 pt) Electrons can transition from one state to another. i) Give the expression for the energy difference $\Delta E = E_{n+1} - E_n$ between two neighbouring states. ii) Use the expression to calculate the energy difference between $n_2 = 4$ and $n_1 = 3$ in Joule.

When the box goes from one dimensional to two dimensional, the total energy is given by:

$$E_{n_x n_y} = \frac{h^2}{8m_e} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right] \quad n_x = 1, 2, \dots \quad n_y = 1, 2, \dots$$

When the two dimensional box is a square, $L_x = L_y$, degeneracy of the energies of the electron can occur.

d) (4pt) Explain the concept 'degenerate' and give an example of a non-degenerate state and a degenerate state. You are meant to give the values for n_x and n_y for these states

Problem 3 (Quantum numbers and electron configuration) (17 points)

a) (5 pt) The electron configuration of atoms is given by four quantum numbers (n , l , m_l and m_s). Indicate which of the following combinations of quantum numbers are allowed and which are not allowed. Explain your answers.

1. $n = 1, l = 1, m_l = 0, m_s = 1/2$

2. $n = 4, l = 3, m_l = 0, m_s = -1/2$

3. $n = 3, l = 2, m_l = -1, m_s = -1/2$

4. $n = 3, l = 4, m_l = 2, m_s = 0$

5. $n = 6, l = 6, m_l = 0, m_s = 1/2$

6. $n = 2, l = 1, m_l = -1, m_s = 1/2$

7. $n = 1, l = 4, m_l = -2, m_s = -1$

8. $n = 13, l = 8, m_l = 0, m_s = -1/2$

b) (5 pt) The four quantum numbers are the building blocks of the periodic system in combination with i) the Pauli exclusion principle and ii) Hund's rule about spins. Explain in your own words what is meant by i) the Pauli exclusion principle and ii) Hund's rule about spins.

c) (3 pt) In one of the course works we saw that under certain conditions the valence shell is spherically symmetric. What are these conditions?

d) (4 pt) Give the electron configuration of the following elements and indicate whether the outer shell is spherically symmetric (the outer shell can be s- or d- orbitals in the case of a metal and s- or p-orbitals for period 2 elements).

Zr, Co, P, Zn

Problem 4 (Wavefunctions hydrogen atom) (16 points)

- a) (2 pt) Describe in your own words the concept of an atomic orbital
 b) (3 pt) The wavefunction of the $2p_z$ orbital of a hydrogen atom is given below:

$$\psi_{2p_z}(r, \theta, \phi) = \frac{1}{24^{1/2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \frac{1}{2} \left(\frac{3}{\pi}\right)^{1/2} \cos(\theta)$$

Indicate when the value of the wavefunction of the $2p_z$ orbital is zero. Explain your answer with a drawing of the $2p_z$ orbital.

- c) (2 pt) The wavefunction of the $2p_z$ orbital is composed of a radial function, $R(r)$, and an angular dependent function, $Y(\theta, \phi)$:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Give the expression for $R(r)$ of the $2p_z$ orbital.

- d) (3 pt) The radial distribution function, $P(r)$, is defined as follows:

$$P(r) = r^2 R^2(r)$$

Give the expression of $P(r)$ for the $2p_z$ orbital.

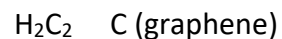
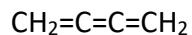
- e) (3 pt) Indicate for which values of r the $P(r)$ function will be zero.

- f) (3 pt) Sketch the radial distribution function, $P(r)$, for the $2p_z$ orbital in a figure and explain your answer in your own words.

Problem 5 (Valence bond theory and MO theory) (15 points)

a) (2 pt) Give a brief description of **i)** a σ bond and **ii)** a π bond.

b) (2 pt) Give the hybridisation of the C atoms in the molecules below

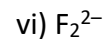


The bonds in molecules can also be described using 'molecular orbital theory'.

c) (3 pt) Draw the MO diagram for **i)** H_2 , **ii)** B_2 and **iii)** F_2 . Place the electrons in the diagrams so that the ground state configuration of **i)** H_2 , **ii)** B_2 and **iii)** F_2 are represented.

d) (4 pt) **i)** Draw the MO diagram for BF and place the electrons in the diagram so that it shows the ground configuration for BF . **ii)** Is BF diamagnetic or paramagnetic?

e) (4 pt) Give the bond order of



$\text{B.O.} = \frac{1}{2}(\text{N} - \text{N}^*)$, N = the number of electrons in a bonding MO, N^* = the number of electrons in an antibonding MO.

Problem 6 (Valence bond theory and MO-theory) (18 points)

Water, H_2O , is a very important molecule for life and in this problem we will study the MO-diagram of water.

a) (3pt) Draw the Lewis structure of H_2O .

b) (3pt) Give the hybridisation of the oxygen atom in H_2O .

c) (8pt) Draw with the help of the figure below a simple MO diagram of H_2O . Indicate which MO's are bonding, non-bonding and anti-bonding.

There are lone pairs present in water, which play an important role in its chemical reactivity, for example during a substitution reaction.

d) (4pt) Reflect on the MO-diagram that you have drawn at c). Indicate the lone pairs of H_2O in the diagram and compare this to the Lewis structure you have drawn at a). How do these two models of the structure of H_2O differ?

