

# Rapport sur les travaux effectués

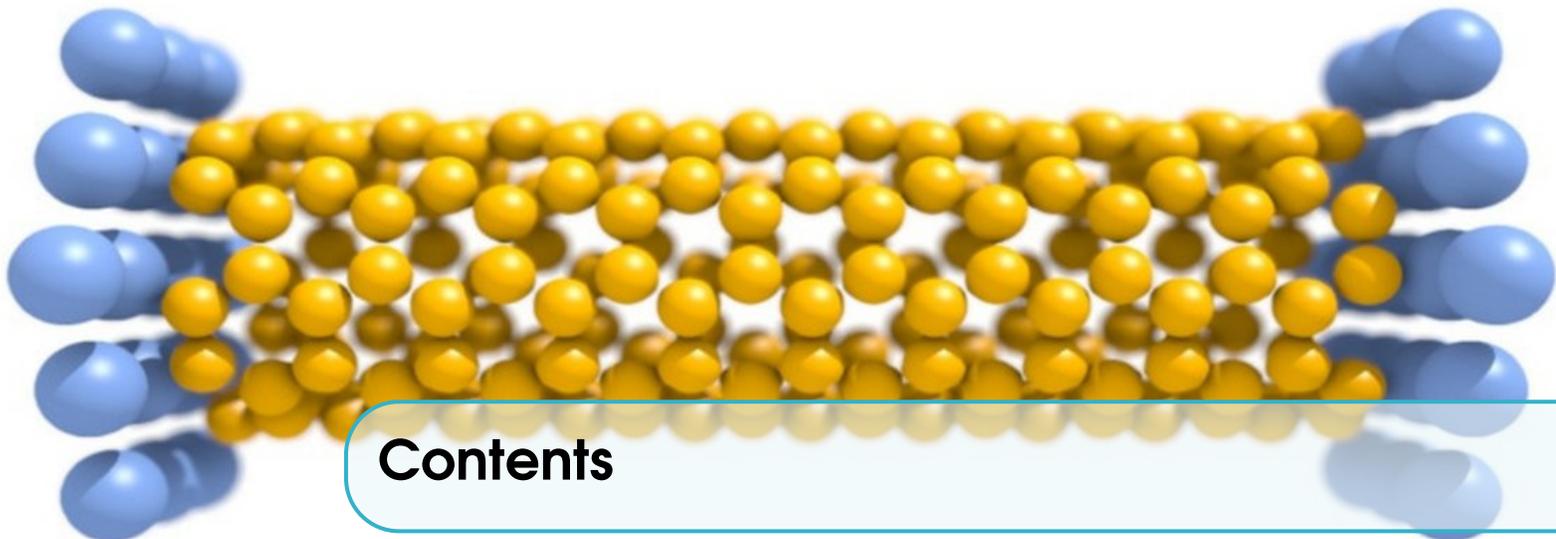
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RAPPORT SUR LES TRAVAUX EFFECTUÉS, CINAM (MARSEILLE)

In this report I present my research activity from the end of my PhD to present day, and focusing in particular on my work after I entered at CNRS.

*December 2021*



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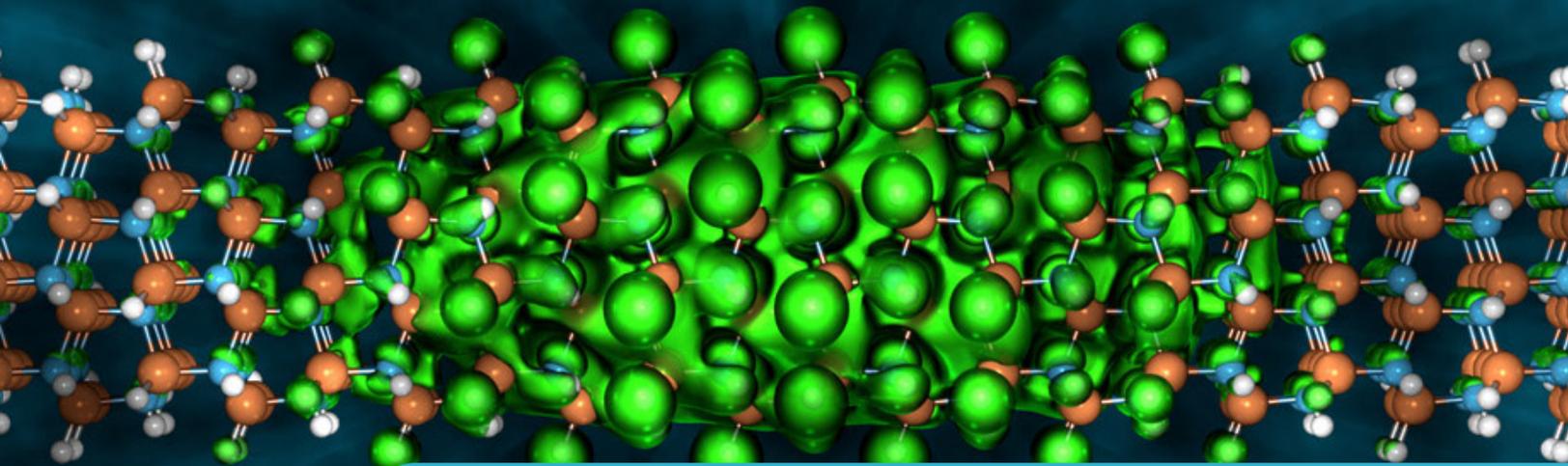
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The following table describes the significance of various abbreviations and acronyms used throughout this report.

Abbreviation	Meaning
BSE	Bethe-Salpeter Equation
BZ	Brilluoin Zone
COH	Coulomb-hole
COHSEX	Coulomb-hole plus Screened Exchange self-energy
DFT	Density Functional Theory
DFTP	Density Functional Polarisation Theory
DMC	Diffusion Monte Carlo
EOM	Equation of Motion
GW	GW approximation for self-energy of a many-body system
$G_0W_0$	Zero order of the GW self-energy
HF	Hartree-Fock
HHG	High Harmonic Generation
IP	Independent Particle
IPA	Indepent particle approximation
KBE	Kadanoff-Baym Equations
KS	Kohn and Sham
KSV	King-Smith Vanderbilt Polarisation
JGM	Jellium with Gap Model
LDA	Local Density Approximation
LRC	Long-range corrected approximation
MBPT	Many-Body Perturbation Theory
PBC	Periodic Boundary Conditions
QMC	Quantum Monte Carlo
QPA	Quasi-particle approximation
RPA	Random Phase Approximation (including local field effects)
SD	Steepest Descent
SEX	Screened Exchange self-energy
SHG	Second Harmonic Generation
SR	Stochastic Reconfiguration
THG	Third Harmonic Generation
RT-BSE	Real-Time Bethe-Salpeter Equation
TDDFT	Time-Dependent Density Functional Theory
TDH	Time-Dependent Hartree
TDHF	Time-Dependent Hartree-Fock
VMC	Variational Monte Carlo





# 1. Introduction

I am theoretical physicist in condensed matter, and my primary interest is the study of materials by means of numerical simulations in such a way to reproduce and predict their properties. I obtained my PhD in 2005 at SISSA(Trieste). After my PhD I spend two years as postdoc in Lille at I.E.M.N. and two year in San Sebastian (Spain) at Universidad de el Pais Vasco. At the end of 2009 I was recruited by the CNRS at the Néel Institut and then in 2014 I moved at CINaM in Marseille. This report presents the most important part of my research activity starting from the end of my PhD. I will pay particular attention to the activities after my recruitment at CNRS.

The report is supplemented by three additional documents: (i) my Curriculum Vitae, (ii) a scientific research project, (iii) my publication list.

The report is divided in five sections:

- **Quantum Monte Carlo**

In this chapter I present my works on Quantum Monte Carlo, in particular: 1) a new correlated wave-function the Anti-symmetric geminal pairing plus Jastrow (JAGP) wave-function for both molecules and solids, 2) a novel *ab-initio* molecular dynamics using QMC noisy forces; 3) the use of Berry-phase to investigate a Mott transition in real-space simulations.

- **Collaboration with experimental groups**

This chapter contains a series of works in collaboration with different experimental groups on ARPES, EELS and optical properties.

- **Theoretical advances in excited states**

In this chapter I discuss some important theoretical advances in the field of excited states. In particular I will present: 1) a new prediction for Bose-Einstein condensation in graphane, 2) a tunable light emission in BN nanostructures, 3) how correlation effects can enhance electron-phonon coupling for particular phonon modes and 4) a new approach to study phonon-assisted luminescence; 5) excited states in Metal Organic Frameworks(MOFs).

- **Non-linear spectroscopy**

This chapter is devoted to the study non-linear optical response, using a new methodology based on dynamical Berry Phase that I have developed.

- **New algorithms and code development**

A consistent part of the work I have done is written not only on papers but also in computational codes that are available to the scientific community. I will present some recent developments in algorithms and codes for material science.

In all the document I will refer to my publications with the blue color respect to the standard black of the other references. At the end of each section I will indicate the principal collaborators, impact and consequences of my research. All the new sections respect to the previous years are marked with *(2018, 2019, 2020, 2021)* in such way to underline the novelties respect to the previous version of the present report.



## 2. Quantum Monte Carlo in real systems

Quantum Monte Carlo (QMC) encompasses a number of numerical techniques for studying correlated systems either on lattice or real Hamiltonians. These techniques range from the simplest one the Variational Monte Carlo (VMC)[1] to the more advanced Diagrammatic one.[2] All these approaches have in common that the solution of the many-body problem is obtained by means of a stochastic equation, within a given statistical precision.

During my research activity on QMC, I mainly focused on searching for new correlated wave-functions for QMC and extension at finite temperature of the zero temperature QMC. The results of this chapter are based on Variational and Diffusion Monte Carlo (VMC and DMC) techniques. However since all advances and new physics can be exclusively understood in terms of Variational Monte Carlo, I will briefly introduce the reader this technique and I will leave the DMC as a way to improve results without modifying the underlying physics.

In an equilibrium situation when no external fields are present, all the physics of a quantum system is described by the Schrödinger equation:

$$H\Psi = E\Psi. \quad (2.1)$$

Since  $H$  is a many-body Hamiltonian, it contains interaction among all the particles and in general the solution of Eq. 2.1 is almost impossible. In Variational Monte Carlo one searches for successive approximated solutions of Eq. 2.1, guided by the variational principle. In fact it is possible to show that, for a generic trial wave-function, the following inequality holds:

$$E_0 \leq \langle \Psi_T | H | \Psi_T \rangle \quad (2.2)$$

where  $E_0$  is the ground state energy of the system and  $\Psi_T$  is a generic trial wave-function. The trial wavefunction can be a complicated wave-function that contains physical insight of the system we are interested in and depends from a given number of parameters  $\alpha_1, \alpha_2, \dots$

The evaluation of variational energy

$$E_T(\alpha_1, \dots, \alpha_N) = \langle \Psi_T(\alpha_1, \dots, \alpha_N) | H | \Psi_T(\alpha_1, \dots, \alpha_N) \rangle \quad (2.3)$$

for a generic wave-function can be a formidable task if the multi-particle integrals cannot be factorized in low dimensional ones. This happens when the wave-function contains correlation effects beyond the single-particle determinant. In Variational Monte Carlo, the integral is rewritten as:

$$E_T = \langle \Psi_T | H | \Psi_T \rangle = \int \frac{H\Psi_T(x)}{\Psi_T(x)} |\Psi_T(x)|^2 dx = \int E_l(x) P(x) dx \quad (2.4)$$

where  $P(x) = |\Psi_T(x)|^2$  is a probability and  $E_l(x) = \frac{H\Psi_T(x)}{\Psi_T(x)}$ , often called local energy, is the function we want to sample.<sup>1</sup> Once the integral is rewritten in the form Eq. 2.4, the probability distribution  $P(x)$  is sampled by means of the Metropolis-Hastings algorithm[3] and then the  $E_l(x)$  is evaluated on this sampling. In this way it is possible to evaluate the integral with an error that scales as the square of the number of sampling points independently from the integral dimension. Once the variational energy  $E_T$  is obtained, also its derivatives respect to wave-function parameters can be evaluated and so the energy can be improved by standard optimization techniques, for a review see Ref. [1]. Notice that not only the mean value of the Hamiltonian can be evaluated using VMC but in general any Hermitian operator can be recasted in the form of Eq. 2.4. After this brief introduction to the VMC method I will present my results in this domain.

## 2.1 Correlated wave-functions

From Eq. 2.4, it is clear that all results we get from VMC depend strongly on the quality of the wave-function. It is therefore extremely important to find wave-functions able to describe the physics we are interested in, not too computational demanding, and easy to be parametrized.

In lattice models physicists developed different wave-functions able to describe physical phenomena produced by strong correlation, as superconductivity, spin liquids, Mott insulators. In the next section I will show how two particular wave-functions, the Resonant Valence Bond and the Gutzwiller one, can be extended to real-space with very interesting results.

### 2.1.1 Resonant Valence Bond (RVB) in real systems

The comprehension of the nature of the chemical bond deeply lies on quantum mechanics; since the seminal work by Heitler and London, a significant progress has been made towards the possibility to predict the quantitative properties of the chemical compounds from a theoretical point of view. Mean field theories, such as Hartree Fock (HF) have been successfully applied to a wide variety of interesting systems, although they fail in describing those in which the correlation is crucial to correctly characterize the chemical bonds. In order to include correlation effects, we proposed a new wave-function in QMC: the Antisymmetrized Geminal Power plus Jastrow (JAGP). This wave-function is inspired by the Resonant Valence Bond wave-function proposed by Anderson on lattice models.[4] In particular in the JAGP all resonances between pairs of localized single particle orbitals are included to form the bond.[5, 6, 7] We show that this wave-function is able to catch a large amount of the correlation energy with only a determinant of singlet pairs between electrons. This wave-function presents different advantages: 1) its evaluation is not computationally expensive compared to a configuration-interaction(CI) expansion; 2) it can describe close-shell as well as open-shell systems; 3) it is size-consistent, in the sense that increasing the size of the systems accuracy is not lost; 4) it reproduces the physics of Valence Bond theory introduced by Linus Pauling[8]. For

<sup>1</sup>In this example I consider only real wave-functions, but the method is easily extended to complex ones

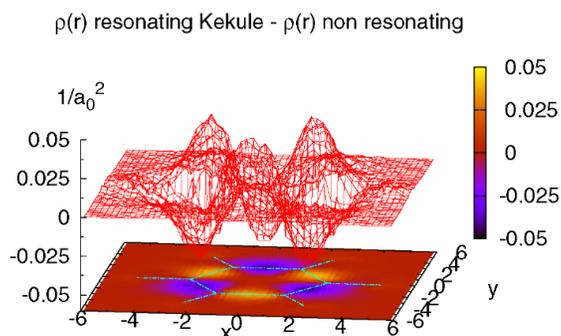


Figure 2.1: Electron density (atomic units) projected on the plane of  $C_6H_6$ . The surface plot shows the difference between the resonating valence, with the correct  $A_{1g}$  symmetry of the molecule, and a non-resonating one, which has the wrong symmetry of the Hartree-Fock wave-function.

example in Fig. 2.1 I show how the JAGP wave-function is able to recover the correct symmetry of the benzene molecule that it would not be correctly reproduced by single-particle wave-functions. Clearly our method is approximate and in some cases not yet satisfactory, but in a large number of interesting molecules we obtained results comparable and even better than multi-determinants schemes based on few Slater determinants per atom that are affordable by QMC only for rather small molecules.

**Principal Collaborators:** Michele Casula and Sandro Sorella

### 2.1.2 From Gutzwiller to the Jastrow

The JAGP wave-function contains a second ingredient to catch correlation effects, the Jastrow. This term is a positive multiplicative factor in front of the determinant. In QMC the Jastrow factor is usually introduced to take care of the electron-electron and electron-nuclei cusp conditions.<sup>2</sup> We introduce a new Jastrow in terms of pairing of localized orbitals[5] that satisfy the previous requirements and it is a generalization of the Gutzwiller projector on lattice[9]. Differently from the standard Gutzwiller projector, it includes also a long-range part, that is a necessary ingredient to describe Mott transition,[10] by suppressing double occupation.

In 2011 we applied the JAGP wave-function to the Mott transition in a one-dimensional hydrogen chain as a function of the interatomic distance. We monitor the transition by means of the many-body Berry phase, that is a measure of the polarization of the system. When the system is in an isolating phase it has a finite polarization while a metal cannot be polarized. This allows us to distinguish the two phases. In Fig. 2.2 I report the complex polarization  $|z|$  for different hydrogen chains as a function of the interatomic distance and the chain length. Thanks to the presence of the Jastrow factor we were able to describe the Mott transition as a function of the distance between the hydrogen atoms. In the same work we also showed that in the limit of large inter-atomic distances the physics of half-filling Hubbard model is recovered.

**Principal Collaborators:** Lorenzo Stella and Sandro Sorella

<sup>2</sup>Strictly speaking the electron-nuclei cusp condition can be also introduced in the orbitals that enter in the determinant, but using the Jastrow for the cusp allows to use of orbitals that do not have cusps, as the Gaussian, without problems

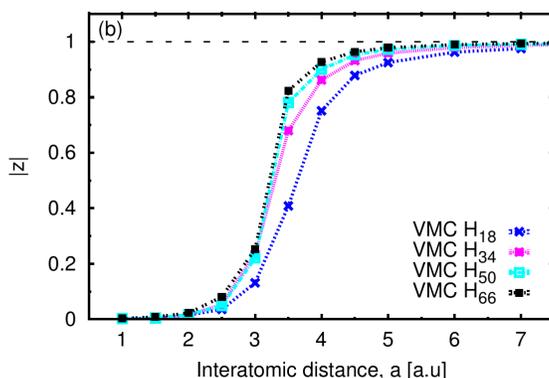


Figure 2.2: Modulus of the complex polarization,  $|z|$  as a function of the interatomic distance for the different chain lengths.

### Impact and consequences

In the last years the JAGP became a standard wave-function in Quantum Monte Carlo, used by different groups in the same form we proposed it or in some of its extensions. Our result on hydrogen-chain was the first QMC simulation of a Mott transition in a realistic system. The hydrogen chain was chosen by the Many Electrons Systems Working Group of the Simons Foundation as benchmark to test many-body approaches.[11]

## 2.2 Cold electrons but finite temperature ions

Ab-initio molecular dynamics (AMD) is a well established and a powerful tool to investigate many-body condensed matter systems at finite temperature. In AMD ions are treated as classical particles in the potential surface generated by quantum electrons. The electrons are usually approximated by means of Density Functional Theory. Different approaches have been developed during the last years to avoid the full solution of the electronic problem but maintaining a good ions dynamics, the most famous the Car-Parrinello method.[12] QMC is an alternative approach that provides better potential energy surfaces than DFT for a large range of materials. However in 2008 few attempts to apply QMC for the ions dynamics or for thermodynamic properties were known, and they were all limited to small number of electrons or to a correction to the total energy without the explicit calculation of the forces.[13, 14]

We introduced a new efficient scheme for the molecular dynamics of electronic systems by means of Quantum Monte Carlo.[16] The evaluation of the (Born-Oppenheimer) forces acting on the ionic positions is achieved by two main ingredients: (i) the forces are computed with finite and small variance, which allows the simulation of a large number of atoms, (ii) the statistical noise corresponding to the forces is used to drive the dynamics at finite temperature by means of an appropriate Langevin dynamics. As first application we studied the liquid phase of hydrogen at high pressure, and showed that the liquid phase is stable at unexpected pressures and temperature, see Fig 2.3. This result was later confirmed by other experimental and theoretical studies.

**Principal Collaborators:** Sandro Sorella

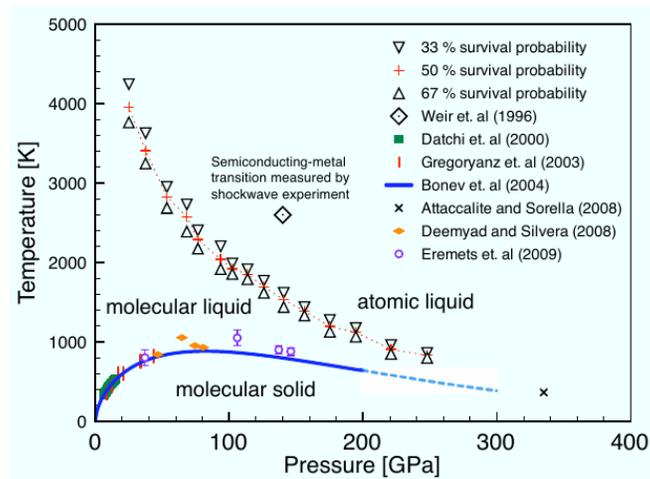


Figure 2.3: Phase diagram of hydrogen at high pressure, results from different experiments and theoretical calculations.[15].

### Impact and consequences

Experimental measurements confirmed that hydrogen is liquid at pressure and temperature where we predicted it.[15] Since then our new molecular dynamics approach has been used many times and it has been extended to include quantum effects in the ions dynamics.[17]





## 3. Collaboration with experimental groups

After my first post-doc I decided to orient my research field in the direction of excited state properties field. I was motivated by the possibility of more contacts with experimental groups carrying out measurements as optical properties, conductivity, magnetic excitations etc.. not often accessible to Quantum Monte Carlo. QMC is indeed a ground state approach, that has few possibilities to deal with response functions probed in the experiments, although a lot of progress has been done in the last years. Therefore I decided to redirect my interest towards Density-Functional and Green's function theory.

### 3.1 From Green's functions to ARPES

In ARPES (Angle-resolved Photoemission Spectroscopy) measurements an high energy photon kicks off an electron from the material. The electron is then captured by a detector that measures its energy and momentum. Combining this information with the one of the photon it is possible to access the full quasi-particle band structure of the material. In order to interpret and reproduce this quasi-particle band structure we used Many-body Green's function theory (MBPT). In MBPT we start from the DFT band structure and correct energies and widths using a perturbative approach in term of a screened electron-electron interaction. In the first work on graphite we show that the DFT band structure underestimates the slope of the bands and the trigonal warping effect. Including electron-electron correlation at the so called GW approximation, however, yields remarkable improvement in the proximity of the Fermi level. This result points toward a pronounced role of electron correlation in a wide range of carbon based materials. Our theoretical results were compared with the full three-dimensional dispersion of the  $\pi$  bands, Fermi velocities, and effective masses measured in angle-resolved photoemission spectroscopy, see Fig. 3.1.[18] This was just the first of a long series of articles in collaboration with two experimentalists A. Grüneis and T. Pichler. In the subsequent months we used the theoretical data obtained with the GW approximation to parametrize a universal set of third-nearest-neighbor tight-binding (TB) parameters for calculation of the quasi-particle (QP) dispersion of N stacked  $sp^2$  graphene layers.

With this new set of TB parameters we determined the Fermi surface and evaluated exciton energies, charge carrier plasmon frequencies, and the conductivities which are relevant for recent angle-resolved photoemission, optical, electron energy loss, and transport measurements. The comparison of these quantities to experiments revealed an excellent agreement.[19]

Then we moved to the intercalate graphite in particular the  $KC_8$ . The  $KC_8$  crystal structure is given by individual graphene sheets separated by layers of potassium. Electrons in the graphene layers behave as a two-dimensional gas of mass-less Dirac Fermions. Since interlayer coupling is very weak, the properties of  $KC_8$  are comparable to the ones of doped graphene, without the inconvenience of the substrate interaction. Our studies of this materials concentrated on Fermi velocity modification induced by doping[20, 21], the electron-phonon coupling.[22]

**Principal Collaborators:** A. Grüenlis, T. Pichler, A. Rubio

#### Impact and consequences

Intercalate graphite was the first material composed of graphene layers alternated to other atomic layers. Today it is possible to create new van der Waals solids made of artificially stacked atomic layers.[23] Many of the results we found for intercalate graphene apply to a large part of these materials.

### 3.1.1 Electron Energy loss spectroscopy (EELS)

In electron energy loss spectroscopy (EELS) a material is exposed to a beam of electrons with a known energy and momentum. Some of the electrons undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the loss. Inelastic interactions involve inter- and intra-band transitions, plasmon excitations and other excitations. If the energy of the electrons is tuned in a range compatible with the valence-conduction transitions, the electron beam is able to probe the inverse dielectric constant. This last quantity can be studied with methodologies similar to the ones presented in the previous section.

For this reason I started a collaboration with A. Loiseau's group at ONERA in Paris, that was measuring EELS on h-BN nanostructures. Our first results were very encouraging, we were able to map the entire inverse dielectric constant in the full Brillouen zone for different energy values.[24] Strong of this result, we have studied another much discussed problem in the literature, the direct or indirect nature of the hexagonal boron nitride. In fact different articles presented contradicting results on this topic.[25, 26] We were able to show that EELS can reveal the nature of hBN band

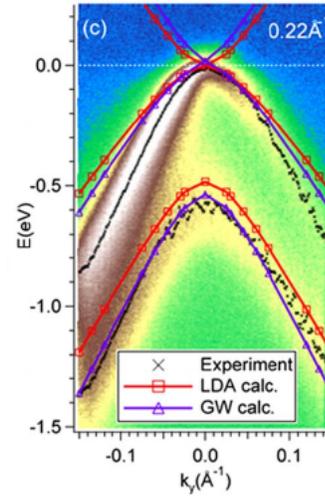


Figure 3.1: Quasi-particle band structure in DFT-LDA and within the GW approximation compared with ARPES measurements.

structure and it shows that h-BN is indeed an indirect gap insulator.[27]

**Principal Collaborators:** F. Ducastelle, H. Amara, L. Sponza, A. Loiseau

#### Impact and consequences

More or less at the same moment we posted our results on arXiv,[27] an experimental group performed the measurements on hBN.[28] The agreement between theory and experiments confirm our findings on this material.

### 3.2 Infrared emission in molecular solids and electric field induced chemical reactions (2019/2021)

In this section I describe two collaboration projects with experimental groups at CINaM. The first collaboration aimed to design new solid state light emitters in the near infrared regime. In this work we combined theoretical predictions with experimental synthesis of borondifluoride complexes derivatives. We show that using halogen atoms substitution provides a useful ingredient for the generation of near infrared emitting organic solids.[29] In the second collaboration we investigated the synthesis of tetraazapentacene(TPA), a very promising analog of pentacene in organic electronics, using a scanning tunneling microscopy (STM). In dihydrotetraazapentacene (DHTPA) molecular bilayers deposited on Au(111), we have induced single or double dehydrogenations by applying high electric field between a STM tip and the substrate. The reaction products have been identified by comparison of Density Functional Theory calculations with experimental images of the molecular orbitals and scanning tunneling spectroscopy. The present results point the way to a synthesis of well-ordered layers of a compound which cannot be obtained by conventional organic chemistry.[30]

**Principal Collaborators:** A. D'Aleo, F. Fages, T. Leoni, C. Becker

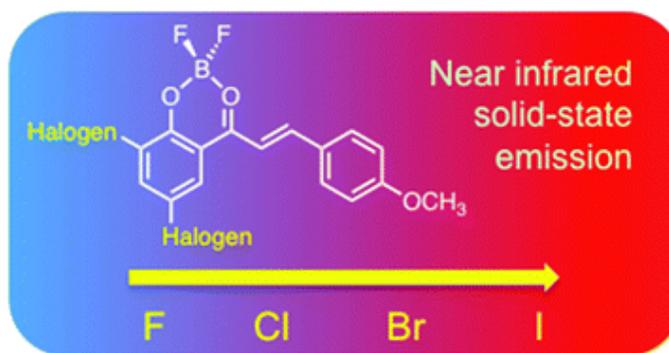


Figure 3.2: Schematic representation of frequency shift of near-infrared solid-state emission in new derivatives of borondifluoride complexes

### 3.3 Materials in extreme conditions (2021-2022)

In 2020 I started a collaboration with the CSIC, the spanish CNRS, on optical properties of materials at high-energies and high pressure. In particular we used ellipsometry to study optical response of hBN up to 25 eV. Combining experiments and theoretical calculations we found a transparency window in the deep ultraviolet region between 7 and 13 eV, that make this material useful for applications in the UV-C.[31]

Then in a second work we extended these studies at different pressures, by combining reflectivity and

ab-initio calculations. We were able to disentangle direct and indirect excitons at different pressure thanks to the comparisons between theory and experiments.[32]

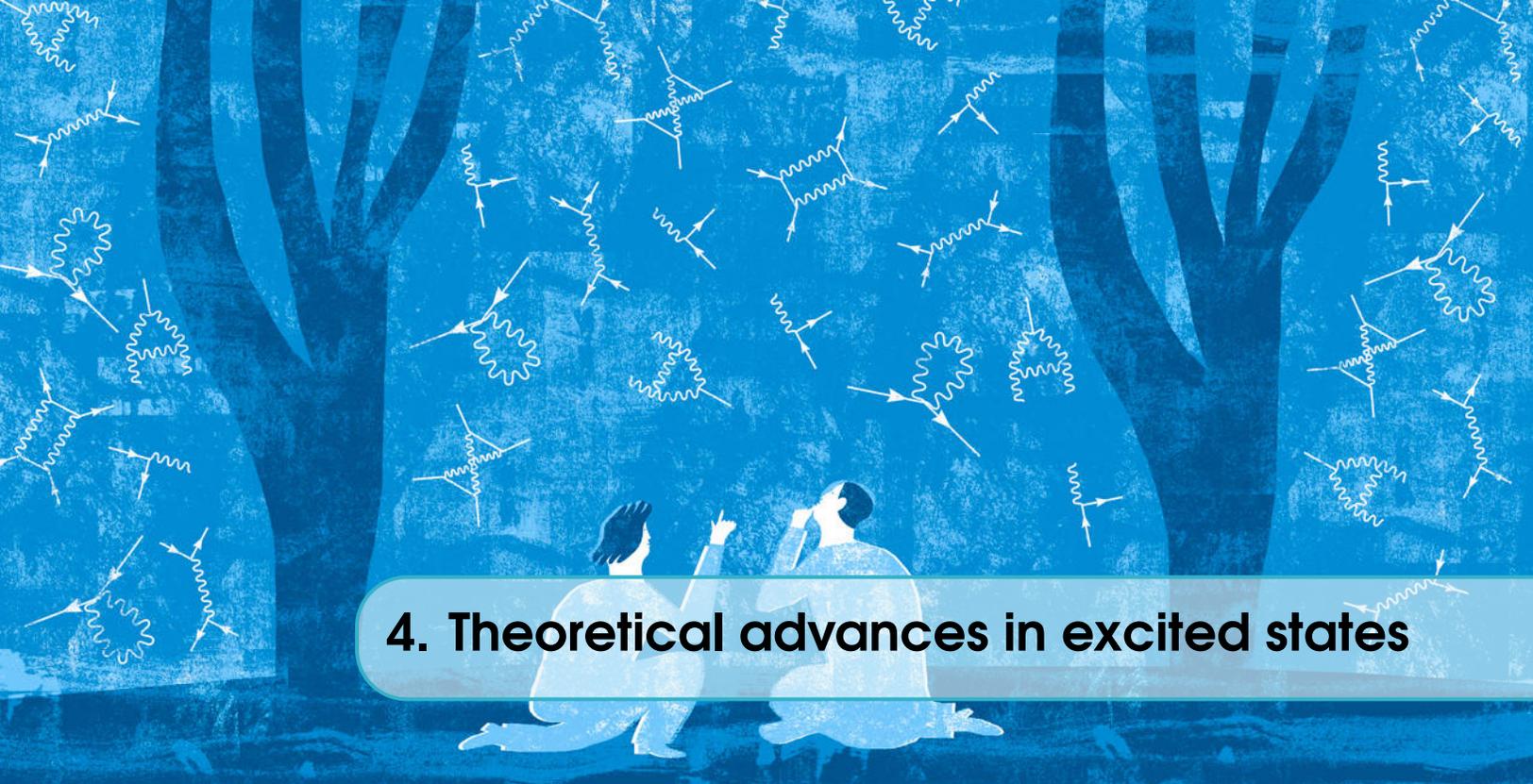
**Principal Collaborators:** L. Artus

### 3.4 Design new materials for non-linear optics (2022)

Starting from 2013 I developed a new approach to study non-linear response in solids based on a real-time solution of an effective Schrödinger equation.[33], this is describe in Chapter 5. This approach is now implemented in the Yambo code and has been used by different theoretical groups.[34]

In 2022 we use this theory in collaboration with an experimental group in Giessen (Germany)[35] to study a family 14 tetraphenyl tetrels with chemical formula  $X(C_6H_5)_4$  and  $X = C, Si, Ge, Sn,$  and  $Pb$  crystals. In particular we investigate second- and third-order optical susceptibilities and found good agreement with the experimentally measurements. The combination theory and experiments yielded a deep insight into this class of materials on the path toward understanding the origin of their characteristic white-light emission and the device of new non-linear optical media.

**Principal Collaborators:** S. Sanna, S. Chatterjee



## 4. Theoretical advances in excited states

In this chapter I discuss some important theoretical achievements in the theory of response functions and electron-phonon coupling. In particular I will present some important predictions as the existence of a Bose condensate in graphene, a tunable light emission in BN nanotubes, and the effect of correlation of the coupling between phonons and electrons in graphene. Some of these prediction have been verified in experiments other are waiting to be tested.

### 4.1 Response functions: optics and EELS

Response functions, and in particular the optical response are quantities easily accessible within Green's function theory. In parallel with my studies on quasi-particle band structures (see previous chapter), I started to investigate optical excitations in nanostructures. We studied graphene, an oxide form of graphene, and found that it could be a good candidate for Bose-Einstein condensation of excitons[36] due to its peculiar excitation spectra.

Then we moved our interest towards another layered material, the hexagonal-boron nitrite (hBN) that is a layered crystal homoe structural to graphite. Differently from graphite, hBN has a large band-gap due the ionic nature. This material emits light in the ultra-violet (UV). At that time, there was an open debate on the nature of this emission (direct or indirect).

The light emission was known to be very efficient, but in contrast with the fact the h-BN is an indirect band gap insulator, which means in principle a less efficient emission. For this reason we investigated the possibility of defect-mediated emission.[37] We showed that excitons couple with defects and form bound states compatible with the experimental measurements. Unfortunately some years later it was discovered that strong light emission efficiency was due to the coupling with phonons and not to defects. Anyway this work was a real challenge for us, because defect calculations require large supercells and we were obliged to develop our own version of code to deal with this problem.

After this work we did not abandon defects, but we searched for an interesting applications of their properties. In that period two groups[38, 39], a theoretical and an experimental one, showed that the gap of h-BN nanotubes can be tuned by means of a transverse electric field. Valence and conduction

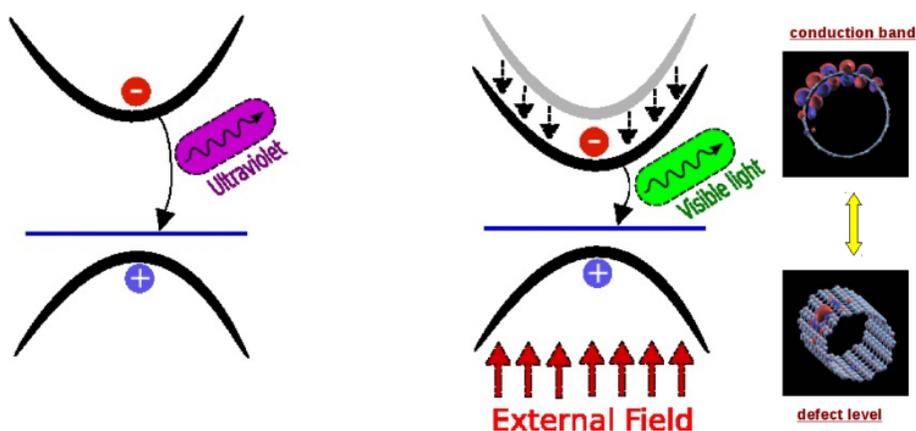


Figure 4.1: Schematic representation of the light emission in presence of defects in hBN under an external electric field.

states can be localized on the opposite sides of the tube. We decided to combine these results with the physics of defects. Defects levels, being localized, are less affected from an external field and therefore they retain their position in the band structure. This means that when one electron jumps from the conduction bands into a defect level its energy loss will depend from the external field, see Fig. 4.1. This idea of tunable light-emission was published in two different papers.[40, 41]

**Principal Collaborators:** A. Marini, A. Rubio, P. Cudazzo, L. Wirtz

#### Impact and consequences

After one year from the publication on light emission from defective nanotubes, we obtained a patent for a device based on these nanostructures,[42] where light emission can be tuned by an external electric field. This result was highlighted on the press, tens of times, but we are still waiting for an experimental realization of the device.[43]

## 4.2 Excitations in molecules and the FIESTA project

During my stay at the Néel Institute I came in contact with Xavier Blase that was working on a new project to bring Green's function theory from bulk materials to molecular systems. I started a collaboration on this new project called FIESTA (French Initiative for Electronic Simulation of Thousands of Atoms)[44] We have developed a GW et Bethe-Salpeter(BSE) code based on a Gaussian basis set.[45] The goal of this code is to make "reasonable", in term of CPU time, the calculations of the quasiparticles (electronic energy levels) and the optical spectra of organic molecules composed of more than one hundred atoms (for the logo see Fig. 4.2).

Using the code we applied this methodology in the study of the excited state properties of different molecules relevant for electronics



Figure 4.2: The FIESTA logo, designed by Carina Faber at that time Phd student in our group.

and photovoltaic interest (acènes, PTCDA, fullerènes, porphyrines, polymères, etc.).[46, 47, 48] Then we started the investigation of charge transfer excitations in donor-acceptor organic complexes and found a remarkable agreement with experiment results (of the order of 0.1 eV) when the approaches based on standard TDDFT (with LDA, PBE or even B3LYP kernels) found an error of the order of the electron-volts.[49] The same methodology was applied to the calculation of electron-phonon coupling that will be described with more details in the next sessions.[45]

**Principal Collaborators:** X. Blase, V. Olevano, I. Duchemin, C. Faber, P. Boulanger

#### Impact and consequences

The FIESTA code is now largely used by the scientific community. Many functionalities have been added to the code since I was working on it, but the core of FIESTA remains the one we worked on, during my stay in Institute Néel. We were one of the first group to apply Green's function theory in chemistry, now different codes appeared that share the same ideas.

### 4.3 Correlation and electron-phonon coupling

Electron-phonon coupling (EPC) is a key quantity in solid state physics. It determines properties as superconductivity, Raman spectra, thermal dissipation and expansion. *Ab-initio* codes based Density Functional Theory(DFT) are able to reproduce these phenomena for a large class of materials. However sometimes there are unexpected experiments that challenge computational approaches even in "simple" materials. In 2008 I entered in contact with the group of F. Mauri and M. Lazzeri in Paris. They were interested in Raman spectroscopy of graphene. In Raman spectroscopy, the system is excited with a laser and then the Raman spectra is measured. Usually the peak of Raman spectra are independent from the exciting laser frequency, being linked to the phononic frequencies of the system. But in the double-resonant Raman, the story is different. The Raman peak moves with the laser frequency because Raman in this case it is mediated by the scattering with a defect (for more detail see [50]). DFT was able to reproduce this behavior qualitative but not quantitative. This fact was quite disturbing because graphene and in general carbon based materials have been always considered weak correlated systems where DFT works well. For this reason we decided to investigate electron-phonon coupling beyond the DFT. By using perturbation theory we corrected the DFT results and were able to reproduce both the Raman shifts and the Kohn-anomaly slope in the phonon spectra.[50] Then we investigated the effect of doping and environment on the electron-phonon coupling constants. We found that many-body corrections on the EPC are much more sensible to these two effects than standard DFT. Therefore we proposed a new way to modify the coupling between electrons and phonons in graphene thanks to the combination of correlations effects and doping.[51]

**Principal Collaborators:** F. Mauri, M. Lazzeri, L. Wirtz, X. Blase, C. Faber

### Impact and consequences

Our results on how correlation effects modify electron-phonon coupling in graphene were verified independently by three experimental groups.[52, 53, 54] One group extracts the electron-phonon coupling coefficients from the Kohn anomalies in graphene,[52] their results coincides with ours. The other two groups measured the effect of doping and environment on the splitting of Raman peaks confirming our theory.[53, 54]

Our work has paved the way for the use of MBTP to correct the phonon electron coupling, after us other groups have used the same methodology to study superconductivity, electron lifetime, band gap renormalization, molecular spectra.[43, 55][45]

## 4.4 Phonon-mediated luminescence (2018)

In standard solid state physics textbooks direct band gap semiconductors are considered efficient light emitters while indirect ones are regarded as inefficient. Hexagonal boron nitride (h-BN) seems to defy this rule. In fact h-BN is an indirect insulator with a large band gap of about 7 eV, but it has recently attracted much attention from the scientific community as a very efficient light emitter in the ultraviolet.[26] An internal quantum yield of 45% has been reported for h-BN, much closer to the 50% one of ZnO (direct band gap) than to the 0.1% one of diamond (indirect band gap).[56] This goes against the common wisdom that indirect band gap insulators are bad light emitters and in fact the strong luminescence signal was initially attributed to direct exciton recombination.[26] In order to shed some light on this phenomenon different theories were proposed, including the presence of defects[37] or a dynamical Jahn-Teller effect.[57]

But only recently, thanks to more accurate and precise measurements, it has been shown that luminescence originates from phonon assisted recombination.[25] This interpretation appeared to be sound, but it was not supported by any theoretical calculations. In this work we developed a new approach to study phonon-assisted luminescence and apply it to h-BN in order to verify this hypothesis. Since excitons play a crucial role in the optical response of h-BN, in order to describe luminescence our theory includes both electron-hole interactions and electron-phonon scattering. We confirm that light emission is due to phonon-assisted transitions, and that in hexagonal boron nitride electron-phonon coupling was enhanced by the strong electron-hole interaction.[58]

**Principal Collaborators:** E. Cannuccia and B. Monserrat

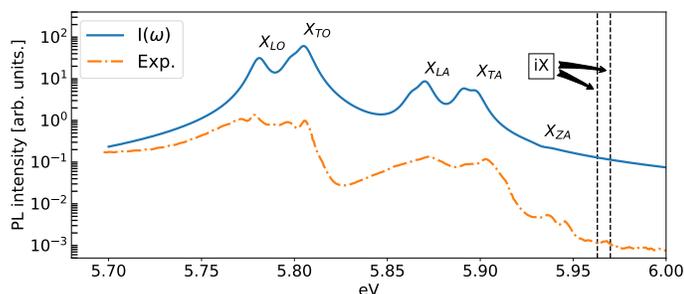


Figure 4.3: Luminescence spectra of bulk h-BN: blue continuous line is the theoretical result and orange dash-dotted the experiments of Cassabois et al. [25]

#### 4.4.1 Role of uniaxial strain on phonon-assisted luminescence (2021)

Then we applied this approach to study phonon-assisted luminescence at the case of strained h-BN. This work was motivated by recent experiments performed by the GEMAC group at Université de Versailles. We found that uniaxial-strain splits the main phonon-assisted peak, and increases the intensity of the peaks due to the acoustic phonons. However the agreement between theory and experiments in this case was not perfect as the equilibrium case. Therefore we are still investigating possible sources of disagreement, like the role of surfaces and some approximation in the calculations.[59]

**Principal Collaborators:** F. Paleari

##### Impact and consequences

In these works[58, 59] we derive a new formula for the phonon-assisted luminescence mediated by excitons, that can be calculated with finite differences using existing codes. This formula was then applied by other groups in the study of light-emission from defects and other 2D materials.

#### 4.4.2 Exciton-phonon coupling from first-principle (2022)

In all my previous works on luminescence, exciton-phonon coupling was calculated by a finite difference approach, by constructing the supercell that contains a given phonon mode and then calculating the exciton-phonon coupling displacing atoms along that mode. This approach works fine in simple situations where phonon-assisted luminescence is due to phonons along high symmetry lines that require small supercell. However in a general situation, for small momentum, low symmetries modes, or complex systems, calculations can become cumbersome. For this reason this year we worked on a new implementation of the exciton-phonon coupling where this coupling is obtained directly from the DFT, using the so-called Density-Functional-Perturbation Theory. This approach allowed us to calculate exciton-phonon coupling without the need for supercells for all momenta.

In addition, thanks to the possibility of sampling the full Brillouin zone and not only selected q-points, we were able to calculate the renormalisation factor of the direct emission peak with respect to the indirect ones, which was not possible with the finite differences approach. [60]

**Principal Collaborators:** D. Sangalli, F. Paleari

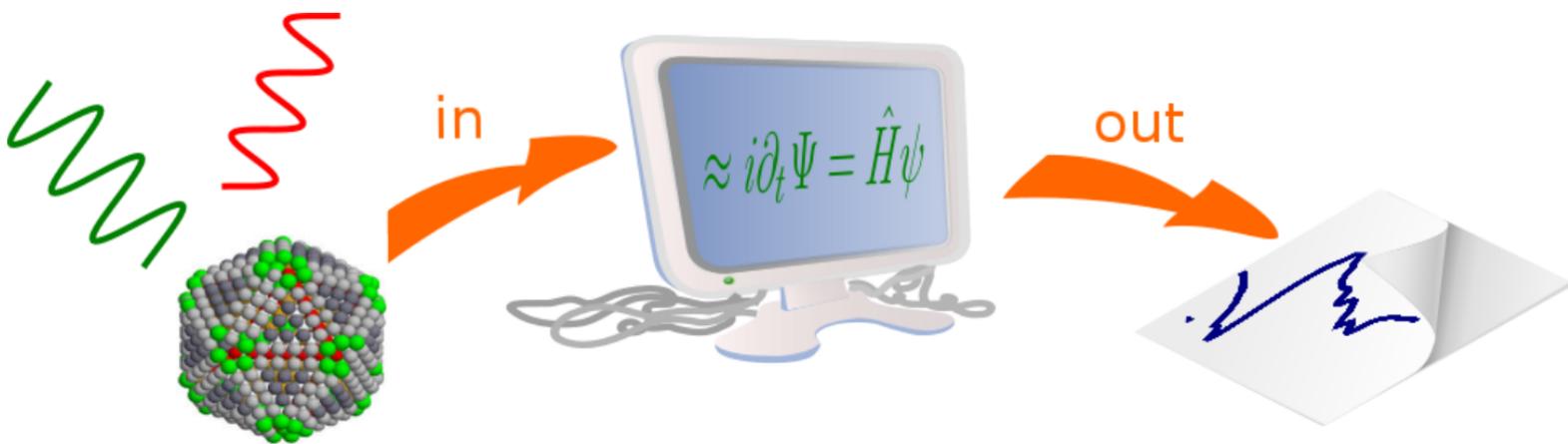
#### 4.5 Optical excitations in Metal-Organic Frameworks (MOFs) (2021)

Metal-organic frameworks (MOFs) have been attracting much attention in the past 20 years as possible candidate materials for a variety of applications, like in catalysis, gas capture and separation, drug delivery, or sensors. Among all families of MOFs, those with photoresponsive properties have been proposed as a potentially efficient technology for gas capture and release as light, possibly in the visible range can be used to change the gas adsorption properties of the material. By employing the Bethe-Salpeter equation (BSE) in conjunction with the GW approximation we studied the excited state properties of photoresponsive MOFs and their similarity with the molecular case. We predict that cis-to-trans isomerization in the photoactive MOF will be faster and more complete than the one of isolated molecules. This has strong implications in the design of MOFs with high photoconversion efficiencies.[61, 62]

**Principal Collaborators:** R. Poloni, X. Blase and J. Li

**Impact and consequences**

Due to their complexity and system size, MOFs have always been challenge systems for the theory. Here we performed the first theoretical calculation of optical properties and excited states in MOFs using many-body perturbation theory, both in a periodic model and using an embedding approach. These works will open the way to many other studies on similar systems.



## 5. Non-linear spectroscopy

When one immerses a solid, either an insulator or a semiconductor, in an electric field (see Fig. 5.1), the dipoles inside the material get oriented along the field lines and create an internal electric field, the polarization  $\mathcal{P}$ , opposite to the field that generates it. This naive picture, even if not correct for extended systems, gives us an idea of the effect of an external electric field on a material. In general the polarization  $\mathcal{P}$  can be expanded in a power series of the total electric field  $\mathcal{E}$ :

$$\mathcal{P} = \chi^{(1)}\mathcal{E} + \chi^{(2)}\mathcal{E}^2 + \chi^{(3)}\mathcal{E}^3 + \dots \quad (5.1)$$

where  $\chi^{(1)}, \chi^{(2)}, \dots$  are the response functions of increasing order.<sup>1</sup> Equation 5.1 is valid for a wide range of situations. However there are cases where this expansion is not valid: for very strong fields, in presence of an hysteresis or close to a phase transition.

In the previous chapter I presented results within linear response, that refers to the first term in Eq. 5.1. In this chapter I will show how methods presented in Chapter 4 can be extended to the non-linear response, namely all terms beyond the first one, as  $\chi^{(2)}, \chi^{(3)}, \dots$ . Non-linear response cannot be appreciated in real-life because it would require a strong laser source to be probed. However non-linear phenomena are used everyday in research laboratories, to change frequency or shape of laser pulses or to probe atomic and electronic structure of solids, interfaces and liquids (for more details see my HDR document[63]).

In this chapter I will present my contribution in this field.

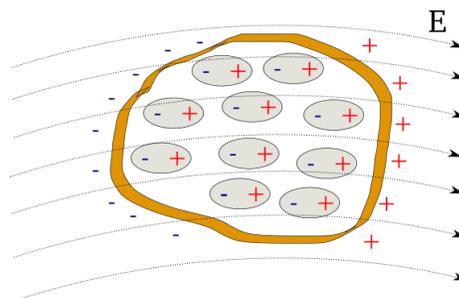


Figure 5.1: A solid immersed in an electric field.

<sup>1</sup>I do not consider here materials with an intrinsic polarization

## 5.1 Berry phase and non-linear spectroscopy

In the first attempts to calculate non-linear optical response from quantum mechanics, an equation for each response function  $\chi^{(1)}, \chi^{(2)}, \dots$  was derived from the equation of motion of the density matrix.[64]

This idea has been later generalized to include correlation effects from TD-DFT or Green's function theory.[63] Although successful, this approach completely lacks in flexibility because there is a different equation for each response function and furthermore it is not possible to study experimental situations where there are more than one lasers, short pulses, etc.

For this reason we developed a new approach to study non-linear response in solids based on a real-time solution of an effective Schrödinger equation.[33] The idea of using real-time dynamics to study non-linear response was not new, but it was applied mainly in molecular systems,[65, 66] The reason lies in the fact that the dipole operator is ill-defined when periodic boundary conditions (PBC) are present and the coupling between light and electrons is more complicated than in molecular systems. This problem has been solved in 1993 by means of Modern Theory of Polarization (MTP) by Resta, Vanderbilt and King-Smith.[67] With MTP it is possible to express the Polarization in terms of the wave-function phase on a closed path of the Brillouin zone (the Berry phase). From the polarization definition it is then possible to derive the correct coupling between light and electrons in periodic systems. This approach has been used to study solids under the effects of static electric fields and also the dynamical response in simple models. In our work we extended this approach to study the non-linear response of solids, starting from ab-initio wave-functions and including correlation effects as local-fields and renormalization of the quasi-particle band structure.[33] We applied this new methodology[68] to study second and third harmonic generation (SHG and THG) in bulk semiconductors. In Fig. 5.2 I report the scheme of our approach, for more details see Ref. [63].

The use of a real-time solution allows to study non-linear response functions that are difficult to simulate with standard methods, as the third-harmonic generation (THG) or the two-photon absorption (TPA).

After this first work we derived an effective Hamiltonian from Green's function theory to include electron-hole interaction effects in the real-time dynamics.[68] This allows us to study non-linear

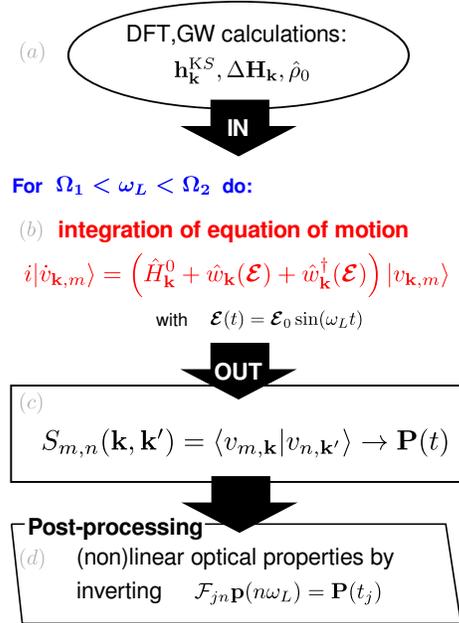


Figure 5.2: Real-time ab-initio scheme to compute SHG and THG spectra in the  $[\Omega_1, \Omega_2]$  energy range for extended systems with PBC: (a) Results from DFT and  $G_0W_0$  are input to determine the zero-field Hamiltonian. (b) The EOMs are then integrated, the polarization is computed. In the post-processing step (d) the nonlinear susceptibilities are obtained by Fourier analysis of the polarization.

response in low-dimensional systems, that present strong bound excitons.[69, 70] In Fig. 5.3 I show

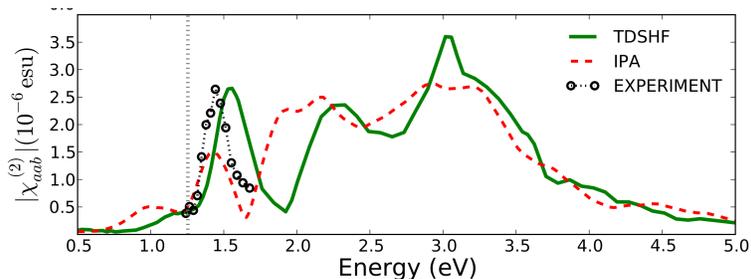


Figure 5.3: Second Harmonic Generation (SHG) in two-dimensional  $\text{MoS}_2$ . The dashed red line is the independent particle approximation, the continuous green line is the theory including electron-hole interaction and the black dots are the experiments from Ref. [71].

the second-harmonic generation (SHG) of  $\text{MoS}_2$  monolayer as function of the laser frequency. We found that in two-dimensional crystals electron-hole interaction can double the intensity of SHG response in comparison to the independent particle case, in better agreement with the experiments.[69, 70]

**Principal Collaborators:** M. Grüning

#### Impact and consequences

We introduce a new methodology to study non-linear response that takes into account correlation effects also in higher order response functions through an effective one-body Hamiltonian. We released a code, Lumen (<http://www.attacalite.com/lumen/>) that implements all the advances presented in this chapter.

## 5.2 TD-DFT and non-linear response

Density functional theory (DFT) is a standard approach for calculating ground-state properties of extended and finite systems. Time-dependent density functional theory (TDDFT) is an extension of the ground-state formalism to investigate many-body systems in the presence of time-dependent external fields. TDDFT is based on the Runge-Gross (RG) theorem that establishes a one-to-one correspondence between time-dependent densities and time-dependent one-body potentials. Despite the success of TDDFT in molecular systems, the situation is more complicated in extended system. In fact, although other methods, as for instance Green's function theory, provide a similar accuracy in extended and finite systems, this is not the case for TDDFT. Due to the lower computational cost of TDDFT respect to Green's function formalism it would be desirable to have the same accuracy in extended and finite systems. This problem originates from the fact the the RG theorem does not hold in extended systems. Different extensions of TDDFT have been presented in recent years in order apply it in periodic systems different extensions.

In our work we used a version of TDDFT where the exchange correlation kernel depends both from the density and the polarization, Density Functional Polarization Theory (DFPT).

In the previous section we included correlation effects from Green's function theory in the non-linear response. This approach is very effective but it is also very computationally demanding. If we could have achieved comparable results with the DFTP it would have been helpful in simulating more complex systems and phenomena. We therefore tested different exchange-correlation kernels within DFTP for linear and non-linear response in solids derived from simple models as the electron-gas or parametrized from more accurate calculations. In general exchange-correlation kernels are built to well reproduce the linear response, so our work for the first time tested their performance in the non-linear regime. As example in Fig. 5.4 I report the second harmonic generation (SHG) for the bulk zinc chalcogenides using different exchange correlation functionals, compared with the experimental results and the independent particle approximation. Although there is an evident improvement respect to the IPA, we still miss a functional that is able to reproduce SHG for a large spectra of materials.[72, 73]

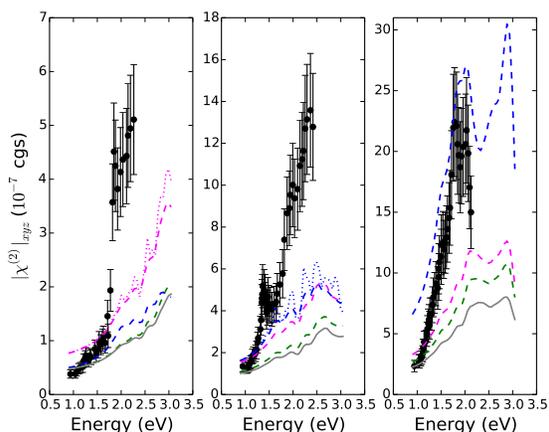


Figure 5.4: From left to right, Second Harmonic Generation (SHG) in bulk ZnS, ZnSe and ZnTe. Grey lines are the independent particle approximation, the other lines correspond to different exchange-correlation functionals and finally the dots are the experiment measurements.

**Principal Collaborators:** M. Grüning and D. Sangalli

### 5.3 Two-photon absorption in 2D materials (2018)

Two-photon absorption (TPA) is a nonlinear optical process in which the absorption of two photons excites a system to a higher energy electronic state. TPA in two-dimensional (2D) crystals have been recently the object of several experiments. For example, a giant TPA has been reported for transition metal dichalcogenides (TMDs); further, TPA has been used to image single quantum emitters embedded in a h-BN multilayer flake; and finally in another study on TMDs, TPA has been used to probe excited states which are dark in linear optics. In fact, two-photon transitions obey selection rules distinct from those governing linear excitation processes and thereby provide complementary insights into the electronic structure of excited states. In particular it is frequently argued that one-photon processes are only allowed for excitons of s symmetry whereas p states can be observed in TPA. These rules can be derived within a continuous hydrogenic model for excitons where full rotational symmetry is assumed. They have been invoked to analyze the excitonic effects observed in carbon nanotubes, and also recently in bulk h-BN. Though it is recognized that these rules are not generally valid if the genuine crystalline symmetry is taken into account, it is claimed they can at least guide interpretations in terms of high or low oscillator strength. For 2D materials, excitonic effects are strong and the exciton wave functions are fairly localized, so that the low threefold symmetry plays an important role. In our work[74] we analyzed the case of the h-BN single layer and bulk, which have the same lattice symmetry as the TMDs and very strongly bound excitons. We combine tight-binding (TB) calculations of the two-photon transition probability with sophisticated

ab-initio real-time Bethe-Salpeter simulations of the two-photon resonance third-order susceptibility. This combination is a unique feature of this work: on the one hand the TB calculations allow us to identify the symmetry properties of the excitons, on the other hand the ab initio real-time Bethe-Salpeter (RT-BSE) simulations provide the TPA spectra—one of the first ab initio TPA spectra at this level of theory which can be compared quantitatively with experiments. Our results show that the 1s exciton is predominant as for one-photon absorption indicating strong deviations from the selection rules based on the hydrogenic model, which are frequently employed to interpret the experimental spectra. Finally we demonstrate that one can measure the Davydov splitting in multilayer stackings with inversion symmetry by using a combination of one and two-photon absorption measurements.

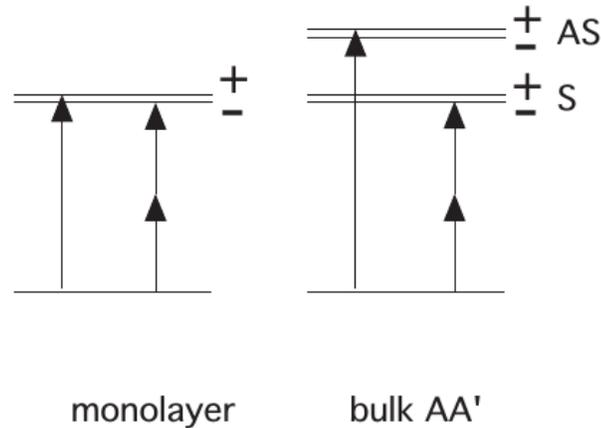


Figure 5.5: Allowed transitions towards the lowest excitonic states with circularly polarized light. (Left) Monolayer; (Right) Bulk AA' stacking; there are now two anti-symmetric (AS, odd, one-photon allowed) and one symmetric (S, even, two-photon allowed) degenerate states, separated by a Davydov splitting

**Principal Collaborators:** F. Ducastelle, H. Amara, M. Grüning

## 5.4 Pump and probe spectroscopy (2022)

In pump-probe spectroscopy, two laser pulses are employed to garner dynamical information from the sample of interest. The pump initiates the optical process by exciting a portion of the sample from the electronic ground state to an accessible electronic excited state, an exciton. Thereafter, the probe interacts with the already excited sample. The change in the absorbance after pump provides information on transitions between the excited states and their dynamics. In this work we study these exciton-exciton transitions by means of a real time propagation scheme based on dynamical Berry phase, the same we used for the non-linear response. Then we analyzed results using a Fermi-golden rule approach formulated in the excitonic basis-set and in terms of the symmetries of the excitonic states. We applied this approach to two systems with strongly bound excitons where hydrogen model fails. This work has been just submitted to Phys. Rev. Materials. [75]

**Principal Collaborators:** D. Sangalli, M. D'Alessandro



How many shortest-length paths are there to get from your house to the doughnut shop?

4 up's  
7 right's

$\binom{11}{7} = \binom{11}{4} = 330$  paths

$\binom{n}{k} = \frac{n!}{(n-k)!k!}$

$e^{i\pi} + 1 = 0$

P	Q	R	P V Q	P V R	(P V Q) $\wedge$ (P V R)
T	T	T	T	T	T
T	T	F	T	T	T
T	F	T	T	T	T
T	F	F	T	T	T
F	T	T	T	T	T
F	T	F	T	F	F
F	F	T	F	T	F
F	F	F	F	F	F

Find  $7 + 12 + 17 + 22 + \dots + 342$

$S_n = 7 + 12 + 17 + 22 + \dots + 342$

$+ S_n = 342 + 337 + 332 + 327 + \dots + 7$

$2S_n = 349 + 349 + 349 + 349 + \dots + 349$

$2S_n = 349 \cdot 68$

$S_n = \frac{349 \cdot 68}{2}$

$S_n = 11866$

Original:  $\exists x \forall y (x \geq 2y \rightarrow x > y + 1)$

Converse:  $\exists x \forall y (x > y + 1 \rightarrow x \geq 2y)$

Negation:  $\neg [\exists x \forall y (\neg (x \geq 2y) \vee x > y + 1)]$

$\forall x \exists y (x \geq 2y \wedge x < y + 1)$

Contrapositive:  $\exists x \forall y (x < y + 1 \rightarrow x < 2y)$

P.I.E. Example:

$6! - \left[ \binom{6}{1}5! - \binom{6}{2}4! + \binom{6}{3}3! - \binom{6}{4}2! + \binom{6}{5} - 1 \right]$

There are six dogs to give 13 tacos. Use a 'stars and bars' diagram to illustrate the first and sixth dog get 3 tacos, the second dog gets none, the third dog gets 5 and the fourth dog gets 0.

$A = \{2, 4, \text{Ⓢ}, \text{Ⓣ}\}$

$(A \cup B \cup C) \cup (A \cap B \cap C)$

Onto

One-to-One

$K_{3,3}$

## 6. New algorithms and code development

Algorithms are the core of numerical calculations. When we write down an equation on a piece of paper it is difficult to imagine how complicated it will be for a computer to solve it. There are power series that converge very slowly, divergences difficult to integrate etc ... Finding new algorithms that can solve these problems is part of the "game" for a theoretical physicist. Here I present my small contribution in this domain.

### 6.1 Algorithms

#### Stochastic reconfiguration method

Stochastic Reconfiguration (SR) method is similar to a standard steepest descent (SD) technique, where the expectation value of the energy is optimized by iteratively changing the parameters  $\alpha_i$  that appear in the wave-function, according to the corresponding derivatives of the energy. The fundamental difference between the SR minimization and the standard steepest descent is just related to the metric they use. SD works with the usual Cartesian metric in the parameter space, instead the SR uses the physical Hilbert space metric of the wave function, namely the square distance between the two normalized wave functions corresponding to the two different sets of variational parameters. The advantage of SR compared with SD is obvious because sometimes a small change of the variational parameters correspond to a large change of the wave function, and the SR takes into account this effect. In my work, Ref. [5] we extended this method to structural optimization for molecular systems.

#### Speed up solution of Bethe-Salpeter Equation by means of Wannier interpolation

The Bethe-Salpeter equation (BSE) is a widely used approach to describe optical excitations in bulk semiconductors, as it is shown in Chapter 3. The solution of the BSE yields spectra that are in very good agreement with experiment, but the price to pay for such accuracy is a very high computational burden. One of the main bottlenecks is the large number of k points required to obtain converged spectra. In order to circumvent this problem we proposed a strategy to solve the Bethe-Salpeter equation based on a double-grid technique coupled to a Wannier interpolation of the Kohn-Sham band structure. We showed that with this approach converged spectra are reached for relatively small

symmetric k-point grids. This allows for a considerably faster calculation of the BSE kernel.[76]

### Fast updating of COHSEX self-energy

In chapter 5 we discussed how electron-hole interaction modify the non-linear response of bulk materials. In order to calculate the non-linear response functions from the real-time dynamics, we need to evaluate the screened exchange (SEX) self-energy, the part that takes into account the electron-hole interaction, thousands of times during a single run. If one used the standard way to evaluate it, calculations would reveal to be impossible to complete. For this reason we devise a new way to update the SEX self-energy when the wave-function evolves in time, with a minimal computational cost, this algorithm is described in Refs. [63, 68]

## 6.2 Codes (2019-2020)

The major part of the advances presented in this report were obtained by means of computational codes. I invested a considerable part my research activity to develop existing codes or develop new ones. Writing a code is a way to translate formulas into concrete results, and face all numerical issues that are often invisible in a formal derivation. In this section I present a short list of codes that I participated in development with a short description of what I have done. For two of them, Yambo and TurboRVB, we submitted in 2019 and 2020 the code reference papers.

### Yambo [<http://yambo-code.org>]

Yambo is a FORTRAN/C code for Many-Body calculations in solid state and molecular physics, that relies on the Kohn-Sham wave-functions generated by two DFT public codes: abinit, and PWscf. In 2019, we published a reference article with the description of all functionalities of the Yambo code, see Ref. [34].

In this computational project, I worked both in the development and maintenance of the code. In particular, I implemented the following parts: parallelization to study large systems,[37] new algorithms to speed up convergence of optical spectra,[76] and real-time electron dynamics.[68] I also actively help in the management of the forum, code testing, web-page, debugging and schools organization.

### Lumen [<http://attaccalite.com/lumen>]

Starting from 2017 I started to develop my own code Lumen. Lumen is based on Yambo and implements a new approach to study non-linear response in solids and nanostructures based on a real-time evolution of an effective Schrödinger equation. All the calculations and all the theory presented in chapter 5 has been implemented and tested with this code.[33, 63, 68]

### Fiesta [<http://perso.neel.cnrs.fr/xavier.blase/fiesta/>]

Fiesta is a code that implements the GW and Bethe-Salpeter formalisms using Gaussian bases for finite systems. During my time at the Néel Institute (20010-2014) I participated in the code benchmarking and testing.[48]

### TurboPair [<http://people.sissa.it/~sorella/web/index.html>]

TurboRVB is a very efficient Quantum Monte Carlo Package for Electronic Structure Calculations, based on a geminal wave-function (AGP) and a highly accurate Jastrow factor containing both spin and density correlations. These ingredients allow to implement the fascinating "Resonating Valence

Bond theory” (RVB) of electronic correlation by Linus Pauling and P.W. Anderson, in a very efficient way. I worked on TurboPair for different years, implementing: periodic boundary conditions; new localized orbitals; finite temperature ions dynamics; polarization in terms of Berry phase to probe metal-insulator transitions.[5, 6, 77, 78]

In 2020, we published a manuscript with the description of the TurboRVB code and all its functionalities[79].





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