

Exam: Modern Quantum Chemistry (MQC)

Date: 22 January 2016

Place: Havinga zaal, Gorlaeus

Time/duration: 3 hours (13.30-16.30)

Lecturer:

Dr. F. Buda

Second lecturer reviewing the exam: Dr. Mark Somers

This written exam will contribute to 80% of the final grade. The remaining 20% is based on the written reports on the computer exercises.

These theoretical questions are organized in 8 sections 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.

Allowed information sources and tools:

Calculator

Please clearly indicate on each sheet: name and student number

Please write with blue or black ink and as clearly as possible.

Good Luck!

Born-Oppenheimer approximation

1. Explain the following statement:
The concept of an "equilibrium molecular structure" relies on the Born-Oppenheimer approximation. (4 p)
2. Assuming that for a given nuclear geometry the energy difference between the lowest electronic state and the first excited state is 0.1 eV, do you expect that non-adiabatic coupling might play a role in this region of the Potential Energy Surface? (Hint: Keep in mind the characteristic energy scale of the nuclear motion. Energy unit conversion: $1 \text{ eV} = 8065.6 \text{ cm}^{-1}$). (4 p)
3. Draw a schematic potential energy curve for a diatomic molecule. Which property (or properties) of the molecule can you extract from this curve? (4 p)

MO theory and variational principle

4. Describe the concept of the Molecular Orbital approximation for a many-electron system. (4 p)
5. What does the variational principle state and how it can be used in actual calculations? (4 p)

Hartree-Fock approximation

6. Which important requirement of a many-electron wavefunction is satisfied by the Slater determinant? (3 p)
7. The Hartree-Fock energy contains terms called "exchange integrals". Which basic principle is at the basis of these energy terms? Are these terms also present in the Hartree approximation? (4 p)

8. To obtain the Hartree-Fock equations we have to minimize the following Lagrangean L

$$L = E^{HF} - \sum_{ij} \epsilon_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})$$

with respect to a variation in the molecular orbitals ψ_i . The first term in the Lagrangean is the Hartree-Fock energy. What is the reason for including the second term in the Lagrangean? (4 p)

9. Describe the concept of the Hartree-Fock limit and how it can be estimated in practical calculations. (4 p)

Beyond HF (Correlation Energy and Configuration Interaction)

10. How can we define the electron correlation energy? (4 p)
11. In the Configuration Interaction (CI) approach, there is a systematic way of improving the accuracy of the computed electronic ground-state energy. Is this statement true or false? Explain your answer. (4 p)
12. Based on the Hartree-Fock orbital energies we can select the active space of orbitals for a CASSCF (Complete Active Space Self Consistent Field) calculation. Draw a schematic orbital energy diagram to explain the meaning of the notation CAS (4,4) used in a CASSCF calculation. (4 p)

Density Functional Theory (DFT)

13. What is the central physical quantity in DFT and how is it related to the many-electrons wavefunction? (3 p)
14. What does the first Hohenberg-Kohn theorem state? (4 p)
15. Within Kohn-Sham DFT, what is the expression for the electronic kinetic energy term? (4 p)

16. Describe briefly the Local Density Approximation for the exchange-correlation energy functional. (4 p)

Force-field and Molecular Dynamics simulations

17. In the AMBER force field the stretching energy term is written as:

$$E_{stretch}(R^{AB}) = \frac{1}{2}k^{AB}(R^{AB} - R_0^{AB})^2$$

In this expression R^{AB} represents the distance between two atoms A and B and R_0^{AB} their equilibrium distance. Discuss how this functional form differs from the more realistic Morse potential. (4 p)

18. Discuss why in normal thermodynamic conditions (room temperature and standard atmospheric pressure) the simpler harmonic approximation for the covalent bond stretching energy is still a valid approximation. (4 p)
19. What are the parameters needed in the electrostatic energy term of a force-field? Mention at least one method to compute these parameters. (4 p)
20. Derive the Verlet algorithm used in molecular dynamics simulations for the numerical integration of the Newton's equations of motion. [Hint: write the Taylor expansion of $R(t+\Delta t)$ and of $R(t-\Delta t)$]. (6 p)
21. Explain the concept of "rare event" in the context of Molecular Dynamics simulations. (4 p)

Ab initio Molecular Dynamics

22. In the Car-Parrinello method for ab initio MD we have to solve simultaneously the following coupled equations of motion for the nuclei and for the Kohn-Sham orbitals:

$$M_I \frac{d^2 R_I}{dt^2} = -\nabla_I E^{KS}[R, \phi]$$

$$\mu \frac{d^2 \phi_i}{dt^2} = -\frac{\delta E^{KS}}{\delta \phi_i^*} + \sum_j \lambda_{ij} \phi_j$$

- a. Which criterion should be used for the choice of the mass parameter μ that appears in the equations for the electrons? (2 p)
- b. In the Car-Parrinello method, which dynamical degrees of freedom will limit the choice of the maximum integration time step Δt ? Explain your answer. (2 p)

23. In which cases the use of ab-initio MD becomes crucially important to overcome some of the limitations of empirical force-field MD? (4 p)

Hybrid QM/MM method

24. Give an example of a problem for which a hybrid quantum-mechanics / molecular-mechanics (QM/MM) approach might be a good computational strategy. (2 p)
25. Which type of interactions will be present in the hybrid part of the Hamiltonian that couples the MM atoms with the QM atoms? (3 p)
26. Explain the concept of "link atom" in the context of the QM/MM method. (3 p)