



Theoretical spectroscopy / Spectroscopie théorique

Foreword

Lucia Reining^{a,b,*}

^a *Laboratoire des Solides Irradiés, École polytechnique, CNRS, CEA/DSM, 91128 Palaiseau cedex, France*

^b *European Theoretical Spectroscopy Facility (ETSF)*

Available online 2 September 2009

Abstract

This issue is dedicated to “Theoretical Spectroscopy”. It is meant to give an overview of what this branch of physics is able to contribute today to the progress of science, combining theory developments, the building of complex computer codes, and large scale numerical calculations. Complementary to experiment and to modeling considerations, theoretical spectroscopy yields new understanding and predictions concerning novel materials. The questions that are treated range from abstract theory to problems of technological interest. Theoretical Spectroscopy is a field that undergoes rapid development; here we give a snapshot of its capabilities today. *To cite this article: L. Reining, C. R. Physique 10 (2009).*

© 2009 Published by Elsevier Masson SAS on behalf of Académie des sciences.

Résumé

Avant-propos. Ce numéro est dédié à la « Spectroscopie théorique ». Son but est de donner une idée de ce que cette branche de la physique peut apporter aujourd’hui au progrès de la science, en combinant les développements théoriques, la mise en place de codes de calcul complexes, et des calculs numériques à grande échelle. Complémentaire des expériences et des modèles, la spectroscopie théorique offre une nouvelle compréhension et prédit les propriétés des matériaux nouveaux. Les points abordés vont des questions théoriques abstraites jusqu’aux problèmes d’intérêt technologique. La spectroscopie théorique est un champ qui se développe rapidement ; nous donnons ici un aperçu de ses capacités actuelles. *Pour citer cet article : L. Reining, C. R. Physique 10 (2009).*

© 2009 Published by Elsevier Masson SAS on behalf of Académie des sciences.

1. Introduction

Our understanding of the interaction between irradiation (by visible or ultraviolet light, X-rays, electron beams, etc.) and matter, and our capability to analyze and predict the reaction of materials as a consequence of the electronic response, condition our ability to design new materials, add new functionalities, improve devices, or simply understand our environment: electronic excitations, and sometimes the consequent structural modifications, are at the origin of a wide range of phenomena, processes or problems such as the colour of materials, photosynthesis, or radiation defects.

A simplified description of electronic structure views the electronic response in terms of transitions of independent electrons between well-defined energy levels. However, the whole problem of this topic lies in the fact that the independent electron picture is a crude approximation, that shows its limits particularly in the context of electronic

* Correspondence to: Laboratoire des Solides Irradiés, École polytechnique, CNRS, CEA/DSM, 91128 Palaiseau cedex, France.
E-mail address: lucia.reining@polytechnique.fr.

excitations. Electrons are subject to the strong Coulomb interaction, and therefore respond collectively to an external perturbation: electrons are *correlated*.

Electronic correlation is by itself the source of a wide range of interesting phenomena. It gives rise to spectacular observations in experiments, such as superconductivity, or the fractional quantum Hall effect. It has a great impact on our surroundings: think about defect creation through a self-trapped exciton, or, in the animal world, the adhesion of a gecko on a surface (through the van der Waals attraction). At the same time, it is a source of excitement and – much trouble for theoreticians: today, although the underlying interaction (the Coulomb interaction) is “simple” and well understood, a unifying framework is still missing that would allow us to describe, analyze, understand and predict all those phenomena on the same footing. Various approaches have led to significant breakthroughs, but are limited to certain domains: a non-exhaustive list includes model approaches [1], renormalization group theory [2], density functional theory (DFT) [3], configuration interaction [4], many-body perturbation theory (MBPT) [5], Quantum Monte Carlo, see e.g. [6] and dynamical mean field theory (DMFT) [7]. The latter, for example, has met a lot of success in describing transition metals and their oxides [8], whereas MBPT (e.g. in the GW approximation [9] to the electron self-energy) is known to predict bandgaps of moderately correlated materials with good precision (contrary to DFT in the Kohn–Sham (KS) formulation) [10]. Much effort is made in the various communities to extend the range of validity of the methods, but this is a tremendous task; to stay just with the latter two examples: One should extend single-site DMFT to cluster DMFT in order to make the method applicable to all those materials (the big majority) where one cannot treat a small number of “correlated” orbitals separately [8]. On the other hand, in order to extend MBPT from GW to a method able to describe a Mott–Hubbard insulator one will probably have to design a vertex correction that cannot be obtained by adding a finite number of diagrams [10].

In the framework of *ab initio* spectroscopy calculations the most frequently used approaches today are either based on density functionals, or on many-body perturbation theory. More recently, model dynamical mean field theory has been combined with *ab initio* calculations to treat the problem of electronic excitations in strongly correlated materials. These are therefore the three lines of theoretical research that are represented in the present volume, and that will be briefly resumed in the following.

2. Density functional based approaches

Ground state static density functional theory (DFT) [3] is a well established tool, especially in its Kohn–Sham formulation, for total energy calculations, structure determination, the description of potential energy surfaces for atomic motion, and as a first guess for electronic bandstructure. A good ground state calculation is the starting point for any spectroscopy work. DFT, often used in the local density approximation (LDA) or other local or semi-local approximations, allows us to obtain efficiently the structure of the system of interest. This can already be a quite complex task (e.g., when amorphous structures, or surface reconstructions, are needed) or in strongly correlated systems like transition metal oxides. The structure, density and Kohn–Sham electronic structure are then the starting point for subsequent spectroscopy calculations. In particular, the latter have to correct for the fact that the Kohn–Sham bandgap is systematically smaller than the experimental quasi-particle (photoemission) gap, which leads e.g. to a redshift of calculated optical spectra with respect to the experimental onset. This is not a failure of DFT – there is no reason for the Kohn–Sham gap to be in agreement with experiment, since the theory is only meant to yield a correct ground state density and total energy.

In order to describe spectroscopy, hence the response of systems to time-dependent external potentials, one has to extend DFT to time-dependent DFT (TDDFT) [11]. The latter describes the evolution of the density under the influence of a time-dependent external potential. It is therefore suitable for the description of excitations that do not change the number of particles in the system, such as optical absorption, electron energy loss, inelastic X-ray scattering. The main theoretical bottleneck is to find good approximations for the time-dependent exchange–correlation (xc) potential and its variation with density (the so-called xc kernel in linear response, as well as higher order variations). The main advantage with respect to other many-body methods is its potential computational efficiency, due to the local nature of the xc potential.

3. Many-body perturbation theory

Whereas TDDFT concentrates on the description of density, Green's functions describe the propagation of one or more particles in the system. Green's functions based many-body methods allow one therefore to access neutral excitations (as TDDFT, e.g. electron–hole pairs) as well as excitations involving a change in particle number (e.g., one additional particle or hole as measured in direct or inverse photoemission) [12]. Another advantage with respect to density-functional based approaches is the relative facility to find good approximations, since the physical picture of quasi-electrons and quasi-holes is used. The main drawback is the rapidly increasing computational load, since already the one-quasi-particle problem involves a “potential” that is non-local in space and time (the self-energy). The so-called GW approximation for the self-energy, introduced in 1965 by Lars Hedin [9], is used for *ab initio* bandstructure calculations since the 1980s. In this approximation the self-energy is expressed as a product of the one-particle Green's function G , and the screened Coulomb interaction W . It successfully describes electron addition and removal energies for metals, semiconductors and insulators, in the bulk as well as at surfaces and for confined structures, and is therefore one of the methods of choice for the description of direct and inverse photoemission experiments. It corrects the problems of the Kohn–Sham bandstructure, in particular the severe underestimation of the bandgap. The main bottleneck is the numerical calculation of the full dynamical inverse dielectric matrix, that is used in order to obtain W . The main limitation is its failure to describe correctly strongly correlated materials, as well as satellites of the spectral function in general. If one wishes to go beyond one-particle excitations, the state-of-the-art method is the solution of the Bethe–Salpeter equation that describes electron–hole excitations. Its ability to reproduce excitonic effects in semiconductors has already been shown in the seventies through semi-empirical work by Hanke and Sham [13]; it is used in the *ab initio* framework since 1995 for clusters, and since 1998 for bulk materials. More complex situations (surfaces, polymers, ...) have been addressed later. Absorption as well as electron energy loss or inelastic X-ray scattering experiments are precisely reproduced and conveniently analysed by this approach, that is therefore clearly predictive. The main bottleneck is the numerical calculation of a two-particle (electron–hole) Hamiltonian as well as, according to the algorithm chosen, its diagonalisation or inversion. Approximations today mostly rely on the GW approximation for the self-energy, and a static electron–hole interaction.

4. Dynamical mean field theory

In the past decade, many-body theory has witnessed the development of a new method for the quantitative treatment of correlated electron materials: the “Dynamical Mean-Field Theory” (DMFT) [7,8]. Originally developed for model Hamiltonians of interacting electrons, this approach has now been implemented successfully in the framework of realistic electronic structure calculations. In this approach, an energy-dependent, local self-energy matrix is calculated from a self-consistent embedding of an atom in an effective medium. While the starting point (a many-body Hamiltonian in a basis set of localised orbitals, constructed from an LDA calculation) is similar to that of LDA + U, DMFT goes considerably farther by fully including local quantum fluctuations. This approach has led to major progress in our understanding of correlated metals, of Mott insulators, and of f-electron materials, both for ground-state properties (e.g. for the equilibrium volume and volume-collapse transitions of rare earth and actinides) and for excited states (e.g. by successfully predicting the photoemission spectra of several transition-metal oxides with a partially filled d-shell). The *ab initio* calculation of the commonly used parameter U is still a major challenge, that might be solved e.g. by combining DMFT and GW.

These efforts indicate that *in fine* a combination of methods may well be a most successful way to go.

References

- [1] J. Hubbard, Proc. Roy. Soc. A 276 (1963) 238.
- [2] K.G. Wilson, Rev. Mod. Phys. 47 (4) (1975) 773;
S.R. White, Phys. Rev. Lett. 69 (1992) 2863.
- [3] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864;
W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 1133.
- [4] Christopher J. Cramer, Essentials of Computational Chemistry, John Wiley and Sons, Ltd., Chichester, 2002, pp. 191–232.
- [5] A.L. Fetter, J.D. Walecka, Quantum Theory of Many-Particle Systems, Dover, New York, 2003.
- [6] Quantum Monte Carlo methods in physics and chemistry, in: M.P. Nightingale, Cyrus J. Umrigar (Eds.), Proceedings of the NATO Advanced Study Institute, Ithaca, New York, 12–24 July 1998, in: NATO Science Series C: (closed), vol. 525, Springer, 1999.

- [7] A. Georges, et al., *Rev. Mod. Phys.* 68 (1996) 13.
- [8] G. Kotliar, S.Y. Savrasov, K. Haule, V.S. Oudovenko, O. Parcollet, C.A. Marianetti, *Rev. Mod. Phys.* 78 (2006) 865.
- [9] L. Hedin, *Phys. Rev. A* 139 (1965) 796;
G. Strinati, *Riv. Nuovo Cimento* 11 (1988) 1.
- [10] F. Aryasetiawan, O. Gunnarsson, *Rep. Prog. Phys.* 61 (1998) 237;
W.G. Aulbur, L. Jonsson, J.W. Wilkins, *Solid State Phys.* 54 (2000) 1.
- [11] E. Runge, E.K.U. Gross, *Phys. Rev. Lett.* 52 (1984) 997.
- [12] G. Onida, L. Reining, A. Rubio, *Rev. Mod. Phys.* 74 (2002) 601, and references therein.
- [13] W. Hanke, L.J. Sham, *Phys. Rev.* 33 (1974) 582;
W. Hanke, L.J. Sham, *Phys. Rev. B* 12 (1975) 5401.