Report on the Cecam School
"Theoretical Spectroscopy Lectures: Theory and Codes"
Zürich, May 2009

http://www.cecam.org/workshop-1-314.html

Introduction

The aim of the school was to give a deep introduction on the theoretical and practical aspects of the electronic excitations. Electronic excitations are probed by experimental techniques such as optical absorption, EELS and photo-emission (direct or inverse). From the theory point of view, excitations and excited state properties are out of the reach of density-functional theory (DFT), which is a ground-state theory. In the last twenty years other ab-initio theories and frameworks, which are able to describe electronic excitations and spectroscopy, have become more and more used: time-dependent density-functional theory (TDDFT) and many-body perturbation theory (MBPT) or Green's function theory (GW approximation and Bethe-Salpeter equation BSE). In fact, computational solutions and codes have been developed in order to implement these theories and to provide tools to calculate excited state properties. The present school focused on these points, covering theoretical, practical, and also numerical aspects of TDDFT and MBPT, and codes implementing them (ABINIT, DP, EXC).

Organization

The tutorial was organized by Francesco Sottile (Ecole Polytechnique, Palaiseau, France), Xavier Gonze and Gian-Marco Rignanese (Universite Catholique de Louvain, Belgium), Valerio Olevano (Institut Neel, Grenoble, France). Invited lecturers: Valerie Veniard (Ecole Polytechnique, Palaiseau, France), Fabien Bruneval (CEA, Saclay, France), Matteo Gatti (Universidad del Pais Vasco, San Sebastian, Spain), Matteo Giantomassi (Universite Catholique de Louvain, Belgium).

The tutorial was overbooked by a factor of two. At the end 22 students had been accepted, representing 8 European countries and 1 African: Belgium (7 + 2 organizers + 1 lecturer), France (5 + 2 organizers + 2 lecturers), Germany (3), United Kingdom (2), Spain (1 + 1 lecturer), Hungary (1), Italy (1), Switzerland (1), Tunisia (1).

Details and timing of the Lectures

The presentation of the theory and theoretical aspects of the implementation took place in the morning sessions, in this order: introduction on spectroscopy, connection between the microscopic simulated world and the real macroscopic world, reminders of Density Functional Theory (Day 1), Time Dependent Density Functional Theory (Day 2), introduction on Green's Function approach, Many Body Perturbation Theory (Day 3), GW approximation (Day 4), Bethe-Salpeter equation (Day 5). The afternoon sessions were devoted to practical hands-on of the theory studied in the morning: DFT with Abinit (Day 1 and Day 3), TDDFT with DP (Day 2 and Day 3), GW with Abinit-GW (Day 4), Bethe-Salpeter with EXC (Day 5). Afternoon session 3 (on Wednesday was considered free, however most of the students stayed in the computer room, working on the previous days' assignments. Animated discussions sessions took place on Day 3 afternoon and Day 5 morning.

Day 1
- Introduction to Spectroscopy (Theory - 1/2 h)
- Density Functional Theory (Theory - 2 h)
- Microscopic-Macroscopic connection (Theory - 1 h)
- DFT with Abinit (hands-on - 3 h)

Day 2
- Time Dependent DFT (Theory - 2 h)
- TDDFT - Casida eqs. (Theory - 1 h)

- TDDFT with DP (hands-on - 3 h)

Day 3
- Brief round table (1/2 h)
- Introduction to Many-Body Perturbation Theory (Theory - 1 h)
- Many Body Perturbation Theory: GW approximation (Theory - 1.5 h)
- Free or Discussion session (2-3 h) and hands-on

Day 4
- MBPT and GW in practice (Theory - 1.5 h)
- GW with Abinit (hands-on - 4 h)

Day 5
- Bethe-Salpeter Equation (Theory - 1 h)
- BSE vs TDDFT (Theory - 1 h)
- BSE with EXC (hands-on - 3 h)

Abstracts

- Introduction to spectroscopy
  In this lecture, I will describe various experimental techniques used to investigate the spectroscopic properties of matter. I will first present the processes (scattering, absorption, and emission) resulting from the interaction of particles with matter, and which are involved in those experimental techniques. The various particle sources will also be described (with a special emphasis on synchrotrons and free electron lasers). Then, I will successively present photoemission spectroscopy (PES), inverse photoemission spectroscopy (IPES), x-ray absorption spectroscopy (XANES, EXAFS, and XANES), electron energy loss spectroscopy (EELS), inelastic x-ray scattering spectroscopy (IXS), reflectance anisotropy spectroscopy (RAS), Auger electron spectroscopy (AES), and X-Ray fluorescence spectroscopy (XRF). For all methods, a link is given to the quantities that can be computed using the theoretical methods in the subsequent lectures.
- Density-Functional Theory
  This two-hour lecture covered the basics of density-functional theory : formalism and implementation. A special care was taken to present the shortcomings of Density Functional Theory as concerns its use for the computation of band structure, and , on the other hand, its usefulness as a starting point for more elaborate theories. The hands-on sessions were also prepared. The following sections were covered :
  A. The electronic N-body problem
  B. Functionals of the density
  C. The Kohn & Sham approach
  D. Density Functional Theory : approximations
  E. The band gap problem
  F. The plane wave basis set / Brillouin zone integration
  G. Pseudopotentials
  H. Computing the forces
  I. Iterative algorithms
  J. ABINIT
- Introduction to TDDFT
  A review of time-dependent density-functional theory and its foundamental assumptions,

theorems, caveats and drawbacks will be presented. In particular, we will illustrate Linear-Response TDDFT in an actual implementation which is in Frequency-Reciprocal space and on a Plane-Waves basis, as implemented in the DP (Dielectric Properties, http://www.dp-code.org) code. This scheme is well suited to EELS and optical spectroscopy calculations, and particularly convenient for infinite periodic bulk solids, but also semi-infinite systems like surfaces, wires and tubes by the use of supercells. A critical analysis of all the classical approximations (RPA, Adiabatic LDA, with and without local-field effects) as well as the most recent ones (long-range contribution only, Nanonoquanta kernel, etc.) will be presented together with illustrating examples of spectra on prototype condensed matter systems, like bulk silicon, graphite, nanotubes, etc. This lecture is followed by a practical session on the use of DP code.

- TDDFT: direct computation of excitation energies.
  This brief lecture (30 minutes) presented the derivation of Casida equations from Time-Density Functional Theory. The later had been presented in th<e previous lecture the same day. The goal was to prepare the student to the type of equations that are obtained in the more elaborate Bethe-Salpether approach. Some application of Casida's approach was also mentioned.
- Green's functions formalism
  In this lecture we will make a link between the Green's function defined as a resolvent of a hamiltonian and the Green's function defined as propagation of an additional particle in presence of all the others. We will discuss the properties of the Green's functions in many-body perturbation theory and introduce the problem of its calculation. This will represent the motivation for the following lecture about Hedin's equation and the GW approximation.
- Many-Body Perturbation Theory
  In this lecture, I present the theoretical basics required to introduce the GW approximation of the many-body problem. The GW approximation has been shown to be very successful in predicting the band gaps of solids. It improses significantly over the standard density-functional approaches for the electronic structure. I introduce the so-called Hedin's equations, which offer an exact formulation of the many-body problem in a functional language. The central quantities are the Green's function G and the screened Coulomb interaction W. In this framework, the GW approximation appears naturally as a first order approximation in the "small" quantity W. This is a formal derivation of the GW approximation. In order to elucidate the physical content of the GW approximation, I show that the GW approximation is a natural improvement over the well-known Hartree-Fock scheme. The only difference comes from the screening of the Coulomb interaction, which accounts for the fact that the interaction between electrons in a solid is decreased by the polarization of the medium.
- Bethe-Salpeter Equation
  This lecture presents the Many-Body approach for the description of polarizability. Within the Green's functions formalism, the linear response polarizability is given by the 2-particle Green's function which obeys to a Dyson-like equation, similarly to the linear response TDDFT eqution. The derivation of the Bethe-Salpeter Equation as well all the approximations involved in the (several) steps are illustrated in this one-hour lecture, before presenting the numerical aspects useful for the afternoon hands-on.
- DFT vs MBPT
  The two basic formalisms are presented together to underline the similarities and the differences. Particular emphasis is devoted to the combination of the two theories in order to merge the advantages. MBPT from DFT: how to use the density functional concept to simplify the Self-Energy (Sham-Schluter equation). TDDFT from MBPT: how to use the screened coulomb interaction coming from the Bethe-Salpeter to devise new and more efficient exchange-correlation kernel for the TDDFT (Mapping theory kernel).

Response from the Students

As tutorial organizers, we were very pleased that most of participants considered as very important a dedicated school focused on electronic excitations. Electronic structures calculations are still very far from being “black box” tools, and require deep and targeted training before being able to obtain sensible results. Thanks to the great effort of the electronic structure community, in the last three decades, many ground state codes are becoming very user-friendly (like Abinit, used in this school). However the number of mistakes made by applying TDDFT or GW approximation is directly proportional to the high expectations that the non-experienced user associates to these approaches. This will only create a negative opinion for the applicability of electronic excitations theories. We are pleased then to notice how favorable our school has always been considered, along these years. As teachers, we were very pleased with audience questions and answers. Student exercises were given along the whole duration of the school (especially concerning what one expect to be the calculated quantity on the basis of the theory studied the very same morning), and most of the students answered correctly to more than 90% of the tests.

Practicals

The tutorial took place in Zurich, which was the first time for us organizers. Most of the things went smooth. We have been assisted by Cecam personnel (many thanks to Emilie Bernard who was there in the first days helping in settling everything up, and to Mauro Ferrario for his presence in the final days), and local ETHZ personnel (many thanks to Micheline, Markus and Eva). Hotel and tutorial locations are quite far apart, but the Zürich transport system is very efficient and no problem arise. The only (little) flaws were a power black-out on the first day (very short, but caused delays in the production of photocopies, while it didn't really caused troubles on the lecture) and the tutorial dinner, which took place on Tuesday (Day 2), not really at the level of the price payed. So very minor shortcomings compared to an evident success (from our point of view).

Conclusions

From the organizers' point of view the school has been a frank success. Thanks also to the cumulated experience of last editions, and to a good team-work among lecturers (and organizers), the lectures have been largely considered appropriate in length, difficulty, and clarity, by the students. The participation level has always been very high, and we have been glad to notice how, sometimes, the discussion time has been stretched much over the allocated time, in particular for the most sensible lectures (MBPT and TDDFT). Almost none of the students took the Wednesday afternoon free, preferring a discussion with the lecturers or continuing the hands-on in his/her own account.

Few problems have been encountered in this school (see above), and only minor ones, while the organization and the connection with the ETHZ and Cecam people was flawless.

Given this, and previous, success of the school, we are going to apply for another tutorial in 2010.

Basic literature

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[4] Strinati, Riv. Nuovo Cim. **11**, 1 (1988)