

Exam (resit): Modern Quantum Chemistry (MQC 2016-2017)

Date: 1 May 2017

Place: Gorlaeus Lab, lecture room 06

Time/duration: 3 hours (14.00-17.00)

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. For those who have followed the course in previous academic years, the grade is based entirely on this written exam.

These theoretical questions are organized in 7 sections 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 (BO) approximation and potential energy surface (PES)

1. Given the following ansatz for the total wavefunction:

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \sum_i \psi_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}, t)$$

where $\psi_i(\mathbf{r}; \mathbf{R})$ are the eigenfunctions of the electronic Hamiltonian, show that

$$\int d\mathbf{r} \psi_j^*(\mathbf{r}; \mathbf{R}) i\hbar \frac{\partial}{\partial t} \sum_i \psi_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}, t) = i\hbar \frac{\partial \chi_j(\mathbf{R}, t)}{\partial t}$$

(Hint: make use of the property that the eigenfunctions are orthonormal to each other)

(3 points)

2. Assuming that the nuclei behave as classical particles, the equations of motion for the nuclei can be written in terms of the Newton's second law of motion. Within the Born-Oppenheimer approximation, which role does the electronic energy play within the nuclear equations of motion?

(3 points)

3. Make a schematic plot of the potential energy surfaces in the ground state and in the first excited state along a reaction coordinate to qualitatively describe in which circumstances the Born-Oppenheimer approximation breaks down?

(3 points)

Variational principle and secular equations

4. What does the variational principle state and how can we make use of it in practical calculations?

(3 points)

5. Given two trial wavefunctions ψ_1 and ψ_2 , and the electronic Hamiltonian operator \widehat{H}_e , how can we judge which one of the two trial wavefunctions approximates better the ground state? (3 points)

6. Describe how we can transform the problem of solving the Schrödinger equation into the solution of a set of linear equations. (The whole mathematical derivation is not required; it is enough to indicate the essential steps of this procedure) (4 points)

Hartree and Hartree-Fock approximation

7. What is the Hartree ansatz for the many-electron wavefunction? (3 points)
8. Which fundamental quantum mechanical property of the many-electron wavefunction is violated by the Hartree product? (3 points)
9. The Hartree equations can be written as follows:

$$\hat{h}_i^{eff} \psi_i = \epsilon_i \psi_i, \text{ with } i=1,2,\dots,n_{el},$$

where the effective Hamiltonian contains the following terms:

$$\hat{h}_i^{eff} = -\frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{I=1}^N \frac{Z_I e^2}{4\pi\epsilon_0 \|\mathbf{R}_I - \mathbf{r}_i\|} + \sum_{j \neq i} \int d\mathbf{r}_j \frac{e^2 \psi_j^*(\mathbf{r}_j) \psi_j(\mathbf{r}_j)}{4\pi\epsilon_0 \|\mathbf{r}_j - \mathbf{r}_i\|}$$

- (a) What is the meaning of each term in the effective Hamiltonian? (3 points)
- (b) Why the Hartree method is a mean-field theory? (3 points)
10. What is a Slater determinant? (3 points)
11. Do the orbital energies obtained by solving the Hartree-Fock equations have a direct physical meaning? (3 points)

12. Make a schematic plot of the Hartree-Fock energy computed for a molecule as a function of the number of basis set functions. Indicate in this plot where the exact ground state energy would be located with respect to the Hartree-Fock limit.
(3 points)

Correlation Energy and Configuration Interaction

13. How can we define the electron correlation energy?
(3 points)
14. How do we construct the CASSCF (complete active space self-consistent-field) wavefunction? (Consider e.g. an active space of 4 electrons in 4 orbitals)
(3 points)
15. The configuration interaction (CI) energies can be determined from the N roots of the CI secular equation:

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & H_{1N} \\ H_{21} & H_{22} - E & \dots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \dots & H_{NN} - E \end{vmatrix} = 0$$

What is the definition of the matrix elements H_{mn} ?
(3 points)

Density Functional Theory (DFT)

16. What does the first Hohenberg-Kohn theorem state?
(3 points)
17. A consequence of the first Hohenberg-Kohn theorem is that the expectation value of the Hamiltonian for a given external potential $V_{nuc,el}$ can be written as

$$E_{V_{nuc,el}}[\rho] = \int \rho V_{nuc,el} d\tau + F_{HK}[\rho]$$

In which sense the functional F_{HK} is a universal functional?
(2 points)

18. In the Kohn-Sham formulation of density functional theory the energy functional is decomposed in several contributions. Describe these contributions and mention which contributions can be calculated exactly and which one has to be approximated.

(4 points)

19. The Kohn-Sham equations can be written as

$$\left(-\frac{1}{2} \nabla^2 + \sum_I \frac{Z_I}{|r - R_I|} + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc}(\rho(r)) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r),$$

where the index i runs from 1 to the number of occupied orbitals.

In which way are these equations coupled to each other?

Discuss briefly the procedure used to solve these equations.

(4 points)

Force-field and Molecular Dynamics simulations

20. Write down the expression of the harmonic potential used to describe the bond stretching energy term in a force-field, such as AMBER.

- Which parameters need to be specified for this term?
- What is the main limitation of such an approximation?

(4 points)

21. Write down the electrostatic potential energy contribution in a force field. Which parameters need to be specified for this interaction? (3 points)

22. Explain briefly the basic idea of molecular dynamics simulations. (3 points)

