

Exam: Modern Quantum Chemistry (MQC)

Date: 22 April 2016

Place: HB218, 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 7 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

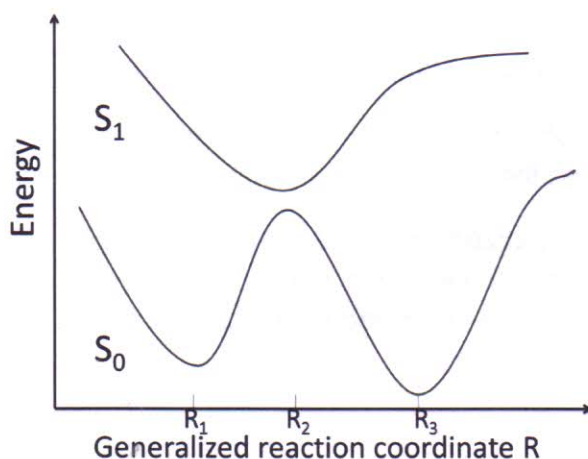
Please clearly indicate on each sheet: name and student number

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

Good Luck!

Born-Oppenheimer approximation

1. Consider the schematic potential energy surfaces (PES) corresponding to the electronic ground state (S_0) and excited state (S_1) shown in the Figure below. For which value(s) of the generalized reaction coordinate R do you expect the Born-Oppenheimer approximation to fail? Explain. (3 points)



2. By considering the general ansatz for the total wavefunction of the form

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

where ψ_i are the orthonormal eigenfunctions of the electronic Hamiltonian with eigenvalues E_i , we derive the following nuclear Schrödinger equation:

$$i\hbar \frac{\partial \chi_j(\mathbf{R}, t)}{\partial t} = (\hat{T}_{nuc} + E_j(\mathbf{R})) \chi_j(\mathbf{R}, t) + \sum_i \sum_I \frac{\hbar^2}{m_I} \int d\mathbf{r} \psi_j^*(\mathbf{r}; \mathbf{R}) \left(-\frac{1}{2} [\nabla_I^2 \psi_i(\mathbf{r}; \mathbf{R})] - [\nabla_I \psi_i(\mathbf{r}; \mathbf{R})] \nabla_I \right) \chi_i(\mathbf{R}, t)$$

Which term(s) is (are) neglected within the Born-Oppenheimer approximation and on which basis this assumption is justified? (4 points)

3. Write down explicitly all the terms in the total Hamiltonian for the hydrogen molecule (H_2). Which term(s) should be included in the non-relativistic electronic Schrödinger equation? Which term(s) of the Hamiltonian is (are) responsible for the electronic energy being parametrically dependent on the nuclear coordinates? (4 points)

Variational principle

4. Let's consider an expansion of the electronic wavefunction Φ in a finite set of linearly independent (basis) functions φ_i :

$$\Phi = \sum_i c_i \varphi_i$$

Evaluate the expectation value of the electronic Hamiltonian using the definition of overlap integrals and resonance integrals. (5 points)

5. Based on the expression for the energy obtained in the previous question (4), how can we now make use of the variational principle? What is the advantage of using a linear combination of known basis functions? (4 points)

Hartree and Hartree-Fock approximation

6. Consider a molecular system with three electrons. The total electronic wavefunction will then in general be a function of the coordinates of all the electrons: $\Psi(r_1, r_2, r_3)$
Write the Hartree approximation for the wavefunction of this system and calculate its norm under the assumption that each molecular orbital is normalized to one. (4 points)
7. Write the Hartree-Fock wavefunction for a system with two electrons and show that this wavefunction satisfies the Pauli principle. (3 points)
8. Suppose to perform a restricted Hartree-Fock (HF) calculation on methane (CH_4).
a. How many molecular orbitals (MOs) will be used to construct the Hartree-Fock Slater determinant? (2 points)

Density Functional Theory (DFT)

13. The first Hohenberg-Kohn theorem proves that the electronic energy can be written as a functional of the electron density. What does the second Hohenberg-Kohn theorem tell us about this functional? (3 points)
14. Write down the electron density in terms of the single-particle Kohn-Sham orbitals. (2 points)
15. 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. Explain why these equations are coupled to each other and describe the procedure to solve them. (4 points)

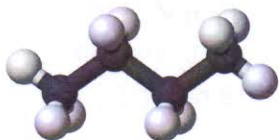
Force-field and Molecular Dynamics simulations

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

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

- What is the physical meaning of the parameter k^{AB} ? (3 points)
 - In which circumstances you would expect this simple functional form to be valid in describing the bond stretching dynamics? (3 points)
 - Consider a molecule in which you have two types of covalent bonds, e.g. single C-C bonds and double C=C bonds with characteristic frequencies of 1000 cm^{-1} and 1500 cm^{-1} , respectively. For which of these two bonds do you expect the parameter k^{AB} to be larger and why? (3 points)
17. Describe the Lennard-Jones potential and discuss the physical origin of the repulsive and attractive parts. (4 points)

18. Consider the butane molecule (C_4H_{10}) represented below:



We have to construct a force field for this molecule: which terms should be included? (5 points)

19. According to the ergodic hypothesis, how can we calculate ensemble averages with Molecular Dynamics simulations? (3 points)

20. How can you test the stability and accuracy of the integration algorithm in Molecular Dynamics simulations? (3 points)

Ab initio Molecular Dynamics and Hybrid QM/MM method

21. An excess proton in water diffuses through the hydrogen bond network of water molecules through the formation and concomitant cleavage of covalent bonds involving neighboring molecules. This is known as the Grotthuss mechanism. Which computational method would you use to describe this process? Explain why. (3 points)

22. In the Car-Parrinello method for ab initio MD an extended Lagrangian is defined that includes both nuclear and electronic degrees of freedom as classical dynamical variables in the system:

$$L_{CP} = K_e + K_I - E^{KS}[\{\phi_i\}, \{R_I\}] + \sum_{i,j} \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij})$$

What is the role of the last term in the Lagrangian? (3 points)

23. What is the main difference between the direct Born-Oppenheimer Molecular Dynamics (BO-MD) approach and the Car-Parrinello (CP-MD) method for ab initio MD? (4 points)

24. In which of these two approaches (BO-MD vs. CP-MD) one can use a larger time step and why? (4 points)
25. How can you deal with the electrostatic interactions between the MM atoms and the QM atoms in the hybrid QM/MM approach? (4 points)