Preface

In recent decades, the modern first-principles theory of real materials and its practical implementation in computer codes has made enormous progress. It is illustrated by rapid advances in basic theory, computational methods, and applications. The electronic structure theory has advanced to the point where not only an accurate description of properties of condensed matter such as solids, nanosystems, and molecules is possible but bold predictions of yet unmade materials and of unsuspected physical properties are being made.

A subdiscipline of the electronic structure field is the investigation of excited states of matter to learn more about materials properties or to find novel physical effects, sometimes called 'theoretical spectroscopy'. It combines quantum-mechanics-based many-body theories and computer simulations to understand the interaction of radiation and matter. The understanding of both the interaction of matter and radiation – visible or ultraviolet light, X-rays, and electron beams – and our capability to analyze and predict the materials reaction enhances our ability to design new materials, improve devices, and understand our environment. Beyond the interpretation of results of experimental spectroscopies from an atomistic quantum-mechanical point of view, the theoretical spectroscopy has reached predictive power for properties of complex materials critical to the development of new technologies. It includes to predict atomic arrangements to design materials with a desired spectroscopic property.

The literature, including the number of good books, on the modern electronic structure theory can hardly be overlooked today. By contrast, the rapidly developing field of electronic excitations of matter has been documented only in very few books, mainly as an appendix to the conventional electronic structure theory with a stronger focus to ground state properties and a reduced relationship to the theory and calculation of spectral properties, which can be directly compared with measurements. The theoretical spectroscopy is based on the many-body perturbation theory (MBPT) developed by Kadanoff, Baym, Hedin, Lundqvist, and many other colleagues already in the 1960s of the last century. However, the first numerical simulation of single-particle excitations by Hybertsen and Louie became possible in the mid-1980s after the implementation of the density functional theory, developed

originally for the ground states. Based on these '*ab initio*' (called in physics but not in chemistry) methods the first simulation of electron-hole pair excitations and the computation of optical spectra from first principles have been demonstrated 1998 by Reining, Del Sole and others. Meanwhile, the solution of Dyson and Bethe-Salpeter equations has been developed to standard methods which supplement many available electronic structure codes. However, there is an increasing opening of a gap between the knowledge of the theoretical basics and the frequent use of such codes to study real problems.

The purpose of this book is therefore to provide a unified exposition of the many-body theory and methods of electronic structure calculations, together with instructive examples for computational methods and actual applications or comparisons with measured data. The theoretical and numerical methods are developed toward the calculation of charged and neutral electronic excitations as well as complete electron or optical spectra. The presentation is focused on the many-body perturbation theory based on Green functions. Other approaches to electronic excitations as the time-dependent density functional theory, the dynamical mean-field theory or the quantum Monte Carlo method are only mentioned for the benefit to follow a clear 'red line' from the basic theory to numerical calculation of spectra. The author apologizes for this and other subjective decisions, for instance the selection of examples. The aim of the book is to serve graduate students as well as researchers in the field. Consequently, it not only provides a text for courses on electronic structure or to serve as supplementary material for courses on condensed matter physics, quantum chemistry and materials science but an advanced text for Ph.D. students and scientists working in the field of theoretical spectroscopy. Even the second half of each part of the book, in particular the final results and the application of the theory to real problems, should be interesting for experimentalists. The book is also intended to improve communication between the two communities in physics and chemistry, despite the fact that the theoretical methods mainly originate from the physics of the inhomogeneous electron gas. All readers are encouraged to provide feedback to the author suggesting updates, corrections, additions, etc.

The text is divided into four parts. Part I describes condensed matter in terms of the many-body quantum mechanics and quantum field theory. Special care is taken to characterize not only the motion of the electrons in the field of nuclei but also the electron-electron interaction. Besides the (longitudinal) Coulomb interaction of the electrons also their (transverse) interaction via the entire electromagnetic field generated by the moving electrons and their spins are described. The terms exchange and correlation are introduced. Electron exchange is described within the Hartree-Fock theory. The description of electronic excitations asks for starting electronic structures. Therefore, Part II is devoted to the density functional theory, in particular to the use of the Kohn-Sham ansatz and to widely used exchange-correlation functionals. Generalizations to spatially non-local functionals and the inclusion of dispersion forces are also presented. This part does not compete with specialized books about density functional theory. Rather, it only serves to illustrate how starting atomic geometries and electronic structures can be made available on a first-principles basis

for the subsequent studies of electronic excitations. The concept of thermodynamic Green functions within the framework of the grand canonical statistics is applied in Part III. It addresses the derivation of the set of fundamental equations of the many-body theory based on Matsubara Green functions. The quasiparticle concept is introduced. The understanding and the explicit use of the developed scheme are mainly illustrated in the framework of the Hedin GW approximation. The success of the approach is demonstrated for all kinds of condensed matter including a comparison with experimental data as, e.g., obtained by means of photoemission spectroscopy. The not fully understood problem of satellite structures to single-particle excitations is discussed in the last chapter. Part IV describes electron-hole-pair and collective excitations. The Bethe-Salpeter equations for the polarization and density correlation functions based on the two-particle Green function are derived. For the description of optical spectra the influence of the spin structure and the inclusion of local-field effects are discussed. The Bethe-Salpeter equation for the macroscopic polarization function is solved within the GW approximation. The relationship to excitons of different kinds and consequences for optical spectroscopies are illustrated. As a culmination of the present-day treatment, it is clearly demonstrated that an optical or energy-loss spectrum can be only computed in agreement with experiment if excitonic and quasiparticle effects are included. Finally, the inclusion of dynamical effects and free carriers and their consequences are described.

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