Computational Strategies for Spectroscopy: From Small Molecules to Nano Systems

Edited by *V. Barone*

*Wiley, **2011**, 608 pp., $125.00*

Computational chemistry has become an important tool for the assignment and interpretation of spectroscopic data. This holds for both high-resolution experiments on small molecules and for spectroscopic investigations of complex biological molecules or nanostructures. At the same time, novel experimental techniques often require the development of new theoretical tools. Thus, computational spectroscopy has become an important subfield of theoretical chemistry. The book edited by V. Barone emerged from an Italian research network on this topic, and aims to provide an overview of the current status of the field.

The book opens with three short introductory chapters by experimental scientists, which briefly sketch the state-of-the-art methods and current challenges in EPR spectroscopy, in linear and nonlinear optical spectroscopy, and in electronic spectroscopy in the gas phase. The following chapters of the book are devoted to computational methods, and are organized in two parts: The first part concerns the calculation of electronic and spin states, whereas the second part deals with effects related to nuclear motion, i.e., rotational and vibrational spectroscopy as well as vibrational contributions to other spectroscopic observables.

The first part starts with a chapter by R. Improta on the calculation of excited electronic states. The main focus is put on time-dependent density functional theory (TD-DFT), because of its ability to treat larger molecular systems, while wavefunction-based methods for excited states are only mentioned in passing. Even more approximate excited states methods are needed for describing nanostructures, as is discussed in the chapter by F. Trani on calculations of optical properties with tight-binding methods. Electronic spectroscopy is also the topic of the chapter by A. Rizzo, S. Coriani, and K. Ruud presenting the theoretical framework of response theory for the calculation of linear and non-linear optical spectra. I particularly enjoyed reading the chapter by V. Carravetta and H. Ågren on computational approaches to X-ray spectroscopy. It gives an introduction to the electronic processes involved in different X-ray experiments and provides a clear overview of the theoretical methods that are available for their description. Finally, the first part is completed by a chapter on magnetic resonance spectroscopy by A. Pedone and O. Crescenzi. This chapter introduces the spin Hamiltonians used to describe NMR and EPR experiments and discusses how its various parameters can be obtained from quantum chemical calculations.

All chapters provide thorough presentations of the theoretical background and emphasize the link between the experimentally accessible quantities and those provided by calculations. In addition, they all include selected applications that serve to illustrate the accuracy and the limitations of the available computational methods and provide some guidelines for an appropriate choice of theoretical approaches.

This also holds for many of the chapters in the second part, which begins with a chapter by C. Puzzarini on rotational spectroscopy. Such high-resolution experiments require very accurate quantum-chemical methods, and the experimental data can in turn serve to benchmark quantum chemistry. The following chapter by C. Cappelli and M. Biczysko introduces the time-independent approach for calculating vibrational spectra within the harmonic approximation, both for standard infrared and Raman spectroscopy and for their chiral analogues VCD and ROA, as well as the inclusion of anharmonic contributions with perturbation theory. Subsequently, the influence of nuclear motion on electronic spectra is the topic of a chapter by V. Barone and coworkers providing an extensive account on the calculation of lineshapes. They focus on the time-independent calculation of vibronic states, ranging from methods including nonadiabatic couplings to single-state methods based on the harmonic approximation. In combination with prescreening techniques, the latter are applicable to rather large molecular systems, in particular for calculating resonance Raman spectra.

After these three chapters on time-independent methods, the remainder of the second part concerns explicitly time-dependent methods for predicting spectroscopic properties. M. F. Gelin, W. Domcke, and D. Egorova introduce time-dependent methods for describing femtosecond spectroscopy. This is followed by a chapter by A. Lami and F. Santoro on time-dependent methods for predicting lineshapes in electronic spectra. Here, numerical methods for propagating the time-dependent Schrödinger equations are introduced, ranging from quantum-dynamical methods to semiclassical approaches. The fully classical dynamics is then covered by G. Brancato and N. Regia. Finally, the chapter by A. Polimeno, V. Barone, and J. H. Freed deals with computational methods for magnetic resonance spectroscopy based on the time-dependent Liouville equation coupled to quantum chemical calculations.

Many chapters in both parts of the book do not limit themselves to isolated small molecules, but discuss the application of the computational methods to molecules in complex environments, with a particular focus on the description of solvent effects with continuum models.

Altogether, the book presents an overview covering a very broad range of topics in computational spectroscopy, while providing numerous cross-references between the different chapters. It does not only discuss the theoretical methodologies, but most chapters give clear prescriptions for their application. Thus, it is useful both for experimentalists interested in using computational tools and for students as well as experienced researchers working on their development. In summary, I believe this book is a valuable reference for anyone interested in computational spectroscopy.

Christoph R. Jacob
Karlsruhe Institute of Technology (KIT)
76131 Karlsruhe (Germany)
DOI: 10.1002/cphc.201200289

