Theory and computation of electronic excitations in condensed matter systems: the ETSF project

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Excited states and electronic excitations are a key for the understanding of condensed matter properties, and for the design of novel materials, systems, and solid-state devices. In fact, many properties of solids depend on their excitation spectrum: from the external aspect (colors), to electrical or thermal conductivity, to the way an LCD screen operates, up to the exotic behaviour of nano-machines such as molecular engines (see, e.g., [1]).

From the physicist's point of view, electronic excitations are at the base of many modern spectroscopic techniques: electrons, photons, or atoms can be sent as probes which, impinging on a sample, induce some kind of excitation. By measuring, e.g., the excitation energies, one can obtain useful compositional and/or structural informations about the sample itself. Typical examples are optical spectroscopy and photoelectron spectroscopy, two of the most widely used characterization techniques in condensed matter laboratories.

Fig.1
Different experimental techniques, and the related different types of electronic excitations which must be considered in the theoretical description.
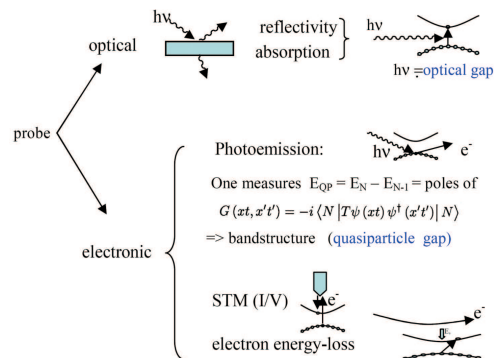
Experiments, of course, are most useful if they can be interpreted in the light of a theoretical model, and theoretical models can be useful in order to suggest how to perform new experiments. For this reason, large efforts are being done in order to deepen and to extend our theoretical understanding of electronic excitations in condensed matter. The task is not an easy one, being the many-body problem very hard to solve for the ground state of a system of interacting electrons.

Among the state-of-the-art theoretical methods and tools, a prominent role is today played by the so-called *ab-initio* approaches. These are characterized by a complete absence of free (adjustable) parameters in the theory: everything is directly derived from the fundamental equations of quantum mechanics (since only Coulomb forces and interactions are relevant in our case, the ingredients from which to start are exactly known). The scope of the calculations is not, however, simply to reproduce the experimental results, which will be of little interest: aim of the theoretician should be to derive from his results some new information about the system, namely informations which are not accessible through experiment. In practice, a theoretical calculation should be thought as an additional "microscope" that can be used, besides the "experimental" one, to look inside the sample in order to understand its behaviour.

Ab-initio methods for the many-electrons system have been developed since many years, starting from the pioneering works of Hartree [2] and Fock [3]. However, in the last 20-25 years the use of ab-initio methods in the study of real systems has become more and more frequent, not only because of the availability of powerful computers, but also thanks to the introduction, between the sixties and the eighties, of novel theoretical approaches which have allowed us to simplify substantially the required numerical calculations. The main progress has been done with the Density Functional Theory (DFT), introduced by W. Kohn and Hohenberg in 1964 [4]. Through suitable theorems, DFT allows one to shift the attention from the many-body wavefunction (a "monster" quantity for a system of many interacting particles [5]) to the much simpler *electronic density*, i.e. essentially to the squared modulus of the N-body wavefunction integrated over $(N-1)$ of its variables.

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In its original formulation, DFT only applies to the system's ground state: it can be found as the minimum of a suitable functional, with respect to the variation of the sole density. Only in 1984 DFT has been generalized by E.K.U. Gross to Time-Dependent DFT (TDDFT) [6], allowing one to study also the excited states. Hence, the available excited state theoretical and numerical tools, being about twenty years younger, are still much more primitive than those dedicated to the ground state, and much work remains to be done in their development.

Another important aspect which explains why the excited-state ab-initio methods are still in their early stage is related to the fact that excitations of many different types are possible, and different excitations often are better studied with different theoretical tools. As shown in Fig. 1, light absorption or electron energy-loss spectroscopy involve an excitation which does not change the number of electrons in the sample, while photoemission (PES), inverse photoemission (IPES), and scanning tunneling microscopy (STM) involve excited states with N-1 or $N+1$ electrons, being hence directly related to the poles of the one-particle Green's function. Different methods, such as the GW method, the Bethe-Salpeter Equation (BSE) method, and the previously mentioned TDDFT, should be selected and used to study these different kind of excitations [7].

Fig.2
Schemes for computing the dynamical polarizability from an ab-initio point of view: Bethe-Salpeter Equation (top), or Time Dependent Density Functional Theory (bottom). See Ref. 7 for details.
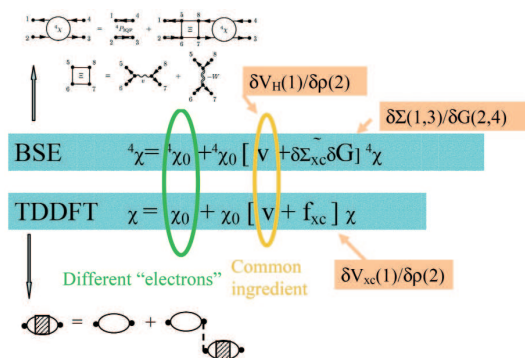
Fig.3
Optical Absorption spectrum of solid Argon (imaginary part of the dielectric function), computed at different levels of the theory: Independent particle (LDA bandstructure); Independent Quasiparticles with self-energy effects (GW); LDA plus Local Fields (RPA); Full calculation with excitonic effects (EXC). The latter curve can be obtained either within the BSE scheme, or using TDDFT. Red dots are the experimental data.
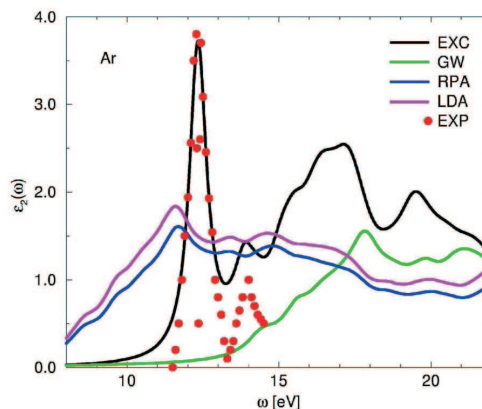
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Nowadays most of these ab-initio approaches can be applied to realistic and complex systems, such as surfaces [8] and nanostructures [9]. However, different degrees of approximation can be considered in order to be able to evaluate numerically the resulting equations and formulas. To this aim, it has revealed particularly useful to make an effort to compare efficiently different approaches, bringing them on similar grounds, and singling out the common ingredients and formulas. For example, this has been done by some of us in the case of TDDFT and BSE approaches in [7]. An example is shown in Fig. 2, where differences and similarities between the BSE and TDDFT equations for the system's polarizability are displayed.

Several successful applications of the ab-initio BSE and TDDFT approaches can be found in the recent literature (see, e.g., [10-12]). Between the most striking results, those concerning optical properties of solids and solid surfaces should be mentioned. In Fig. 3 we reproduce the absorption spectrum of solid Argon, which is very well described both within BSE and TDDFT, while standard bandstructure calculation (RPA or independent quasiparticles approaches), neglecting the excitonic effects, fail to describe the absorption peaks, even qualitatively.

Other applications, between the most recent ones, are those realized by some of the authors in the case of semiconductor surfaces, namely silicon and oxidized silicon reconstructed surfaces. Fig. 4 shows surface optical anisotropic reflectivity spectra for the Si(100) surface, decomposed in its contributions coming from different layers below the surface [13]. This technique allows one to associate some of the spectral features to specific bonds or structures, like silicon dimers at the surface.

Fig. 4
Optical anisotropy spectra calculated for Si(100), an important surface of Silicon since it is used in microchips and semiconductor device technology. The possibility to look at contributions coming from different atomic layers is a nice example of the use of calculations as a "theoretical microscope" (see text).
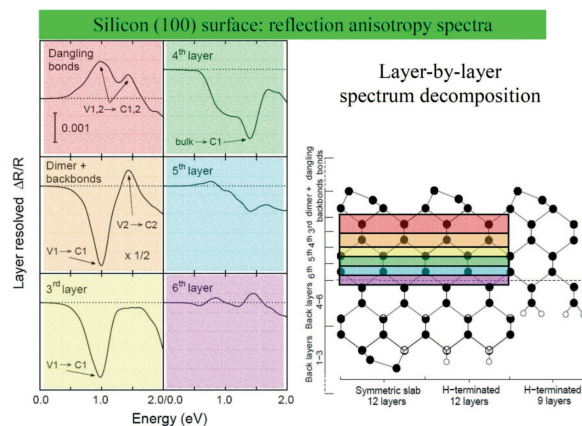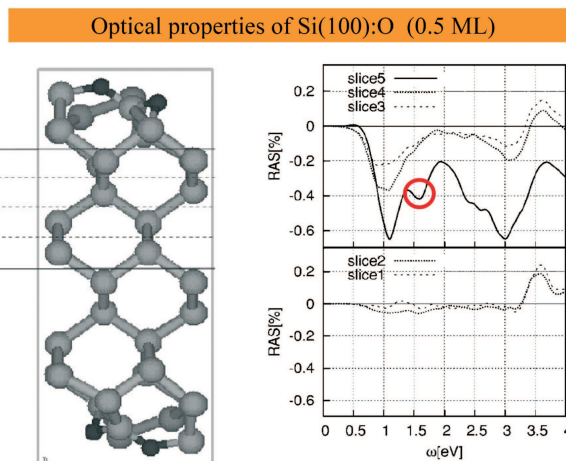

Fig. 5
Same as Fig. 4, but for an half-monolayer oxidized surface: the red circle shows a spectral feature which is associated to the presence of oxygen on surface dimers and backbonds.

104

Surface optical spectra are very sensitive to compositional and structural details. Si(100) has hence also been studied in presence of oxygen, in connection with its interest for semiconductor technology. In fact, thin oxide layers can be grown on Si(100) as insulating layers for building MOS devices. Fig. 5 shows a spectral feature which can be associated to the presence of oxygen atoms on specific adsorption sites, namely surface dimers and surface backbonds in a 0.5 ML oxygen-covered surface [14].

As shown by the examples above, the development and the numerical implementation of reliable ab-initio theoretical tools for computing the spectra of real systems is an important issue in today's condensed matter and solid state physics. In many cases, expertises from different research groups must be put together in order to realize and apply such tools in the most effective way. In fact, the demand for collaborations using state-of-the-art software -and for support- is rapidly growing, amongst both the theoretician and experimentalist communities. Starting from this observation, the idea of creating a dedicated collaborative structure was born, building on an existing 15-years ongoing and expanding collaboration between a number of condensed-matter theory groups in Europe.

In 2004, a NoE (network of excellence) named "Nanoquanta", funded by the European Community under the 6th Framework program, has been set up with the major aim to find a long-term answer to this challenge. Nanoquanta is a substantial undertaking, involving many research groups and interested users across Europe. Today, the ten nodes constituting the network are in charge of building up the so called "European Theoretical Spectroscopy Facility" (ETSF).

The ETSF, inspired to the large experimental facilities, will be a "knowledge center" in which expertise, theory, and the associated software for excited-state calculations will be developed

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and used in different ways, according to the interests and background of the users. Its aim will be to make available the "integrated resources" developed within Nanoquanta to a wide scientific community, after the end of the EU-funded period.

These "integrated resources" consist in the theoretical tools, computer codes, and scientific know-how, which is strongly complementary between the groups forming our network. ETSF will be a distributed structure, with offices in different countries, and will be open to the insertion of new research groups which can contribute with their expertises, specially if it is complementary to the already present ones.

One of the primary objectives of ETSF will also be that of fostering the scientific and cultural interchange with researchers from other scientific disciplines, like chemists and biologists who could be interested in the use of theoretical tools and computational codes available within the ETSF.

Fig. 6
The European Theoretical Spectroscopy Facility (ETSF), an initiative of the "Nanoquanta" Network of Excellence, has been devised to ease and encourage the sharing of theoretical tools and computer codes for the calculation of electronic excitations and related spectra. Significant progress has already been made, and the ETS Facility is planned to become a lasting structure after the end of the Nanoquanta NoE in 2008, independent of support from the EU.
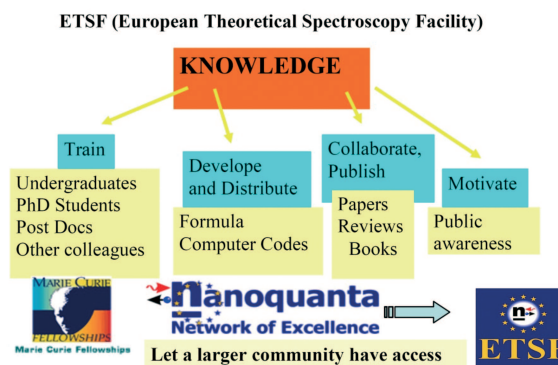
The Nanoquanta groups will constitute the core of ETSF, which will also build a broad and federal community of research groups working on similar topics. Besides those groups directly involved in the theory and software development, users of the facility will be a larger and varied group, composed of researchers from the public and private sector wishing to benefit from the developments in the field of electronic excitations (see Fig. 6).

The ETSF concept is hence introducing an important novelty with respect to the past, when EU and national organisations were supporting scientific collaborations for fundamental developments of theory and computational approaches by funding self-contained, fixed-term research projects and networks, with no permanent opportunity for other researchers to benefit from the "products".