CHE 458 / 506, Spring 2010: Physical Chemistry 2 "Quantum Chemistry"

Instructor: Jochen Autschbach

Syllabus Revision 1.5. Last updated: January 9, 2010

Time, Dates, Location, Office Hours, Contact Info

Class Room: 4 Knox, North Campus
Lecture Times: T,R 1100 – 1220
First lecture: Tue, Jan 12, 2010
Last lecture: Thu, Apr 22, 2010
Office Hours: Tue, 4 – 5 pm, or by appointment, NSC Room 313
Holidays etc.: Spring Break March 8 – 13
Deadline for course resignation: Friday, Mar. 26

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Course web site at UBLearns, https://ublearns.buffalo.edu. The course web site will contain downloadable (PDF) versions of the syllabus, all assignments, and most handouts (except where restricted by copyrights). You can also find some links to quantum chemistry program sites, announcements about the course, assignments, and other material.

Textbook

The recommended textbook for the course is: Thomas Engel: *Quantum Chemistry & Spectroscopy*, © 2006 Pearson Education (published by Benjamin Cummings), ISBN 0–8053–3843–8. The textbook is not required; the lecture will proceed according to the instructor's notes which are posted at UBLearns.

Other excellent quantum chemistry textbooks from which handouts might be supplied are:

– Ira N. Levine: "Quantum Chemistry", 5th ed., Prentice Hall (2000)

– Atkins & Friedman: "Molecular Quantum Mechanics", 3rd ed., Oxford University Press (1997)

Please note that the books by Atkins and Levine are also suitable as textbooks for this course. If you have a chance to compare the books (library, bookstore) I recommend that you buy the textbook that you find most easy to read. The textbook will mostly be used as a reference for the material presented in the course, and to provide additional reading material. The recommended text by Engel has some nice interactive material available on–line with the book purchase. I also recommend the textbook for additional exercises. There is a student's solution manual available. I will present the lectures on the blackboard from my own notes, and on occasion use transparencies (with handouts for everybody) and the classroom's computer equipment. Your lecture notes will be the prime source of information when preparing for an exam or working on the assignments. The textbook will also provide alternative derivations of important results, numerous problems & answers, and it will serve as a quick tutorial in case you forgot most of your calculus. There will be a few reading assignments for which I recommend the "official" textbook, but the same material is also covered in the two other books, too. The chapters listed in the syllabus refer to the text by Engel, but the course material is also covered by the other books.

Further, I will provide Handouts from McEvoy & Zarate: "Introducing Quantum Theory", handouts from Wilson: "Quantum Psychology", handouts from Hofstadter: "Metamagical Themas", and one of the chapter's from levine's textbook.

Overview, Goals

"What exactly is a molecular orbital?"

If you have ever wondered what a molecular orbital really is, you will find out in CHE506. The answer to this question is the central topic of the course. Apart from this, we'll explore basic quantum chemistry, the nature of the chemical bond, the theoretical basics of various spectroscopic tools which are most frequently applied in chemical research, and basic computational chemistry as well as how to use the "Gaussian" (TM) quantum chemistry program through the graphical interface "webMO" (www.webmo.net). Computer resources will be provided by UB's Center for Computational Research.

These days quantum chemistry programs are not only used by theoreticians but also in many experimental groups in order to assist the research. The course is designed to give you an overview of frequently applied computational methods. This includes the underlying theoretical approach as well as practical computational exercises. The first part of the course will cover basic quantum mechanics and the discussion of simple model systems. Next, the molecular orbital (MO) model and its application to molecules will be introduced. Exercises will emphasize both the qualitative and quantitative aspects of the MO model. Further, common computational methods that build upon the MO model will be discussed. The last part will be concerned with the calculation of spectroscopic molecular properties and visualizations.

By the end of the course you should have a clear understanding of the origin of molecular orbitals in chemistry, how they are used to understand chemical binding, and know how simple quantum model systems can be applied to understand spectroscopic data. Further, you should be able to understand basic computational chemistry lingo which will enable you to read contemporary research literature that contains results from quantum chemical computations, and to assess the quality of such calculations. Finally, you will learn how to carry out your own quantum chemical calculations for small molecules.

It is strongly recommended that you study the relevant pages in the textbook *before* the lectures.

Contents

(Chapter numbers refer to Engel's textbook):

Week 1 (see Math appendices in the textbook): Mathematical tools needed for this course. Reading assignment: Linear Algebra handout. Homework assignment: Functions, vectors, matrices.

Week 2 (Chapters 1 – 3): Historical overview: Why Quantum Theory? Postulates of quantum mechanics, particle waves, time-dependent and time-independent Schrodinger equation, atomic units. Reading assignment (handout): Heisenberg's uncertainty principle.

Week 3 (Chapters 1–4,7): Recap of undergraduate PChem: Particle–in–a–Box (PB), Harmonic oscillator, quantum effects and uncertainty principle. Homework assignment: PB and Harmonic oscillator.

Weeks 4+5 (Chapter 7 & 9): Hydrogen atom, spherical coordinates, angular momentum, quantum numbers, atomic orbitals, how to graphically display atomic orbitals. Assignment: H–atom and angular momentum.

Week 6 (Chapter 6): Electron spin, spin operators, spin functions, total angular momentum, spin-orbit coupling (one electron systems only).

Mid Term Exam 1 (Thursday of Week 6)

Week 7 (Chapter 10 & 12): Many electron systems and the molecular orbital (MO) model, many electron Hamiltonian, Born-Oppenheimer separation, correlated electrons, Hartree product.

Week 8 (Chapter 10 & 12): Antisymmetry and Pauli principle, Slater determinants, spin and spatial orbitals, Pauli exclusion principle. Hartree–Fock method — Part 1. Assignment: Essay about the MO model (about

3 to 5 pages)

Spring break (Week 9)

Week 10 (Chapter 10 & 13): Hartree–Fock method — Part 2, Hartree–Fock equations, spin and energy, Hund's rule. Assignment: singlet vs. triplet energies

Week 11 (Chapter 14 & 16): Basis set approximation, secular equation, generalized eigenvalue problem, variational principle, types of basis sets. Computational assignment: Calculating H_2O and NH_3 with various basis sets, MO coefficients, MO diagram

Week 12 (Chapter 10 & 12): The chemical bond: kinetic energy and virial theorem, H_2 and H_2^+, minimal basis sets, 1st row diatomics, electronic configurations, excited states, Koopmans' theorem.

Mid Term Exam 2 (Tuesday of Week 13)

Week 13 (based on handouts from Levine): Beyond the MO model (a survey): CI method, equivalence of lowest order CI and VB functions for H_2, truncated CI, coupled cluster method, DFT. Handouts from Levine's book (DFT). Computational assignment: Calculate H_2 potential curve with various methods and basis sets.

Week 14 + 15 (Chapter 16 & 8): Potential energy surface, geometry optimizations, harmonic approximation, normal coordinates, vibrational spectra of polyatomic molecules, symmetry classifications. Computational assignment: Calculation of optimized structures and vibrational frequencies of molecules, symmetry considerations

Week 16: Final exam. Date, location, and time to be announced

Exams, Assignments, Grades, Policies

The course's grade will be based on 6 assignments, one essay, two mid term exams, and a final exam (see below for details). I do not explicitly grade your attendance. However, each class of the course builds upon the material covered until that point. Thus, you can expect difficulties if you do not attend the lectures. The grading will be adjusted somewhat depending on the overall performance of the class. I.e. if you get 50% for an assignment that does not necessarily mean a bad grade unless most other students have much higher scores consistently (they usually do). Typically, however, you should not expect a grade of A− or better unless you score higher than 85% in the exams and in the assignments. Based on the student performance of the last 5 years in this course it is unlikely that adjustments to the grading scheme will be necessary. Last year's grading scheme was: A: 85% or better, A-: 80, B+: 75, B: 70, B-: 65, C-: 50. Undergraduate students who take this course may receive a bonus between 5 and 10% when determining the final grade because of their additional course workload.

Assignments typically consist of short calculations that are designed to get you familiar with the (sometimes strange) properties of quantum systems. They occasionally provide additional information about such systems that is not covered in the lectures (often as part of the bonus questions). I will provide detailed solutions for each assignment. Exam questions will be different. I will rarely ask you to calculate something during an exam, but rather ask questions of the type: "Explain what an orbital is?", "What is the origin of Hund's rule?", etc., where the answer consists of a mix of text and some very basic equations. Or I will ask you to sketch graphs of, say, radial functions of atomic orbitals for the hydrogen atom or the potential curve of a diatomic molecule, and explain some chemical or spectroscopic facts with the help of these graphs. Multiple choice questions will be used sparingly.

The most successful students will not only be able to carry out correct calculations for the assignments, repeat a definition, or reproduce graphs and equations that were shown in the lectures, but also understand the motivation behind the concepts introduced in this course. They will be able to transfer their knowledge in order to solve problems that are not exactly the same as those from the lecture or from the homework.

If they make mistakes in the assignments or an exam, they find out, with the help of the solutions that I provide, what the origin of their mistake was. They won't make the same mistake twice.

For most assignments and exams I will provide a bonus question worth about 10% of the total score. It can be used to compensate for mistakes made elsewhere in an assignment or other assignments. Therefore, the maximum score for assignments is 100% plus the score of the bonus question. For exams, however, correct answers of a bonus question can only compensate for errors made in the same exam. The maximum score for an exam is 100% even if all question plus the bonus question are answered correctly.

Assignments are due at the end of the lecture one week after they were handed out. Late submission will not be accepted. Academic integrity will be strictly enforced (e.g. regarding plagiarism). Make sure you contact me before you hand in an assignment or paper in case you are not sure what is meant by "academic integrity".

Grade details:

Two mid term exams (during regular lecture times), 70 minutes each. Total of 35% of final grade (17.5% each)

3 assignments with theoretical problems, 1 essay, 3 computational assignments (5% each, total of 35% of final grade)

Final exam, 110 minutes (30% of final grade)