NOCturNE **PRC** **Défi ≪ des autres savoirs≫** **2016**

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

General subject	Theoretical description of nonlinear processes in condensed matter and nano-structures, studied through Second- and Third-Harmonic Generation
Objectives	• Fundamental understanding and theoretical modeling of the nonlinear interaction of electromagnetic fields with solid targets 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	362k€ - 36 months

1. 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) and third-harmonic generation (THG).

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 $\chi^{(2)}$. Doubling the frequency allows the access to higher energy domain, that would not be normally possible. $\chi^{(2)}$ is non-zero in systems which have no inversion symmetry. SHG is thus a prominent tool for probing crystal structure and low-dimensional materials. 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 [1], generation of entangled photons for quantum information [2], in-vivo imaging [3]. Note also that among the related second-order processes, frequency-difference is at the basis of most of the optical amplifiers (OPO) for the mid-infrared regime [4].

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. 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. 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 macroscopic susceptibilities $\chi^{(n)}$ should include these many-body effects. For complex materials, it is well beyond the present state-of-the-art first-principles approaches.

In the last years, several *ab initio* approaches, in order to include many-body effects, have been proposed, mainly for SHG. Nevertheless, their application has been reserved to simple bulk materials due to the huge computational effort required. For complex materials, the theoretical investigations of nonlinear optical response have been performed at the lowest level of *ab initio* theory that is the independent-electron approximation. 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, with the development of new theoretical approaches and numerical tools, at elucidating the physics involved in the interaction of electromagnetic fields with solid targets and nano-objects in the nonlinear regime, opening the possibility for new and potentially breakthrough in the nonlinear regime. 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), see Fig. 1 for a schematic representation. Besides these theoretical approaches, we will take advantage of the fact that numerical methods are also developed by the partners for the calculation of the optical response both in the frequency and real-time domain.

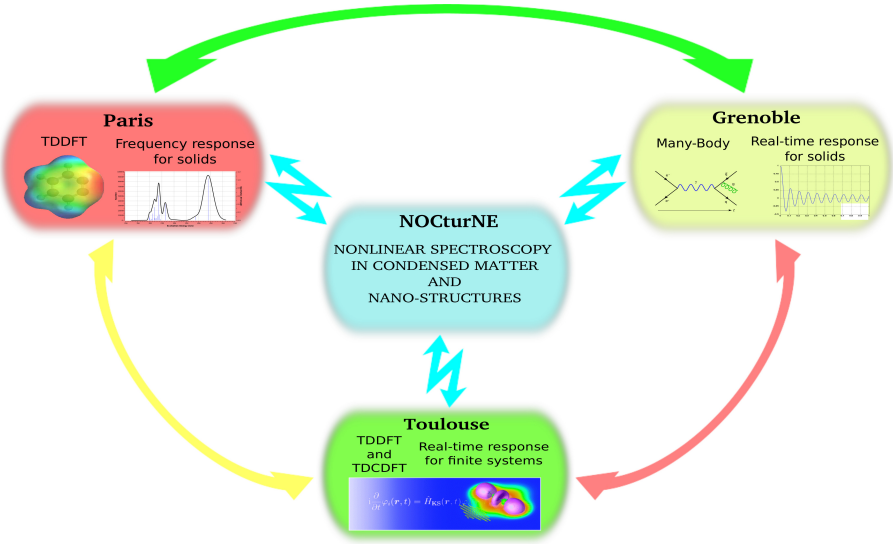

FIGURE 1 – Schematic representation of NOCturNE project research structure.

Fundamental aspects

This project plans to tackle nonlinear interaction of light with matter using state-of-the-art theoretical description of electronic excitations. It relies on first principle framework, to account for interactions between electrons. These many-body effects have of course to be approximated, and two ab initio formalisms will be used. One is MBPT, where physical approximations can be found in a **systematic way**, but with the price of being too costly for complex systems. To overcome this drawback, one will use TDDFT, where the many-body problem is replaced by a one-particle description in which the many-body effects enter through an effective potential called **exchange-correlation potential** (V_{xc}). 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. TDDFT in frequency domain 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. 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, to get accurate potentials for response functions to all orders.

V_{xc} appears to be the key-quantity in TDDFT. Different paths can be followed to obtain accurate V_{xc} for all orders of response functions. The most natural one is to directly derive efficient kernels from TDDFT. Another approach is to take benefit of insights from MBPT to design approximations with a clear physical meaning 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. Another key-task in TDDFT is the development of 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. Adding the knowledge and expertises of each pertners of the consortium, we want to define accurate and efficient exchange-correlation potentials for nonlinear processes by combining the **efficiency** of TDDFT, the **non-locality of TDCDFT** and the clear **physical picture** of MBPT.

Finally, once these new theoretical developments achieved, it will open the way to various applications. Among those presenting potential breakthrough and for which we have indentified a need for methodological

developments to meet the expectations of the community, one finds ferroelectric materials and silicon nanoclusters. To deal with the first ones, we need to extend our formalism to spin polarized systems. To deal with nano-objects, it will be essential to reach the efficientcy of reciprocal-space and the accuracy of real-space calculations.

Synergy

None of the objectives proposed in the project can be achieved by one of the partners alone and can only be the result of the collaboration between the participating groups :

- Paris - Grenoble : the link between MBPT and TDDFT for the second-order response will be established.
- Paris - Toulouse : Efficient kernels will be derived using TDCDFT.
- Paris(LCT)-Paris(LSI) : Efficient kernels will be derived using TDDFT (Bootstrap, range separation)
- Paris-Grenoble-Toulouse : spin will be included in SHG.
- Paris-Grenoble-Toulouse : Numerical implementation in the frequency domain for THG in the framework of TDDFT and comparison with the real space approach, using the kernels derived in the previous steps.

This project allows to formalise an ongoing collaboration and to strengthen a small but efficient community, in the field of the theoretical description of nonlinear processes.

Discussion of risks

Concerning the link between MBPT and TDDFT, the risk is low, as it has already been done for optical linear properties by one member of the consortium. The implementation for THG can be more problematic : the use of the dipole approximation implies heavy analytical calculations, but helps greatly the insight we get from the numerical results. If it turns out to be too heavy, a second strategy is possible, relying on a full numerical procedure. The development of new kernels within TDCDFT is the most risky part of this project. This is a long standing problem, but the framework of NOCturNE is a favourable context, since several experts are part of this collaborative project. Concerning the implementation of spin, the risk is low. Moreover, the available codes have been developped in the participating groups, so the work starts on a quite advanced level.

Potential breakthrough

Second-harmonic generation is a key ingredient to monitor phase transitions in **ferroeletric materials** [5]. In that case, the magnetic symmetry determines the polarization $P(2\omega)$ 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. These ferroelectric materials are fundamental for optical data storage. The extension of the formalism, developed for unpolarized systems to polarized systems, will allow us to treat the different phases of ferroelectric materials. Using our ab-initio approach, we will be able to disentangle the ionic and electronic contribution to the SHG. Since excitonic effects are known to be important in this class of strongly correlated materials, accurate exchange-correlation kernels are mandatory.

Silicon nanoclusters : The potential for incorporating photonic functionality in silicon integrated circuits is extremely exciting [6, 7] in particular for applications such as high-speed chip-to-chip data communication, spectroscopy and sensing. However, there remain significant scientific and engineering challenges before the full potential of this integration is achieved : 1) indirect bandgap which makes spontaneous emission unlikely and thus impedes lasing, 2) centrosymmetry which prevents second-order nonlinear process and 3) variety of fast and slow higher-order nonlinear effects that result in both slow and fast recovery times when the material is exposed to high field strengths. The way to turn silicon into an active photonic material is based on Nanosilicon Photonics : manipulations at the nanometer scale demonstrate that desirable optical properties can be generated just by changing the system dimension and shape [6]. By combining Si nonlinear optical properties and nanodimension, it is possible to design materials that can be used for high speed optical communications. The possibility to describe theoretically the nonlinear optical phenomena in Si-based nanostructures will allow to fully understand the experimental observations on nanosystems, in particular the role of the size, surface, composition in the nonlinear optical response and the correlation between the nonlinearities and the local structure of the nanosystems.

2. Organisation du projet et moyens mis en oeuvre

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 (64 publications in peer-reviewed international journals, impact factor H=24)

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	LSI : V. Véniard, C. Giorgetti and F. Sottile. LCT : E. Luppi and J. Toulouse
Cutting-edge expertises	• Linear and nonlinear (SHG) processes in extended systems • Functionals development in DFT/TDDFT
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	Institut Neel : C. Attacalite and V. Olevano
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/TDCDFT : real time response for finite systems
Human resources	LPT : P. Romaniello and Phuong Mai Dinh. LCPQ : A. Berger
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	Physics Reports **562**, 1 28 (2015) ; PRL **114**, 066404 (2015)

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 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 expertise is presently available in these french laboratories is an asset for this ambitious collaborative project. The amount of work proposed in the NOCturNE project is huge and cannot be tackled by the permanent researchers only. The possibility to offer three one-year fellowship is important for the success. On the other hand, a strong support for the organisation of workshops will reenforce the synergy of the groups and allow an efficient dissemination

of the deliverables. A funding from the ANR is required to push forward the very promising field of theoretical nonlinear optics.

Required budget for 36 months
Staff : 210 k€ (Experienced Post-doc= 3 × 12 months)
Equipment : 60 k€ (Computation machines to be integrated in existing clusters)
Travel money : 45 k€ (1.5k€ per person and per year)
Workshops organisation and visitor scientists : 20 k€
Other expenses : 27k€ (overhead for partners' institutions)

3. Impact et retombées 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. It is done upstream of experiments and can benefit to experimentalists or industrial laboratories, showing what is potentially promising. The theoretical design is a tool reducing costs and time to achieve a specific application.

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 or optical data storage.

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 des autres 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".

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 dissemination of knowledge will be made thanks to publications. Small workshops , inviting the community to gather for discussing about breakthrough and problems encountered will be held. This way of working has shown its potential success in the past (see for instance the organisation of the "theoretical days" in Toulouse , "Informal Scientic Discussion" and the "Correlation meeting" in Palaiseau) . The organisation of tutorials and hands-on will allow also the dissemination and the use of the codes made available.

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.

Références

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