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BOOK OF ABSTRACTS

Spectral properties of molecules and solids from a functional approach

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Accurate first-principles predictions of spectral properties – such as band gaps, band structures, photoemission and absorption spectra – attract considerable attention because of their critical impact on the design and characterization of optical and electronic devices. To date, the most common approaches to compute these quantities are still limited in system size and complexity due to their computational cost an accuracy.

We present a novel functional approach [1,2] that is derived from the density-functional theory by enforcing the correct response to the removal or addition of one electron to the interacting system (Koopmans's condition). We show that Koopmans-compliant functionals provide a novel framework where spectral properties, and not only total energies, can be efficiently and accurately predicted.

As an example, ionization potentials of a large set of molecules [3] (the GW100 test set), photoemission and absorption spectra [4] of organic donors and acceptors, band gaps and band structures of solids [5] and liquds [6] are presented, showing very good agreement with experiment or higher-order theories. Being this a functional framework, the straightforward advantages are that forces and other derivatives are also readily accessible, that the computational costs and complexity are much reduced, and the numerical parameters are those typical of density functional calculations.

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Frequency dependence in GW made simple using a multi-pole approximation

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In the GW approximation, the screened interaction W is a non-local and dynamical potential that usually has a complex frequency dependence. A full description of such dependence is possible but leads to computationally demanding methods. For this reason, it is still common practice to approximate it using a plasmon pole (PP) model. The PP approach has however limitations that prevent an accurate description of inhomogeneous systems, such as interfaces and defects, and some bulk materials, such as metals.

In this work we explore a multi-pole (MP) approach and develop an effective representation of the frequency dependence of W. We show that an appropriate sampling of the polarizability in the frequency complex plane and a multi-pole interpolation can lead to a level of accuracy comparable with full-frequency methods at much lower computational cost, therefore, naturally bridging from the PP to a full-frequency treatment of the GW self-energy. Numerically, the MP technique has been implemented and tested by using the Yambo code [1, 2], and in this work we discuss the application of such strategy to relevant prototype systems.

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Solving the Dyson equation via the algorithmic inversion

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Frequency-dependent potentials appear in several electronic structure formulations including self-energies from many-body perturbation theory, dynamical mean-field theory, electron-boson coupling, embedding problems, or spectral potentials. Once determined (via e.g. many-body-perturbation theory), the solution at all frequencies of non-linear-Dyson-like equations is needed to retrieve spectral and thermodynamic quantities of the system. Suffering from not having solved the equation at all-other frequencies, current approaches enforcing point-wise inversions are unable to provide accurate frequency-integrated results. Here we propose to solve the Dyson equation exactly and at all frequencies using the algorithmic-inversion method for homogeneous and non-homogeneous systems. The Green's function obtained from the solution of the non-linear problem, via the algorithmic-inversion method, allows for the analytic calculation of the thermodynamics of the system, and for the self-consistent solution of the Dyson equation.

HIgher-order many-body perturbation theory benchmarked on atoms

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While the GW method has been the subject of an intense work of validation, higher-order many-body perturbation theory (MBPT) methods have received much less attention. Here we investigate the performance of beyond-GW MBPT approaches in atoms described within the spherical approximation. By using a dedicated numerical treatment based on a B-spline/spherical harmonics representation [1, 2], we obtain benchmark results avoiding many commonly adopted approximate procedures (including complete basis set extrapolations, pseudopotentials and frequency descriptions). We consider the GW, 2nd Born and GW+SOSEX [3] self-energies and apply the many-body treatment on top of a number of starting points (HF, PBE, PBE0) to compute the ionization potentials (IPs) of atoms (see FIgure 1). We also use these self-energies within the optimized effective potential (OEP) method to compute xc correlation potentials and related IPs within a KS-DFT scheme.

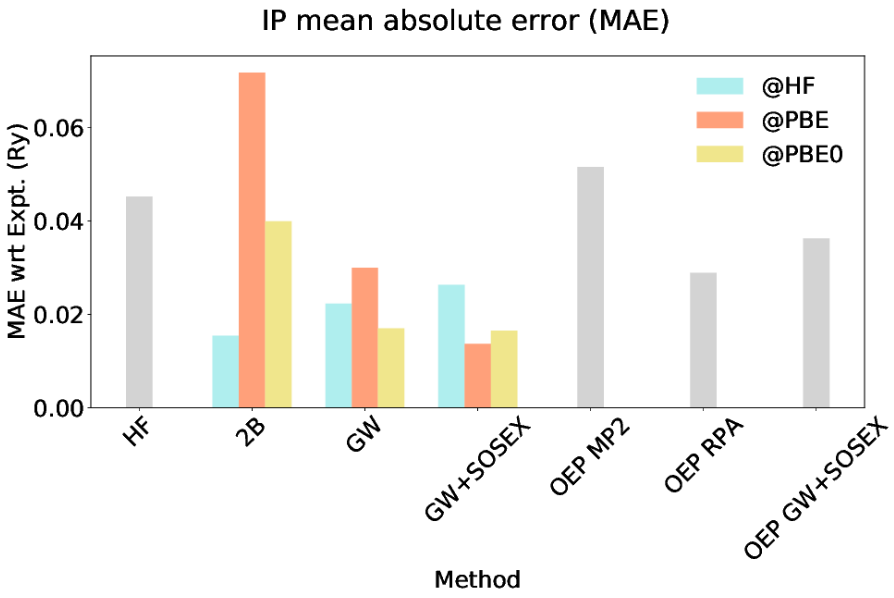

Figure 1: Mean absolute errors (MAE) on the IPs for each method and starting point.

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First-principles electronic and structural properties of BNC nanomaterials

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Advanced Silicon-based device components are moderately chemically tunable, which restricts the realistic prospect of current technology transitioning into flexible and miniaturized devices. Graphene is a promising candidate [1] to replace Silicon as semiconducting material and heteroatom co-doping has emerged as an appealing strategy to tune its electronic and structural properties. Since the existing BN-doped carbon-based materials are not periodically doped, their properties are not reproducible [2] hence a substantial challenge is to gain control in the incorporation of these BN rings in a reproducible manner. The present study aims to search for an entirely new class of BCN hybrid 2D materials in order to construct a high-accuracy reference database with key electronic and optical properties. This goal is achieved by using *ab initio* quantum mechanical calculations relying on density functional theory (DFT) and many-body perturbation theory (MBPT). A large set of BNC materials exhibiting different doping parameters (Figure 1) is considered in order to search for the best configuration in terms of both stability and band gap. These models are then compared to benchmark systems, displaying high stability. The corresponding cohesive energy presents comparable values and well-defined linear trends with BN-ring concentration. Within the same doping patterns, different ring orientations are also considered suggesting that the cohesive energy does not qualitatively change. On the other hand, the band gap is found to be sensitive on the doping pattern and its value is considerably higher when BN rings are in the same orientation.

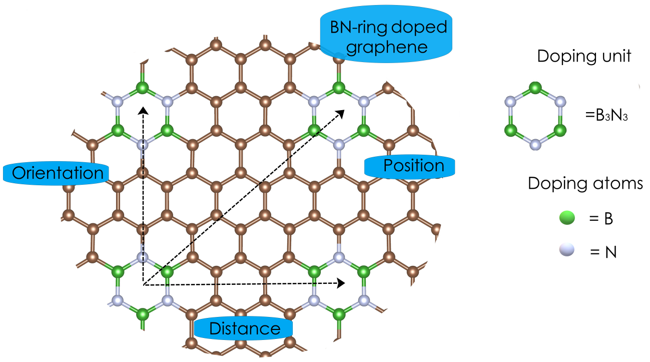

Figure 1: BN-ring doped Graphene. Different doping parameters, such as orientation, position and distance, are considered herewith to search for an optimal doping configuration in terms of stability and band gap in order to possibly replace Silicon in future opto-electronic nanodevices.

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A GW study of dielectric screening effects on the quasiparticle properties of monolayer MoS_2

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Monolayers of transition-metal dichalcogenides (TMD) hold great promise as future nanoelectronic and optoelectronic devices. A unique feature of these atomically thin semiconducting TMDs is the tunability of their properties by the dielectric environment for which suitable supporting substrates are needed to achieve high-performing devices. Using many-body GW method, we have investigated the change in the electronic structure of monolayer MoS_2 by an effective dielectric screening, which correspond to hexagonal boron-nitride (hBN) and silica (SiO_2) substrates. In this talk, I will, first, give a short overview on the GW method and the Sternheimer formalism and then present the results of the dielectric screening effects on the band gap, carrier effective masses and spectral properties of MoS_2 monolayer[1].

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Modelling magnetism and strong correlations in real materials

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In the past decades there has been an enormous progress in developing the realistic electronic structure theory for strongly correlated systems. Most of the modern first-principles studies are based on a combination of density functional theory and dynamical mean field theory (DFT+DMFT) [1]. Within this approach, the DFT is used as a starting point for more sophisticated DMFT calculations for a selected subset of “correlated” orbitals. The approach has proven to be extremely successful and is commonly employed to model the electronic structure of a wide range of *d*- and *f*-based correlated materials. In my talk I will show various applications of DFT+DMFT with particular emphasis on magnetic properties.

Magnon excitations are non-local and are therefore not directly accessible within DMFT. Thus we have to employ a so-called two-step approach. We first map the system on a Heisenberg model and extract the effective exchange parameters *Jij*’s from DFT+DMFT, following Ref.[2]. Then the atomistic spin dynamics simulations are employed to simulate magnon spectra and predict the magnetic ordering temperatures [3]. I will demonstrate how such a combined approach can successfully predict properties of different types of materials from transition metal oxides to rare-earth metals.

The *Jij*’s in real materials have a complicated nature and depend on how the correlation effects are taken into account [4]. I will show how the decomposition of the exchange parameters in terms of their orbital contributions can provide a useful insight into the essence of magnetism in a material. In particular, we found an intrinsic competition between ferromagnetic and antiferromagnetic interactions between different orbitals in elemental Mn and Fe [5]. Moreover, I will demonstrate that iron is a unique example where one can even distinguish RKKY, double- and super-exchange contributions to the magnetic couplings [6].

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A density-corrected DFT scheme applied to the calculation of spin-state energetics

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The accurate description of spin-state energetics of transition-metal complexes represents a great challenge for electronic structure ab initio methods. This challenge stems from the lack of error cancellation when computing energy differences using approximate electronic structure methods between spin states exhibiting different types and amounts of electronic correlations.

In DFT for example, local and semilocal functionals (e.g. LDA and GGA), systematically overstabilise low spin state while Hartree-Fock, which only treat exchange correlations, overstabilises HS. Thus, depending on the system under investigation, a balanced description of the spin energetics can be achieved by adopting a global hybrid with a suitable choice of the amount of exact exchange that may depend on the system under study.

In this work, we propose an alternative method which is computationally more efficient compared to the hybrids and does not require a system-dependent parametrization. The premise of our approach is that the calculation of adiabatic energy differences is largely affected by errors in the electronic density. Thus we employ a non-self consistent density-corrected DFT scheme where the corrected density is the DFT+U density with a linear-response self-consistent U [1, 2]. The total energy is thus evaluated on the PBE+U density by employing the PBE functional, i.e. without inclusion of the Hubbard term and we name this approach PBE[U].

In my talk I will explain the rationale behind this approach and will show that our results are in excellent agreement with coupled-cluster-corrected multiconfigurational calculations, i.e. CASPT2/CC, and with experiments [2, 3].

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Alchemical Perturbation Density Functional Theory: Scaling with chemical space

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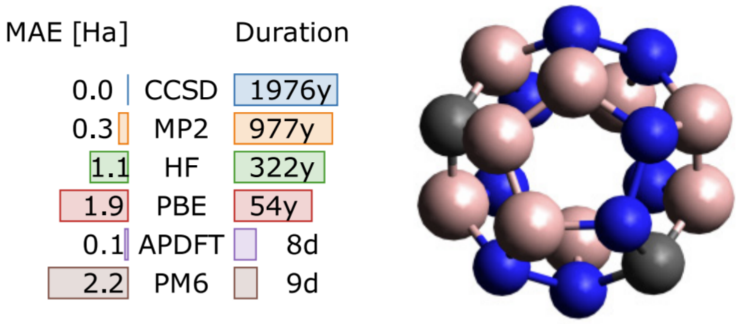
Chemical Compound Space (CCS) is so vast, that even simple enumeration is unfeasible, let alone property estimation. Therefore, molecular or materials design requires approaches which implicitly assess multiple compounds at once, effectively reducing the search space. Alchemical Perturbation Density Functional Theory (APDFT) [1] is a perturbative approach that treats a change in elemental composition as a perturbation to the system Hamiltonian and allows to estimate properties of millions of compounds at once rather than enumerating them one-by-one. The perturbations are obtained from electron density derivatives, thus benefiting from highly accurate reference methods. Applying the chain rule to the leading orders of that expansion creates a highly efficient computational scheme where few explicit derivatives cover a vast part of chemical space. APDFT is applied to covalent bonding, non-covalent interactions and deprotonation energies[1,2] and clearly outperforms approaches applying the same level of theory to all the millions of target compounds.

Rooted in quantum mechanics and perturbation theory, APDFT is a valuable tool for deriving constraints in chemical space. Based on APDFT, we show the existence of alchemical enantiomers [3] which are pairs of compounds that need to be degenerate in their electronic energy up to third order of the perturbative expansion. Most interestingly, this new and fundamental constraint on chemical space is independent of bond topology, which simplifies material design problems due to the effectively reduced dimensionality of the search space. We use alchemical enantiomers to obtain new rules for electronic energy contributions to chemical bonding and for ranking over 2000 and 400 million BN-doped naphthalene and picene derivatives, respectively. We thus demonstrate how alchemical chirality as a result of APDFT deepens our understanding of CCS and enables the establishment of trends without empiricism for any materials with fixed lattices.



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New approximation to the exchange correlation potential from connector theory, application to the density of silicon and sodium chloride

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In the Kohn-Sham formulation of density functional theory (DFT) [1], the ground-state density of interacting electrons can be obtained from a fictitious system of independent particles in an effective potential. Although DFT is in principle exact the effective potential contains an unknown quantity called the exchange-correlation (xc) potential. In this talk we propose a new approximation to the xc potential using a general approach called "Connector Theory" (COT) [2]. This approach is a prescription of how to use data from models to calculate quantities in materials. COT is in principle exact but in practice approximations are needed to make it useful. After introducing the general scheme of this approach, we explain how to use our approximate xc potential in the self-consistent Kohn-Sham loop to calculate the electronic density. Then, we compare the resulting electron densities of Si and NaCl with benchmark Quantum Monte Carlo (QMC) results [3], and we find a good agreement. Finally, by inverting the QMC densities, we derive accurate xc potentials for Si and NaCl.

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Photoemission spectroscopy from the three-body Green's function

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We present an original approach for the calculation of direct and inverse photoemission spectra from first principles.
The main goal is to go beyond the standard Green's function approaches, such as GW and T-matrix, in order to find a good description not only of the quasiparticles but also of the satellite structures, which are of particular importance in strongly correlated materials.
Our method uses as a key quantity the three body Green's function, or, more precisely, its hole-hole-electron and electron-electron-hole parts.
We will show that, contrary to the one-body Green's function, satellites are already present in the corresponding non-interacting Green's function. Therefore, simple approximations to the three-body self-energy, which is defined by the Dyson equation for the three-body Green's function and which contains many-body effects, can still yield accurate spectral functions. In particular, the self-energy can be chosen to be static which could simplify a self-consistent solution of the Dyson equation.
We also show how the one-body Green's function can be retrieved from the three-body Green's function.
We illustrate our approach by applying it to the symmetric Hubbard dimer.

Calculation of phonon dispersion and thermal conductivity in various systems using DFT

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First-principles calculations have gained increased interest in recent years for the description of vibrational properties in condensed matter thanks to enhanced computational power and improved methods. Using density functional perturbation theory (DFPT) and the response of the system to atomic displacements the phonon dispersion, or vibrational spectrum, can be calculated from the interatomic force constants. Information of the phonon band structure is important for the prediction of many thermodynamic properties, such as thermal transport coefficients. A correct description of the acoustic phonon frequencies is in particular crucial. Special care needs to be taken for the calculation of interatomic force constants in polar materials. Here, long-range dipole-dipole interactions need to be treated separately from short-range interactions. In piezo- and ferroelectric materials, even higher order long-range interactions (dipole-quadrupole, quadrupole-quadrupole, quadrupole-octupole) need to be considered in the treatment of the interatomic force constants in order to obtain an accurate description of the acoustic phonon frequencies. This concept is elucidated on the example of BaTiO3. The concept of DFPT furthermore allows for the calculation of third order interatomic force constants. Based on these anharmonic phonon-phonon interactions can be determined which give rise to the intrinsic thermal conductivity of a system. Evaluation of the thermal conductivity of real systems based on first-principles calculations usually requires however the consideration of additional scattering terms such as isotope or grain boundary scattering. Here, a systematic study of the intrinsic thermal conductivity is presented including mass disorder in bulk SiGe as a function of temperature, composition and carrier concentration.

Phonon-limited carrier mobility in semiconductors from first principles

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Carrier mobility is an essential property in many different applications. Solar cells, thermoelectrics, transparent conductors or even light-emitting devices are all areas that would benefit from a better understanding of transport quantities. Therefore, for the design of new devices, it is essential to have an efficient and low-cost method for calculating fully *ab initio* carrier (electron or hole) mobilities. Despite significant progress in the field since the late 2000s, very few bulk semiconductors have been investigated so far due to the complexity of the current methods.

Recently, various works have reported the *ab initio* calculation of phonon-limited mobility for semiconductors using different methodologies [1-4]. In this work, we present the latest developments in ABINIT regarding the calculation of the phonon-limited mobility within the semi-classical Boltzmann transport formalism and results for new and state-of-the art materials. The prospect of highly efficient and automatic calculations using this methodology in the future will also be discussed.

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Perturbation theory beyond GW introduction to the GW-GWGWG approximation.

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In Many Body Perturbation Theory (MBPT), the state-of-the art approximation for the self-energy is the GW approximation (GWA). It is widely used in condensed matter physics and it has been a standard calculation to get the band structure of materials, since it leads to very good agreement with experiments for large range of materials. Many more observables, such as density, density matrix, total energy and spectral function can also be written explicitly in terms of the one-body Green's function. However, any kind of approximation has an error and it will be limited for some cases. The GWA has two main problems: first it suffers from a self-screening error and second, GW is designed for weakly to moderately correlated systems, whereas it fails to describe system with strong correlation [1].

My work concerns theoretical developments in MBPT to go beyond GW in order to solve its problems . The target of my thesis is to improve the total energy of materials. The error of GW is due to the absence of the induced exchange-correlation energy represented by the vertex corrections that are neglected in GWA.

On the other hand, the power of GWA is due to the fact that the bare Coulomb interaction V in the exchange self-energy GV is replaced by the screened Coulomb interaction W . In this way, the GW self-energy has an additional term on the top of the Fock term, which is the screening of charges! This screening is an important part to describe many body problems because the interaction between two particles is strongly modified by the the rearrangement of the other particles. That is why GW has a great success. Starting from this result, we decided to go beyond GW (first order in W) by performing different perturbative expansions in terms of W and adding higher orders. We study problems and solutions using as model system the two site Hubbard model (Hubbard dimer) at quarter and half-filling. This model is very useful for theoretical investigation, since the exact results can be obtained analytically. In my talk, I will present results for the second order self-energy in W, comparing GW-GWGWG results to the GWA and exact results.

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Chiral valley phonons and flat phonon bands in moiré patterns of WSe_2

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A chiral object is not the same as its mirror image. The chirality of quasiparticles is a critical concept behind many modern developments of condensed matter physics. Some recent examples include Klein tunneling and chiral magnetic effect due to chiral Fermions. Here, we show that phonon modes, an example of Bosonic collective excitation, in moiré pattern created with WSe_2 can be chiral [1,2]. Furthermore, we observe the flattening of bands near the phononic band-gap edges in these systems. Our findings, which are expected to be generic for moiré materials created with two-dimensional materials that break inversion symmetry, are important in understanding the electron-phonon, exciton-phonon scattering and in designing efficient phononic crystals.

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Polar optical phonons in one-dimensional materials

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Abstract

The need for an accurate description of the vibrational properties of 1D materials is strongly motivated by the growing interest in low-dimensionality systems - semiconductor nanowires in particular - with vibrational spectroscopies probing accurately their properties. At small momenta (those probed by IR and Raman spectroscopies), longitudinal polar-optical modes are known to undergo a frequency shift which depends upon the phonon wave-vector, the effective charges and the dielectric properties of the material and the surrounding medium. This dielectric shift also crucially depends on the dimensionality of the system. Indeed, in the long-wavelength limit, the amount of electrostatic energy built up by the longitudinal polar-optical phonons is finite in 3D, but it vanishes in 2D. Here, using analytical models and density-functional perturbation theory in a newly-implemented one-dimensional framework, we show that it also vanishes in 1D, but with a different asymptotic behavior which is logarithmic in nature. We demonstrate the relevance of our work by studying a representative portfolio of materials: BN atomic chains and nanotubes, as well as GaAs nanowires. Moreover, we discuss how the long-wavelength phonon dispersion is affected by the radius, which is particularly relevant for characterization through Raman spectroscopy. The present work not only provides useful insight into the vibrational physics of nanowires but also a ready-to-use tool for the experimental community to encourage further studies.

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Simulating Vibronic Spectra without Born-Oppenheimer Surfaces

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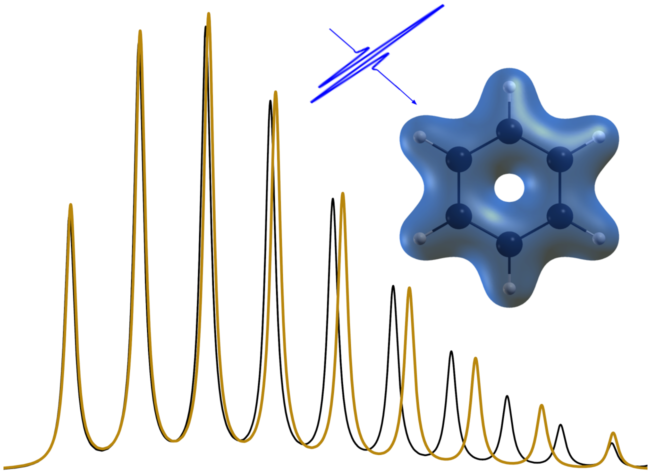

Being able to simulate coupled electron-nuclear processes for large molecular systems in a computationally tractable manner is a defining challenge of ab-initio condensed matter quantum dynamics. While the Born-Oppenheimer (BO) framework is a powerful tool, it's applicability is limited by the computational bottleneck of potential energy surface fitting and the calculation of non-adiabatic coupling terms. In this talk, we show how vibronic spectra in molecular systems can be simulated in an efficient and accurate way using first principles approaches without relying on the explicit use of multiple BO potential energy surfaces.

We demonstrate [1] and analyze the performance of mean-field Multi Trajectory Ehrenfest (MTEF) and beyond mean-field Interacting Conditional Wavefunction [2] (ICWF) dynamics techniques for the H_2 molecule in one dimension, in the both cases capturing the vibronic structure, including quantum Franck-Condon effects, with the ICWF results converging quite accurately to the exact results. In a practical application of this methodology we simulate the absorption spectrum of benzene in full dimensionality using Time-Dependent Density Functional Theory and MTEF, finding good qualitative agreement with experiment.

The extension of the ICWF method via utilization of Tensor Network algorithms to represent the multi configurational wavefunction in ab-initio molecular and condensed phase systems are also briefly discussed. These results show promise for future applications of this methodology in capturing phenomena associated with linear and nonlinearly driven correlated electron-nuclear dynamics.

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The problem of exciton-phonon interaction

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The problem of exciton-phonon interaction in crystals entails the simultaneous description of the coupling of excited electron-hole pairs both between themselves and with lattice vibrations. It has become increasingly relevant to both experimental and theoretical research. It is invoked, for example, to explain fine structures in optical absorption and luminescence spectra of low-dimensional semiconductors, to model the width of excitonic spectral peaks, and to explain the out-of-equilibrium carrier dynamics in ultrafast spectroscopy. In the first part of the talk, I will introduce both the concepts of phonons and excitons from a many-body point of view. In the former case, we will analyze the equation of motion for the quantized atomic displacements and make the connection to density functional perturbation theory in the static approximation. In the latter case, we will find the equation of motion for the electronic response function and get to the static Bethe-Salpeter equation, which is the state-of-the-art tool to compute excitons. In the second part, I will describe the exciton-phonon interaction model, which in most cases is based on the approximation that the exciton is a bosonic quasiparticle. We will discuss pros and cons of this model with some examples from both the theoretical and experimental literature. Finally, I will briefly sketch a more general treatment of the exciton-phonon interaction which may overcome the failures of the exciton-as-quasiparticle model, along with some numerical examples from first principles.

Phonon-assisted luminescence in defect centers from many body perturbation theory: the boron vacancy in 2D hBN

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Phonon-assisted luminescence is a key property of defect centers in semiconductors, as it can be measured to perform the readout of the quantum information stored in their energy states or detect temperature variations. The techniques adopted in literature to investigate the phonon-assisted luminescence are usually based on phenomenological models as the Huan Rhys model, which adopt very restrictive assumptions, thus not being predictive. In this work, we address this problem by studying exciton-phonon coupling under a rigorous many-body perturbation theory framework. We point out that this kind of analysis has never been performed for defect centers.

We study the emission of the negatively-charged boron vacancy in 2D hexagonal boron nitride, which currently stands out among defect centers in 2D materials for its promise for quantum information and quantum sensing applications. We show that phonons are the responsible for the observed luminescence, which otherwise would be dark due to symmetry reasons. We also show that the symmetry-break induced by static Jahn-Teller effect is not able to describe the presence of the peak at 1.5 eV which is observed experimentally.

Direct and indirect excitons in monolayer and bilayer Molibdenum Ditelluride

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After the discovery of graphene and its unique properties, broad families of atomically thin two-dimensional (2D) materials are continuously under scrutiny in view of their interesting physical properties and of the large number of envisaged device-oriented applications. Because of their atomic scale thickness, they are characterized by weak dielectric screening, strong light-matter interaction, and highly bound excitons.

Layered group VI Transition Metal Dichalcogenides (TMD) are particularly attractive for their interesting opto-electronic properties characterized by the presence direct and indirect excitons whose fine structure depends on spin-orbit coupling (SOC) and Van-der-Waals (vdW) interlayer interaction. Differently from the others, characterized by IR-VIS light-emission only in the monolayer (ML) form, $MoTe_2$ shows quite intense near-infrared photo-luminescence (PL) also in the bilayer (BL) form opening a discussion about its direct or indirect band-gap nature [1,2]. While studies based on Many Body Perturbation Theory (MBPT) on top of DFT calculations have been carried out for $MoTe_2$ ML and BL [3], a complete picture of direct and finite-momentum exciton fine structure is still missing.

We carry out a complete DFT + post-DFT (GW and BSE) study of the electronic and optical properties of $MoTe_2$ ML and BL. We discuss how strain and k-dependent quasi-particle corrections influence the bandgap nature [4]. We further study their q-resolved exciton bandstructure and calculate the ML radiative lifetimes. Since the indirect nature of the BL is confirmed by our calculations, we start to explore by frozen-phonon approach similar to [5,6], how phonon assisted radiative recombination can be at the origin of the PL emission in the BL case.

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First-principle study of the luminescence spectrum of Eu^{2+} - doped phosphors

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Predicting the photo-luminescence spectrum of phosphor materials from first principles is of significant technological interest. For instance, to produce white light, a blue primary LED chip can be coated with one or more phosphor materials that convert a fraction of the initial high-frequency photons into lower-frequency photons, with the resulting mixture appearing white. To fairly reproduce the low concentration of Europium, large supercells are needed, which ask for a computationally manageable theoretical methodology to simulate the Eu ($4f^65d^1$) excited state. To this aim, we use the DFT- ΔSCF scheme, whereby the eigenfunction associated to the highest occupied state of the ground state is constrained to be unoccupied in the excited state while the next higher state is filled. Transition energies are then computed as differences of two total energies and shows reasonable agreement with experiment [1]. One can also predict the shape of the emission spectrum by projecting the atomic displacements induced by the Eu: $4f^65d^1 \rightarrow 4f^7$ electronic transition onto the vibrational eigenvectors of the system. This gives access to the spectral function of electron-phonon coupling and ultimately to a detailed understanding of the vibronic luminescence spectrum [2].

In this contribution, after a description of the above-mentioned methodology, I will describe how we used it to characterize the emission spectrum of the promising $Sr[Li_2Al_2O_2N_2]:Eu^{2+}$ red phosphor [3]. It belongs to the UCr_4C_4-structure family of phosphors, whose small linewidth has drawn the attention of researchers in the last five years. This small linewidth has been tentatively ascribed to the high-symmetry cuboid environment of the doping site, with the underlying assumption that only the first coordination shell was significantly relaxing under $4f^65d^1 \rightarrow 4f^7$ transition. Our computations indicate that this vision is incomplete. Indeed, we observe an additional one-dimensional long-range collective displacement of Strontium atoms forming a channel along the tetragonal axis (see figure 1). We show that the dominant phonons that shape the emission spectrum are low-frequency modes that strongly couple with this long-range relaxation [4]. This finding sheds a new light on the emission properties of UCr_4C_4 phosphors, possessing similar Ca/Sr/Ba channel structure.

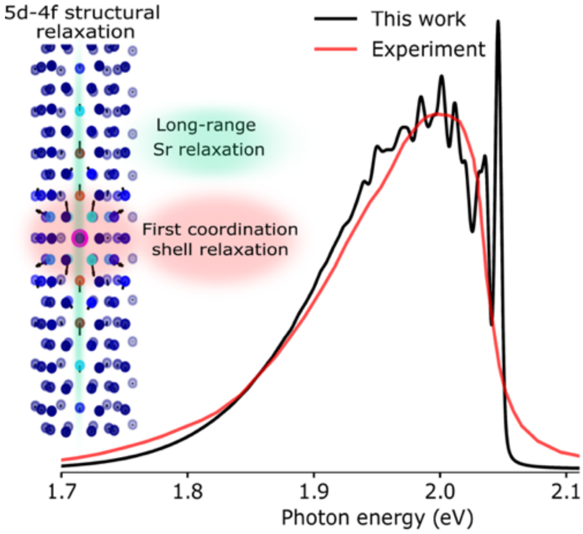

Figure 1

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Advances in strong-field and ultrafast optical spectroscopies of solids

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All-optical spectroscopy of matter is a well established technique to access properties of electrons and quasi-particles in matter. The description of these optical properties is usually done employing *ab initio* methods such as linear response time-dependent density functional theory (TDDFT) or Green functions based methods.

Recent advances in experimental techniques have opened up the possibility to develop novel types of spectroscopies based ultrashort and intense laser pulses, allowing for instance to access non-equilibrium dynamics of electronic systems or to allow for exploring non-equilibrium phase diagram of correlated materials.
The strong-field electronic dynamics in solids have received a lot of attention, in particular due to the experimental observation of high-harmonic generation in solids. The dynamics associated with strong laser fields requires a non-perturbative description of the electronic dynamics. One possible way of describing this dynamics by *ab initio* methods is to use real-time TDDFT, which will be introduced.

In this talk, I will first discuss the standard optical spectroscopies and how they are usually modeled using *ab initio* methods. Then, I will present how now novel experimental methods can be simulated and what are the remaining challenges posed by recent experimental advances.

Orbital Magnetism in Nanoparticles from Real-Time TDDFT

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Transfer of angular momentum from helicity-controlled laser fields to a nonmagnetic electronic system can lead to the creation of magnetization. Recently optically induced magnetization in plasmonic gold nanoparticles has been also quantified [1].

The underlying mechanism, the inverse Faraday effect, in metallic nanoparticles has been studied using different theoretical approaches, e.g., using quantum hydrodynamic modelling of electrons [2]. However, an understanding of the dynamics using an orbital-based quantum-mechanical method within the many-body theoretical framework is still due. To this end, the real-time formulation of time-dependent, density-functional theory is used to study induced orbital magnetism in metallic nanoparticles (clusters) excited by circularly (and elliptically) polarized light. The nanoparticles are described by a spherical jellium model on a real-space grid. The polarized laser field gives rise to an angular momentum and, hence, a magnetic moment, which is maximum at the surface plasmon frequency of the nanoparticle, revealing that this is a resonant plasmonic effect. The primary contribution to the magnetic moment comes from surface currents generated by the plasmonic field, although some bulk contributions due to the quantum-mechanical nature of the system (Friedel oscillations) still persist. We compare nanoparticles of K, Na, and Au having different size and excited at resonant and non-resonant frequencies.

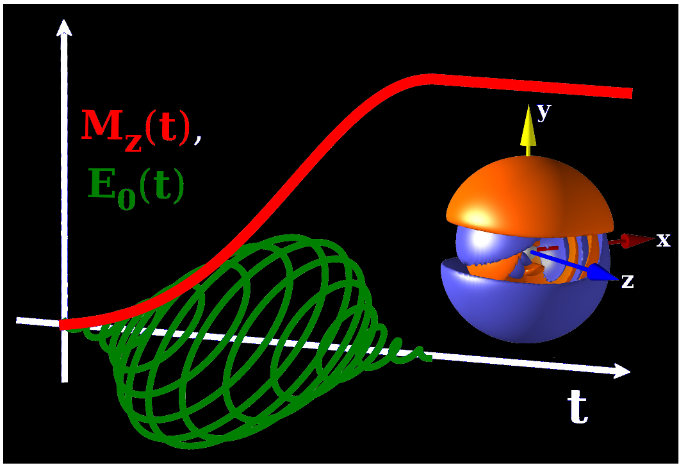

Figure 1: Time dependence of driving field (green) and induced magnetization (red). Snapshot of the corresponding induced density.

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Ab-initio investigation of electronic excitations in bulk v_2o_5

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We present an *ab-initio* investigation of electronic excitations in bulk V_2O_5. Time-dependent Density-Functional Theory (TDDFT) calculations were performed to obtain the dielectric function within linear response. When crystal local field effects are included, we find a quantitative agreement between theoretical and experimental electron energy loss spectra (EELS) for all the momentum transfers considered in the experiment [1]. We further discuss optical absorption and excitonic effects obtained by solving the Bethe-Salpeter equation (BSE). The comparison between the BSE and experimental absorption [2] is provided. We find a strong exciton binding energy ~1.2eV for a first bright exciton and two dark excitons with binding energy ~1.7eV. Exciton analysis reveals that the suppressed (enhanced) intensity for dark (bright) excitons is due to the crystal symmetries.

Funding Acknowledgement: Financial support by the Chaire Energies Durables EDF – Ecole Polytechnique is acknowledged.

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Investigating dynamical Franz—Keldysh effects and beyond in bulk Germanium via TDDFT

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Understanding and manipulation of out-of-equilibrium quantum states is a growing area of scientific and industrial research. Modern experimental techniques are able to probe dynamics of electrons at the atomic level and on attosecond timescales [1]. Considering bulk systems, Franz and Keldysh could explain key features for semiconductors with simple parabolic-like bands for moderate laser intensities [2-4]. For stronger laser fields, non-linear effects open new intriguing questions and novel opportunities. When considering non-trivial materials, it is necessary to investigate these phenomena computationally. For this goal, time-dependent density functional theory (TDDFT) may provide us an acceptable trade-off between accuracy and computational cost. In particular, TDDFT has enabled the simulation of transient reflectance maps and helped to assign their features to the relevant electronic transitions in Diamond [5] and Silicon [6]. In this talk, I will present the case of pristine and doped germanium, whose d-levels add extra dynamical features as well as extra computational challenges.

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Impact of electron correlation on the light-induced demagnetization of elemental ferromagnetic metals

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The local spin-density approximation (LSDA) is known to describe poorly the electronic structure of 3d transition metals, yet most density-functional-based ab-initio studies of ultrafast demagnetization rely on it. One way to account for Coulomb correlations among the localized d electrons and go beyond LSDA is to include the effective correlation energy (or Hubbard) U. In this talk I will show that electronic correlations lead to a significant decrease of the laser-induced demagnetization of iron, cobalt, and nickel. I will also show how the various laser parameters, such as pulse duration or intensity, change the magnetization dynamics. It turns out that the total laser fluence is not suitable to quantify how much a laser pulse demagnetizes a material, as changes in pulse duration and shape influence significantly the outcome. The findings are traced back to the electronic structure of the material, and explained based on phase space for optical transitions.

Excitonic effects in graphene-like C_3N

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Monolayer C_3N [1] is an emerging two-dimensional indirect band gap semiconductor with interesting mechanical, thermal and electronic properties. In this work we present a full description of C_3N electronic and dielectric properties, focusing on the so-called momentum-resolved exciton bandstructure (Fig.1). The study is performed using GW+BSE approach for zero and finite momentum transfer, as implemented in the Yambo code [2].

Excitation energies and oscillator strengths are computed in order to characterize bright and dark states. Activation of excitonic states is observed for finite transferred momentum. We find an indirect excitonic band gap of 0.8 eV, significantly lower than the direct optical gap of 1.96 eV. Excitonic binding energies ranging from 0.6 to 0.8 eV for the lowest excitonic states, are indicative of strongly bound excitons. Excitonic wavefunctions are discussed with respect to crystal symmetries.

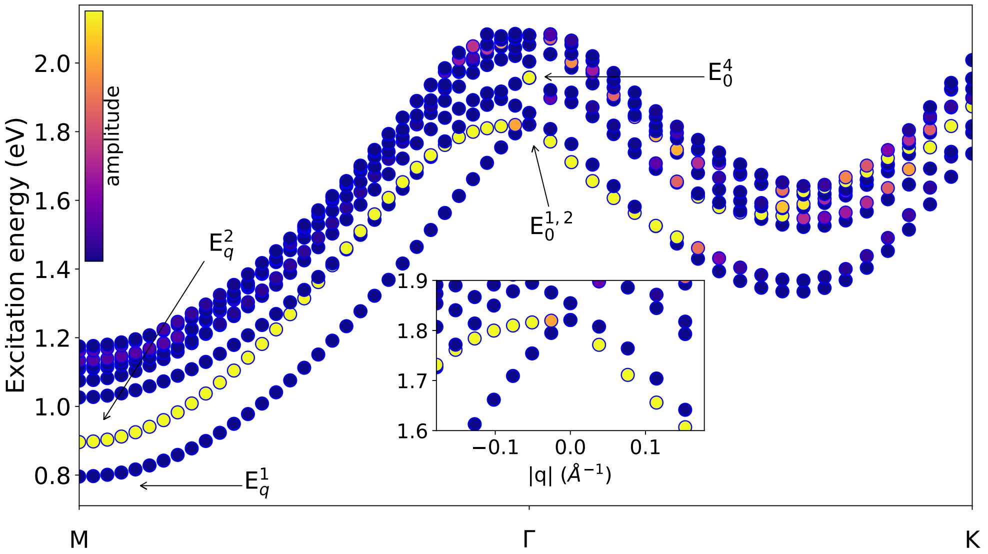

Figure 1: Momentum-resolved exciton bandstructure of C_3N for high-symmetry directions.

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Electron energy loss spectroscopy (EELS) for 2D materials

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The theoretical scattering cross section of electron energy loss spectroscopy (EELS) is essentially given by $\mathrm{Im}\,\epsilon^{-1}(\mathrm{k},\omega)$ with the energy loss $\hbar\omega$ and the momentum transfer $\hbar k$. The macroscopic dielectric function $\epsilon(k,\omega)$ can be calculated from first principles using the Random Phase Approximation (RPA).
However, experimental EELS measurements have a finite k resolution or, when operated in spatial resolution mode, yield a k-integrated loss spectrum, which deviates significantly from EEL spectra calculated for specific k momenta. On the other hand, integrating the theoretical spectra over k is complicated by the fact that the integrand varies over several orders of magnitude around $k = 0$.
Here we present a stable technique for integrating EEL spectra over an adjustable range of momentum transfers. The important region around $k = 0$, where the integrand is nearly divergent, is treated partially analytically, allowing an analytic integration of the near-divergence. When applying this scheme to slab systemes (with additional vacuum to create a monolayer), we are confronted with the added difficulty that the long-range Coulomb interaction leads to a very slow supercell (vacuum size) convergence. This difficulty is addressed by employing an extrapolation scheme, enabling an efficient reduction of the supercell size and thus a considerable speed-up in computation time. The calculated k-integrated spectra of MoS_2 (semiconductor), hexagonal BN (insulator), and graphene (semimetal) are in very favourable agreement with experimental EEL spectra.

Acknowledgement: We are grateful to Volkswagen Stiftung for the support of this work.

Optical properties of defect centers on 2D transition metal dichalcogenides

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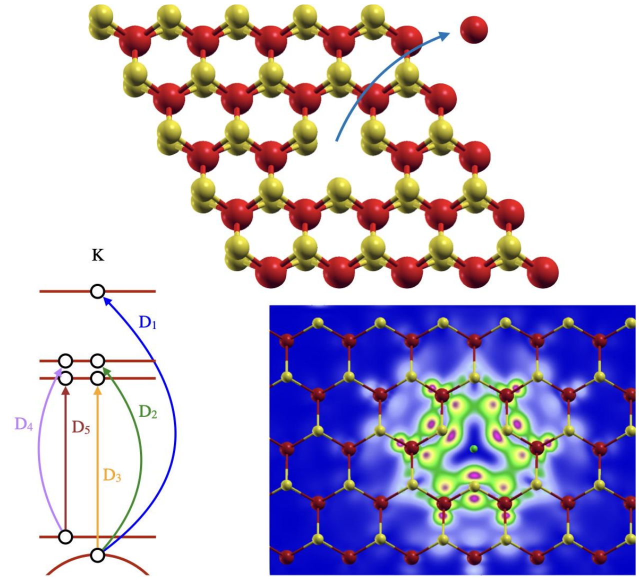
Hard to avoid even in the best quality samples of 2D materials, vacancies and impurities are often present, even at non-negligible concentrations[1,2]. Their presence will alter intrinsic properties, so it becomes crucial to understand how we can take advantage of the presence of defects to generate functionality. In this work we employ many-body perturbation theory to obtain the optical absorption spectra of defected transition metal dichalcogenides using the yambo code[3]. New optical features arise in the presence of vacancies, especially in the largely unreported metal vacancies[4]. These show a large manifold of sub-optical-gap excitons, whose wave-functions are highly localized, making them good candidates for quantum dots. For the cases where isovalent substitutional defects are present, both the spin texture and the pristine excitonic energies are preserved, despite the strong interaction with the defects. There is, however, some redistribution of spectral weight between the A and B excitons which is visible in both cases and may allow for the quantification of the defect concentration. With this work we establish how excitonic signatures characterize defects in 2D materials and highlight vacancies as qubit candidates for quantum computing.



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Real Time Observation of Correlated Electrons Response to Photo-Ionization

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Cytosine (***C***) is a heterocyclic nucleic acid base present in DNA and RNA, and hence any alteration in structure of ***C*** may ultimately affect the genetic stability. However, biological systems are interestingly designed to show photo-protective response to alteration caused by interaction with high energy radiation.[1] Due to the presence of multiple solvent-exchange protons cytosine can adopt multiple tautomeric form.[2] This rapid inter-conversion between tautomeric structures could be well understood with help of correlated photo-induced ultrafast charge distribution on cytosine after sudden ionization. In this study we will study five different tautomeric systems of cytosine using the single particle Green's function Non-dyson ADC(3) method, to understand the initial charge migration dynamics. From the time evolution of the initially created averaged hole density of each system, we identify distinctly different charge dynamics response in the tautomers. Additionally, the dynamics following the sudden ionization of chosen molecular orbitals of different symmetry reveal that speed and extent of charge delocalization strongly depends on orbital symmetry. These observations indicate why and how different tautomers may respond differently to an XUV ionization, and might explain the subsequent different fragmentation pathways. An experimental schematics allowing detection and reconstruction of such charge dynamics is also proposed. Although the present study uses a simple, prototypical bio-relevant molecule, it reveals the explicit role of molecular symmetry and tautomerism in the ionization-triggered charge migration that controls many ultrafast physical, chemical, and biological processes, making tautomeric forms a promising tool of molecular design for desired charge migration. This study could be of interest to design photo-responsive or photo-protective materials, to reveal the subsequent nuclear dynamics.

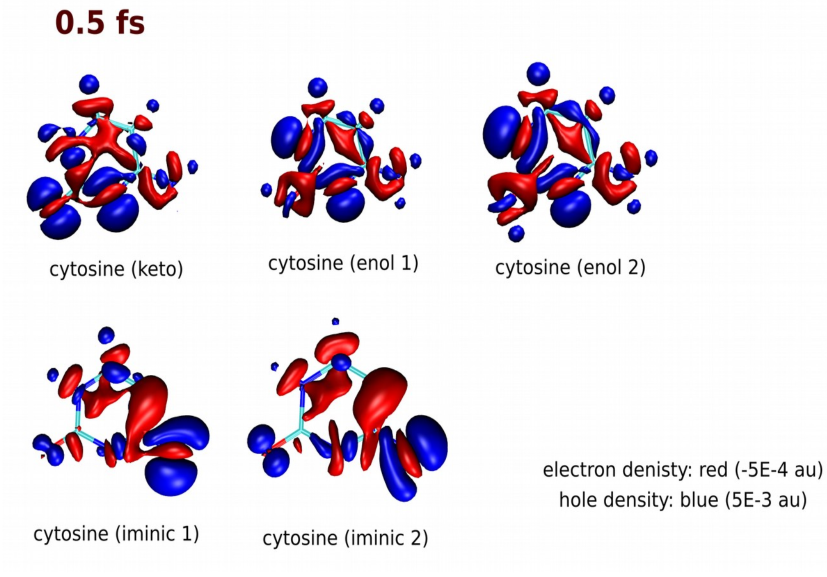

Figure 1: Comparing the charge density distribution on five different tautomeric forms of cytosine, 0.5 fs after sudden ionization of HOMO-2 molecular orbital.

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Quasi-equilibrium states in heterobilayers of transition metal dichalcogenides

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Transition metal dichalcogenides (TMDs) are a class of two dimensional van der Waals materials that received the attention of the scientific community for their interesting physical properties. The strong interaction with light and the possibility to assemble multilayer structures are essential for device applications and, in particular, to achieve efficient solar cell systems[1].

These multilayer 2D structures enhance the Coulomb interaction between charge carriers leading to strongly bound electron-hole (exciton) pairs. It has been shown that optical properties of such structures are controlled by excitons. Due to the stacking of layers of different TMDs we can access interlayer excitons, where the electron and the hole are localized in different layers. The interlayer character[2,3] of heterobilayers (HBLs) is, surprisingly, a new feature in these materials where the electron and hole create a permanent out-of-plane dipole which can be manipulated by an external electric field. These excitons have a clear optical signature, with a new peak showing at lower energies than the intralayer excitons, due to the strongly reduced screening in their dipolar interaction.

In this work we study the optical properties of two heterobilayers (WS2/MoS2 and WSe2/MoSe2) by solving the Bethe-Salpeter equation on top of a G_0W_0 calculation using the yambo code[4], which corrects the independent-particle eigenvalues obtained from density-functional theory. We continue the work that has been done on these systems by looking at several quasi-equilibrium states varying the chemical potential and the temperature to reproduce real life measures. These simulations are a first approximation to resource-demanding real-time calculations, which would be the next step to simulate the interaction between carriers and an incoming time-dependent electric field. We also further simplify the problem of diagonalising the BSE kernel matrix by employing an iterative algorithm using the SLEPC library.

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Ab-initio calculations for materials with correlated 3*d* and 4*f* shells

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Strongly correlated materials host a rich variety of exotic phases. This reaches from unconventional superconductivity in layered cuprates and nickelates, to the Kondo effect in heavy fermion systems and orbital and charge order in various transition-metal oxides. At the same time, correlated materials are challenging to tackle theoretically since standard mean-field theories and approaches based on an effective single-particle picture—such as density functional theory (DFT) in its local density approximation—are not able to comprehensively capture their correlated nature. The dynamical mean-field theory (DMFT) includes local electronic correlations in a non-perturbative fashion and has become a state-of-the-art method for strongly correlated electron systems. When combined with DFT, in the so-called DFT+DMFT approach, it allows for first-principles calculations of correlated materials such as materials with partially filled 3*d* or 4*f* shells.

In this talk, I will introduce the DFT+DMFT approach and present recent results on cerium-based hard-magnets and new inorganic pigment materials. I will show how one can tackle the Kondo effect in the Ce-4*f* shell and how the optical gaps and conductivities in novel correlated pigment materials can be determined from first principles. Eventually, I will compare the theoretical results to experiment.

Wigner localization in one, two and three dimensions: an *ab initio* approach

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In this work we investigate Wigner localization at very low densities by means of the exact diagonalization of the Hamiltonian. This yields numerically exact results. In particular, we study a system of two electrons in one, two and three dimensions. Our approach consists of three main principles: (i) the creation of a supercell that has the topology of a Clifford torus, which is a flat, finite, and borderless manifold; (ii) the renormalization of the distance between two points on the Clifford torus by defining it as the Euclidean distance in the embedding space of the Clifford torus; (iii) we use a grid of equidistant spherical gaussians as a basis for the Hamiltonian. To characterize the Wigner localization in a quasi-one-dimensional Clifford Torus we study several appropriate observables, namely the two-body reduced density matrix, the localization tensor and the particle-hole entropy. We show that the localization tensor is the most promising quantity to study Wigner localization since it accurately captures the transition from the delocalized to the localized state and it can be applied to systems of all sizes. [1] We have extended the approach to two and three dimensions by using the translational symmetry of the system to efficiently calculate the electronic wave function. We are thus able to accurately describe the wave function up to very low density. We validate our approach by comparing our results to a semiclassical model that becomes exact in the low-density limit. With our approach we are able to observe the Wigner localization by computing the two-body reduced density matrix without ambiguity.

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First-order in the Mott transition induces a quantum critical point at finite doping

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In a Hund metal - a system the metallic properties of which are highly influenced by Hund's coupling[1],[2] - the Mott transition of the half-filled system is typically first order at zero temperature[3]. We show, in a two-orbital Hubbard model within dynamical mean-field theory (DMFT), that this entails a first-order transition at finite doping between the two metals connected, respectively, to the half-filled metal and to the Mott insulator. This frontier is characterized by a zone of phase separation - already seen in previous works[4],[5] - ending in a quantum critical point (QCP) at finite doping. This traces a robust parallel between the physics of copper- and iron-based superconductors. We unveil the continuous structure of the various stable and unstable solutions mapped in this phase diagram, implying the common nature of the first-order transitions at and away from half filling. We finally analyze the Mott transition within Landau theory and show that the ultimate cause of the first order transitions is the lifting of the atomic ground state multiplet by a small energy scale, in this case Hund's coupling itself.

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Excitonic vs Mott insulator in carbon nanotubes: a proposed experimental test

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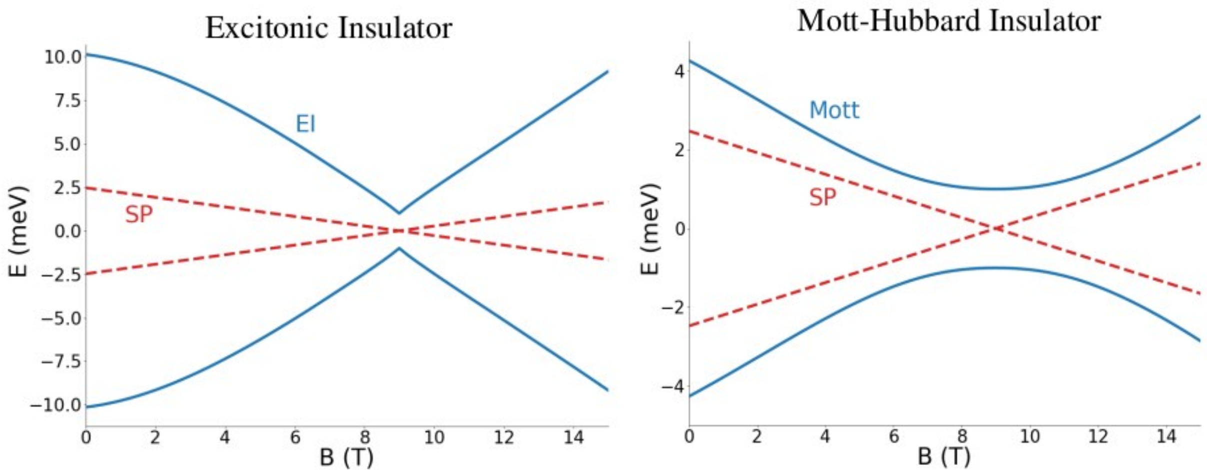
Ultraclean, undoped carbon nanotubes are always insulating, even when the gap predicted by band theory is zero. The residual, intrinsic gap is thought to have a many-body origin, associated with either a Mott[1] or an excitonic phase[2]. Whereas the two scenarios are fundamentally different, as they are driven by the short- and long-range part of Coulomb interaction, respectively, a conclusive experiment has been missing so far. Here we propose as a unique fingerprint of the excitonic insulator the presence of a cusp in the evolution of the gap with the axial magnetic field, close to the gap mimimum. On the contrary, the Mott phase exhibits a featureless, rounded profile. The non-analytic spike originates from the extreme sensitivity of electron-electron interactions to the Aharonov-Bohm gap modulation, as we demonstrate by combining a first-principles analysis of screening with extensive model calculations for tubes of different size and chirality.



Dispersion of the gap with the magnetic field in the Excitonic Insulator phase and in the Mott insulator phase of a carbon nanotube. We plot with a dashed line the single-particle energies for guidance.

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Exploring new exchange-correlation kernel in the Bethe-Salpeter equation: a study on the Hubbard dimer

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The Bethe-Salpeter equation (BSE) is the key equation in many-body perturbation theory based on Green's function to access response properties [1,2]. Within the GW approximation to the exchange-correlation (xc) kernel the BSE has been successfully applied to several finite and infinite systems. However, it also shows some failures, such as too low triplet energies, lack of double excitations, ground-state energy instabilities in the dissociation limit etc. [3].
In this talk we will show the performance of the BSE within the GW approximation and beyond, e.g. using the T matrix approximation, for the excitation energies of the exactly solvable Hubbard dimer [4]. This model allows one to study various correlation scenarios by varying the on-site Coulomb interaction *U*, and therefore it offers an ideal platform for testing approximations to correlation. We will show that the T matrix approximation gives better excitation energies than GW over a wide range of *U*. However, the strongly-correlated limit $U \rightarrow \infty$ still remains a challenge.

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Optical properties of strained hexagonal Boron Nitride

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Hexagonal Boron Nitride is a material of interest, due to its strong luminescence in the ultraviolet domain, with an indirect band gap. This luminescence originates from strongly bound indirect excitons, and is assisted with phonons. One can expect that changes in the atomic structure of this layered material will have strong effects on both the absorption and emission of light. In this work we investigated the effect of uniaxial strain on the optical properties of bulk hexagonal Boron Nitride. We used *ab initio* calculations to study strained structures and then we investigated exciton-phonon coupling by finite differences in order to obtain luminescence spectra under strain.

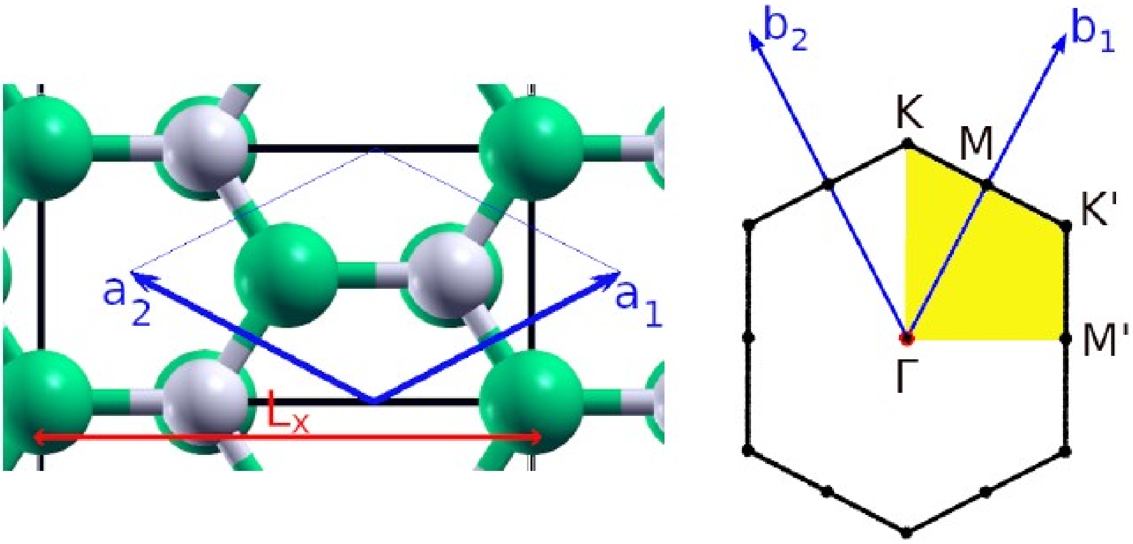

Figure 1: Structure of strained hexagonal Boron Nitride and the corresponding Brillouin zone.

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Predicting material properties with the help of machine learning

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A central goal of computational physics and chemistry is to predict material properties using first-principles methods based on the fundamental laws of quantum mechanics. However, the high computational costs of these methods typically prevent rigorous predictions of macroscopic quantities at finite temperatures, such as chemical potential, heat capacity and thermal conductivity.

In this talk, I will first discuss how to enable such predictions by combining advanced statistical mechanics with data-driven machine learning interatomic potentials. As an example, we computed the phase diagram of water from density functional theory at the hybrid level, accounting for thermal fluctuations, proton disordering and nuclear quantum effects. As another example, we simulated the high-pressure hydrogen system with converged system size and simulation length, and found, contrary to established beliefs, supercritical behaviour of liquid hydrogen above the melting line. Besides thermodynamic properties, I will talk about how to compute the heat conductivities of liquids just from equilibrium molecular dynamics trajectories.

During the second part of the talk, I will rationalize why machine learning potentials work at all, and in particular, the locality argument. I'll show that a machine learning potential trained on liquid water alone can predict the properties of diverse ice phases, because all the local environments characterising the ice phases are found in liquid water.

Doping solid-state electrolytes: a pinball model study

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Lithium-ion solid-state electrolytes hold promise of becoming the key component of next-generation batteries, by addressing the increasing demands for improved safety and higher energy density. In the last 20 years, several compounds featuring high-ionic and low-electronic conductivities have been identified, but no known material satisfies all the requirements needed for a successful deployment. In particular, high-throughput computational studies have proven successful in identifying new promising compounds by screening large materials databases, based on empirical descriptors [1], molecular dynamics simulations [2], or machine learning methods [3]. Nevertheless, chemical substitutions represent a powerful strategy to tune the properties of promising candidates. In particular, aliovalent dopants can introduce vacancies and disorder on the Li sublattice, thus enhancing the Li mobility, but at the same time they may perturb the potential-energy landscape, possibly hindering Li-ion diffusion [4].

We study these two interwoven effects by means of molecular dynamics and the Pinball model [5], a hybrid ab-initio/semi-empirical potential able to describe the diffusion of Li ions in a host lattice at the level of accuracy of DFT but at a much reduced cost. We explore the compositional space of halogenated argyrodites such as Li_6PS_5Cl [6], in order to optimize their ionic conductivity, and we shed light onto the effects of substitutional anion disorder on Li-ion transport [7].

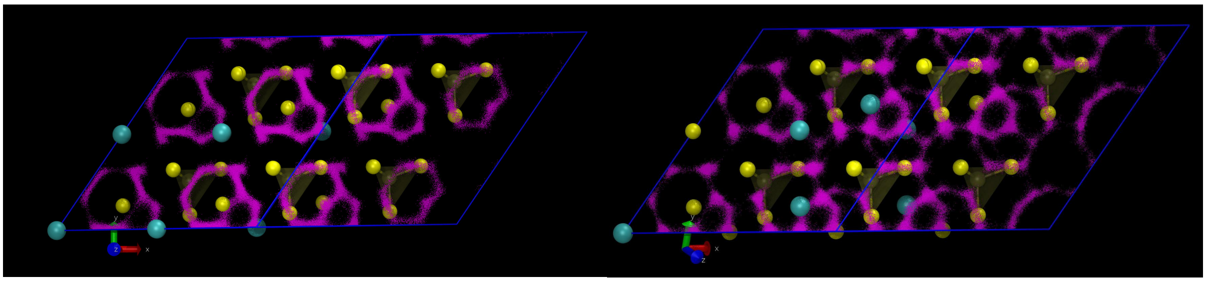

Figure 1: Effect of anion disorder on Li-ion diffusion in Li_6PS_5Cl. The sites occupied by Li during the dynamics are represented by pink dots. Left: ordered anion sublattice; right: disordered anion sublattice.

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EMBEDDED MANY-BODY PERTURBATION THEORY FOR COMPLEX MOLECULAR SYSTEMS: FUNDAMENTALS AND APPLICATIONS TO DOPED SEMICONDUCTING POLYMERS

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ABSTRACT

We present a general multiscale method based on embedded many-body perturbation theory for the calculation of the photoemission and optical spectra through the *GW* and Bethe-Salpeter formalisms, accounting for the electrostatic screening of the excitations in a QM/MM fashion. After discussing the general characteristics of the methodology, we apply it to investigate the electronic structure of a semiconducting polymer (PBTTT) doped by a strong electron acceptor molecule (F4TCNQ). Our calculations address the relationships between the structure of the doped semiconductor (viz. the location of the dopant with respect to the polymer backbone) and the energetics of the charge-transfer process governing doping. We observe a strong role of the electrostatic landscape of the host polymer in determining the advent of spontaneous charge-transfer. We demonstrate the essential role of excitonic interactions in the stabilisation the charge-transfer ground-state, a feature of critical importance for efficient doping of organic semiconductors.

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Materials property prediction for limited datasets and bias-imbalance in data-driven materials science

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In order to make accurate predictions of material properties, current machine-learning approaches generally require large amounts of data, which are often not available in practice. The proposed talk will present MODNet [1], an all-round framework, which relies on a feedforward neural network, the selection of physically meaningful features, and when applicable, joint-learning. Next to being faster in terms of training time, this approach is shown to outperform current graph-network models [2,3] on small datasets. In particular, the vibrational entropy at 305K of crystals is predicted with a mean absolute test error of 0.009 meV/K/atom (four times lower than previous studies) and is shown to outperform current leaders on 4 of the 13 tasks against the recently released MatBench v0.1 [4], a curated test suite of materials datasets. Furthermore, joint learning reduces the test error compared to single-target learning and enables the prediction of multiple properties at once, such as temperature functions. Moreover, the selection algorithm highlights the most important features and thus helps to understand the underlying physics.

The second part of the proposed talk will cover the uncertainty assessment of a model towards a target domain. Significant variations in validation errors can be observed in most models, depending on the imbalance and bias in the training set (i.e., similarity between training and application space). By using an ensemble MODNet model, confidence intervals can be built and the uncertainty on individual predictions can be quantified. Imbalance and bias issues are often overlooked, and yet are important for successful real-world applications of machine learning in materials science and condensed matter.

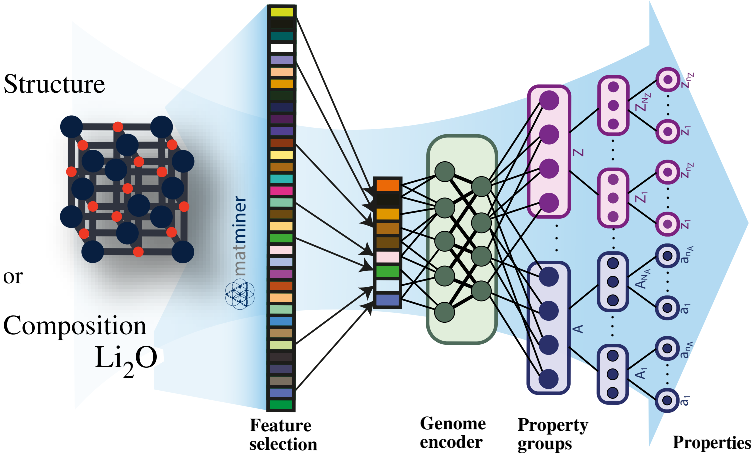

Figure 1: MODNet schematic (adapted from Ref. [1]). The feature selection on matminer (from structure or composition) is followed by a hierarchical tree-like neural network.

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Lanczos recursion on a quantum computer for the Green's function and wavefunctions

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A state-preserving quantum counting algorithm is used to obtain coefficients of a Lanczos recursion from a single ground-state wave function on the quantum computer [1]. This is used to compute the continued fraction representation of an interacting Green's function for use in condensed matter, particle physics, and other areas. The wave function does not need to be reprepared at each iteration. The quantum algorithm represents an exponential reduction in memory over known classical methods. An extension of the method to determining the eigensolutions is also possible. Similar techniques can be used to determine the density functional and will be discussed, time provided [2].

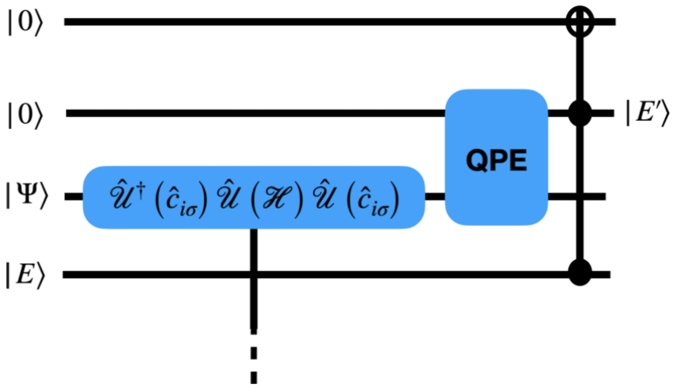

Figure 1: C ng algorithm [1].

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Efficient GW calculations in two dimensional through the interpolation of the screened potential

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The GW self-energy approximation is able to accurately predict quasiparticle (QP) properties of several classes of materials. However, the calculation of the QP band structure of 2D semiconductors is challenging due to the sharp q-dependence of the dielectric function in the long-wavelength limit ($q \rightarrow 0$). In this case, a very dense q-sampling of the Brillouin zone is usually needed to obtain properly converged quantities. In this work, we assess the possibility to drastically improve the convergence of the QP corrections of 2D semiconductors with respect to the q-sampling, by combining Monte Carlo integration techniques and interpolation schemes of the screened potential.

We test our method by computing the bandgap for three prototypical materials: a wide bandgap insulator (hBN), a transition metal dichalcogenide (MoS_2), and an anisotropic semiconductor (phosphorene). A speed-up of at least two orders of magnitude is found for all the systems considered.

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Towards the electronic density response of borophene polymorphs

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In the recent years, with the successful synthesis of four diffentent borophene polymorphs, this material has attracted attention for its promising electronic and structural properties, for example in superconductivity, catalysis and energy storage [1]. Given the polymorphism and anisotropy of this material, and its plasmonic features in the visible range, it constitutes an ideal prototype for the study of 2D plasmonics. It is therefore interesting to investigate how the structure of the material influences the propagation of the plasmons, and whether one can detect interference effects and use them to tune the material properties.

In this poster we explore the structure and electronic properties of four essentially different borophene polymorphs known as δ_3, β_{12}, α, and “stripped” borophene [2-5]: the main structural characteristics that make these cases relevant for our study, and how these differences affect the electronic structure of the material and therefore its ground state properties. Moreover, the polarizability is studied in the linear-reponse regime in the framework of the Time-Dependent Density Functional Theory within the Random Phase Approximation, showing the strong influence of the anisotropy of the sytem, and the local field effects.

From these preliminary results we set the basis for the understanding of the plasmonic behavior of these polymorphs, from a currently-developing tool made to visualize the electronic density response in real time [6]. In summary, we aim to study the relevance of the structure on the density response, and the upcoming effects towards their application as a new tool to tune the properties of the material.

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Dielectric properties of metallic nanosystems from second-principles computations

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Surface-Enhanced Vibrational Spectroscopy (SEVS) is a powerful tool to characterize molecules [1]. Due to its numerous advantages (non-destructive, ultra-high energy resolution, identification capabilities, etc.), it is widely used as sensing of systems in fields ranging from polymer sciences to biochemistry. Due to the combined need to describe a molecule and the enhancing surface (usually a metallic nanoparticle with much over thousands of atoms), the accurate simulation of SEVS is a challenge.

This is the problem addressed by the SURFASCOPE project. In the frame of this project, one of the most important issue that must be tackled is the computation of the dielectric response of a metallic nanoparticle to which a molecule is close. These are key elements of SEVS as they are responsible for the high enhancement factor of this kind of experiment. Classical models are often used to simulate the dielectric response of the metallic system but none of them are sufficient to answer all the questions about the interpretation of the experimental data [2]. Moving to first-principles computation might help to better understand the various phenomena occurring during the SEVS. However, this type of technique requires an increasing amount of time as the size of the system increases making it impractical to simulate systems of thousands of atoms (about the size of small nanoparticles). Therefore second-principles methods (i.e., methods building up on several first-principles computations [3]) might become handy, allowing one to preserve the accuracy of the first-principles computations while keeping the time required to perform the computation to its minimum.

In this poster, we will present different ways to derive dielectric properties of metallic nanoparticles from second-principles. The function of interest will be the density response function as it is a central quantity in this frame and can easily be derived from first-principles computations (e.g., via Adler-Wiser formula [4-5] in the frame of GW computations). The poster will present how, by working on a few relatively small unit cells cells (primitive or slab models), one can recover the properties of larger systems, and point out difficulties and solutions.

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ABINIT GW Benchmarks

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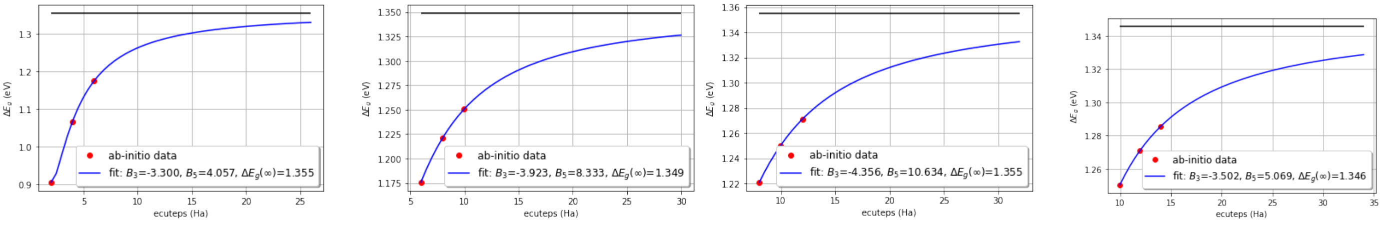
Dealing with GW calculations is always challenging, especially when the system is large and symmetries cannot be exploited. In this work, we present benchmark results for the GW part of ABINIT [1] in the high-accuracy regime, in order to understand the limitations of the standard formulation in Fourier space. Besides, the parallel speedup and efficiency of the implementation within a convergence criterion of 0.02 eV in the GW band gap have been investigated. This criterion is more stringent, in comparison to the target of a previous large-scale study (70 materials) with ABINIT that was only 0.05 eV [2]. Moreover, the latter study used a plasmon-pole model, while the present analysis also focus on contour-deformation and analytic continuation methodologies which are computationally more expensive.

We focus on two oxydes labelled A_1 (with 3 atoms) and C_1 (with 11 atoms).The former contains one Zirconium and two Oxygen atoms (ZrO_2) while in the latter the ZrO_2 crystal is doped by 50% of Yttrium ($2ZrO_2 + Y_2O_3$). The geometry of both systems are optimized at the Kohn-Sham level using PBESol pseudopotentials [3]. For GW calculations, a double convergence study must be performed over the number of bands (nband) and the energy cut-off for the dielectric matrix (ecuteps). Reaching convergence within our criterion (0.02 eV) for C_1 structure benefits from techniques introduced in [5] and [6]. In the latter, the gap is extrapolated as a function of ecuteps (noted E_c^χ), as $\Delta E(E_c^\chi) = \Delta E_g(\infty) + B_3 \times E_c^{\chi(-3/2)} + B_5 \times E_c^{\chi(-5/2)}$. With these techniques the convergence criteria are met, as it is shown in Fig. 1.



(a) **(b)** **(c)** **(d)**

Figure 1: QP-KS energy as a function of energy cut-off for the dielectric matrix for different range of ecuteps.

Using contour deformation technique and the optimized parameters, the GW band gap is 5.353 eV and 4.272 eV for A1 and C1 systems respectively. The time scaling analysis confirms that the most time consuming part of the calculation is the calculations of the screening matrix.

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Molecular modeling of TADF blue light emitters with a dibenzofuran spacer

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Over the last few decades, technological advances have pushed forward the search of new and more efficient light sources. One of them are organic light-emitting diodes (OLEDs), which have been developed rapidly for the past 30 years [1]. Some of the modern OLEDs rely on fluorescent or phosphorescent emitters. Nowadays, there is great interest towards devices that operate on the principle of thermally activated delayed fluorescence (TADF) [2]. This process employs transition from triplet to singlet excited state, which increases the efficiency of the diode. One of the most serious challenges industry faces is the development of such blue light emitters [3]. It can be aided by molecular modeling.

The present study summarises the results of (TD)DFT calculations aimed at designing potential compounds that are suitable for blue light emission enhanced by TADF. Molecules containing a dibenzofuran π-conjugated bridge fragment substituted with various electron donors and electron acceptors are considered. Their geometries in the ground and several excited states are optimized with B3LYP/6-31G*. Absorption and emission transitions are obtained with the TDDFT approach. Based on the results, the possibility of TADF in different molecules and their capacity to emit blue light are evaluated. The most promising candidate is a structure in which the diphenylamine donor and the cyano acceptor fragments are o,p-substituted at the bridge. It is proposed for synthesis and experimental characterization.

Acknowledgements:
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Ab initio study of graphene/hBN Van der Waals heterostructure: from bilayer phase to coincidence lattices

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One of the most important and attractive property of 2D materials is the possibility to design brand-new structures, without a bulk counterpart, with innovative features. These systems, known as Van der Waals heterostructures (VdW-hs), are characterized by strong covalent bonds between atoms in the same plane and weak Van der Waals interaction among the layers. The key point in the design of new VdW-hs lies in the possibility of finely tuning the optoelectronic properties of the system by changing structural parameters like stacking sequences, number of layers and different rotation angles. This aspect is one of the most widely used approaches in the study of novel graphene-based nanodevices. The aim of this work is to study, via DFT calculations, performed with the *Quantum ESPRESSO suite*, VdW-hs based on graphene and hexagonal boron nitride (hBN), two systems with a very similar crystal structure (they have almost the same lattice parameter), but with totally different electronic properties, in order to modify the optoelectronic properties of graphene. Starting from the monolayers, several VdW-hs have been designed changing both the number of layers and their relative rotation angle in the structure. In particular, the attention has been focused on the bilayer phase (CBN-AB), the quadrilayer (CBNBNC), and the coincidence lattice achieved by rotating graphene on hBN by 21.8°. For all these systems stability analysis, structural relaxation, band structure calculation and optical properties study have been performed. The goal was to explore the changes induced by both the structural design itself and by the external environment, investigating the response to an external electric field.The calculations show a small but significant modification [1] of the optoelectronic properties of graphene and hBN when they are paired in a VdW-hs, that results in particular in the opening of a tunable [2] band gap at the Dirac cone of graphene, even if the optoelectronic *fingerprint* of the starting monolayers is still preserved. This makes graphene/hBN hs exploitable for nanoelectronic applications like THz devices.

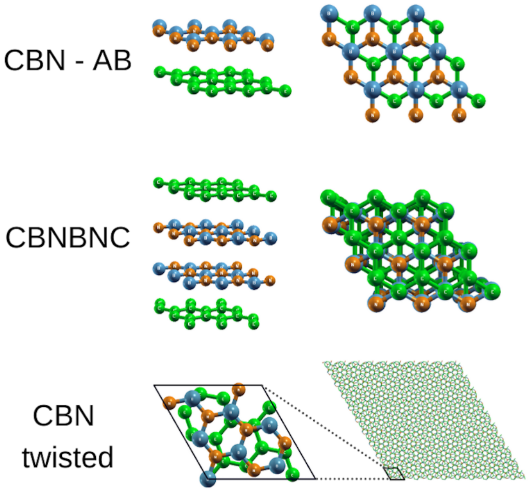

Figure 1: Bilayer, quadrilayer and twisted bilayer for a graphene/hBN VdW-hs

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From bulk tellurium to 2D tellurene: an *ab-initio* study

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Tellurene (Te) is an emerging 2D anisotropic semiconductor, with fascinating electric and optical properties that differ dramatically from its bulk counterpart, which has come to us owing to its unique chained structures. Te is the 2D form of tellurium and it was proposed by theoretical calculations and then verified by experiments in 2017 [1].

The main intent of this work was to provide a better understanding of the evolution of the physical properties of Te with increasing number of layers. Indeed, the lack of systematic and clear studies in this sense has made this research an opportunity to try putting the pieces together.

By means of *ab-initio* calculations, using Density Functional Theory, structural relaxations, electronic band structures and optical properties calculations have been carried out for different allotropic forms (α-, β- and γ-phase) of Te using the *Quantum* ESPRESSO integrated suite [2]. Comparing the few available information [1, 3] with the results obtained, an overall qualitative and (often) quantitative agreement was found with all the studied systems. Our calculations confirm that γ-Te is the most stable phase in the monolayer configuration; on the other hand, α-phase is more stable if the number of layers (L) is greater than 1; moreover, for the case of α-phase, lower values of the gaps were discovered thanks to a more accurate sampling of the Brillouin Zone. Finally, using an analytical model for 2D materials, we have evaluated the excitonic binding energies and radii [4, 5, 6, 7] for the different phases, and their evolution with the number of layers (ranging from 1 to 4). The results show interesting implications regarding the properties of electron-hole interaction in this material.

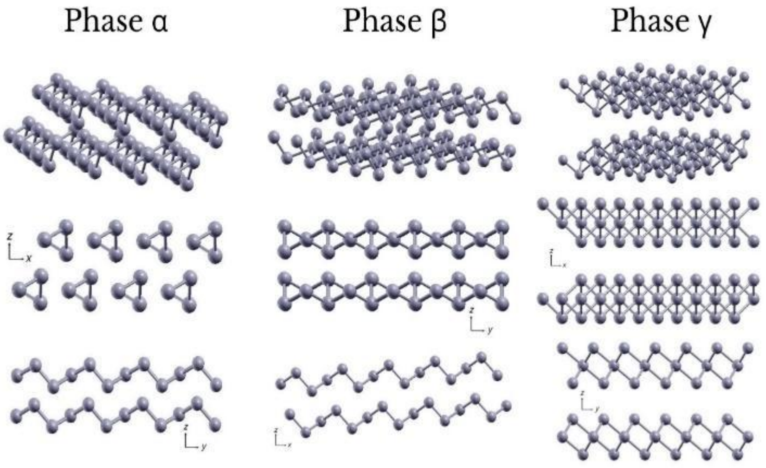

Figure 1: Different studied phases of few-layer Te (bilayer).

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Machine Learning on Topological Electronic Materials

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Topological electronic materials is concerned due to their importance in basic physics and their potential application value. Recent years, through high-throughput calculations that combine density functional theory [1, 2] (DFT) theory and topological quantum chemistry theory [3] (TQC), a huge number of materials have been proved to be topological non-trivial [4-6]. However, this approach is time consuming and limited to the non-magnetic system with well-defined symmetry. Machine learning method provide a way that overcome the above shortcomings, base on the dataset from the Materiae [5], we compare the results of several machine learning models[7-11] and discovery some important features that affect there topological properties.

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Nonlinear optical properties calculation with OCTOPUS

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OCTOPUS is a real-time, real space simulation code based on the time-dependent density functional theory, it can successfully calculate some optical properties in the regime of linear response theory. Now we are exploring the nonlinear properties calculation under strong field laser with OCTOPUS.

The idea starts from the Kerr effect, in the refractive index – intensity curve which shown in Fig.1, the slope represent the Kerr coefficient n2, from n2 we can calculate the other nonlinear parameters such like third order susceptibility and two-photon absorption coefficient and so on. So the key problem is how we calculate the refractive index for different pump intensity? Fortunately, we just need some modification from OCTOPUS defaulting method, then we can calculate the dielectric function freely, and also refractive index.

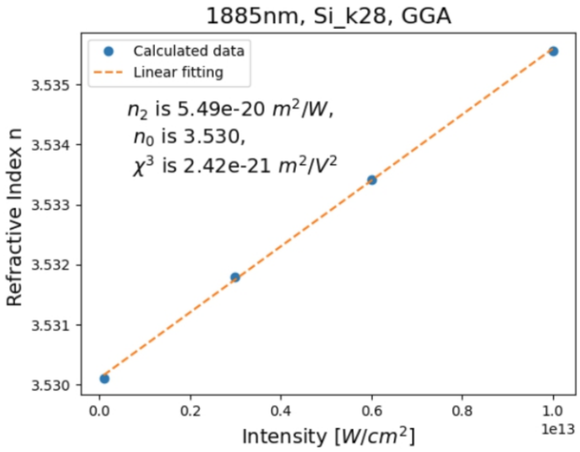

Fig1: Refractive index - Intensity curve for Silicon. With 1885nm pump laser.

Our calculated Kerr coefficient have the same order of magnitude with experimental data for diamond, but for Silicon and ZnO, the calculated data is smaller 10~100 times than reference, which is waiting to be modified and improved.

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Polaron effective mass and localization length in cubic materials: degenerate and anisotropic electronic bands

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We present our recent progress in treating the polaron effective mass and localization length for the case of cubic materials. Most works on polaron models, to understand their characteristics such as radius, effective mass, mobility and energy dispersion, have focused on the original Fröhlich model for large polarons, with a simple (non-degenerate) parabolic isotropic electronic band coupled to one dispersionless longitudinal optical phonon mode [1]. Real cubic materials have electronic band extrema that are often degenerate (e.g. 3-fold degeneracy of the valence band), or anisotropic (e.g. conduction bands at X or L)[2]. A couple of attempts have been made towards a generalization of the Fröhlich polaron model[3-5], yet these left aside the important consequences of band warping and/or ignored the effect of multiple phonon modes or electronic degenerate bands. In this work, we keep the continuum hypothesis inherent to large polaron models, but go beyond the existing isotropic and non-degeneracy hypotheses, and also include multiple phonon modes. For polaron effective masses, working at the lowest order of perturbation theory, we provide (i) the analytical result for the case of anisotropic electronic energy dispersion, with two distinctive effective masses (uniaxial), (ii) an approximate expression for the case of three distinctive axes (ellipsoidal), (iii) numerical simulations for the 3-band degenerate case, typical of III-V and II-VI semiconductor valence bands. We also deal with the strong-coupling limit, using a variational treatment: we propose trial wavefunctions for the three above-mentioned cases as well, providing polaron radii and energies. We gauge such approaches for the case of a dozen of II-VI, III-V and oxide semiconductors treating both electrons and hole polarons.

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Optical properties of armchair Graphene nanoribbons under strain

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In this paper, using the Tight-Binding approximation (TB), the influence of uni axial strain is studied on the band structure and optical properties of Geographer nanobots with armchair edges (Agnes). Furthermore, with the dielectric function of the system, we obtain the imaginary part of the dielectric function, absorption and reluctance coefficients of the nanobots. Our results indicate that the presence of the uniaxial strain induces the increase of the energy band gap in the band structure of the Graphene nanobots. We found, under the uniaxial strain, the optical absorption of AGNRs increases.

Graphene is a material in which carbon atoms are covalently bonded together in a hexagonal lattice composed of Benzene rings. Graphene was synthesized for the first time by Novoselov in 2004 [1]. In this magical substance, electrons behave like Dirac massless fermions, which increase the mobility of electrons and lead to interesting electrical, magnetic, and transport properties. These properties make Graphene one of the suitable candidates for using in nano-electronics components. Wallace obtained the Graphene band structure and predicted its electronic structure using a narrow-band approximation [2].According to Wallace's observations, a Graphene sheet has metallic like behaviour with zero energy band gap. This is a limitation for the use of Graphene in the electronics industries. Restricting Graphene sheets to ribbons with limited widths is introduced as an effective solution to this problem. Accordingly, with synthesis and modelling the AGNRs, which exhibit interesting electronic and optical properties due to the non zero energy band gap in the structure, new physical perspectives opens for Graphene applications. For this purpose, the application of strain may alter the energy bad gap of the Graphene nanoribbons so that by controlling the band gap, electronic and optical properties of the structure can be improved such that the converting Graphene into a functional material in the electronics industry [3].

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X-ray Absorption Spectrum: Boron K edge of Monolayer and Bulk Hexagonal Boron Nitride

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Abstract

Hexagonal boron Nitride (hBN) is a two dimensional (2D) material with a wide-band-gap and polar covalent B-N bond. Both monolayer and bulk hBN emerge as an optoelectronic material with various applications in photodetectors, and additionally for photocatalysis. We present calculations for the K-edge absorption spectra of monolayer and bulk hexagonal boron nitride (hBN). X-ray absorption near edge spectra of hBN are calculated as a function of field polarization and satisfactory agreement with the recent experimental data is obtained. Similarly, transient absorption spectroscopy (TAS) for monolayer and bulk hBN using a pump and probe numerical simulations. The dynamics was modelled with time dependent density functional theory $TDDFT$by solving the Time Dependent Kohn-Shams (TDKS) equations as implemented in the octopus code.

Keywords:- Transient absorption spectroscopy (TAS) Xray absorption spectroscopy (XAS), time-dependent density functional theory (TDDFT), hexagonal boron nitride (hBN).

THz-induced high-order harmonic generation in graphene

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High-order harmonic generation (HHG) is one of the most important nonlinear optical effects, opening a novel possibility for new light sources. An extremely efficient generation of terahertz high harmonics in graphene has been observed [1], which was interpreted with the thermodynamic response of Dirac electrons to the driving terahertz fields [2]. To develop the microscopic understanding of the THz-induced HHG in graphene from the viewpoint of nonequilibrium dynamics, we employ a quantum master equation approach with relaxation time approximation [3]. The electronic structure of graphene is modeled by a simple tight-binding model. We evaluate the time-dependent electric current from the time-dependent density matrix. Furthermore, the HHG spectra are evaluated from the current with the Fourier transform. By comparing the quasi-static picture and thermodynamic picture, we explore the role of the nonequilibrium electron dynamics in the HHG.

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A high-throughput study of the defect tolerance of halide perovskites solar absorbers

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Charge transport and recombination probabilities in semiconductors are determined to a large extent by the presence of defects. Defects can act as scattering or trapping centres of electrons or holes, changing the device's optoelectronic properties. In photovoltaics, it is essential to minimize the amount of these scattering/trapping centres, or, at least, their impact, to achieve long diffusion lengths of carriers. This leads to the question of how to achieve materials that are good solar absorbers and, at the same time, show low defect densities or a certain insensitivity to their presence. The ability of semiconductors to retain their optoelectronic properties in the presence of defects [1] or to eliminate defects by a self-reorganization mechanism [2,3] is collectively known as defect tolerance.

We present a high-throughput search for defect tolerant [4,5] metal-halide perovskites for photovoltaic applications based on their deformation potential. The deformation potential gives a measure of the changes of the bandgap of material upon compression of the bonds, helping identify the valence and conduction bands have a bonding or anti-bonding nature. This bonding nature is an indicator of a material's tendency to shallow or deep intrinsic defect levels. Our high-throughput search is based on all-electron density functional theory. We find that among the 700 studied halide perovskites, only 30% present a favourable anti-bonding valence band and therefore defect tolerance. In addition, we also explore emerging trends from the calculated values.

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Electron-Phonon Beyong Fröhlich: Dynamical Quadrupoles in Polar and Covalent Solids

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First-principles computations of electron-phonon related properties in polar and covalent solids have gained popularity in the last five years. In polar semiconductors, the long-range electrostatic interactions lead to the dipolar Fröhlich divergence of the electron-phonon matrix elements. This contribution was recently generalized to anisotropic materials, opening up a first avenue for computations of electron-phonon effects in polar materials [1].

In this work, we include the treatment of quadrupolar fields beyond the Fröhlich interaction in the first-principles electron-phonon vertex in semiconductors. Such quadrupolar fields, as illustrated in Fig. 1 in the case of Si, induce additional long-range interactions that have to be taken into account for accurate physical results. We apply our formalism to Si (nonpolar), GaAs, and GaP (polar) and demonstrate that electron mobilities show large errors if dynamical quadrupoles are not properly treated.

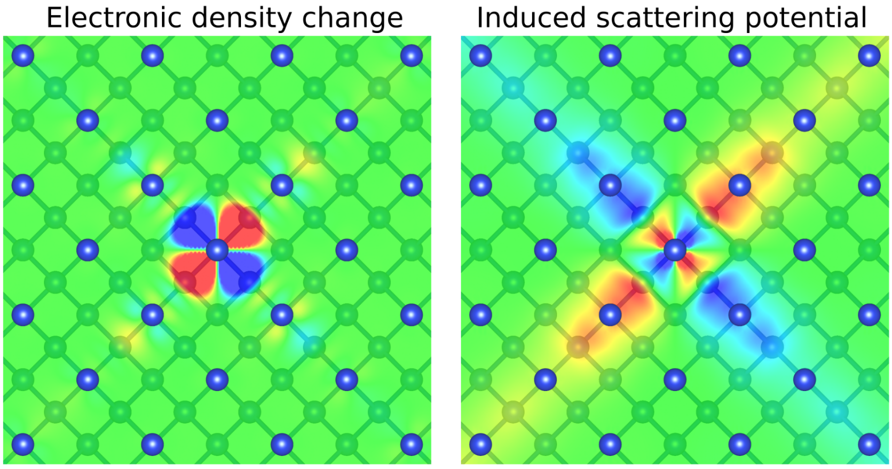

Figure 1: (Left) In-plance change of the electronic density in Si due to the displacement of the central atom in and out of the place. (Right) Scattering potential induced by this atomic displacement.

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Implementation of the Bethe-Salpeter Equation in the SPEX Code

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The Bethe-Salpeter Equation (BSE) and GW approximation are two many-body perturbation theory techniques that together form the state-of-the-art method to include electron-hole interaction in periodic systems [1]. The BSE has proven to be the most accurate tool to compute optical absorption for the valence and core energy region, as well as electron energy loss. In recent developments the BSE has been applied to compute the exciton band dispersion and exciton effective masses, inelastic electron scattering, and many more.

We have implemented the BSE in the SPEX code, a full-potential linearized augmented planewave (FLAPW) code that supports a range of Green function based methods including the GW approximation, optical spectra in the random phase approximation, and more [2, 3]. The BSE is run on top of a one-shot G_0W_0 calculation with SPEX, or directly on top of the underlying density functional theory (DFT) calculations from FLEUR [4, 5].

Our code has been tested for various bulk, layered and monolayer semiconductors, among them LiF and MoS_2, and includes spin-orbit coupling. The results agree with the literature. We also use the crystal symmetries to achieve a significant computational speedup, and maintain good scalability of the code for parallel computing.

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