Ab initio calculation of Photo-emission and Coherent Inelastic X-ray Scattering Spectroscopies

F.Sottile, M.Gatti (LSI, UMR7642 CEA-DSM-Iramis, CNRS, Ecole Polytechnique)

Collaborations: Maison de la Simulation, TEMPO and GALAXIES beamlines at SOLEIL

The computational design of materials is gaining broad recognition as an effective mean of reducing the number of experiments that can ultimately lead to the discovery of materials with tailored properties. Notably, the ability to devise new functionalities for specific applications crucially depends on the microscopic understanding of the elementary excitations induced by external perturbations.

Spectroscopy, by probing the response of materials to those perturbations, allows the analysis of the induced elementary excitations and hence the characterisation of the material properties. Photoemission spectroscopy (PES) [1] is the standard tool for studying the electronic structure of materials, measuring the electron addition and removal energies that define the band structures (including the band gap of semiconductors and insulators). Alternatively, scattering experiments like inelastic X-ray scattering (IXS), both in its non-resonant (NIXS) and coherent (CIXS) versions, are techniques able to probe neutral elementary electronic excitations, including their energy and momentum dependence [2-4].

These experimental techniques are rapidly developing, and benefit from the last-generation synchrotron light sources. The accuracy and resolution (in energy, space, and momentum) achieved today are so high that many-body effects are strongly enhanced in experimental spectra making their interpretation far from being trivial. Therefore, a combined experimental and theoretical effort clearly is a very promising strategy in order to foster the design of material properties. However, concerning theory and especially the numerical implementation, ab initio simulations of PES or IXS spectra often lie a long way behind experiments. This doctorate work rightly aims at closing this gap with experiment, thanks to the help of cutting edge numerical implementation, optimization and parallelization.

In order to tackle this ambitious plan, we have been working in the last couple of years on both the theoretical and numerical levels: i) on one side we have recently developed a method to evaluate the microscopic screened Coulomb interaction W for a wide range of momentum transfers, including excitonic effects [5]. This method permits the ab initio description of IXS of materials (also complex ones [6]), and opens the way to a whole series of spectroscopies that contains the physics described by W ; ii) on the other side, a collaboration with the Maison de la Simulation has been already established, with a two year project that lead to the massive parallelization of the DP code, a Time Dependent DFT (TDDFT) open source code for the determination of the dielectric function. The DP code runs today over more than 1000 procs and has been the objective of a successful PRACE preparatory access that has ported the code to run over multiple GPUs.

It is timely to propose the next step: thanks to the newly developed description of the dielectric function including excitonic effects for the whole range of momentum transfers, we propose to:

- investigate, beyond today state-of-the-art, the role of excitonic effects in the screening of the Coulomb interaction W=v/epsilon on spectral functions, band structures and band gaps (quantities to be experimentally measured via PES). In particular, we predict the possibility to observe what we call “excitonic satellites”, and we will propose the pertinent experiment to Synchrotron SOLEIL;
- extend the target of the IXS, to non-diagonal response. CIXS is on one side a challenge for numerical calculation (instead of one, many element of the final dielectric matrix have to be calculated) and experiment (corresponding to particularly low signal/noise setup), but on the other side it is very rich for not only gives a complementary description of the material, but will also permit to construct the visualization of the excitations in real space.

The work

The doctorate work is composed of two main tasks: description of exciton satellites and coherent inelastic X-ray scattering.

1. The state of the art for the calculation of band structures in a wide range of materials is today the GW approximation (GWA) of many-body perturbation theory (MBPT) [8, 9]. Here G is the

Green's function and W the screened Coulomb interaction of the system. Today's calculations are at best represented by the so-called quasiparticle self-consistent GW (QSGW) method [10, 11], which however (though greatly improving with respect to any one-particle approach) sistematically overestimates the band-gap of materials. We plan to systematically investigate, beyond the state-of-the-art GW approximation, the role of excitonic effects in the screening for band structures and band gaps. This will be possible thanks to the solution of the Bethe-Salpeter equation (BSE) and in particular with our recently devoloped method to calculate W in a wide range of energy and momentum transfers [5, 6]. On this basis, a BSE calculation of W will provide a quantitative evaluation of the improvements with respect to the GWA. This doctorate work will definitely confirm or dismiss the expectations about the role played by excitonic effects in W. On another hand, we also aim to predict qualitatively new phenomena. In particular, using a recent development in the group [12, 13], we will investigate the possible existence of "exciton satellites", i.e. many-body fingerprints in PES spectra of the coupling between the photo-hole and additional excitons in the system. We will calculate exciton satellites in the spectral function of prototypical excitonic materials, which will be verified by photoemission experiments that we will propose to experimentalists.

2. CIXS permits one to obtain the non-diagonal elements of the dielectric function, which means measuring directly the plasmon bands of an anisotropic material, and giving extra information on the local field effects. However, the experimental setup is complicate and the intensity low, so with the exception of a pionnering work from Schulke [15], no other experiment has been carried out for CIXS. The theoretical counterpart is, on the contrary, very easy in principle, but it requires the evaluation of many matrix elements of epsilon. We believe timely to propose a new set of experiments of CIXS at the synchrotron, for several reasons: i) the experimental resolution and intensity achievable today are much better than fifteen years ago; ii) the theoretical counterpart contains today the excitonic effects, thanks to our recently developed method, so to give real reference high-quality results to the experimentalist to compare with (especially in terms of absolute intensities); finally the knowledge of the non-diagonal response function permits one to infer about the density variation upon perturbation in real space so to graphically plot the plasmons, the excitons, or the orbitals.

Computational challenges

there are at least two important issues related to this project, for which the help of the Maison de la Simulation is envisaged. On one side we aim at massively parallelize the EXC code: as it has been demonstrated by a previous collaboration (on the DP code), this can be very effective. This parallelization will permit to tackle the ab initio description of excitonic effects for very large systems. On the other side, given the new physical quantities we will be able to measure/calculate, it will be important a professional help in graphical output and post-processing tools. This is not only for the final output visualization, but especially to use intermediate visual aid to guide and drive the next simulation (techniques also called collaborative on-the-fly visualization).

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