The “Marseille Condensed Matter Workshop” will bring together specialists from different computational fields working on optical and magnetic properties of complex materials.

**Invited Speakers:**

- Cyrille Barreteau, CEA, Paris (France)
- Arjan Berger, Université Paul Sabatier, Toulouse (France)
- Friedhelm Bechstedt, Jena University (Germany)
- Marie-Bernadette Lepetit, ILL, Grenoble (France)
- Alfredo Correa, Lawrence Livermore National Laboratory, (USA)
- Pierluigi Cudazzo, Ecole Polytechnique, Paris (France)
- Dinh Phuong Mai, Université Paul Sabatier, Toulouse (France)
- Antonio Fernández-Domínguez, UAM, Madrid (Spain)
- Nicola Ferre, ICR, Aix-Marseille Université (France)
- Pablo Garcia Gonzalez, UAM, Madrid (Spain)
- Myrta Grüning, Queen’s University Belfast (UK)
- Roland Hayn, IM2NP, Aix-Marseille Université (France)
- Miquel Huix-Rotllant, ICR, Aix-Marseille Université (France)
- Jorge Kohanoff, Queen’s University Belfast (UK)
- Eleonora Luppi, LTC, UPMC, Paris (France)
- Thomas Niehaus, ILM, Lyon (France)
- Xavier Rocquefelte, ISCR, Université de Rennes (France)
- Davide Sangalli, CNR, Milano (Italie)
- Lorenzo Stella, Queen’s University Belfast (UK)
- Alexander Smogunov, CEA, Paris (France)
- Lorenzo Sponza, King’s College, London (UK)
- Jaejun Yu, Seoul National University (Korea)
**Posters**

**Shuming Bai** : "Effects of Different Quantum Coherence on the Pump-Probe Polarization Anisotropy of Photosynthetic Light-Harvesting Complexes: A Computational Study”.

**Benjamin Grenier** : "Azacalixarenes, structure/activity relationship: a theoretical study”.

**William Lafargue-dit-Hauret** : "Magnetic anisotropy and magnetoelectric coupling in LiNbO$_3$-type InFeO$_3$”.

**Grégoire David** : "Decomposition of the magnetic exchange coupling $J$”.

**Claudio Attacalitte** : "Dielectrics in a time dependent electric field: density polarization theory approach”.
Recently there has been a lot of interest in iridium oxides because of the possibility of realizing topological insulators, quantum magnets and spin liquid. Further pyrochlore iridates have been widely studied due to their geometrical frustration, and novel topological phases have been theoretically proposed. We predict an interesting magnetic ground state for the A-site deficient spinel Ir$_2$O$_4$ based on first-principles calculations with LDA+U+SOC method as implemented in the OpenMX code. The A-site deficient spinel Ir$_2$O$_4$ is a Mott-Hubbard insulator driven by the formation of the J=1/2 state, which is the same spin-orbit entangled state demonstrated in Sr$_2$IrO$_4$. We show that the magnetic ground state of the Ir pyrochlore lattice in spinel Ir$_2$O$_4$ has a non-collinear antiferromagnetic ordering with easy-plane anisotropy relative to the local (111) axis at the vortex corners of each tetrahedron, which corresponds to an effective 3-dimensional XY-model embedded in a spinel lattice. Using spin-constraint density-functional-theory calculations for non-collinear spin configurations together with various models for the effective spin interactions, we investigate an origin of such unusual magnetic ordering in the spinel Ir$_2$O$_4$. Both anisotropy Heisenberg exchange and Dzyloshinskii-Moriya interactions are found to be effective in connection with the J=1/2 spin-orbit coupled state. By fine-tuning the structural parameters, one can explore more interesting characteristics of transition metal oxides with competing strong SOC and Coulomb correlation such as topological insulators and exotic magnetic phases.
The development of ultra–short laser pulses has opened the opportunity to investigate the dynamics of electrons on the $fs$ time–scale ($1\, fs = 10^{-15}$ seconds). After the photo–excitation with such lasers pulses, electrons are in a regime which is highly out–of–equilibrium. Here we present a novel numerical approach, based on the merging of the out–of–equilibrium Green’s function method with the \textit{ab-initio}, Density–Functional–Theory, to describe this regime in semi–conductors. Silicon is used as reference material to show the physical process involved. The simulations are also compared with recent two photon photo–emission and transient–reflectivity measurements.

In the 2PPE experiment we show that different processes take place: (i) scattering between degenerate states, activated by the pump–pulse induced symmetry breaking, (ii) $L \rightarrow X$ inter–valley scattering, and, finally, (iii) the relaxation towards the thermal equilibrium.

In the TR experiment we underline the key role of optical–gap renormalization induced by the pump pulse, combined with bleaching, needed to explain the experimental signal.
In this talk I will discuss two advances we recently made within time-dependent current-density functional theory.

1) A solution to the problem of the gauge dependence of molecular magnetic properties (magnetizabilities, circular dichroism) [1,2].

2) A parameter-free exchange-correlation functional that accurately describes the optical absorption spectra of insulators, semiconductors and metals [3].

Topological surface and interface states from first principles

Friedhelm Bechstedt
Friedrich-Schiller-Universität Jena, Germany

Topological insulators (TIs) have opened a new fascinating field for solid state physicists. They are based on small-gap semiconductors with large spin-orbit interaction (SOI). At their surfaces and interfaces metallic edge states with linear bands (Dirac cones) and spin polarization are formed. In the talk two classes of TIs are investigated, (i) the three-dimensional (3D) zero-gap semiconductors -Sn and HgTe with inverted bands, and (ii) two-dimensional (2D) graphene-like honeycomb crystals such as germanene, its chemically functionalized derivatives, and its one-dimensional (1D) nanoribbons. The ab-initio calculation of topological invariants is demonstrated for systems with and without inversion symmetry. The edge states of -Sn surfaces [1] and -Sn or HgTe quantum wells formed with CdTe [2, 3, 4] are investigated with respect to the appearance of topological states, their localization and spin polarization. We demonstrate that the graphene-like, buckled group-IV-derived crystals with small gap and strong SOI are also topological insulators [5]. Their ribbons show topological edge states which however are sensitive to any kind of edge magnetization [6]. The 2D systems represent the quantum spin Hall (QSH) phase [4, 5]. That is shown by the quantization of the spin Hall conductivity [7].

Fig. 1 (a) Wave-function localization, (b) band dispersion, and (c) spin polarization of topological states at HgTe/CdTe interface

Highly spin-polarized electron transport in atomic-scale nanojunctions: ab initio study

Alexander Smogunov
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Achieving highly spin-polarized electric currents across atomic-scale junctions connecting two ferromagnetic electrodes is of great importance in the field of nanoelectronics and spintronics. Moreover, high "spin-filtering" of such junctions is inevitably accompanied by another very important effect - a large magnetoresistance characterized by a drastic change in electrical conductance when magnetizations of two electrodes are rotated from parallel to antiparallel orientation. I will discuss our recent idea [1,2], based on robust symmetry considerations, to block completely one of spin channels ("majority" one, more precisely) by a clever choice of a connecting junction, providing thus a 100 % spin-polarized currents and very high (ideally, infinite) magnetoresistance ratios. These junctions must have no s-symmetry states around the Fermi level which results in complete reflection of "majority" spin electrode electrons, which are all of s-orbital origin, at the electrode-junction connection. We demonstrate the mechanism for several possible types of junctions - short Carbon chains and ?-conjugated molecules - by carrying out ab initio electron transport calculations with the Quantum-ESPRESSO package [3]. We then further elaborate on possible ways to control the "spin-filtering" ratio by some external influence such as mechanical strain or gating. In particular, we show that for Si (zigzag) chains connecting two Ni electrodes the degree of spin-polarization of the current can be tuned by their stretching due to appearance of additional Si chain s-like band at the Fermi level switching on the "majority" spin conductance.

2. D. Li, Y. J. Dappe, A. Smogunov, PRB 93, 201403 (2016).
How a single atom changes the optical properties of a nanosystem

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Plasmonic nanostructures are able to confine and enhance light in sub-wavelength regions in a unique tuneable manner. This is the basis of a number of applications including surface-enhanced spectroscopies, designing of light-harvesting devices, molecular sensors, and hybrid optoelectronic devices. A prototypical system is made up by two metallic nanoparticles separated by a narrow spatial gap, that is, a nanoparticle dimer. These systems have been extensively studied using classical-optics prescriptions as well as under a quantum description of the electron light-induced dynamics [1]. However, only recently fully ab-initio simulations of the optical response of nanoparticle dimers have been carried out [2, 3].

First, we present ab-initio time-dependent density functional theory (TDDFT) studies of the anisotropy and atomic relaxation effects on the optical properties of nanoparticle dimers. Special emphasis is placed on the hybridization process of localized surface plasmons, plasmon-mediated photoinduced currents, and electric-field enhancement in the dimer junction. We show that there is a critical range of separations between the clusters in which the detailed atomic structure in the junction and the relative orientation of the nanoparticles have to be considered to obtain quantitative predictions for realistic nanoplasmonic devices. The orientation of the particles not only modifies the attainable electric field enhancement but can lead to qualitative changes in the optical absorption spectrum of the system [4].

Second, we discuss the effects of different atomic junctions on the optical properties of these nanoparticle dimers, as well as the corresponding plasmon-induced electric currents through the junctions. We show that, besides the appearance of well-defined signatures in the infrared absorption spectrum associated to a quantized electric current, the plasmonic response itself is affected by such a current. A deeper understanding of the physical process behind is given with the aid of a simple model system.

Work done in collaboration with: Alejandro Varas, Mónica Sánchez-Barquilla, Pu Zhang, Johannes Feist, Angel Rubio, and F.J. García-Vidal.

Tuesday 13/9  9:00 - 9:30

Optical properties of diluted magnetic semiconductors

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A review is given on the electronic structure of diluted magnetic semiconductors (DMS) with a special emphasis on Co doped ZnO and Mn doped GaN. By combining first principle LSDA+U (local spin density approximation with Hubbard U correction) calculations with a ligand field analysis important insights into the d-impurity multiplet structure are obtained. The calculated multiplet structure corresponds well to experimental data obtained by optical measurements and electron paramagnetic resonance.
Tuesday 13/9   9:30 - 10:00

Transformation optics approach to plasmon-exciton strong coupling in nanocavities

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In this talk, I will present a transformation optics description of the electromagnetic interaction between a single quantum emitter and the localized plasmonic modes supported by a dimer of metal particles separated by a nanometric gap. I will employ this methodology, which incorporates naturally the full richness of the plasmonic spectrum supported by this system, to explore the conditions yielding plasmon-exciton strong coupling at the single emitter level in this archetypal nano-optical cavity.
Since the discovery of graphene there has been an increasing interest for 2D materials, and new classes of materials are regularly proposed with the hope that their specific properties could lead to new applications. Very recently, a new class of 2D materials has appeared, based on the bottom-up synthesis of metal-organic coordination networks. These systems elaborated at the interface of two media (liquid-liquid or liquid-air) present the advantage that they do not need to be grown on a substrate which could be beneficial for the growth of large-scale defect-free 2D networks.

We have investigated, by means of electronic structure calculations, the electronic and magnetic properties of metal-organic 2D networks for which small “flakes” of organic ligands with delocalized $\pi$-electrons are connected by individual metal atoms $M=$Fe,Co,Ni (see Fig1). We have shown that the electronic properties are very much dependent on the nature of the metallic atom as well as on the atom $X(=\text{NH},\text{S}, \text{O})$ connecting the metal to the ligand. Basically these networks can be (half)-metallic or semi-conducting, magnetic or not, which offers a tremendous playground to tailor their properties. In addition these systems fall into a class of very specific Honeycomb-Kagome lattices with many very specific features that we have started to elucidate by means of simplified tight-binding (Huckel) models.

Figure 1: Schematic representation of a 2D metal-organic coordination network. The metallic atoms M are in red, the ligand (here a simple benzene ring) in black and the connecting atoms X in blue.
The progress in laser technology over the last decades has opened up new avenues for the exploration of properties of clusters and molecules. A laser pulse is characterized by its frequency but also by the laser intensity as well as the laser time profile. While for years the variations of these parameters were heavily constrained by technology, the last two decades, and even more so the last years, have seen tremendous increases in the range of attainable parameters. This is true for intensity: since the 1990’s, it can reach huge values which can lead to very large energy deposits and possibly violent disintegration of the irradiated species. But this is also true for the tuning of the time profile which can now be tailored up to time scales of the order of magnitude of electronic motion and even below. This allows the follow up of the detail of electronic dynamics at its own "natural" time. The latest breakthroughs were attained in terms of laser frequency with the ongoing possibility of reaching very large frequencies up the X domain. This opens up new possibilities of imaging which are progressively being explored.

Benefiting from the development of various coherent light sources and experimental setups, photo-electron spectra (PES) are widely used as a valuable tool to analyze the structure and dynamics of electronic emission in atoms, molecules or solids. One usually identifies the peaks observed in a PES with the mere density of states. However, this labelling can be cumbersome, or can simply fail, when several laser frequencies are used, as in a complex combination of an IR femtosecond pulse and a UV attopulse train. In this talk, we will first explain how time-dependent density functional theory in real time and real space can be used to compute PES. Then we will present a new interpretation of PES patterns in terms of spectral distributions of electronic dipole, monopole, and quadrupole moments, giving a relevant picture for the analysis of PES, especially in involved experimental setups, in the He atom and in a small sodium cluster.
The initial stage of the irradiation process, both via energetic particles or electromagnetic radiation, consists of ionizing the material generating secondary electrons and holes. These species diffuse through the sample experiencing inelastic collisions with the medium until they find an opportunity to react, producing chemical modifications that can lead to various types of damage. In the case of biological matter, damage to the genetic component (DNA) may cause the arrest of the cell cycle. It is linked to diseases like cancer and constitutes the basis for radiotherapies. But materials are subject to ionizing radiation in many other areas, such as radiation detectors, electronic devices in spacecrafts and satellites, structural components in nuclear power plants, and nuclear waste forms encapsulating disposed radioactive fuel and contaminated components. While the type of damage and its consequences depend on the specific material and application, the underlying physics is quite similar, and it is related to the fate of secondary electrons and holes.

We have studied the problem of electron and hole localization and chemical reactivity in a variety of systems of interest using electronic structure calculations and first-principles molecular dynamics simulations (FPMD). Here we will present results for strand breaks in DNA due to low-energy electrons in the condensed phase, which is representative of the physiological environment. We will show that there are a variety of protection mechanisms that are not present in gas phase models, which are important to assess the feasibility of strand breaks [1-5]. We will also discuss recent results for the localization of electrons and holes in Mg(OH)2 (brucite), which is one of the main phases in the UK nuclear waste inventory, and cement that is the most common material used for the immobilization of nuclear waste. In both cases we will show that electrons tend to localize in interstitial regions while holes are generally located in OH groups, and discuss the implications. FPMD simulations are used to examine the initial stages of the radiolytic road to hydrogen gas production.

Quantum dynamics of singlet fission: coherent versus thermally activated mechanisms

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\textsuperscript{4} Laboratory of Chemistry of Novel Materials, University of Mons, Mons (Belgium)

In certain -stacked molecular crystals, carrier multiplication can occur by splitting singlet excitons into two triplets in a process called singlet fission. The mechanism of singlet fission is still under debate. In this talk, we resolve some controversies by developing a first principles nonadiabatic quantum dynamical model that reveals the critical role of molecular stacking symmetry in determining the mechanism. Additionally, it provides a unified picture of coherent versus thermally activated singlet fission mechanisms in different types of acenes. The slip-stacked packing of pentacene derivatives is found to enhance ultrafast singlet fission mediated by a coherent superexchange mechanism. By contrast, the electronic couplings for singlet fission strictly vanish at the C2h symmetric equilibrium -stacking of rubrene. In this case, singlet fission is driven by excitations of symmetry-breaking intermolecular vibrations, rationalizing the experimentally observed temperature dependence.

Magneto-electric multiferroics materials are characterized by the simultaneous presence, and the coupling between magnetic and electric orders. They respond to the application of both electric and magnetic fields and the coupling allow the control of the magnetic properties by an electric field and the control of the electric properties by the application of a magnetic field. One can for instance reverse the sign of the system polarisation by the application of a magnetic field. Direct application of multiferroics is data storage. For example, a four-state logic (2 magnetisation states + 2 polarisation states) in an ultimate memory device is now worth considering. Beyond that, the electrical control of magnetization using the magnetoelectric coupling in a single device [2], offers the unrivalled opportunity to write a magnetic information by application of a small voltage instead of a large current.

The coupling between the magnetic and electric properties is characterised by the magneto-electric tensor which is the second derivative with respect to both the electric and magnetic fields of the free energy potential.

The present paper will present a methodology for the direct calculation of the magneto-electric coupling tensor. For this purpose a multi-step method [3] as been developed, using ab initio methods (combining density functional theory calculations and embedded fragment, explicitly correlated, quantum chemical calculations [4].) to evaluate the microscopic contributions such as the spin-orbit or the magneto-strictive contributions. This method allows the evaluatating of the evolution of the magnetic couplings as a function of an applied electric field. Further this ab initio information is integrated into a spin-wave derivation in order to obtain the macroscopic magneto-electric tensor. The method allows in addition to evaluate individually the contribution of the different microscopic effects to the ME tensor.

It was successfully applied on the YMnO3 compound [5] on which we were able to show that the Dzyaloshinskii-Moriya contribution (originating in the spin-orbit coupling) is three orders of magnitude weaker than the electrostrictive contribution to the magneto-electric tensor.

Tuesday 13/9 15:00 - 15:30

Applications of TDDFT to non-linear response of materials

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Real-time Time dependent density functional theory gives us access to detailed evolution of quantum electronic system, both in the linear and the non-linear regime. As the power and scale of TDDFT computer simulations grows, new phenomena can be capture and studied. In this talk I am going to present simulation results regarding materials undergoing particle radiation and their non-linear optical response and conductivity.
Semiclassical optical response by means of the Generalised Langevin Equation

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The coupling of a small, controllable, system (e.g., a molecule or atomic cluster) to a larger, possibly structured, environment can be modelled using the projection techniques introduced by Mori and Zwanzig [1]. In a similar way, the optical response of a semiconductor nanocrystal coupled to a larger metallic nanoparticle can be modelled using a set of projected equations of motion (PEOM) [2]. The PEOM approach makes possible to achieve high accuracy in the electronic structure of the system along with a scalable description of the collective response of the system and its environment. The PEOM in the case of an isotropic dielectric environment are presented in the first part of this talk, while in the second part we consider an extension through the generalised Langevin equation (GLE) formalism [3]. The advantages of the PEOM over the standard rotating wave approximation (RWA) are highlighted, along with the possibility to model quantum delocalisation and electronic dephasing by means of a semiclassical GLE. The domain of applicability of the semiclassical GLE formalism is finally discussed.

Multiferroic materials [1], in which ferroelectric and magnetic ordering coexist, are of fundamental interest for the development of multi-state memory devices that allow for electrical writing and non-destructive magnetic readout operation. The great challenge is to create multiferroic materials that operate at room temperature and have a large ferroelectric polarization. Cupric oxide, CuO, is promising because it exhibits a significant polarization, that is, \( P \approx 0.1 \mu \text{C cm}^{-2} \), for a spin-spiral multiferroic [2]. Unfortunately, CuO is only ferroelectric in a temperature range of 20 K, from 210 to 230 K. Here we propose an original theoretical investigation of the magnetic and ferroelectric properties of CuO under high-pressure based on first-principles and Monte-Carlo calculations.

We have established that pressure-driven phase competition renders CuO multiferroic at room-temperature [3-7], while preserving its large polarization and strong magneto-electric coupling. Moreover, under pressure values of 20-40 GPa the multiferroic phase becomes stable in a very broad temperature domain extending above 300K (from 0 to \( T \approx 300\text{K} \)). We will also show that our theoretical approach allows to simulate the temperature dependence of the optical and NQR (nuclear quadrupole resonance) properties of CuO [8].

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Projected equations of motion (peom) approach to hybrid quantum/classical dynamics in composite materials

Myrta Gruening    Ryan McMillan, Lorenzo Stella
Atomistic Simulation Centre, Queen’s University Belfast, United Kingdom,

TDDFT and Greens function approaches have become standard in the numerical simulation of spectroscopic properties in a wide variety of materials. The computational requirements of such calculations grow with the size of the simulated system. For composite systems one often uses hybrid methods, treating the constituent subsystems using different levels of theory where treating the entire system using the same theory would be computationally impractical. In this presentation, we introduce a hybrid method (PEOM) which describes the dynamics of the larger system classically whilst retaining a fully quantum mechanical description of the smaller system. As a testbed, we look at two composites: a quantum dot-metal nanoparticle hybrid and a system of MoS2/Graphene monolayers. In the first case, we compare the results of the PEOM method with analytical results based on the rotating wave approximation. In the second case we compare the method with the standard super-cell approach which uses linear response TDDFT. We then go on to examine MoS2 on a gold substrate where excitonic effects are important [1] using a real time Bethe-Salpeter equation (BSE) [2] coupled with the PEOM. In this case, a super-cell approach cannot be used due to the computational demand of the BSE.

Spin fluctuations and itinerancy: Combining GW and DMFT in ferromagnetic Nickel

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King’s College London

In this talk I present a recent investigation on ferromagnetic Nickel. Very high quality measurements are available for the magnetic moment and the exchange-splitting (distance between two band of different spin character) in this material [1]. In order to account quantitatively for these data, a theory able to account at the same time for the itinerancy of the electrons and their local spin-fluctuations is demanded.

The width of the d-band and its alignment with respect to the sp-states are accurately predicted by means of the Quasiparticle Self-consistent GW theory, a single-particle theory based on the non-local GW self-energy [2]. However this approximation alone lacks spin-fluctuation diagrams thus leading to overestimated predictions.

I will illustrate how spin fluctuations have been included in our calculations [3]. Results from a static ad-hoc model will be compared to the experimental data and to the bare QSGW calculation. Then I will discuss some results obtained by merging the QSGW theory with the Dynamical Mean Field Theory. This strategy, still under development, is intended to lead to a more general and robust theory.

Wednesday 14/9  9:30 - 10:00

Approximate time-dependent density functional theory

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Institut Lumire Matière, Université Claude Bernard Lyon 1

In this contribution, we summarize recent advances in the development of the time-dependent density functional based tight-bind method (TD-DFTB) [1,2]. The scheme is characterized by (i) the use of a limited, usually minimal basis, (ii) a two-center approximation for the Kohn-Sham Hamiltonian, (iii) a second-order functional expansion of the total energy and (iv) the simplification of two-electron integrals in the Mulliken approximation. The range of validity of these approximations is assessed by comparison to first principles time-dependent density functional theory (TDDFT) calculations in converged basis sets. The approach is free of empirical parameters and can be used to evaluate optical spectra for systems with several hundred atoms.

If time allows, we will also present a generalization of the ground state DFTB method to cover range separated exchange correlation functionals (LC-DFTB) [3,4]. In contrast to the traditional DFTB scheme, the density matrix is used as basic variable in an expansion of the energy functional in generalized Kohn-Sham theory. The theory provides access to hybrid functionals in DFTB as a special case. Implementation issues and numerical aspects of the new scheme are also covered. We present results for quasiparticle gaps in organic molecules and discuss polaron formation in polymers.

Large magnetic systems are challenging for quantum chemistry, due to the intrinsic multireference character of their low-energy states. While detailed wavefunction-based analysis have evidenced the relative importance of several mechanisms (direct exchange, kinetic exchange, spin and core polarization), the systematic decomposition of the magnetic exchange coupling into its various physical contributions is still in its infancy. In that talk, I will introduce such a decomposition scheme using one of the simplest approach for large molecular systems: the broken-symmetry DFT Kohn-Sham method with selective freezing of orbitals. After a quick review of the different steps entering in our calculation protocol, particular emphasis will be placed on the kinetic exchange contribution for which we will show an improved evaluation, based on the energy of the broken-symmetry solution built on orbitals describing the true low-spin state.
Nonlinear optical spectroscopy in finite and infinite systems

Eleonora Luppi
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Nonlinear optics is an exciting field which has many applications in different areas like materials science and chemistry. Its beginning date back to 1961 when second-harmonic generation (SHG) was observed for the first time by P. Franken et al. [1]. The nonlinear phenomena were treated in the perturbation regime which made possible to develop techniques for efficiently converting laser light from one wavelength to another. However, the situation completely changed when high-harmonic generation (HHG) were discovered by Mcpherson et al. in 1987 [2]. In fact, new non-perturbative understanding of nonlinear optics was necessary to explain the nature of HHG. Moreover, recently, the unique physics of HHG was used to produce the first attosecond pulse source [3] which makes possible the real-time observation of atomic-scale electron dynamics.

In this seminar I will present my work on theoretical nonlinear optical spectroscopy on SHG in solids and HHG in atoms and molecules. I will present a new theoretical approach based on Time-Dependent Density-Functional Theory (TDDFT) for the calculation of second-order susceptibility. In this formalism it is possible to include straightforwardly many-body effects such as crystal local fields and excitons. I will show SHG spectra for different materials such as semiconductors and interfaces. Beyond the perturbative regime, I will show HHG spectra calculated with the Time-Dependent Configuration-Interaction (TDCI) putting in evidence the role of Rydberg bound-states and continuum levels in the field-induced electronic dynamics.

strongly reduced[1,2]. As a consequence, the binding energy of both Wannier and Frenkel excitons in the optical spectra is large and comparable in size. Therefore, contrarily to bulk materials, it cannot serve as a criterion to distinguish different kinds of excitons. Here we demonstrate that the exciton band structure, which can be accessed experimentally, instead provides a powerful way to identify the exciton character. By comparing the ab initio solution of the many-body Bethe-Salpeter equation for graphane and singlelayer hexagonal BN, we draw a general picture of the exciton dispersion in twodimensional materials[3], highlighting the different role played by the exchange electron-hole interaction and by the hopping terms related to the electronic band structure.