1
Introduction

1.1
Basics of Computational Chemistry

Computational chemistry has become an indispensable tool for the experimental chemist. Today, computational chemistry is used by the chemistry community to back up experimental results not only in many scientific publications, but also in textbooks and theses. The level of involvement varies strongly. Computational chemistry is, for example, employed to interpret and rationalize results, to compare experimental with simulated data, to get an idea of a molecular structure, or just to create a graphical representation of a molecule, its molecular orbitals or its electrostatic potential. Though only a small percentage of all chemists would call themselves computational, quantum or theoretical chemists, computational chemistry is indeed applied by the majority of modern chemists. This is due to the tremendous progress that the field has made in the past years. In contrast to the time a few decades ago, today we have powerful computers and – probably more importantly – modern, easy-to-use and robust chemistry software.

Progress in computational chemistry has allowed a new quality of research in chemistry. Most modern chemists actively use the computer at various levels of their work, for example to get an idea of the three-dimensional structure of molecules of interest, and to understand chemical bonding, stability and so on. It is now possible to calculate the stability of a molecule, or even a reaction path, before going into the laboratory to try the synthesis in practice. Also, it is common practice to simulate properties and to compare them with experiment, most importantly for infrared (IR), Raman and nuclear magnetic resonance (NMR) spectra.

Still, this exciting development comes with a dark side. Very often, the calculations are performed using the "black-box" strategy: well-established recipes are used to obtain a computational result of a particular problem, while very little is known about what exactly happens in the computer simulation. This unsatisfactory state of affairs

is not the fault of today's experimental chemists. While the theoretical chemist receives all the education that is necessary to understand laboratory synthesis or analytics, sufficient theoretical chemistry education does not reach students who concentrate on experiments. We think that the reason for this problem stems from the history of computational chemistry: it is necessary to know a great deal of higher mathematics to develop quantum chemical methods, and a lot of programming, programming languages, and computer hardware to write efficient computer algorithms. Most chemists are not used to apply higher mathematics and are not trained in computer science or advanced quantum physics. This makes communication between experimentalists and theorists difficult.

Furthermore, when lecturing computational chemistry, it is difficult if not impossible to find typical "example problems" to practice what has been taught in class. Computer laboratory courses, where students have the chance to solve example problems on computers, are a way to bridge this gap. Again, courses for training the fundamental methods and algorithms that are used in a computer simulation are rare, and laboratory courses are usually unique, developed locally to accompany a certain lecture. In worst cases they are even restricted in providing technical instructions for the use of some special software.

1.2
Aim of This Book

The headmost aim of this workbook is to reduce this gap. We have demonstrated in several years at Dresden University of Technology that second- and third-year chemistry students can understand the basic principles of computational chemistry and create a solid basis to advanced quantum and computational chemistry education.

We do not expect that an undergraduate chemistry student will master tasks that are taught to physicists in their Master courses, such as many-body quantum mechanics, or which involve advanced mathematics, such as how to solve multi-dimensional partial differential equations. Instead, we avoid the whole topic of how the electronic Schrödinger equation of a molecule has to be solved. This is a subject for later studies. We concentrate instead on the concepts that are necessary to understand many phenomena in chemistry, and must be understood before computational chemistry can be used effectively in a more elaborate way. Whenever mathematics is necessary – and this is quite often the case – we try to be as explicit as possible and to illustrate the procedure to arrive at the result in great – for some people's taste probably too great – detail. However, we are sure that many students will appreciate these efforts, since they are often skipped or implied

in many textbooks. Certain examples are carried out using spreadsheets. They allow one to apply geometry optimization or molecular dynamics algorithms, and students, even those without any programming knowledge, are able to "program" an algorithm for doing important tasks of computational chemistry.

This book comes with a CD, containing a full `Linux` operating system based on the `Knoppix` Live system, enriched with various computer programs that allow the computer experiments to be practiced on any reasonable Intel x86-compatible computer that can boot from a CD drive (Windows, Mac OS, `Linux`). It is also possible to work more effectively by running the CD as guest operating system in a virtual machine, by copying it to a pen drive, or by copying the book-related software to an existing `Linux` installation. This allows a straightforward application of the software in any computer pool or on any laptop or office PC without disturbing the local hard- and software setup. File transfer is easily possible through USB data storage media or the Internet. The system is kept up to date on a web site accompanying this project at http://www.compchem.jacobs-university.de/workbook.html.

It is, however, not necessary to use the software delivered with this book. All chapters are formulated in a neutral way and can be solved by employing different software to the taste, for the convenience and within the budget of the reader.

1.3
How to Use This Book

This book can be used in various ways. *Instructors* may take advantage of the book to design quickly a computational chemistry laboratory course. The book comes with all the software necessary to run the experiments, and the accompanying CD can be installed in any computer laboratory, even on the fly, leaving the standard system untouched. It might also be a convenient basis to set up some selected computer laboratory sessions, which may accompany courses in general chemistry, physical chemistry, but possibly also in analytic, organic or inorganic chemistry. The computer experiments can be easily adopted to include different example systems. It might also be interesting to distribute selected chapters – or modifications of it – as homework hands-on tasks: the individual chapters are self-contained, and detailed instruction is given to be able to solve the problems. To assist this purpose, the accompanied CD can be redistributed without charge, and newer versions will be available through the Internet.

For *students*, the book tries to close the gap between theory lectures and textbooks on the one hand and applications in typical "black-box computer programs" on the other, where it is hard to

understand what exactly happens in the computer calculations. This book offers the possibility to practice various topics learned in class and to take the first steps in using professional computational chemistry software. The experiments may invite one to use computational chemistry in more advanced situations, and the distributed methods and software are a solid basis to do so.

1.4
Structure of This Book

Each chapter contains one type of computer experiment and is structured in sections following the same pattern:

- **Aim:** The aim of the computer experiment is briefly described. Here you can find the methods that will be introduced as well as the chemical problems that will be tackled.

- **Theoretical background:** As far as necessary the theory needed for the chapter will be reviewed. Bibliography to milestone papers in the original literature are given as well as the recommendations of standard textbooks. As this workbook is not intended to replace a standard text, we cover only the part of the theory that is relevant for the computer experiment, and sometimes we replace complex discussions that are not appropriate at this level by figurative explanations.

- **Demonstration:** A particular example is chosen and its solution is demonstrated in detail. If possible, the example is simplified to an extent that it can be treated by the student using only pencil and paper. Afterwards, the example is repeated using computer tools. After this demonstrative example, the reader is familiar with the practical realization of the theoretical concepts.

- **Problems:** This is the most important section. First, the hands-on tasks will be given. Then, general hints for their solution are provided. These hints are general recommendations to solve the hands-on tasks and do not cover any particular features of specific software. Technical assistance to solve the hands-on tasks using the specific software delivered with this book is then given in the "Technical Details". It is, however, straightforward to solve the problems using various different software products other than those found on the CD.

- **Review and summary:** Here, the computer experiment is summarized and its key elements are discussed briefly.

- **Bibliography:** This gives a general list of milestone papers in the original literature and the recommendations of standard textbooks and a selection of chapters therein.

1.5
The Chapters

The book contains 16 chapters of computational chemistry "experiments", each designed as a laboratory session to cover a certain topic. The Appendix gives technical advice on the use of the CD that is distributed with this book. Further technical information material can be found on the CD, which is regularly updated and available for download. The 16 chapters can be worked through successively. However, in many cases, specific chapters may be useful to accompany a certain course. Here, we give a recommendation on the context of the usage of each chapter.

Chapter 2 is an introductory chapter in which students learn how to communicate molecular structures with the computer. Essential software such as a molecular editor will be introduced. In this vein, the Cartesian and internal coordinates (Z-matrix) will be introduced. We take advantage of the visualization of molecular structures and introduce symmetry elements and point groups.

If the content of Chapter 2 is not yet known from an earlier introductory computational chemistry lab course, this chapter is highly recommended as a starting point. It also provides exercises for the introduction of molecular symmetry in a general chemistry or physical chemistry freshmen course.

Chapters 3 and 4 are one unit, introducing the computational approach to calculate the vibrational frequencies of diatomic molecules. In Chapter 3, we introduce the Morse potential to describe the potential energy surface (PES) of the diatomic molecule. We motivate the harmonic approximation to calculate the vibrational frequencies, and use the concept of reduced mass to solve the resulting differential equation. After obtaining the vibrational frequencies, we discuss the relative mobility of the two nuclei of the diatomic molecule depending on their relative masses. Chapter 3 can be skipped if all those concepts are already clear to the student. Chapter 4 starts by discussing the limitations of the classical approach of Chapter 3, and introduces the stationary Schrödinger equation to solve the motion of the nuclei on the PES of a diatomic. The important concepts of quantum mechanics are introduced here: quantization, the quantum mechanical state, the discrete set of eigenenergies and corresponding eigenfunctions, probability densities, and tunneling. Students understand that only discrete amplitudes are allowed for molecular vibrations, and that light quanta (photons) of the same frequency as the molecular vibrations are needed to excite a vibration or to emit a photon. Finally, the zero-point energy is introduced and discussed.

These two experiments are helpful for students who are confronted with quantum mechanics for the first time, for example in a physical

chemistry course, and have a limited background in mathematics and in particular in quantum physics. In some cases Chapters 3 and 4 may be combined into a single practical course, or as a homework to refresh the knowledge of physics (Chapter 3), and to prepare for the lab course in Chapter 4.

In **Chapter 5** the electronic stationary Schrödinger equation is solved for some noble gas atoms. The typical textbook example, the analytical solution of the Schrödinger equation of hydrogen, is skipped, due to the involved mathematics. Instead, we state at this point that the exact solution of the electronic Schrödinger equation is impossible for any realistic system, that high-precision numerical approaches are very sophisticated, and that we will not look into this matter within this book. However, we are aware that there are means of computational chemistry that are able to approximate the solution of the electronic Schrödinger equation of a molecule, and that we will use such tools here and in the following. Details can be taught to an audience with stronger mathematical background, for example in a more advanced lecture or text. At this stage of education, however, it is important to develop a figurative understanding of the solution of the electronic Schrödinger equation. We discuss in detail the results of the calculation, in particular the orbital energies and the molecular orbitals, and allow the student to gain an insight into the energy and length scales for the core area and the valence area of atoms. We allow the student to visualize atomic orbitals using graphical software, to see nodes, orbital shapes, and the like. Finally, we request some mathematical skills by solving some calculus problems, where students show that atomic orbitals are normalized and orthogonal to each other.

Chapter 5 is designed to suit two purposes. It contains a lot of technical information, which will be necessary later. It also allows a better understanding of the spatial form of atomic orbitals, the extensions of atoms, nodes, and so on, to be obtained. We recommend it as a training tool for the quantum chemistry software. It might be combined with Chapter 1 for more advanced students to provide the technical background for further experiments.

In **Chapter 6**, the ionization potential and electron affinity of a selection of atoms will be determined. To understand the important concept of electron screening, we start the discussion with the Slater rules. We also use the figuratively clear scheme of Koopmans' approximation to the ionization potential, before we perform more sophisticated calculations using computational chemistry software.

This chapter allows students to reproduce popular diagrams in physical chemistry and inorganic chemistry freshmen texts using the software the students know by that time. We find the Slater rules – even though nearly forgotten – an interesting approach to develop

understanding of the screening concept, which is used for all discussions that involve only valence electrons.

Chapters 7 and 8 are devoted to Hückel theory. We use Hückel theory to motivate the linear combination of atomic orbitals (LCAO) ansatz, which is quite important for any chemical discussion of the electronic properties of molecules. In this book Hückel theory is discussed well beyond the typical *n*-annulenes and linear chain examples. We use this method to show how one can solve the approximate Schrödinger equation within the LCAO concept for quite large systems with no more mathematical tools other than a program to diagonalize a matrix. We apply Hückel theory to determine fullerene stabilities, a method that was even used in "professional computational chemistry" up to the late 1990s. While Chapter 7 is focused on stabilities and the LCAO concept, Chapter 8 discusses bond order, the quantum chemical prediction about the strength of individual bonds, and the resulting molecular orbitals.

Hückel theory is a very intuitive way to teach LCAO, a method that governs quantum chemistry today. Our students found it appealing to work with more "fancy" systems such as fullerenes in addition to the standard ones found in the primary literature. Chapters 7 and 8 form a unit. If there is enough time, they can be performed together. If there is no time, Chapter 8 might be dropped.

While Chapters 2 to 8 have been taught to second-year students, **Chapter 9** is the first of a series that we have designed for third-year students. Chapter 9 provides the basis for geometry optimization. Whereas we cannot discuss the rather complex mathematical apparatus of the large variety of modern algorithms to optimize molecular geometries, we can explain the principal functioning of the steepest descent optimizer and of the Hessian-based Newton–Raphson optimizer on the example of a diatomic. Both algorithms are programmed in a spreadsheet and applied to a diatomic with the PES given by a Morse potential. As more sophisticated algorithms employ the same or similar approximations, this chapter explains why it is important to choose good starting geometries, and why geometry optimizations may fail to find an equilibrium structure. Besides, the typical way to characterize an equilibrium structure by the first and second derivatives of the PES with respect to the coordinates is motivated.

We strongly recommend Chapter 9 to everybody who is going to perform a geometry optimization. It develops the students' sense for iterative algorithms; in principle, they program a geometry optimizer in a spreadsheet that does – essentially – the same as the advanced computer code they are using later. If the student is familiar with a programming language or a math processor the chapter could be adopted to use this knowledge, as a much more useful tool may result from performing the tasks of Chapter 9.

In **Chapter 10** molecules with unpaired spins are treated. Quantities such as the electron spin and multiplicity are introduced. It is shown that it is not always straightforward to predict the spin state of a molecule, and how it can be determined. We further discuss the Jahn–Teller distortion.

This chapter is necessary if systems with unpaired electrons are investigated. You may use this chapter together with Chapter 13 in a course for more advanced students.

Chapters 11 and 12 introduce vibrational spectroscopy of polyatomic molecules. They are based on Chapters 3 and 4, but extend the approach to large systems. In Chapter 11 a simplified calculation of vibrational frequencies and normal modes is given for the carbon dioxide molecule. The assignment of external degrees of freedom to translation and rotation is also discussed. The comparison with IR and Raman spectroscopy experiments is motivated, and the means of coupling of molecular vibrations and light is briefly discussed. Chapter 12 is more advanced. It gives, in a mathematically somewhat more involved way, the calculation of the vibrational spectrum as a system of uncoupled harmonic oscillators and shows that molecular vibrations are indeed independent. More importantly, it relates the molecular vibrations to the symmetry of the molecule, and shows how vibrational frequencies can be analyzed in terms of normal modes.

Chapter 11 is designed to introduce vibrational spectroscopy to undergraduates. It might be combined with Chapters 3 and 4. Chapter 12 is definitely beyond the level of a freshmen lab course. It should be given to very interested students, and may accompany a course for higher semesters in computational, analytical or physical chemistry.

Chapter 13 builds on Chapter 6 and shows how ionization potentials and electron affinities can be calculated for molecules. Adiabatic and vertical values (adiabatic and vertical ionization potential and electron affinity as well as vertical detachment energy) are discussed, and their importance for the detection of species with short lifetimes is motivated.

Chapter 13 is a simple lab session that practices the topic of ionization potentials and electron affinities. It is useful as a lab course as well as a hands-on task for a homework accompanying a lecture.

Chapter 14 discusses thermochemistry. The entropy and energy contributions due to translation, rotation, and vibration of the molecule are calculated and used to calculate the thermodynamic properties of the molecule. We also compare relative energies of molecules where the thermodynamic distribution of isomers changes with the temperature.

This chapter looks – at first glance – very difficult. We have used it for third-year students, and, after the initial shock because of the cumbersome mathematical formalism, they really enjoyed it, as the bridge from the single-molecule calculation to statistical thermodynamics

is indeed one of the more difficult topics for an undergraduate chemistry student.

Chapters 15 to 17 are devoted to molecular dynamics (MD). We used a combination of these chapters for fourth-year students, but the content is simple enough to be taught to undergraduates. In Chapter 15, the Verlet and velocity Verlet algorithms are introduced, and an MD simulation of diatomic molecules is carried out in a spreadsheet. Emphasis is given to the numerical pitfalls of the MD approach. Chapter 16 introduces thermodynamic ensembles – microcanonical (constant particle number, volume, and energy; *NVE*) and canonical (constant particle number, volume, and temperature; *NVT*) – and discusses averaging procedures. It further introduces MD simulations for larger molecules. In Chapter 17 we introduce the simulated annealing approach to search for isomers and the global minimum of molecules and to overcome transition states.

Molecular dynamics is becoming more and more popular in computational chemistry. In a similar way as in Chapter 9 we write a simple MD program in a spreadsheet. Again, this series is easily adoptable to a more advanced programming tool. We use Born–Oppenheimer molecular dynamics, as Chapter 17 (simulated annealing) requires a quantum method for the calculation of forces.

1.6
The Software

This book is accompanied by a CD, which contains a `Linux` operating system based on the `Knoppix` Live system. The CD contains, besides the operating system, a software collection that allows to carry out the tasks in this book to be carried out. The software can be transferred to any computer with a `Linux` system. Most of the programs on the CD, however, can be obtained free of charge for academic usage. The CD compilation on the CD is freeware. You can freely use and redistribute it. We also welcome improvements and further developments. Note that some of the software, in particular the `deMon` computer code, the `CaGe` program, and the `Molden` molecular editor, have different license agreements. They can be used, freely redistributed with this CD or with improvements of the CD project. However, their modification has to be agreed with the original authors.