CHEM356: Physical Chemistry II — Exam II - 16^{th} of April, 2019

Name: _____

The exam consist of 5 questions, 25 points each. Only 4 highest score questions will make the final score.

Total - 100 Pts.

Problem I — 25 Pts

1. Write down the hamiltonial for LiH molecule and identify respective terms. You can write it in atomic units.
2. Draw a molecular orbitals diagram and populate it with electrons. Next, write down the electronic wave function in a form of (Single) Slater Determinant.
3. Show that the determinant is zero if two electrons occupy same state.
4. Calculate the bond orders and molecular term symbols for LiH and LiH^+ species.

Name: _____

Problem II 25 Pts

1. Derive atomic terms for a $3d^2$ electronic configuration (for instance Ti^{2+} cation), including J numbers, and order them according to their energy.

2. What other d-electronic configuration has same term symbols? How does ordering of terms change in this configuration?

Name: _____

Problem III 25 Pts

1. Explain the variational princple.
2. A trial function for 1s electron in hydrogen atom has a form of $\Phi(r) = e^{-\alpha r^2}$. Derive the normalization constant for the function.
3. The expression for energy as a function of α for the H-atom using above trial function is given by:

$$E(\alpha) = \frac{3\hbar^2\alpha}{2m_e} - \frac{e^2\alpha^{1/2}}{2^{1/2}\epsilon_0\pi^{3/2}}$$

Derive α that minimizes the energy and confirm that the variational principle holds.

Two useful relations, remaining integrals you will find in the provided sheet of paper:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$

$$E_H = \frac{m_e e^4}{16\pi^2\epsilon_0^2\hbar^2}$$

Name: _____

Problem IV 25 Pts

1. The first three hydrogen atomic wave functions for s-type electrons are given by following equations:

$$\Psi_{100} = \frac{1}{\pi^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\Psi_{200} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\Psi_{300} = \frac{1}{81(3\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$$

   Calculate the position of radial nodes and sketch the probability density, $r^2|\Psi(r)|^2$, of these wave functions.

2. Show that Ψ_{100} and Ψ_{200} are orthonormal to each other.

3. Compute the average distance from the nucleus for electron at 1s orbital.

Problem V 25 Pts

1. Plot a molecular orbital diagram for N_2 molecule.
2. Write down the ground-state electronic configuration for a following series of species: N_2^+, N_2, N_2^- and N_2^{2-}. Assign the bond order and determine the molecular term symbol.
3. Calculate the energy (in wavenubers) of allowed $3d\ ^2D \rightarrow 2p\ ^2P$ transitions in hydrogen atom. The energies of different terms are:

$$E(2p\ ^2P_{1/2}) = 82258.917\ \text{cm}^{-1}$$
$$E(2p\ ^2P_{3/2}) = 82259.272\ \text{cm}^{-1}$$
$$E(3d\ ^2D_{3/2}) = 97492.306\ \text{cm}^{-1}$$
$$E(3p\ ^2D_{5/2}) = 97492.342\ \text{cm}^{-1}$$

Show that the energies of these states are approximated well with the Rydberg law ($R_H = 109677.581\ \text{cm}^{-1}$).