Exam MQM (MST) - theoretical questions –
17 January 2012, 9-12, Room C2

1) The H_2 molecule

a) Write the total Hamiltonian for the H_2 molecule. Explain the meaning of each term. (5 points)
b) Using the Born-Oppenheimer approximation, write the Schrödinger equation for the electronic problem and the Schrödinger equation for the nuclear motion. (5 points)
c) Explain the concept of potential energy surface (PES) as it emerges from the Born-Oppenheimer approximation. (5 points)
d) Make a schematic drawing of the PES for the H_2 molecule in the electronic ground state. (5 points)
e) How can you in principle compute this PES? (5 points)

Total question 1: 25 points

2) Hartree-Fock approximation

a) Does the Hartree-Fock wavefunction satisfy the Pauli principle? (3 points)
b) If this is the case, explain how this is mathematically achieved. (5 points)
c) Assuming that we are computing the Hartree-Fock energy using a very large basis set (Hartree-Fock limit), is this energy higher or lower than the exact ground-state energy? And why? (5 points)
d) How is the energy difference between the Hartree-Fock energy and the exact energy called? (3 points)
e) Suppose to perform a Hartree-Fock calculation on a molecule with N electrons. Each Molecular Orbital (MO) is written as a linear combination of M basis functions (with M>N). How many occupied MO's would you get? How many virtual orbitals? (Assume that we are dealing with a singlet state and each MO's can accommodate two electrons with spin up and spin down respectively) (4 points)

Total question 2: 20 points

3) Configuration Interaction (CI)

a) In the configuration interaction method there is a systematic way of improving the ground-state electronic wavefunction (and thus the ground-state energy). Is this statement true or false? Explain your answer.

Total question 3: 10 points

4) Density Functional Theory (DFT)

a) Explain why we need an iterative self-consistent field (SCF) procedure to solve the Kohn-Sham equations in DFT.

Total question 4: 10 points

5) Force field

a) What is the simplest functional form to describe a stretching energy term in a force-field? (5 points)

b) How many parameters need to be determined in this case for each stretching term? (5 points)

Total question 5: 10 points

6) Molecular Dynamics

a) What are the criteria that should be used in choosing the value of the time step in a Molecular Dynamics simulation? (5 points)

b) What are the main limitations of the Molecular Dynamics simulations based on empirical force-field? (5 points)

c) Is it possible to overcome these limitations and with which approach? (5 points)

Total question 6: 15 points

7) Quantum-Mechanics / Molecular Mechanics (QM/MM)

Can you describe a problem in which a hybrid QM/MM approach is an appropriate method to use?

Total question 7: 10 points