“NONLINEAR SPECTROSCOPY IN CONDENSED MATTER AND NANO-STRUCTURES” (NOCturNE)

KEY FACTS

General subject	Theoretical description of nonlinear processes in condensed matter, surface/interfaces and nano-structures, studied through Second- and Third-Harmonic Generation
Objectives	• Fundamental understanding and theoretical modeling of the interaction of electromagnetic fields with solid targets, surfaces/interfaces and nano-objects. • New and potentially groundbreaking applications for nonlinear spectroscopy
Partners	• Theoretical Spectroscopy group, Laboratoire des Solides Irradiés (LSI), X, CNRS, CEA/DSM , Palaiseau • Electronic Structure Theory group, Laboratoire de Chimie Théorique (LCT), Sorbonne Universités, Université Pierre et Marie Curie, Paris • Abineel group, Institut Neel (Abineel), CNRS/UJF, Grenoble • Laboratoire de Physique Théorique (LPT), Université Paul Sabatier, Toulouse • Laboratoire de Chimie et Physique Quantiques (LCPQ), Université Paul Sabatier, Toulouse
Cutting-edge expertises	• Time-Dependent Density Functional Theory (TDDFT) and its derivatives • Time-Dependent Current-Density Functional Theory (TDCDFT) • Many-Body formalism (GW) and Bethe-Salpeter Equation (BSE)
Required budget	539k€

1. Pertinence et caractère stratégique du projet

Theoretical design offers the opportunity to test a large number of model systems without the need and the cost of an experimental setup. It allows the calculation of tailored properties, as well as the study of their evolution in terms of specific variables, to extract trends and identify key parameters.

The NOCturNE project has the aim to develop a theoretical and numerical tool to describe nonlinear optical phenomena in matter to theoretically design new materials for a wide range of applications like lasing, optical fibers, optical data storage or in-vivo imaging.

Nevertheless, before designing technological materials, one first needs to understand the nonlinear interaction between light and matter, which involves processes that require state-of-the-art quantum mechanical approaches, regardless of the field of application. For these reasons, NOCturNE falls naturally into the generic “Défi de tous les savoirs” call for upstream and/or exploratory research projects. This project focuses on basic-science development and it is not specific to one of the nine “défis sociétaux".

Besides the expected new and potentially groundbreaking applications for nonlinear spectroscopy, one of the major realizations of this project will be new computational tools, which will be made available for the scientific community. This way of working is inheritated from the successfull experience of the European Theoretical Spectroscopy Facility (ETSF), a research network dedicated to providing support and services for ongoing research in academic, government and industrial laboratories. Indeed, most of the researchers involved in NOCturNE are current or former members of ETSF, and know the power of this kind of partnership.

The consortium is composed of three partners, located in french research intitutions. All of them have a huge expertise in the joint area of nonlinear optics and condensed matter physics, where a concurrent development of theory and modeling is required. In such a context, the ANR funding of this project seems perfectly suited. It will allow the improvement of the theoretical investigation of nonlinear optical properties of bulk materials and nanostructures by combining a well-founded theory and accurate computational tools with the in-depth knowledge of systems which are potential candidates for optoelectronic applications. One of the key aspect of this project is the genuinely collaborative and complementary character of the consortium we built for its realization : achieving the ambitious goals setted by NOCturNE would be impossible for any of the partners alone.

2. Objectifs scientifiques et technologiques

State of the Art

The optical science studies the interaction of light with matter. Nonlinear optics, in particular, is specific to those regime of electromagnetic-field intensity for which the response of the system is nonlinear. For this reason it was not until the advent of the laser in 1960 that nonlinear optical phenomena have been observed. Over the following four decades, the area of nonlinear optics has witnessed an enormous growth, leading to the observation of new physical phenomena and giving rise to novel concepts and applications. Among the nonlinear process, the main role is played by second- (SHG), third-harmonic generation (THG) and two-photon absorption (2PA).

SHG converts two photons of frequency ω to a single photon of frequency 2ω. It can be described by the macroscopic second-order nonlinear susceptibility χ^2. Doubling the frequency allows the access to higher energy domain, that would not be normally possible. χ^2 is non-zero in systems which have no inversion symmetry. SHG is thus a prominent tool for probing surfaces and/or interfaces. The interest of SHG and THG has now gone beyond fundamental research since they are exploited in many technological applications ranging from laser frequency multipliers, in-vivo images, generation of entangled photons for quantum information, self-focusing in optical fibers.

However, despite the great interest in nonlinear optics, the scientific community continues to have a poor understanding of several key aspects of the nonlinear optical response of solids. The reason is the enormous difficulty in the theoretical and numerical developments in this field. For example, the dynamics of a nonlinear electron-hole excitations represents a huge challenge, whose description in complex materials is well beyond the present state-of-the-art first-principles approaches. Moreover, the recent advent of stronger laser-light source made phenomena such as high-harmonic generation accessible thus increasing the gap with theory even more profoundly.

The challenge of an accurate theoretical description of the physical mechanisms behind the nonlinear optical processes is to take into account the many-body interactions among the electrons of the system. Among these complex effects the most important are (i) the screening of the electromagnetic fields due to the microscopic nature of the material and (ii) the excitonic effects which describe the interaction between the excited electron and the remaining hole. The macroscopic susceptibilities $\chi^{(n)}$ include these many-body effects.

In the last years, different *ab initio* approaches that include many-body effects have been proposed, mainly for SHG. However their application has been reserved to simple bulk materials due to the huge computational effort required. Therefore, the theoretical investigations of nonlinear optical response of surfaces, superlattices, interfaces have been performed at the lowest level of theory that is the independent-electron approximation. Instead, studies on these complex systems that include many-body effects are usually restricted to phenomenological, semi-empirical, or classical models. However, these many-body effects are expected to give important contributions to the nonlinear response.

General objectives of NOCturNE

NOCturNE project lies at the frontier of nonlinear optics and condensed matter physics. Therefore its realisation will permit us to provide considerable inputs in both fields. NOCturNE aims at elucidating the physics involved in the interaction of electromagnetic fields with solid targets, surfaces/interfaces and nano-objects and at using such interaction for new and potentially breakthrough in the nonlinear regime. The goal is the development of new theoretical approaches and numerical tools taking advantage of the knowledge and expertises of each partners in the consortium (see Fig. 1 for a schematic representation). NOCturNE will benefit of three different theoretical approaches developed by the partners : Time-Dependent Density Functional Theory (TDDFT), its current counterpart (TDCDFT) and Many-Body perturbation Theory (MBPT). Besides these theoretical approaches, we will take advantage of the fact that numerical methods are also developed by the partner for the calculation of the optical response both in the frequency and real-time domain.

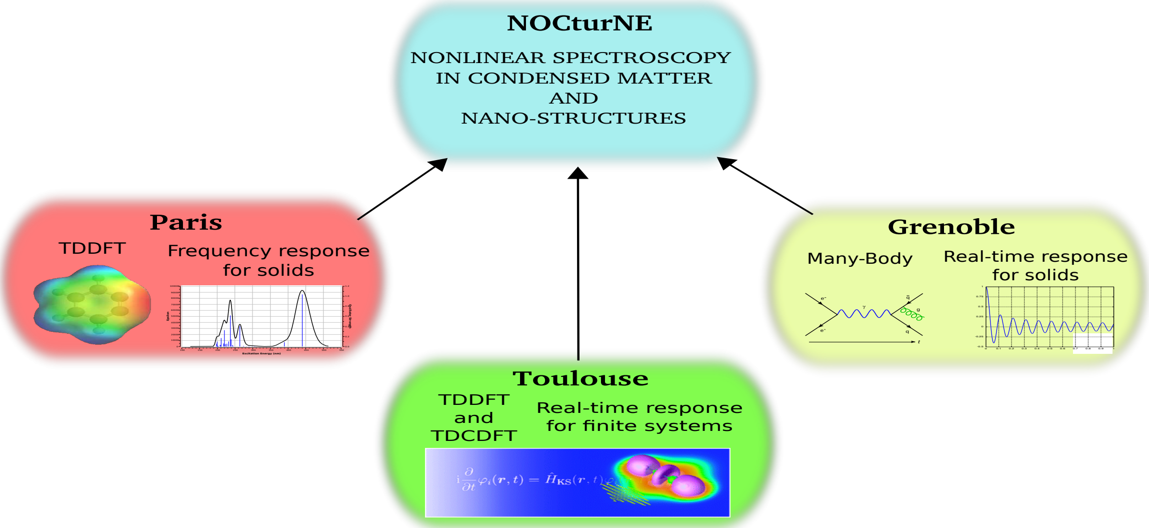

FIGURE 1 – Schematic representation of NOCturNE project research structure.

Fundamental aspects

The basic idea of TDDFT is to replace the many-body problem by a one-particle description in which the many-body effects enter through an effective potential called **exchange-correlation potential**. The main ingredients for the description of optical processes are response functions. Two approaches are used for their calculation : a direct evaluation in the **frequency domain** and an indirect evaluation through a **real-time propagation** of the system. By using TDDFT in frequency domain we will have the advantage that the exchange-correlation potential has to be evaluated only once, but the complexity of the equations grows with the order of the nonlinearity. Instead by using TDDFT in real-time domain, response functions at any order can be evaluated with the same equations, but the price to pay is that the exchange-correlation potential has to be evaluated hundreds of times during the time evolution. The collaboration between the different teams aim to combine the advantages of the two approaches, namely very accurate potentials for response functions in frequency domain and less accurate but fast potentials in real-time in order to calculate higher response functions.

In TDDFT, any observables are based on the density of the system. An important issue is hence to find the expression of the observables in terms of the density. This is an even greater challenge in solids, since some expressions which are valid for **finite systems** are no longer well-defined in **extended systems** when using periodic boundary conditions. We have already expertise in SHG calculations for unpolarized systems, we propose to extend our formalisms for polarized systems and also to third-order nonlinear optical response functions.

Another key-task in TDDFT is the development of accurate exchange-correlation potentials allowing for **memory effects**. The present development of TDCDFT, which, unlike TDDFT, allows for approximations which are **non-local in time**, appears to be a promising way. On the other hand, many-body effects can also be included by using Many-Body Perturbation theory (MBPT). **Many-body effects** have, of course, also to be approximated, but these approximations can be found in a **systematic way**, with now the price of being too costly for complex systems. Therefore, passing through MBPT has the advantage that approximations with a clear physical meaning can be designed more easily than in the context of density functionals and introduced in a second-step into the more efficient TDDFT. This strategy has been successfully used in solids to introduce excitonic effects in TDDFT absorption spectra. We now want to use a similar strategy for nonlinear processes by **combining the efficiency of TDDFT, the non-locality of TDCDFT and the clear physical picture of MBPT**.

Applications

Second-harmonic generation is a key ingredient to monitor phase transitions in **ferroeletric materials** [1]. In that case, the magnetic symmetry determines the polarization P(2ω) of the material, so that SHG reveals the underlying arrangement of spins in the solid. In these materials the temperature dependence of the SHG intensity is used to probe phase transitions and the appearing of magnetic order. In this project we plan to extend our formalism developed for unpolarized systems to noncolinear spin, to treat the different phases of ferroelectric materials. Our ab-initio approach will allow us to disentangle the ionic and electronic contribution to the SHG. We will first concentrate on materials where giant second-harmonic response has been found and then we will deal with the phases at different temperature. These ferroelectric materials are fundamental for optical data storage.

Carbon Nanotubes : Thanks to their low dimensionality and strong anisotropy, they are expected to exhibit enhanced properties. The second harmonic signal is expected to be 10 times larger than the best nonlinear crystals [2]. However these predictions are based on simple calculations. The comparison between theory and experiments remains problematic due to the drastic approximations in the calculations and the difficulty to measure the response of nanotubes. Regarding the third harmonic generation (THG) the situation is even more intricate. Our goal is to provide a solid basis to interpret experimental findings and shed light on the intricate interaction of light and confined electrons in low dimensional structures.

Nanoclusters : Manipulations at the nanometer scale demonstrates that desirable optical properties can be generated just by changing the system dimension and shape [3]. For example silicon nanoclusters offer a large variety of nonlinear optical effects. By combining Si nonlinear optical properties and nanodimension, it is possible to design materials that can be used for high speed optical communications. The objective is to predict these properties for the development of nonlinear devices and in-vivo imaging.

Two-photon absorption. Among the new techniques based on nonlinear optics, those in which two photons are absorbed simultaneously to excite a material, are of particular importance [4]. By focusing an intense laser field, there is a significant probability, that at the focal point, two photons can be absorbed simultaneously. As a result, the small focal volume allows an excellent spatial resolution. This property is used in highly innovative technologies such as microfrabrication in molecular engineering and optical data storage. Moreover, in bulk materials, the presence of a gap can prevent the traditional one-photon absorption, inducing transparency at the fundamental frequency. The penetration depth becomes much larger, allowing to probe deeper inside the material. The two-photon microscopy and photo-therapy are based on the joint use of these two properties, improved spatial selectivity and greater penetration in tissues. One of the technological key points is the development of new nonlinear materials, with a large two-photon cross section, combined with an important physical and chemical stability under the action of radiation.

3. Cohérence de la préproposition

CV of the coordinator - Valérie VENIARD

Education

June 1983 : Ingénieur de l'Ecole Centrale Paris.

February 1986 : PhD thesis, Pierre and Marie Curie University, Paris(Adv. : Pr. Maquet).

April 1999 : Habilitation à diriger les recherches, Pierre et Marie Curie University, Paris.

Professional experience

1986 : Chargée de Recherche 2ème classe, CNRS.

1990 : Chargée de Recherche 1ère classe, CNRS.

2003 : Directrice de Recherche 2ème classe, CNRS

August 2013-Décembre 2013 : Directrice Adjointe du Laboratoire des Solides Irradiés.

Thematic mobility

1986-2004 : Dynamics of atomic and molecular systems in the presence of an intense laser field.

Since 2005 : Nonlinear optics in solids.

5 selected publications (61 publications in peer-reviewed international journals, impact factor H=22)

Two-color multiphoton ionization of atoms using high-order harmonic generation,V. Véniard, R. Taïeb and A. Maquet, PRL **74**, 4161 (1995).

Signature of relativistic effects in atom-laser interactions at ultra-high intensities, R. Taïeb, V. Véniard and A. Maquet, PRL **81** 2882 (1998).

H_2^+ *in intense laser field pulses*, B. Rotenberg, R. Taïeb, V. Véniard and A. Maquet, J. Phys. B **35**, L397 (2002).

Ab initio second-order nonlinear optics in solids, E. Luppi, H. Hübener and V. Véniard, PRB **82**, 235201 (2010).

Second-harmonic generation in silicon waveguides strained by silicon nitride, M. Cazzanelli, F. Bianco, E. Borga, G. Pucker, M. Ghulinyan, E. Degoli, E. Luppi, V. Véniard, S. Ossicini, D. Modotto, S. Wabnitz, R. Pierobon and L. Pavesi, Nature Materials **11**, 148 (2012).

The partners consist of five well-established research groups which have already developed an efficient synergy in previous years. Along with a common base of expertise, the consortium exhibits a genuine complementarity of the partners in terms of expertise. Three thematic poles can be identified :

Paris	TDDFT : Frequency response for solids
Human resources	6 persons including 5 permanent researchers + support from a computer ingeneer
Cutting-edge expertises	• Linear and nonlinear (SHG) processes in extended systems • Third harmonic generation is currently under development
available codes	• DP : ab initio Linear Response TDDFT code. • 2light : ab initio second-order TDDFT code. • EXC : ab initio Bethe-Salpeter Equation code.
Related publication	Nature Materials **11**, 148 (2012)

Grenoble	Real time response for solids
Human resources	2 permanent researchers
Cutting-edge expertises	• Bethe-Salpeter Equation (BSE) • Many-Body formalism (GW)
available codes	• YAMBO : real-time non-linear spectroscopy
Related publication	PRB **88**, 235113 (2013)

Toulouse	TDDFT/TDCDDFT : real time response for finite systems
Human resources	3 permanent researchers
Cutting-edge expertises	• Time-Dependent Current-Density Functional Theory (TDCDFT) • Real-time dynamics
available codes	• ADF : TDDFT (non)linear response of finite systems, TDCDFT linear response of solids • TELEMAN : real-time TDDFT dynamics of finite systems
Related publication	Phys. Rep. in press ; PRB **74**, 245117 (2006)

In this project, these three internationally recognized research nodes join together their cutting-edge and complementary expertise in order to further extend their basic understanding of nonlinear interaction between electromagnetic fields and solid targets, surfaces/interfaces and nano-objects and propose to the experimental community new and potentially breakthrough for nonlinear optics. TDDFT, BSE and TDCDFT are at the forefront of the theoretical development in solid states physics ; existing codes, developed by the partners, are already available and can be used directly for some of the applications. The complementarity of the partners and the fact that the exertise is presently available in these french laboratories is an asset for this ambitious collaborative project. A funding from the ANR is required to push forward the very promising field of nonlinear optics.

Required budget

Staff : 315 k€ (Experienced Post-doc= 54 months)
Equipment : 90 k€ (Computation machines to be integrated in existing clusters)
Travel money : 73 k€ (1.5k€ per person and per year)
Workshops organisation and visitor scientists : 20 k€
Other expenses : 41k€ (overhead for partners' institutions)

Références

[1] T. Lottermoser *et al*, Nature, **430**, 541(2004) ; T. Lottermoser D. Meier, R. V. Pisarev, and M. Fiebig Phys. Rev. B **80**, 100101(R) (2009).

[2] P. Avouris, M. Freitag et V. Perebeinos, Nature Photonics **2**, 341 (2008).

[3] L. Pavesi *et al*, Nature, **408**, 440(2000).

[4] Ziliang Ye *et al*, Nature, **513**, 214(2014).