



Electronic Structure of Materials by Ab Initio Methods: Overview

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Abstract

The next set of 12 chapters provides an overview of the new advances since the first edition of the *Handbook of Materials Modeling* in 2005 regarding the description of the ground-state and excited-state electronic structure of complex many-body systems by ab initio electronic structure methods. In this section we present contributions aiming to providing an up-to-date description and illustration of the main theoretical methods used by the electronic structure community for the study of problems of actual materials, of prediction of properties, and for the design of novel materials.

1 Introduction

Back in September 2015, I was contacted by Wanda and Sidney, who proposed me the idea of joining the editorial board of the second edition of the *Handbook*

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of *Materials Modeling* as well as being the editor in charge of one section on electronic structure and ab initio methods, which should work as a fundamental point of reference for the following chapters within the volume. I thought this was an excellent idea. After a lot of hard and excellent work by the contributors to this section, I am delighted to welcome you to the introduction of the section on “Electronic structure of materials by ab initio methods” in the *Handbook of Materials Modeling (2nd edition, Vol. 1)*.

A large part of research in condensed matter science is related to the characterization of the electronic, structural, and bonding properties of interacting many-electron systems. An accurate description of the electronic structure and its response to external probes is essential to the understanding of the behavior of systems ranging from atoms, molecules, and nanostructures to complex materials. Solving for the electronic structure of an interacting electron system (in terms of the many-particle Schrodinger equation) has an intrinsically high complexity: while the problem is completely defined in terms of the total number of particles N and the external potential $V(r)$, its solution is a task of exponentially increasing complexity. Fortunately, in the study of either ground- or excited-state properties of interacting many-body systems, we seldom need the full solution to the Schrodinger equation. When one is interested in structural properties, the ground-state total energy is sufficient. In other cases, we want to study how the system responds to some external probe; thus, the knowledge of a few excited-state properties is needed.

In the last two decades, we have seen a continuous but impressive improvement in the accuracy of the approximate methods to deal with many-body electronic systems together with a tremendous increase of computing power as well as improved numeral algorithms. In this realm, ab initio computational sciences have become a fundamental tool to understand, discover, and predict materials properties, as well as to guide experimental efforts along those lines. Therefore, in this set of chapters, we aim to lay out the fundamental concepts providing the basis for the development of increasingly more realistic models and more powerful multi-scale simulation methods as they are being applied nowadays in the materials science community. We address in particular the development and application of a broad range of experimental and computational methods to describe the electronic, optical, and magnetic properties of matter, including nonadiabatic ultrafast phenomena and non-equilibrium dynamical processes at different size and time scales. This section plays a pivotal role in the whole structure of the *Handbook of Materials Modeling* by providing the fundamentals of the methodologies used in the two volumes. In particular, it has close ties with this volume’s sections on atomistic simulations, materials informatics, molecular dynamics-thermodynamics, and magnetism-spintronics. Furthermore, it offers complementary information to many of the sections in the second volume of the Handbook that focus on applications to demonstrate and expand the capabilities of current models and simulation methods, in particular the one dealing with photovoltaics from first-principles.

At the simplest level of treating the many-electron problem, the Hartree-Fock theory (HF) is obtained by considering the wave function to be a single Slater determinant. In this way the N -body problem is reduced to N one-body

problems with a self-consistent requirement due to the dependence of the HF effective potential on the wave functions. By the variational theorem, the HF total energy is a variational upper bound of the ground-state energy for a particular symmetry. The HF eigenvalues may be used as estimates of the true excitation energies. The HF theory is far from accurate because the wave function of a system in general cannot be written as a single determinant for the ground state and Koopman's theorem is in general a poor approximation. On the one hand, a rigorous method is to employ the many-particle Green's function approach in which the poles of the one-particle and two-particle Green's function give the quasiparticle energies and optical transition energies, respectively. On the other hand, within the density-functional theory (DFT), the ground-state energy of an interacting system of electrons in an external potential can be written as a functional of the ground-state electronic density. When comparing to conventional quantum chemistry methods, this approach is particularly appealing since it does not rely on the complete knowledge of the N -electron wave function but only on the electronic density. However, although the theory is exact, the energy functional contains an unknown quantity called the exchange-correlation energy, $\text{Exc}[n]$, that has to be approximated in practical implementations. For excited-state properties, the DFT has been extended to a time-dependent formalism (TDDFT) and applied with success to the calculations of optical properties and excited-state dynamics of finite and extended systems. However, the commonly used adiabatic functionals in DFT and TDDFT encounter problems when studying correlated materials and spectroscopic properties of extended systems and excitation energies in molecules. Of course, when going to more complex systems, the key to describe and model most physical effects in chemistry and materials is not achieving "chemical accuracy" but being able to theoretically describe and capture the relevant physical-chemical processes.

When describing light-matter interactions, those theoretical tools have a certain range of validity as they often treat electromagnetic radiation and matter on a different level of approximation. Photons are usually only treated as an external perturbation that probes matter without any further influence and vice versa. The standard theoretical modeling can thus be insufficient when photon and matter degrees-of-freedom become equally important (as in the case of polariton condensates). Indeed, these matter-only approaches can be viewed as approximations to a density functional or Green's function formulation of nonrelativistic quantum electrodynamics (QED). In my group we have recently introduced a novel quantum-electrodynamical density-functional approach (QEDFT) to describe such complex dynamics of interacting electrons, photons, and phonon systems all on the same theoretical footing (Ruggenthaler et al. 2018; Flick et al. 2015, 2017). QEDFT is a novel framework to deal with electron-photon interactions from first-principles (opening up the fields of cavity QED-chemistry and QED materials). Hybridizing light strongly with the electronic structure of the system, novel effects appear providing a promising route for new design of material, for example, Floquet engineering (quantum topological matter), valley Hall effect in 2D materials, chiral plasmonics, or phonon-driven spin-magneto valleytronics. Moreover, hidden

aspects of photon-matter interaction can be revealed with new tailored spectroscopic tools (Ruggenthaler et al. 2018; Flick et al. 2015, 2017).

2 Contributed Chapters to “Electronic Structure of Materials by Ab Initio Methods”

The carefully chosen contributions presented here handle fundamental aspects of the different frameworks to deal with static and dynamical properties of many-body interesting systems (from molecules to solids). We touch up on basic ideas coming from traditional quantum chemistry methods, condensed matter approaches based on different flavors of many-body perturbation theory as well as static and time-dependent density (and density matrix) functional approaches. Thus, the articles collected in this section cover a wide and impressive range of topics in the fields of chemistry, physics, and material science.

In the next 12 chapters (and in some of the 4 plenary presentations), we provide an in-depth discussion of the basic concepts of density-functional theory and the development of exchange and correlation functionals (► Chap. 11, “Recent Developments in Density Functional Approximations,” L. Li and K. Burke), which are able to cope with strong correlations, charge transfer phenomena (► Chap. 12, “Charge Transfer in Molecular Materials,” T. Zhu, T. Van Voorhis, P. de Silva) and dispersion (van der Waals) (► Chap. 13, “Van der Waals Interactions in Material Modelling,” J. Hermann and A. Tkatchenko) forces within a DFT formalism and beyond, both in the static as well as in time-dependent domains (touching on the efficient ab initio modeling of pump probe spectroscopies (► Chap. 14, “Pump-Probe Photoelectron Spectra,” U. De Giovannini)). After having presented the approach to solve the many-body problem from a density-functional perspective, we change gear and address the recent exciting developments in correlated many-body techniques based on Green’s functions methods, including new developments on the GW+BSE framework for fermions (► Chap. 15, “Modeling Excited States of Confined Systems,” L. Hung and S. Ögüt) and coupled fermion-boson systems (► Chaps. 16, “Many-Body Calculations of Plasmon and Phonon Satellites in Angle-Resolved Photoelectron Spectra Using the Cumulant Expansion Approach,” F. Caruso, C. Verdi, F. Giustino, and ► 17, “Non-equilibrium Green’s Functions for Coupled Fermion-Boson Systems,” D. Karlsson and R. van Leeuwen), non-equilibrium dynamical mean field approaches (► Chap. 18, “Non-equilibrium Dynamical Mean-Field Theory,” M. Eckstein), quantum (► Chap. 19, “Correlations and Effective Interactions from First Principles Using Quantum Monte Carlo,” L. Wagner), and diagrammatic Monte Carlo approaches (► Chap. 20, “Diagrammatic Monte Carlo and GW Approximation for Jellium and Hydrogen Chain,” K. Van Houcke, IS Tupitsyn and NV. Prokof’ev) as well as coupled cluster and quantum chemistry schemes (► Chap. 21, “Coupled Cluster and Quantum Chemistry Schemes for Solids,” A. Grüneis). This section ends with a contribution on how those different electronic structure methods could be combined with optimal control theory in order

to design protocols that allow one to achieve specific predefined targets (► [Chap. 22, “Optimal Control Theory for Electronic Structure Methods,”](#) A. Castro), i.e., bring a system into a specified electronic state, maximize a higher order response function, improve the yield of a chemical reaction, etc. Those methods are just several selected from a lot of examples, given to illustrate the current status in ab initio calculations. Yet work needs to be done toward the inclusion of higher order vertex effects into the many-body description of electron-electron and electron-phonon interactions in order to have a more general ab initio theory of the spectra of weak and strongly correlated electronic systems.

3 Final Concluding Remarks

In conclusion, this section is a journey through some of the recent advances in solving the many-body electronic problem in complex materials, which have been enabled by major theoretical and methodological developments. Some of the methods and ideas discussed are very recent and will clearly evolve in the next years. Also, I want to mention here three other schemes that have emerged as powerful tools to deal with correlated many-body systems that have not been addressed by any of the chapters in this section, just to name a few: density-matrix renormalization group (Schollwöck 2011) and embedding methods (Wouters et al. 2016), stochastic method for DFT (Cytter et al. 2018) and many-body schemes (Neuhauser et al. 2014), auxiliary field quantum Monte Carlo (Motta and Zhang 2017), (the recent advances on this topic are reviewed in ► [Chap. 7, “Ab Initio Electronic Structure Calculations by Auxiliary-Field Quantum Monte Carlo”](#) by S. Zhang in this volume) machine learning for many-body problems (Carleo and Troyer 2017), quantum electrodynamical density-functional theory (Ruggenthaler et al. 2018; Flick et al. 2015). This is just an indication of the dynamism and wealth of ideas and methodologies being explored in our community to enable to tackle the many-body problem in realistic interacting quantum materials. This is clearly an exciting field of research.

Especially in this field, we have been witness of a real knowledge transfer from academia to society in the last years, with the rise and establishment of many start-up companies based on such accumulated knowledge (we are clearly entering the age of big data analytics in many fields arounds us, and computational materials science has joined the wave since the start). In this context, the whole Handbook and in particular this fundamental section on electronic structure will play an important role in further enabling and strengthening such synergy between fundamental research and society.

I don't want to take more space and much rather would like to leave you enjoying the reading of the next articles in which many experts have laid out the fundamentals of the electronic structure methods being in use now, which will shape the field of chemistry and condensed matter physics in the next years. I hope you will find those contributions interesting and relevant for your scientific work or scientific curiosity.

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