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Patrick Norman, Kenneth Ruud,
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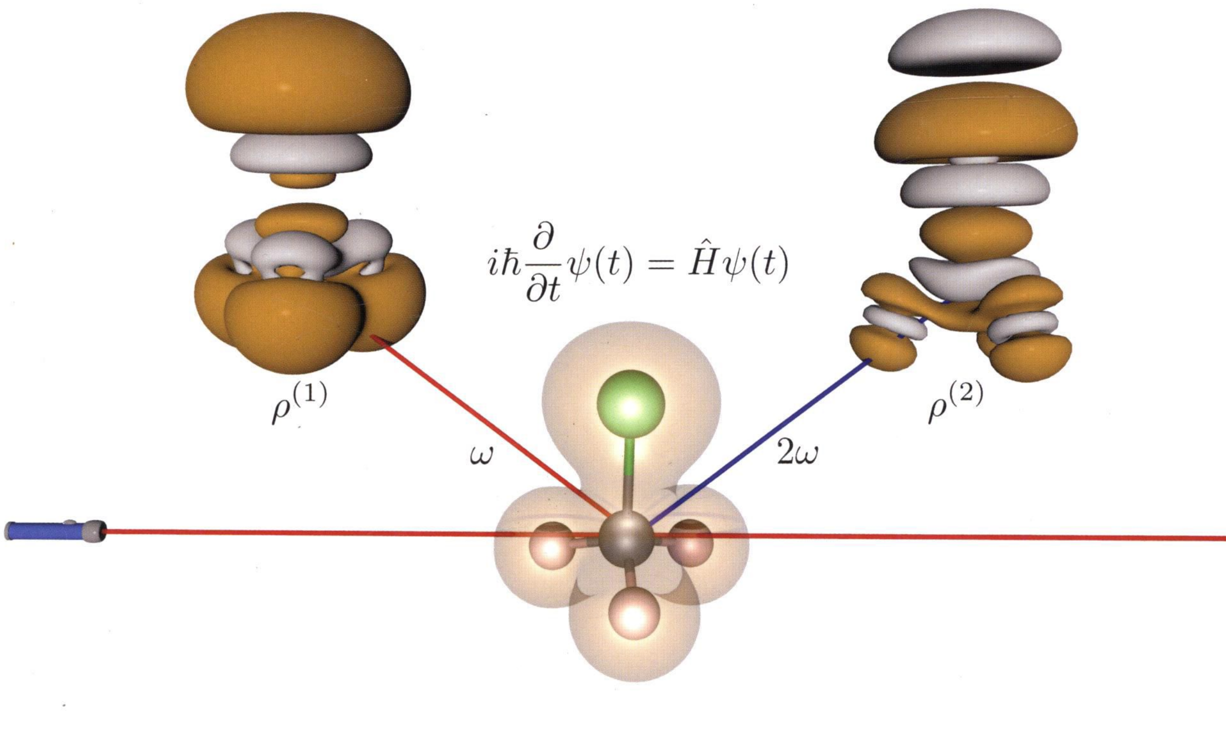
Principles and Practices of Molecular Properties

Theory, Modeling, and Simulations



Principles and Practices of Molecular Properties

Theory, Modeling, and Simulations

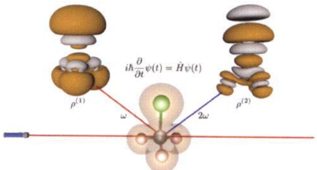
A comprehensive yet accessible exploration of quantum chemical methods for the determination of molecular properties of spectroscopic relevance

Molecular properties can be probed both through experiment and simulation. This book bridges these two worlds, connecting the experimentalist's macroscopic view of responses of the electromagnetic field to the theoretician's microscopic description of the molecular responses. Comprehensive in scope, it also offers conceptual illustrations of molecular response theory by means of time-dependent simulations of simple systems.

This important resource in physical chemistry offers:

- A journey in electrodynamics from the molecular microscopic perspective to the conventional macroscopic viewpoint
- The construction of Hamiltonians that are appropriate for the quantum mechanical description of molecular properties
- Time- and frequency-domain perspectives of light–matter interactions and molecular responses of both electrons and nuclei
- An introduction to approximate state response theory that serves as an everyday tool for computational chemists
- A unified presentation of prominent molecular properties

Principles and Practices of Molecular Properties: Theory, Modeling, and Simulations is written by noted experts in the field. It is a guide for graduate students, postdoctoral researchers and professionals in academia and industry alike, providing a set of keys to the research literature.



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Principles and Practices of Molecular Properties:
Theory, Modeling, and Simulations

Preface

This book has grown out of an ambition to collect the basic theoretical foundations needed in our daily work as computational chemists with a focus on calculating molecular spectroscopic properties. The result is of course a product strongly influenced by our past experiences and will, as such, provide both a subjective and selective view of the field. It is subjective in the ways we choose to present the subject matter and it is selective in the inclusion of some topics but leaving out others that by many may be deemed just as important. But it is our hope that we provide a basic understanding of key concepts so as to enable further reading of research articles providing either a more detailed treatment of theoretical specifics and algorithmic implementations, or covering any one of the several spectroscopies not mentioned in the book.

Every chapter in this book expresses a balance between *principles* and *practices*. A principle (such as the variational principle) can typically be expressed in an extremely compact manner and governs the practices in a wide range of applications (such as a whole category of methods in electronic structure theory). After an introductory chapter aimed at getting the reader into the right mind-set, the second chapter (on the topic of *quantum mechanics*) almost exclusively deals with principles. It sets the stage and introduces much of the notation used in the remainder of the book. This chapter, as well as this book, is best appreciated after having completed a dedicated course on quantum mechanics[1] at the level of the second cycle in higher education. The third chapter is devoted to *electrodynamics* and here we attempt not only to provide principles but also practices in a form adapted to its use in theoretical chemistry. It represents a core chapter of this book and it should be possible to study it even without any particular background in the field. The fourth chapter is devoted to the topic of *symmetry* and it focuses on principles and is hardly the material for a first time encounter. We expect that the reader is well familiar with the use of molecular point groups and one finds here merely a brief recapitulation of this topic.[2] However, we have tried to provide a novel perspective that takes the reader a bit further than the standard presentation, which will help prepare the reader to handle not only spin-free nonrelativistic wave functions, but also systems where the two-component (or four-component) nature of electronic wave functions must be considered. In the fifth chapter of this book, we reach the core of the theoretical exposé and become familiar with molecular *response properties*. This is intended to be a self-contained chapter and it is followed by the sixth chapter that explains the *separation of electronic and nuclear degrees of freedom* and discusses nuclear contributions to molecular properties. The seventh chapter provides a glimpse into the vast amount of work devoted to implementing the ideas of *response theory in approximate-state theory*. This chapter treads somewhere right in between principles and practices. It treats with certain detail some wave function models but leaves out much of

1 A recommended textbook is *Quantum Mechanics* by B. H. Bransden and C. J. Joachain.
2 A recommended reading is *Group Theory and Chemistry* by D. M. Bishop.

the background in electronic structure theory.[3] Our book is completed with the eighth chapter that illustrates the use of molecular response theory for the calculation of spectroscopic properties. We exemplify nuclear structure and spin properties, dispersive and absorptive electronic response properties, electronic birefringences and dichroisms, and vibrational spectroscopies. Needless to say, the list of examples in this final chapter could be made much longer, but we hope that our selection is diverse enough to provide compelling evidence for the impact and use of response theory in molecular modeling.

Before proceeding, let us note some notational conventions that will be used in this book. We will use the Système International d'unités (SI units). Vectors are typeset in boldface and operators are denoted by a hat, as for instance the molecular Hamiltonian $\hat{H}$. When referring to a specific matrix representation of an operator, we leave out the hat. We will indicate the real and imaginary parts of complex quantities by Re and Im, respectively. For compliance with the literature on electrodynamics, we will in Chapter 3 use **E** to denote the electric field. In the rest of the book, however, we will use **F** for the electric field in order to avoid confusion with the molecular energy that will be denoted by E. We will use implicit summation of repeated indices (the Einstein summation convention), such that

$$A_{\alpha\alpha} \Rightarrow \sum_{\alpha=x,y,z} A_{\alpha\alpha}.$$

Over the course of time spent in writing this book, we have discussed the material with a large number of people. We have organized several week-long courses where the manuscript has been used as teaching material and we have received numerous comments and corrections during these events. We are greatly indebted to all the enthusiastic students attending these schools on response theory, taking place in Chamonix and Luchon in France, as well as at Virginia Tech in the United States. The school at Virginia Tech has been co-organized with Daniel Crawford, who has provided excellent local arrangements and shared his expertise with us in a series of lectures. The U.S. variant of this school could never have been realized without his kind help. We have also benefited from the dedicated proof reading by several people, including Daniel Friese (Düsseldorf), Bin Gao (Tromsø), Michal Jaszuński (Warsaw), Marius Kadek (Tromsø), Nanna H. List (Stockholm), Roberto Di Remigio (Tromsø), and Magnus Ringholm (Tromsø).

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Things take longer time than one thinks, even when one takes into account that things take longer time than one thinks. Trond and Patrick would like to thank Hélène, Aurélien, and Sigurd and Dorthe, Jonathan, and Alexander, respectively, for their patience and understanding over the several years it has taken to complete this work.

Patrick Norman, Stockholm
Kenneth Ruud, Tromsø
Trond Saue, Toulouse

June, 2017

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3 The most comprehensive treatment of today on this topic is found in *Molecular Electronic-Structure Theory* by T. Helgaker, J. Olsen, and P. Jørgensen.

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Appendicies

1

Introduction

If you want to find the secrets of the universe, think in terms of energy, frequency and vibration.

Nicolas Tesla

This is a book about molecular properties, or to be more specific, molecular response properties. Response properties tell us about how molecules respond to electromagnetic fields. To understand these responses, we have to enter the microscopic world of atoms and molecules, governed by the laws of quantum mechanics. For that reason, the reader of this book can expect several intellectual challenges ranging from profound and conceptual cornerstones of quantum theory itself to trivial, yet mind-boggling, issues relating to the smallness of atomic sizes. Consider for instance the situation in which a collection of molecules are being exposed to the intense electric field of a laser, as illustrated in Figure 1.1. From a human perspective, the focal point of a laser is a dangerous place to be, but, from the atomic perspective, it is far less dramatic. In our example, there will be fewer photons than molecules, and, for instance, if the purpose is to protect the eye by efficient optical power limiting, only about every second molecule needs to absorb an incoming light quanta in order to reduce the energy in the transmitted light pulse to an eye-safe level. Furthermore, as strong as the electric field may appear to our eyes, to the individual electron it is several orders of magnitude smaller than the dominating forces exerted by the atomic nuclei and fellow electrons. To get an idea of magnitudes, one may note that the electric field below overhead power lines may reach 10^4 V m^{-1} and the maximum electric field strength possible in air without creating sparks is 3.0×10^6 V m^{-1}. In contrast, at the Bohr radius a_0 in the hydrogen atom, the electric field strength is 5.1×10^{11} V m^{-1}. This is a key point, namely, that we can expose molecules to fields that are strong enough so that we can detect the responses of their charges (nuclei and electrons) while at the same time the fields are weak enough to act as probes, not significantly perturbing the electronic and nuclear structure of the molecule.

Take a very simple example: What happens if a neutral atom (not even a molecule) is placed in a uniform electric field? An experimentalist will ask nature—that is, he or she may perform an experiment, where every macroscopic experiment relates to a very large number of probabilistic microscopic quantum events—by probing how the charge distribution of the atom is modified by the applied field. A theoretician will ask the wave function ψ. The quantum-mechanical equivalent to the outcome of the experiment is the expectation value

$$\langle \hat{\Omega} \rangle = \langle \psi | \hat{\Omega} | \psi \rangle, \tag{1.1}$$

where $\hat{\Omega}$ is the quantum-mechanical operator corresponding to the observable monitored by the experiment. Quantum mechanics is a probabilistic theory. The link between theory and

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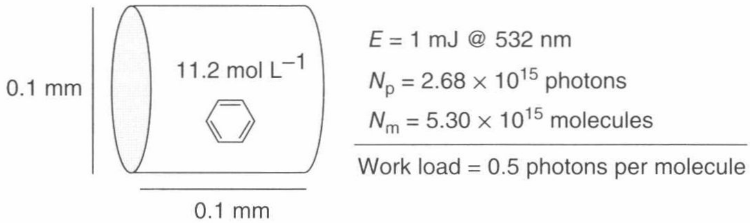

Figure 1.1 Liquid benzene in a small volume corresponding to the focal point of a laser operating at 532 nm and releasing pulses with an energy of 1 mJ.

experiment is made by considering a large number of systems prepared in the same state, prior to switching on the field. If we disregard measurement errors, then the possible outcomes of the individual quantum events are given by the eigenvalues $\{\omega_n\}$ of the operator $\hat{\Omega}$, defined by the eigenvalue equation

$$\hat{\Omega}\psi_n = \omega_n \psi_n. \tag{1.2}$$

Following the postulates of quantum mechanics, the operator $\hat{\Omega}$ is by necessity Hermitian, and the eigenvalues are thus real (corresponding to real-valued observables), and there is a probability $p_n = |\langle \psi_n | \psi \rangle|^2$ for the outcome ω_n in each of the single quantum events, leading to an expectation value that is

$$\langle \hat{\Omega} \rangle = \sum_n \omega_n \, p_n. \tag{1.3}$$

For example, indirect information about the charge distribution of the atom can be obtained from measurements of the electric dipole moment since the two quantities are connected through an expectation value of the form

$$\boldsymbol{\mu} = \left\langle \psi \right| - e \sum_{i=1}^{N_e} \mathbf{r}_i \left| \psi \right\rangle = \int \mathbf{r}\rho(\mathbf{r}) \, d^3\mathbf{r}, \tag{1.4}$$

where N_e denotes the number of electrons and e is the elementary charge. However, the electronic charge density can in itself also be expressed as an expectation value

$$\rho(\mathbf{r}) = \left\langle \psi \right| - e \sum_{i=1}^{N_e} \delta(\mathbf{r} - \mathbf{r}_i) \left| \psi \right\rangle, \tag{1.5}$$

and it is possible to probe $\rho(\mathbf{r})$ in for instance X-ray diffraction experiments.

If the external electric field is weak compared to the internal atomic fields, we can expand the induced electronic charge density in a Taylor series with respect to field strength. In Figure 1.2, such a perturbation expansion is illustrated to fifth order for a neon atom. The electric field of strength F is applied along the vertical z-axis (directed upward in the figure) and will tend to pull the positive charge along the field and the negative charge in the opposite direction, resulting in an electronic charge density that can be expanded as

$$\rho(\mathbf{r}) = \rho^{(0)}(\mathbf{r}) + \rho^{(1)}(\mathbf{r})F + \frac{1}{2!}\rho^{(2)}(\mathbf{r})F^2 + \frac{1}{3!}\rho^{(3)}(\mathbf{r})F^3 + \frac{1}{4!}\rho^{(4)}(\mathbf{r})F^4 + \frac{1}{5!}\rho^{(5)}(\mathbf{r})F^5 + \cdots . \tag{1.6}$$

The zeroth-order density $\rho^{(0)}$ refers to that of neon in isolation and integrates to $-10e$. It follows from charge conservation that the higher-order densities all integrate to zero. The first-order density $\rho^{(1)}$ shows the charge separation of a dipole, and we then get more and more complicated