

Exam MQM (MST) - theoretical questions –
15 January 2013, 9-12, Room C1

1) The H₂ molecule and the Born-Oppenheimer approximation

Using the Born-Oppenheimer approximation we can separate the electronic problem from the nuclear motion. The electronic Schrödinger equation is written as:

$$\left[\hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \right] \psi(r; R) = E_{el}(R) \psi(r; R)$$

- Why the electronic energy $E_{el}(R)$ depends parametrically on the nuclear positions R ? (5 points)
- Which term in the electronic Hamiltonian above is a constant within the Born-Oppenheimer approximation? (3 points)
- The electronic energy $E_{el}(R)$ appears in the Schrödinger equation for the nuclei as an effective potential and is indeed called the potential energy surface (PES). Make a schematic drawing of the PES for the H₂ molecule in the electronic ground state. Indicate in your drawing the equilibrium distance and the dissociation energy (5 points)
- Consider now the H₂⁺ case obtained by extracting one electron from the H₂ molecule. Can you qualitatively indicate how the PES for H₂⁺ will differ from the H₂ molecule case? (You can add a schematic drawing of the PES for H₂⁺ as well) (5 points)

Total question 1: 18 points

2) Force field

You want to build up a force field for liquid water which is able to describe also the internal degrees of freedom of each water molecule.

- Which terms (bonded and non-bonded) should be included in the force-field? (5 points)
- Give the simplest functional form to describe the bending energy term and indicate which parameters need to be specified in this case. (5 points)

- c) Which term in the force field prevents two atoms of opposite charge to come too close to each other? (5 points)

Total question 2: 15 points

3) Hartree-Fock approximation

- a) Explain how a Slater determinant wavefunction satisfies the Pauli principle. (You can use a two-particle case to illustrate this point) (5 points)
- b) Consider the case of the Li_2 diatomic molecule. Imagine to compute the Hartree-Fock energy for this molecule by writing each molecular orbital (MO) as a linear combination of 10 basis functions. How many orbitals will you get by solving the corresponding secular equations (also called Roothaan equations)? How many orbitals are occupied and how many are empty (virtual orbitals)? Add a schematic drawing of the molecular orbital diagram in order of increasing energy indicating the occupation of each MO with up and down arrows. (10 points)
- Note: We are dealing with a singlet state and each MO's can accommodate two electrons with spin up and spin down respectively.
- 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)

Total question 3: 20 points

4) Configuration Interaction (CI)

- a) Which Slater determinants are included in the Configuration Interaction Single (CIS) wavefunction approximation?

Total question 4: 10 points

5) Density Functional Theory (DFT)

The Kohn-Sham equations in DFT are written as

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

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:

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

- Explain why we need an iterative self-consistent field (SCF) procedure to solve the Kohn-Sham equations? (8 points)
- Which term in the effective potential is not known exactly? Mention some of the most commonly used approximations. (7 points)

Total question 5: 15 points

6) Molecular Dynamics

The Verlet algorithm in Molecular Dynamics simulations is:

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

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

- How does the force field enter in the Verlet algorithm? (6 points)
- What are the criteria that should be used in choosing the value of the time step? (6 points)

Total question 6: 12 points

7) Ab initio Molecular Dynamics

In ab initio molecular dynamics we derive the forces acting on the nuclei by solving the quantum-mechanical electronic problem, usually within DFT, for each time step. There are two possible strategies in ab initio MD: (i) the Born-Oppenheimer MD and (ii) the Car-Parrinello extended Lagrangian scheme. Explain shortly what is the main difference between these two approaches?

Total question 7: 10 points