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Topics in Current Chemistry

Aims and Scope

The series Topics in Current Chemistry presents critical reviews of the present and future trends in modern chemical research. The scope of coverage includes all areas of chemical science including the interfaces with related disciplines such as biology, medicine and materials science.

The goal of each thematic volume is to give the non-specialist reader, whether at the university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to larger scientific audience.

Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years should be presented. A description of the laboratory procedures involved is often useful to the reader. The coverage should not be exhaustive in data, but should rather be conceptual, concentrating on the methodological thinking that will allow the non-specialist reader to understand the information presented.

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First Principles Approaches to Spectroscopic Properties of Complex Materials

With contributions by

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Preface

The development of ever more advanced technologies depends very critically on the definitions of materials with appropriate characteristics. For example, specific combinations of optical and electronic properties (e.g., band gap and conductivity) are essential in materials employed in solar energy technologies, such as photovoltaics, photocatalysis, photoelectrochemical cells, water splitting photosystems, or artificial photosynthesis, but also in medical diagnostics, sensor technology, optoelectronics, and photonics, where photosensitive materials can be either used as artificial antennas capturing light or as emitters and scintillators. Other kinds of applications present equally specific requirements of, e.g., magnetic properties and, as a result, the number, variety, and complexity of systems under development are constantly growing. Current technological investigations span, in fact, a vast class of materials with varied properties. A partial list could easily include inorganic (sp) and organic semiconductors, transition metal compounds (e.g., oxides, sulfides, or chalcogenides), perovskites, inorganic quantum dots, rare earth compounds, heterojunctions, composite systems (e.g., dye-sensitized semiconducting oxides), and nanoconjugate materials. The ability to characterize electronic, magnetic, and optical properties of broad families of different materials, to predict and possibly control them through proper design is crucial for the above-mentioned technological applications.

Spectroscopy is undoubtedly the prime tool to investigate electronic, optical, and magnetic properties of materials. Over the last few decades, experimental spectroscopy has undergone tremendous progress and a substantial improvement in its accuracy has been achieved through the differentiation of the type of radiation used to probe the samples: light of different frequencies, electrons, neutrons, etc. More recently, in parallel with the growth of experimental spectroscopy, theoretical computational spectroscopy has also gained an increasing relevance. The field has greatly benefited, on the one hand, from the development and improvement of new theoretical approaches and algorithms and, on the other hand, from the availability of more powerful computational infrastructures. It is well understood that the synergy between experimental and computational spectroscopy can lead to a higher level of understanding, and to a more precise interpretation and rationalization of the observed data. The achievement of this goal, however, requires an effort from both communities to establish a common language, and to assess and understand

each other's capabilities and limitations. To discuss the potential of state-of-the-art computational spectroscopy is, in fact, one of the main goals of this volume.

There is a long list of critical physical and chemical quantities which can be accurately determined through calculation, including the electronic (or fundamental) and optical band gaps of the materials, the positions of defects, impurities and dopants, electronic levels in the band gap, the nature (e.g., the degree of localization) of their states, the level alignment with respect to the vacuum and at the interfaces, the excitation and emission energies involved in optical processes, in photoabsorption, and in photoemission, the energy associated with spin excitations, etc. However, when the systems are complex or require large models to be described, sophisticated techniques rapidly become unaffordable. For this reason, developing reliable and accurate computational approaches which can keep computational costs to a reasonable level, is perhaps more critical than ever.

In this respect, Density Functional Theory (DFT) has gained a prominent position in the general scenario of computational chemistry and materials science because of the excellent accuracy achievable at a relatively low cost compared to the highly expensive post-HF methods. It is thus not surprising that most of the computational approaches discussed in this volume are, to various extents, based on DFT. Because of the approximations in the exchange-correlation functional, however, DFT is limited by a residual electron self-interaction and by an improper description of electronic correlations, causing a number of problems, such as the over-delocalization of electrons in defects or impurity states, which are often shallower than they should be, or the impossibility of capturing metal-insulator transitions. In addition to these problems, which can be traced back to the approximations employed for the exchange-correlation functional, a major issue of DFT is the fact that, being a ground-state theory, it is intrinsically unsuitable for describing elementary excitations in an electronic system.

Viable approaches for the correction of electronic self-interaction, such as scissor operators or the more refined DFT+U and hybrid functional methods, are quite effective in fixing certain aspects of the one-electron spectrum (e.g., the fundamental gap and photoemission energies). However, if one wants to calculate neutral excitation energies (i.e., the optical spectrum) including many-body effects, the knowledge of the static ground-state density is no longer sufficient. There are two main ways to go beyond DFT in these cases.

The first way involves studying particle propagation and fluctuations in the system. This approach results in correlation functions which can be related to response functions, yielding spectroscopic quantities. These correlation functions are one- or two-body Green's functions. The one-body Green's function can be essentially understood as a time-dependent particle and hole density matrix. Its phase fluctuations (or poles in frequency space) are given by electron addition and removal energies, measured, e.g., in photoemission or inverse photoemission experiments. The particle-hole part of the two-particle Green's function, in turn, has poles at the energies of neutral excitations. Many-body perturbation theory is the framework where suitable approximations for Green's functions can be found. In particular, the GW approximation, introduced in 1965 by Lars Hedin, is extremely successful in evaluating quasiparticle energies for bulk materials, as well as at

surfaces and in confined structures. Restricted self-consistent procedures were recently proposed for transition metal oxides, where standard perturbative GW fails. With regard to neutral excitations, the Bethe–Salpeter equation is state-of-the-art for obtaining optical spectra of solids. The price to pay for a physically intuitive and in general quite reliable description is, however, high in terms of computational cost, because four-point functions appear instead of the simple electron density.

The second way involves exposing (in the computer) the system to a time-dependent external potential and calculating the evolution of the density over time. Response functions can be directly determined from linear response relations between the variation of the external potential and the induced density. This route has become accessible thanks to the extension of DFT to its time-dependent formulation (TDDFT). Put on a rigorous basis by the Runge–Gross theorem, one can intuitively understand that in TDDFT the quantum-mechanical "trajectory" of the system under the influence of a time-dependent external potential is found by searching for the extrema of an action, by analogy to classical mechanics. One thereby obtains the time-dependent Kohn–Sham equations as a generalization of the static case, and from these, response functions describing excitations of the system. At this point the difficulty lies in finding suitable approximations for the time-dependent exchange-correlation potential. Note that now the functional dependence is on the density in the whole space and at all past times.

Both these broad families of approaches to computational spectroscopy are presented in depth in this volume, together with some of the most recent corrective approaches to improve the accuracy of exchange-correlation functionals in describing ground state properties of materials and in reproducing selected aspects of their single-particle energy spectrum.

More specifically, the volume pursues four main aims: (1) to offer a birds-eye overview of the state-of-the-art theoretical approaches and computational methods (based on and beyond DFT) currently used to characterize the spectroscopic properties of materials; (2) to discuss the most significant theoretical and computational challenges inherent in this field, and to provide a guide on the most relevant approximations currently used; (3) to illustrate some of the most recently defined theoretical approaches, developed to expand further the descriptive and predictive power of computational spectroscopy techniques and to discuss the most recent solutions to some of the long-standing problems; and (4) to provide an instantaneous picture of the evolution of computational spectroscopy, discussing the ongoing refinement of well-established approaches, the emergence and optimization of new ones, and the progress on open problems of the field.

The structure of the volume reflects this system of aims. Even though different chapters are not explicitly linked to each other, their order is consistent with a logical and progressive development of their topics across the volume, evolving from a panoramic view of systems and problems being currently tackled, towards a detailed illustration of the various methods developed to capture or improve particular aspects of materials spectroscopy, to end with a stimulating discussion on some of the "frontier" problems of the field and on the challenges they pose to

the theoretical and computational methods recently defined or still under development.

The opening chapter of the volume by Pastore et al. provides a review of recent computational studies of the electronic and optical properties of dye-sensitized solar cells, discussing the use of DFT/TDDFT and GW approaches, and highlighting the need for "post-DFT methods." A comparative analysis of TDDFT and GW is also proposed in the second chapter by Bendavid and Carter, discussing the calculation of neutral and charged excitations in transition metal oxides and effective methods (such as DFT+U, hybrid functional, embedded correlated wavefunctions) to improve the evaluation of their fundamental gap. The third chapter by Bruneval and Gatti focuses on the use of GW for photoemission spectroscopy, with particular emphasis on how a quasi-particle self-consistent implementation of the method (QSGW) significantly improves its accuracy when used on both band and strongly correlated insulators, thus broadening the range of materials whose spectral properties can be reliably predicted. Computing photoemission spectra is also the main topic of the fourth chapter by Kronik and Kummel which discusses the possibility of approaching this type of calculation within the framework of TDDFT. The chapter also reviews some of the most used corrections to DFT functionals (e.g., exact exchange, self-interaction correction, etc.) developed to improve the estimate of band gaps and to evaluate spectroscopic properties from ground state calculations. In the chapter "Piecewise Linearity and Spectroscopic Properties from Koopmans-Compliant Functionals" by Dabo et al., the latter theme is actually expanded with the discussion of a recently elaborated corrective functional able to impose the Koopmans condition onto the Kohn–Sham spectrum. Through the elimination of electron self-interaction, this correction is shown to improve significantly the accuracy of evaluated spectroscopic properties while maintaining a reasonable computational cost. The chapter "Optical Response of Extended Systems Using Time-Dependent Density Functional Theory" by Sharma et al. specifically focuses on the calculation of neutral excitations (optical spectra) by TDDFT; after a thorough review of its fundamental theorems, the chapter discusses a linear-response approach to this method and reviews the performance and accuracy of several exchange-correlation kernels in predicting the optical response of a quite broad spectrum of systems. The topic of the chapter "Spin Excitations in Solids from Many-Body Perturbation Theory" by Friedrich et al. is magnetic excitation. The chapter shows how to compute the spin excitation spectrum of materials with a new method based on many-body perturbation theory and illustrates how including vertex corrections in the form of a multiple scattering T matrix allows capture of both spin-flip Stoner and collective spin-wave excitations. The calculation of the spectroscopic properties of correlated materials is the focus of the chapter "Dynamical Mean Field Theory-Based Electronic Structure Calculations for Correlated Materials" by Biermann which contains a thorough discussion of the DFT+DMFT method, and how to use it to improve the description both of the ground state and also of optical properties of these materials. The last part of the chapter presents the recent GW+DMFT approach for accurate calculation of quasi-particle excitation. Finally, the chapter "Probing Strongly Correlated Materials in

Non-equilibrium: Basic Concepts and Possible Future Trends in First Principle Approaches" by Hopjan and Verdozzi, after summarizing the state-of-the-art of the field with a synthetic review of the themes treated in the previous chapters, offers a perspective outlook on one of its unfolding directions, namely time-resolved spectroscopy, by discussing (also in comparison with TDDFT) the theory of the non-equilibrium Green's function technique and the ability to apply it to model correlated systems. The volume is completed by an appendix (by the Editors) on the Bethe–Salpeter equation which, although referred to by several chapters, was not explicitly treated by any of them.

The wide spectrum of topics and computational approaches covered makes the volume suitable for a broad readership. While the researcher who is new to this field can find a useful introduction to it, with excellent samples of topics and relevant literature, the discussion of typical problems and a critical review of computational methods designed to solve them, a scientist with more expertise in computational spectroscopy can certainly use this volume to learn more about recent progress and for an in-depth study of specific problems and techniques such as, for instance, quasi-particle or optical excitations, magnetic spectra, Green-function-based and beyond-DFT methods, etc.

Because of its focus, the volume will be most useful to readers who are already familiar with DFT, the limits of approximate exchange-correlation functionals, and its range of applicability. The less experienced reader will, however, find in the various chapters ample literature references to the above-mentioned basic topics if he/she wants to establish his/her understanding on more solid theoretical ground.

The Editors would like to take this opportunity to thank all the authors for accepting the invitation to write a chapter, for their work, and for their efforts to make their manuscripts as complete and self-contained as possible, as required by a volume covering such a wide variety of topics such as this. Special thanks go to M. Hopjan and C. Verdozzi for agreeing to write the final chapter of the volume which contains a review of the state-of-the-art of computational spectroscopy and an outlook on approaches yet to be fully developed and on problems still existing in this important field. The Editors are also grateful to the many referees who critically and thoroughly reviewed the various chapters.

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