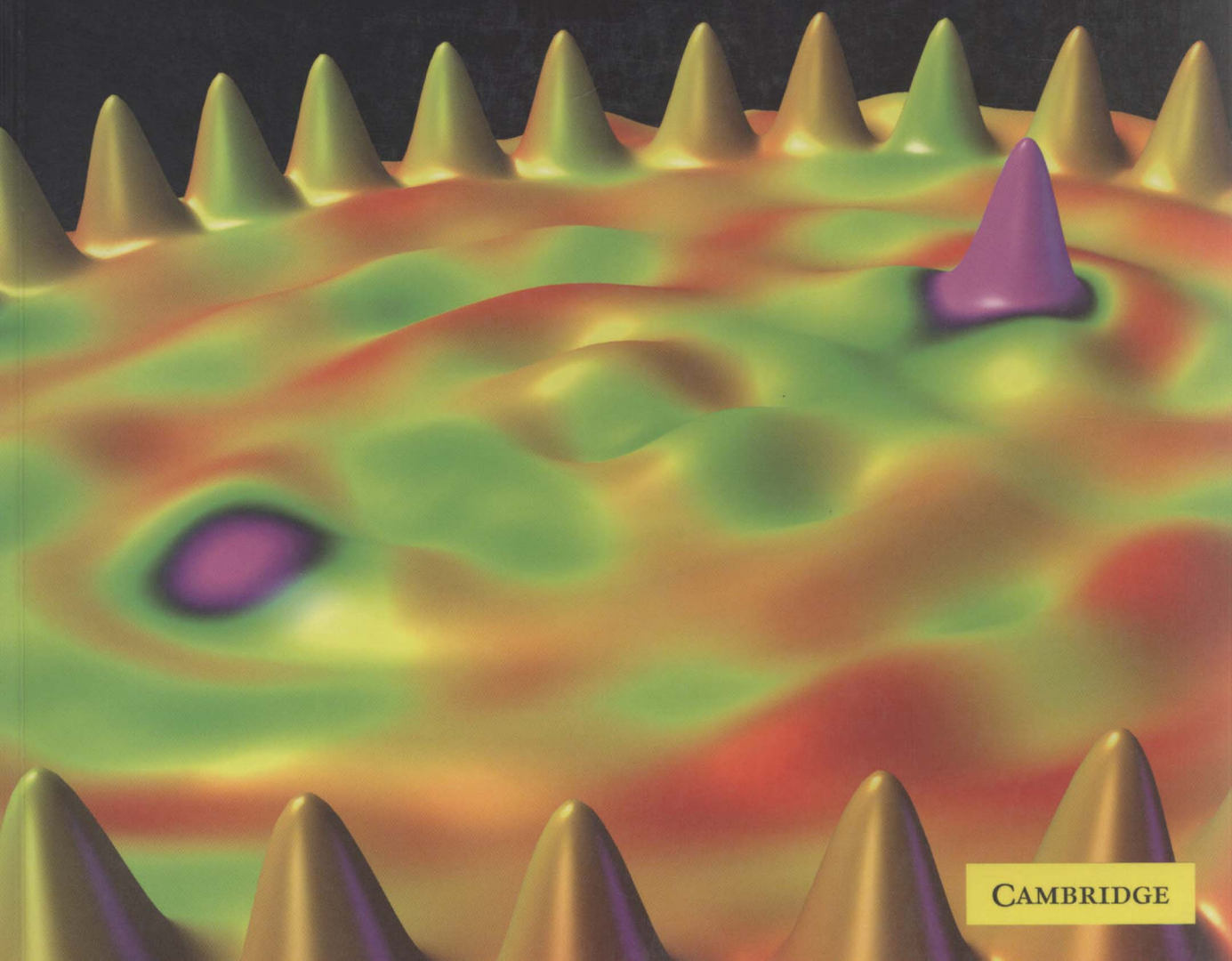


An Introduction to  
**Theoretical Chemistry**

Jack Simons



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# An Introduction to Theoretical Chemistry

**Jack Simons**

University of Utah, Salt Lake City, Utah

Introductory remarks

Acknowledgements

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## **An Introduction to Theoretical Chemistry**

In this unique textbook Jack Simons goes back to basics and focuses on the foundations that lie at the heart of modern day theoretical chemistry. Emphasis is on the concepts, tools and equations that govern the three main theoretical chemistry sub-disciplines: electronic structure, statistical mechanics and reaction dynamics.

Part I provides the foundations of quantum mechanics and molecular spectroscopy as applied to chemistry today. This section can be used either as stand alone material in a junior level physical chemistry class or to provide the reader with the tools and background needed to cover the second part of the book. Part II starts with a general overview of theoretical chemistry and then gives a very accessible introduction to each of the three main sub-disciplines in the subject.

Highly illustrated with numerous exercises and worked solutions, this book provides a concise, up-to-date treatise on the underpinnings of modern theoretical chemistry.

Born April 2, 1945 in Ohio, JACK SIMONS earned a B.S. degree (Magna Cum Laude) in Chemistry from Case Institute of Technology in 1967. His Ph.D. degree, in 1970 as an NSF Fellow, is from the University of Wisconsin, Madison. After serving an NSF Postdoctoral Fellowship at MIT, he joined the University of Utah Chemistry Faculty in 1971, where he was appointed to the Henry Eyring Chair in 1989. He is the author of more than 270 scientific papers and four books, and has mentored more than sixty Ph.D. and postdoctoral students. He is the recipient of many awards including Sloan, Dreyfus, and Guggenheim Fellowships, the Medal of the International Academy of Quantum Molecular Science and the R. W. Parry Teaching Award.



## Introductory remarks

Let's begin by discussing what the discipline of theoretical chemistry is about. I think most young students of chemistry think that theory deals with using computers to model or simulate molecular behaviors. This is only partly true. Theory indeed contains under its broad umbrella the field of computational simulations, and it is such applications of theory that have gained much recent attention especially as powerful computers and user-friendly software packages have become widely available.

However, this discipline also involves analytical theory, which deals with how the fundamental equations used to perform the simulations are derived from the Schrödinger equation or from classical mechanics, among other things. The discipline also has to do with obtaining the equations that relate laboratory data (e.g., spectra, heat capacities, reaction cross-sections) to molecular properties (e.g., geometries, bond energies, activation energies). This analytical side of theory is also where the equations of statistical mechanics that relate macroscopic properties of matter to the microscopic properties of the constituent molecules are obtained.

So, theory is a diverse field of chemistry that uses physics, mathematics and computers to help us understand molecular behavior, to simulate molecular phenomena, and to predict the properties of new molecules. It is common to hear this discipline referred to as theoretical and computational chemistry. This text is focused more on the theory than on the computation. That is, I deal primarily with the basic ideas upon which theoretical chemistry is centered, and I discuss the equations and tools that enter into the three main sub-disciplines of theory – electronic structure, statistical mechanics, and reaction dynamics. I have chosen to emphasize these elements rather than to stress computational applications of theory because there are already many good sources available that deal with computational chemistry.

Now, let me address the issue of “who does theory?” It is common for chemists whose primary research activities involve laboratory work to also use theoretical concepts, equations, simulations and methods to assist in interpreting their data. Sometimes, these researchers also come up with new concepts or new models

in terms of which to understand their laboratory findings. These experimental chemists are using theory in the former case and doing new theory in the latter. Many of my experimental chemistry colleagues have evolved into using theory in this manner.

However, for several decades now there have also been chemists who do not carry out laboratory experiments but whose research focus lies in developing new theory (new analytical equations, new computational tools, new concepts) and applying theory to understanding chemical processes as a full-time endeavor. These people are what we call theoretical chemists. I am proud to say that I am a member of this community of theorists and that I believe this discipline offers the most powerful background for understanding essentially all other areas of chemistry.

Where does one learn about theoretical chemistry? Most chemistry students in colleges and universities take classes in introductory chemistry, organic, analytical, inorganic, physical, and biochemistry. It is extremely rare for students to encounter a class that has "theoretical chemistry" in its title. This book is intended to illustrate to students that the subject of theoretical chemistry pervades most if not all of the other classes they take in an undergraduate chemistry curriculum. It is also intended to offer students a modern introduction to the field of theoretical chemistry and to illustrate how it has evolved into a discipline of its own and now stands shoulder-to-shoulder with the traditional experimental sub-disciplines of chemical science.

I have tried to write this book so it could be used in any of several ways:

- (i) As a textbook that could be used to learn the quantum mechanics and molecular spectroscopy components of a typical junior-level physical chemistry class, including an overview of point group symmetry. This would involve covering Part I (the Background Material covered in Chapters 1–4) and then Chapter 5 and Sections 5–7 of Chapter 6. It would also be wise to solve many of the problems that I offer. Certainly, any student who has not yet taken an undergraduate class in physical chemistry should follow this route.
- (ii) As a first-year graduate text in which selected topics in the areas of introductory quantum chemistry, spectroscopy, statistical mechanics, and reaction dynamics are surveyed. This would involve covering Chapters 5–8 and solving many of the problems. Although the Background Material of Chapters 1–4 should have been learned by such students in an undergraduate physical chemistry class, it would be wise to read this material to refresh one's memory. It is likely that full-semester classes in statistical mechanics and in reaction dynamics will require more material than offered in Chapters 7 and 8, but these chapters should suffice for briefer classes and for gaining an introduction to these fields.
- (iii) As an introductory survey source for experimental chemists interested in learning about the central concepts and many of the most common tools of theoretical chemistry. To pursue this avenue, the reader should focus on Chapters 5–8 because

the Background Material of Chapters 1–4 covers what such readers probably already know.

Because of the flexibility in how this text can be used, some duplication of material occurs. However, it has been my experience that students benefit from encountering subjects more than one time, especially if each subsequent encounter is at a deeper level. I believe this is the case for subjects that are covered in more than one place in this text.

I have also offered many exercises (small problems) and problems to be solved by the reader, as well as detailed solutions. Most of these problems deal with topics contained in Chapters 1–4 because it is these subjects that are likely to be studied in an undergraduate classroom setting where homework assignments are common. Chapters 5–8 are designed to give the reader an introduction to electronic structure theory, statistical mechanics, and reaction dynamics at the graduate and beginning-research level. In such settings, it is my experience that individual instructors prefer to construct their own problems, so I offer fewer exercises and problems associated with these chapters. Most, if not all, of the problems presented here require many steps to solve, so the reader is encouraged not to despair when attempting them; they may be difficult, but they teach valuable lessons.

The reader will notice that I do not provide many references, nor do I mention many names of theoretical chemists who work on the subjects I discuss. I avoided such citations because most of the people who have pioneered or are now actively working on the theories I discuss are friends of mine. I felt that mentioning any of them and not citing others would risk offending many colleagues, so I decided to severely limit such references. I hope the readers and my friends in the world theory community will appreciate my decision.

Before launching into the subject of theoretical chemistry, allow me to mention other sources that can be used to obtain information at a somewhat more advanced level than is presented in this text. Keep in mind that this is a text intended to offer an introduction to the field of theoretical chemistry, and is directed primarily at advanced undergraduate- and beginning graduate-level readerships. It is my hope that such readers will, from time to time, want to learn more about certain topics that are especially appealing to them. For this purpose, I suggest two sources that I have been instrumental in developing. First, a World Wide Web site that I created can be accessed at [simons.hec.utah.edu/TheoryPage](http://simons.hec.utah.edu/TheoryPage). This site provides a wealth of information including:

- (i) web links to home pages of a multitude of practicing theoretical chemists who specialize in many of the topics discussed in this text;
- (ii) numerous education-site web links that allow students ranging from fresh-persons to advanced graduate students to seek out a variety of information;

- (iii) textual information much of which covers at a deeper level those subjects discussed in this text at an introductory level.

Another major source of information at a more advanced level is my textbook *Quantum Mechanics in Chemistry (QMIC)* written with Dr. Jeff Nichols (Past Director of the High Performance Computing Group at the Pacific Northwest National Laboratory and now Director of Mathematics and Computational Science at Oak Ridge National Laboratory). The full content of that book can be accessed in .pdf file format through the TheoryPage web link mentioned above. In several locations within the present introductory text, I specifically refer the reader either to my TheoryPage or *QMIC* textbook, but I urge you to also use these two sources whenever you want a more in-depth treatment of a subject.

To the readers who want to access up-to-date research-level treatments of many of the topics we introduce in this text, I suggest several recent monographs to which I refer throughout this text:

*Molecular Electronic Structure Theory*, T. Helgaker, P. Jørgensen, and J. Olsen, J. Wiley, New York (2000),

*Modern Electronic Structure Theory*, D. R. Yarkony, Ed., World Scientific Publishing, Singapore (1999),

*Theory of Chemical Reaction Dynamics*, M. Baer, Ed., Vols. 1–4; CRC Press, Boca Raton, Fla. (1985),

*Essentials of Computational Chemistry*, C. J. Cramer, Wiley, Chichester (2002),

*An Introduction to Computational Chemistry*, F. Jensen, John Wiley, New York (1998),

*Molecular Modeling*, 2nd edn., A. R. Leach, Prentice Hall, Englewood Cliffs (2001).

*Molecular Reaction Dynamics and Chemical Reactivity*, R. D. Levine and R. B. Bernstein, Oxford University Press, New York (1997),

*Computer Simulations of Liquids*, M. P. Allen and D. J. Tildesley, Oxford University Press, New York (1997),

as well as a few longer-standing texts in areas covered in this work:

*Statistical Mechanics*, D. A. McQuarrie, Harper and Row, New York (1977),

*Quantum Chemistry*, H. Eyring, J. Walter, and G. E. Kimball, John Wiley, New York (1944),

*Introduction to Quantum Mechanics*, L. Pauling and E. B. Wilson, Dover, New York (1963),

*Molecular Quantum Mechanics*, 3rd edn., P. W. Atkins and R. S. Friedman, Oxford University Press, New York (1997),

*Modern Quantum Chemistry*, A. Szabo and N. S. Ostlund, McGraw-Hill, New York (1989).

Because the science of theoretical chemistry makes much use of high-speed computers, it is essential that we appreciate to what extent the computer revolution



has impacted this field. Primarily, the advent of modern computers has revolutionized the range of problems to which theoretical chemistry can be applied. Before this revolution, the classical Newton or quantum Schrödinger equations in terms of which theory expresses the behavior of atoms and molecules simply could not be solved for any but the simplest species, and then often only by making rather crude approximations. However, present-day computers, which routinely perform  $10^9$  operations per second, have  $10^9$  bytes of memory and 50 times this much hard disk storage, have made it possible to solve these equations for large collections of molecules and for molecules containing hundreds of atoms and electrons. Moreover, the vast improvement in computing power has inspired many scientists to develop better (more accurate and more efficient) approximations to use in solving these equations. Because this text is intended for both an undergraduate and beginning graduate audience and is designed to offer an introduction to the field of theoretical chemistry, it does not devote much time to describing the computer implementation of this subject. Nevertheless, I will attempt to introduce some of the more basic computational aspects of theory especially when doing so will help the reader understand the basic principles. In addition, the TheoryPage web site contains a large number of links to scientists and to commercial software providers that can give the reader more detail about the computational aspects of theoretical chemistry.

Let's now begin the journey that I hope will give the reader a basic understanding of what theoretical chemistry is and how it fits into the amazing broad discipline of modern chemistry.

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## Background material

## Part I Background material

The first part of the book, Part I, is devoted to the background material. It is divided into two main sections. The first section, Chapter 1, is devoted to the general background of the book. The second section, Chapter 2, is devoted to the specific background of the book. The first section is divided into two main parts. The first part is devoted to the general background of the book. The second part is devoted to the specific background of the book. The second section is divided into two main parts. The first part is devoted to the general background of the book. The second part is devoted to the specific background of the book.

# Chapter 1

## The basics of quantum mechanics

### 1.1 Why quantum mechanics is necessary for describing molecular properties

We know that all molecules are made of atoms which, in turn, contain nuclei and electrons. As I discuss in this introductory section, the equations that govern the motions of electrons and of nuclei are not the familiar Newton equations,

$$\mathbf{F} = m\mathbf{a}, \quad (1.1)$$

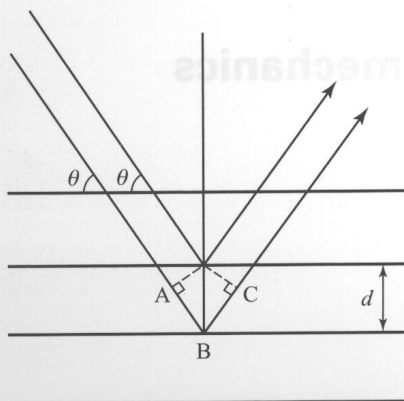
but a new set of equations called Schrödinger equations. When scientists first studied the behavior of electrons and nuclei, they tried to interpret their experimental findings in terms of classical Newtonian motions, but such attempts eventually failed. They found that such small light particles behaved in a way that simply is not consistent with the Newton equations. Let me now illustrate some of the experimental data that gave rise to these paradoxes and show you how the scientists of those early times then used these data to suggest new equations that these particles might obey. I want to stress that the Schrödinger equation was not derived but postulated by these scientists. In fact, to date, no one has been able to derive the Schrödinger equation.

From the pioneering work of Bragg on diffraction of x-rays from planes of atoms or ions in crystals, it was known that peaks in the intensity of diffracted x-rays having wavelength  $\lambda$  would occur at scattering angles  $\theta$  determined by the famous Bragg equation:

$$n\lambda = 2d \sin \theta, \quad (1.2)$$

where  $d$  is the spacing between neighboring planes of atoms or ions. These quantities are illustrated in Fig. 1.1. There are many such diffraction peaks, each labeled by a different value of the integer  $n$  ( $n = 1, 2, 3, \dots$ ). The Bragg formula can be derived by considering when two photons, one scattering from the second plane in the figure and the second scattering from the third plane, will undergo constructive interference. This condition is met when the “extra path length”





**Figure 1.1** Scattering of two beams at angle  $\theta$  from two planes in a crystal spaced by  $d$ .

covered by the second photon (i.e., the length from points A to B to C) is an integer multiple of the wavelength of the photons.

The importance of these x-ray scattering experiments to the study of electrons and nuclei appears in the experiments of Davisson and Germer, in 1927, who scattered electrons of (reasonably) fixed kinetic energy  $E$  from metallic crystals. These workers found that plots of the number of scattered electrons as a function of scattering angle  $\theta$  displayed “peaks” at angles  $\theta$  that obeyed a Bragg-like equation. The startling thing about this observation is that electrons are particles, yet the Bragg equation is based on the properties of waves. An important observation derived from the Davisson–Germer experiments was that the scattering angles  $\theta$  observed for electrons of kinetic energy  $E$  could be fit to the Bragg  $n\lambda = 2d \sin \theta$  equation if a wavelength were ascribed to these electrons that was defined by

$$\lambda = h/(2m_e E)^{1/2}, \quad (1.3)$$

where  $m_e$  is the mass of the electron and  $h$  is the constant introduced by Max Planck and Albert Einstein in the early 1900s to relate a photon’s energy  $E$  to its frequency  $\nu$  via  $E = h\nu$ . These amazing findings were among the earliest to suggest that electrons, which had always been viewed as particles, might have some properties usually ascribed to waves. That is, as de Broglie suggested in 1925, an electron seems to have a wavelength inversely related to its momentum, and to display wave-type diffraction. I should mention that analogous diffraction was also observed when other small light particles (e.g., protons, neutrons, nuclei, and small atomic ions) were scattered from crystal planes. In all such cases, Bragg-like diffraction is observed and the Bragg equation is found to govern the scattering angles if one assigns a wavelength to the scattering particle according to

$$\lambda = h/(2mE)^{1/2}, \quad (1.4)$$

where  $m$  is the mass of the scattered particle and  $h$  is Planck’s constant ( $6.62 \times 10^{-27}$  erg s).