

Materials Design: Theoretical Methods. 07/04/2017, 09.00 – 12.00, 5115.0013

- Read the exercises carefully
- **Explain all your answers (no explanation, no points)**
- Do not forget to write your name and student number.

Question 1 (10 points (2,3,2,3))

- a) Calculate the commutator $\left[\hat{x}, \frac{d^2}{dx^2} \right]$.
- b) Are the following functions eigenfunctions of $\frac{d}{dx}$? If yes, what are the eigenvalues?
- $f(x) = ax + b$
 - $g(x) = e^{ax}$
 - $h(x) = e^{ax^2}$
- c) Normalize the function $f(\varphi) = e^{i\varphi}$, where φ ranges from 0 to 2π .
- d) The wavefunction of particle in a 1-dimensional box is given by:
 $\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$, where L is the length of the box and n is the quantum number.
- For the ground state, what is the expression for the probability of finding the particle in the range x and $x + dx$?
 - What is the probability of finding the particle in the centre of the box ($x = L/2$)?

Question 2 (6 points (2,3,1))

- Write down the expression for the Hamiltonian of the helium atom (use atomic units). Explain each of the terms.
- If one wants to apply perturbation theory to the He atom (treat electronic repulsion as perturbation), what is the way to divide this Hamiltonian into $H^{(0)}$ and V ? Which system is described by $H^{(0)}$? What is the eigenfunction of $H^{(0)}$, $\Psi^{(0)}$?
- Give the general expression for the first order correction to the energy E^1 .

Question 3 (8 points (2,3,3))

You would like to carry out variation theory treatment of the CO molecule, where we consider only one π bond. The trial function ψ is then a linear combination of the atomic p_z orbitals of C and O, $\psi = c_1 p_z(O) + c_2 p_z(C)$.

a) Write down the secular determinant for the problem.

You are given the following matrix elements:

$$\langle p_z(O) | H | p_z(O) \rangle = -1 \text{ eV}$$

$$\langle p_z(C) | H | p_z(C) \rangle = 0$$

$$\langle p_z(O) | H | p_z(C) \rangle = -0.5 \text{ eV}$$

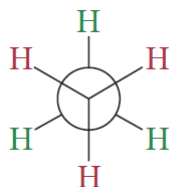
You also know that the $p_z(O)$ and $p_z(C)$ are orthogonal to each other and normalized.

b) Calculate the energy of the ground state. Comment on how this energy compares to the true energy of the system.

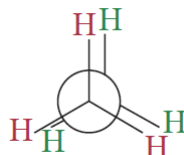
c) Calculate the corresponding wavefunction.

Question 4 (10 points (2,1,2,2,1,2))

You are interested in finding out the energy difference between the staggered and eclipsed conformations of ethane (see figure). You have thus carried out a Hartree-Fock geometry optimization of the two conformations, followed by vibrational analysis. You have used the STO-3G basis set.



a. Staggered conformation



b. Eclipsed conformation

a) How many atomic orbitals will you have in your calculation?

b) How many vibrational modes do you have?

In the table below you can find the results of your calculations.

| | Staggered ethane | Eclipsed ethane |
|--------------------------------------|------------------|-----------------|
| Total HF energy (a.u.) | -78.30618 | -78.301605 |
| Zero point vibrational energy (a.u.) | 0.089703 | 0.089313 |

c) Calculate the energy difference between the conformations; give your answer in kcal/mol (1 a.u.=627.52 kcal/mol). **Note: question 4 continues on the next page!**

- d) You would like to improve your calculation by using a larger basis set, 6-31G* (also called 6-31G(d)). How many atomic orbitals do you have now in your calculation?
- e) Which of the two basis sets will give a lower HF energy?
- f) How will the number of 2-electron integrals used in the 6-31G* calculation compare with the case of the STO-3G basis set?

Question 5 (11 points (2,2,2,2,3))

You are performing a closed shell Hartree-Fock calculation on the hydrogen fluoride (HF) molecule.

- a) Give the Hartree-Fock wavefunction for this closed shell system. Use abbreviations a, b, c , etc. for the molecular orbitals.
- b) The Hartree-Fock energy in this case is given by $E_{HF} = \sum_i 2h_{ii} + \sum_i \sum_j 2(ii|jj) - (ij|ji)$ Explain what the various terms are in this expression and indicate the limits of summations.
- c) What is the ionization potential of the molecule according to Koopman's theorem?
- d) You are also interested in the dissociation energy of this system. Do you expect closed-shell Hartree-Fock to perform well for dissociation energy of hydrogen fluoride? Explain why yes or why not.
- e) Give a short description of **one** of these methods:
- Configuration interaction (CI)
 - Density Functional Theory (DFT)
 - Møller-Plesset perturbation theory (MP)

Question 6 (10 points (2,4,4))

Different spinfunctions can be generated for a system with four electrons in four singly-occupied orbitals.

- b) Give the number of different spinfunctions that can be generated.
- c) For all spinfunctions that can be generated give the eigenvalues of the S^2 and S_z operators.
- d) Give the unnormalised spinfunction with $M_S = 1$ for the highest possible multiplet.

Question 7 (8 points (2,4,2))

- a) In a band structure plot, what is plotted on the y-axis and what on the x-axis?
- b) Sketch schematically 2 band structure plots: for a conductor and for an insulator.
- c) Say you perform a calculation on NaCl. You have one atom of each of the elements in the unit cell. Each atom is described by 10 basis functions (6-31G basis set). How many bands do you expect to find in the band structure diagram? How many of them below the Fermi energy level?

The End.

Examination mark: $\frac{\#p + 7}{7}$; final mark: $0.25 * \text{report} + 0.75 * \text{examination}$