

Exam Molecular Quantum Mechanics - MST

Course code: 4052MOLQM

14 January 2014, 9-12, Room C1

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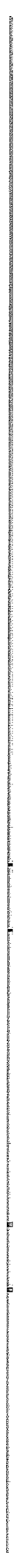
Theoretical questions: This written exam will contribute to 40% of the final grade. The remaining 60% is based on your written report on the computational project.

These theoretical questions are organized in seven parts with sub-questions and cover most of the material discussed during the course. For each question the associated points are indicated explicitly. The total number of points is 100.

Please clearly indicate on each sheet your name and student number.

Please remember at the end to fill out the evaluation form.

**Good luck!**



### 1) The Born-Oppenheimer approximation and the Potential Energy Surface

The total Hamiltonian of a system of nuclei and electrons can be written as follows:

$$\left[ -\frac{\hbar^2}{2m_e} \sum_i \nabla_{r_i}^2 - \frac{\hbar^2}{2M_I} \sum_I \nabla_{R_I}^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{i,I} \frac{Z_I e^2}{4\pi\epsilon_0 |r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |R_I - R_J|} \right]$$

where  $r_i$  are the electronic positions and  $R_I$  are the nuclear positions.

- Explain the meaning of each term in the Hamiltonian (7 pts)
- What is the physical basis for the Born-Oppenheimer (BO) approximation which allows to separate the electronic problem from the nuclear motion? (3 pts)
- The electronic Schrödinger equation within the BO approximation is written as:

$$\widehat{H}_{el} \psi(r; R) = E_{el}(R) \psi(r; R)$$

Which terms of the total Hamiltonian are included in the electronic Hamiltonian  $\widehat{H}_{el}$ ? Explain your answer. (5 pts)

- The electronic energy  $E_{el}(R)$  depends parametrically on the nuclear positions  $R$  and is called the Potential Energy Surface (PES). Make a schematic drawing of the PES for a diatomic molecule (e.g.  $H_2$ ) in the electronic ground state. In which way this curve will change if we consider two different diatomic molecules, e.g.  $H_2$  and  $N_2$ ? (5 pts)

Total question 1: 20 points



## 2) Variational principle:

- What does the variational principle (also called variational theorem) state? (5 pts)
- How can we use this principle in practical calculations? (5 pts)

Total question 2: 10 points

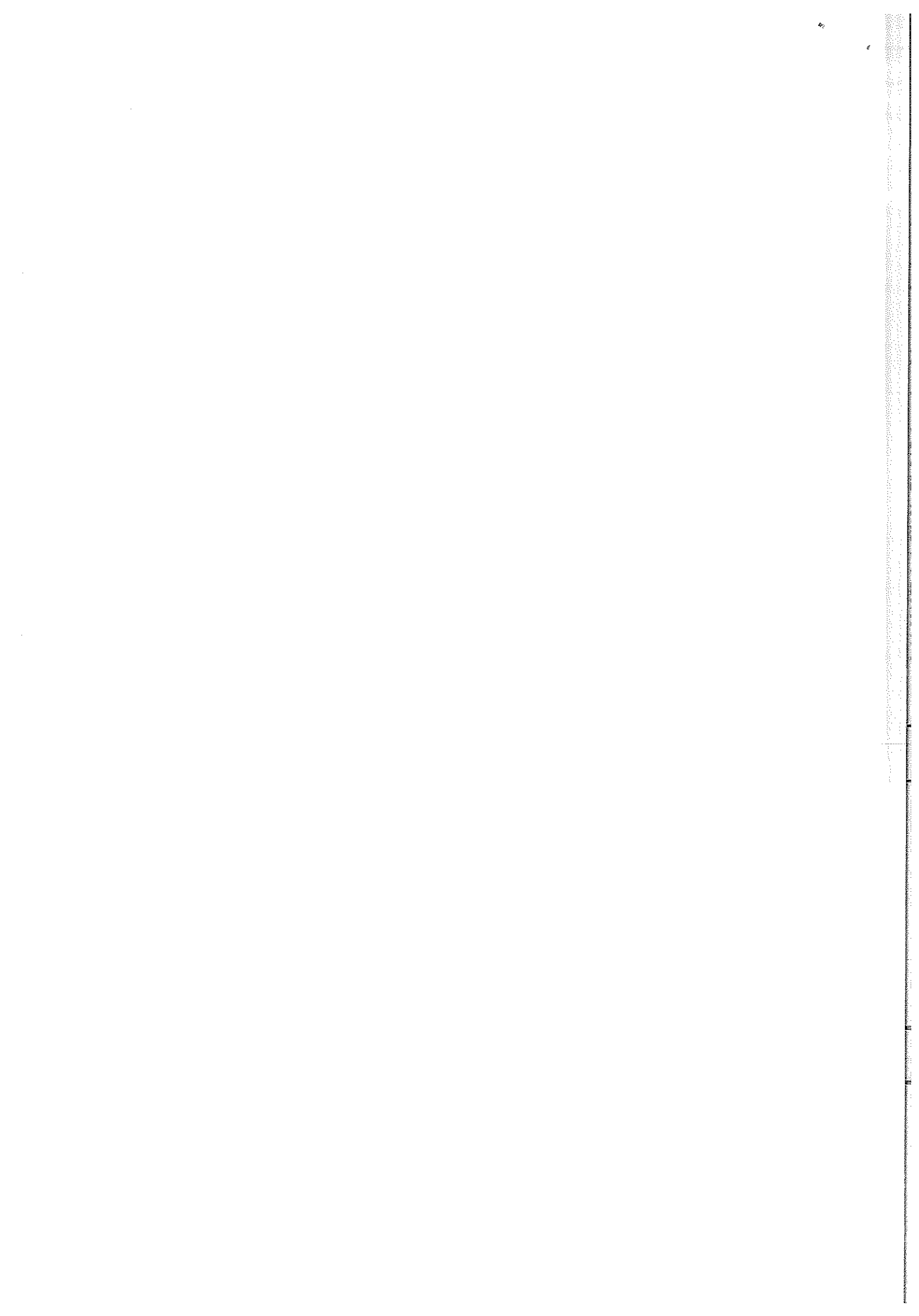
## 3) Force field

The form of the potential energy within the AMBER force field is given below (the indexes  $i$  and  $j$  in the last summations run over the number of atoms  $N$ ):

$$\begin{aligned} V(r^N) = & \sum_{\text{bonds}} k_b(l - l_0)^2 + \sum_{\text{angles}} k_a(\theta - \theta_0)^2 \\ & + \sum_{\text{torsions}} \sum_n \frac{1}{2} V_n [1 + \cos(n\omega - \gamma)] \\ & + \sum_{j=1}^{N-1} \sum_{i=j+1}^N f_{ij} \left\{ \epsilon_{ij} \left[ \left( \frac{r_{0ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{r_{0ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\} \end{aligned}$$

- Explain the meaning of each term in the potential energy. (10 pts)
- When the functional form in the first term of the potential  $\sum_{\text{bonds}} k_b(l - l_0)^2$  can be considered a valid approximation to the actual potential? (5 pts)
- Assume that in the system under consideration there are two types of covalent bonds, i.e., single C-C bonds and double C=C bonds, with characteristic frequencies of  $1000 \text{ cm}^{-1}$  and  $1600 \text{ cm}^{-1}$ , respectively. For which of these two types of bonds you expect the parameter  $k_b$  in the first term of the AMBER force field to be larger, and why? (5 pts)

Total question 3: 20 points



#### 4) Hartree-Fock approximation

- a) Write the Hartree-Fock wavefunction for a system with two electrons. (5 pts)
- b) Show that this wavefunction satisfies the Pauli principle. (5 pts)
- c) Imagine to compute the Hartree-Fock (HF) energy for the  $\text{Li}_2$  molecule. Each molecular orbital (MO) is written as a linear combination of basis functions. We begin calculating the HF energy with 10 basis functions, then with 20 basis functions, and finally with 30 basis functions. Plot schematically how these computed energies vary as a function of the basis set. (5 pts)
- d) We say that we have reached the Hartree-Fock limit if by increasing further the number of basis functions, the energy does not change any more significantly. Is this energy higher or lower than the exact ground-state energy? And why? (5 pts)

Total question 4: 20 points

#### 5) Electron correlation and Configuration Interaction (CI)

- a) What is the definition of electron correlation energy? (5pts)
- b) In the Complete Active Space Self-Consistent Field (CASSCF) method the electron correlation energy is computed by performing a full Configuration Interaction calculation within the active space. The smallest active space that we could consider includes two electrons in two orbitals, which is indicated with the notation (2,2). Which electronic configurations and thus Slater determinants are included in the CASSCF (2,2)? *Hint*: Draw a schematic molecular orbital diagram with corresponding occupation of all the possible electronic configurations within the active space. (5 pts)

Total question 5: 10 points





## 6) Density Functional Theory (DFT)

The Kohn-Sham equations in DFT are written as

$$\left( -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right) \phi_i(r) = \epsilon_i \phi_i(r)$$

where the index  $i$  runs from 1 to the number of electrons in the system. The effective potential in these equations contains the following terms:

$$V_{\text{eff}}(r) = \sum_I \frac{Z_I}{|r - R_I|} + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc}(r)$$

- Explain why we need an iterative self-consistent field (SCF) procedure to solve the Kohn-Sham equations? (5 pts)
- Which term in the effective potential is not known in its exact functional form and needs to be approximated? (5 pts)

Total question 6: 10 points

## 7) Molecular Dynamics

The Verlet algorithm in Molecular Dynamics simulations is given below:

$$R(t + \Delta t) = 2R(t) - R(t - \Delta t) + (\Delta t)^2 \frac{d^2 R(t)}{dt^2}$$

where  $R(t)$  is the position of one of the particles in the system at time  $t$  and  $\Delta t$  is the time step.

- How does the force field enter in the Verlet algorithm? (5 pts)
- Assuming that the highest vibrational frequency in the system corresponds to a time period of 10 fs, what would be a suitable value of the time step  $\Delta t$ ? (5 pts)

Total question 7: 10 points

