

## ETSF - 19<sup>th</sup> Young Researchers' Meeting June 11 – 16<sup>th</sup>, 2023



## **ABSTRACT BOOKLET**

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	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
	Session 1: Electronic structure methods	Session 2: Optical properties of materials	Session 3: Vibrational properties of materials	Session 4: Strongly correlated systems	Session 5: Quantum computing*
9:30-10:00	Registration + Welcome talk				
10:00 - 11:00	M. Mayorga Is there any recipe for using RPA?	Y. Liu (online) Calculations of absorption tail in mixed halide perovskite	M. Kotiuga Insights from vibrational properties in determining structural prototypes of ferroelectrics	M. Chatzieleftheriou Metal-insulator transitions in the Hubbard model: local vs non-local correlation effects	X. Bonet-Monroig Quantum computing: why should I (and you) care?
11:00- 11:30	A. El Sahili Beyond GW:non-unique method and diversity of choices	H. Fried Calculation of optical signatures of deffects: comparing different methods	A. Castellano Mode-coupling theory anharmonic lattice dynamics	B. Chatterjee Ground state symmetries collective modes in TA2NISe5 - an excitonic insulator candidate	C. Emeis Electron-plasmon satellites in the spectral function of highly-doped HfS2
11:30 - 12:00	COFFEE BREAK	COFFEE BREAK	COFFEE BREAK	COFFEE BREAK	COFFEE BREAK
12:00 - 12:30	M. Gunes Charge density as a functional of the potential: Connector theory approach	L. Biancorosso Plasmon-assisted electron dynamics in photocatalysis: hydrogen production from formic acid	J. Batista Machine learning assisted calculation of phonon properties in layered hBN	A. Carrasco Alvarez Charge ordering as the driving mechanism for superconductivity in rareearth nickel oxides	D. Corona Encapsulated BN nanocages and nanocapsules as anode materials for magnesium-ion batteries: A DFT study
12:30 - 13:00	M. Sadegh Shakeri Many-body GW calculation od X-ray absorption spectra of Cu0, Cu+, Cu2+ and Cu3+ structures	M. Marino Ab initio study of Fe-phthalocyanine adsorption on the antiferromangetic NiO(001) surface	M. Lezoualc'h Charge density waves in 1T-VeS2	A. Osorio Understanding borophene: From the atomic structure to the electronic response	
13:00 - 13:30	I. Mukatayev Investigation of atomic core levels with ab initio many body theories	S. Grillo Non-trivial excitonic fingerprints and optical anisotropy of 2D Tellerium	A. Custodio Nitrogen-vacancy center: understanding the electronic structure from ab-initio calculations	C. Morassut Analysis and comparison of optimal-continuum Gaussian basis sets for high harmonic generation spectra for atoms and molecules	END OF CONFERENCE

13:30 - 15:30	LUNCH BREAK	LUNCH BREAK	LUNCH BREAK	LUNCH BREAK
15:30 - 16:30	A. Ammar Transcorrelated Selected Configuration Interaction	S. Canola Molecular systems probed by near-field spectroscopy	C. Verdi Phonon anharmonicity in quantum paraelectrics beyond density-functional theory	C. Yue BStrong correlation and and unconventional superconductivity in bulk and trilayer alkali-doped fullerides
16:30 - 17:00	Coffee break	Coffee break	Coffee break	Coffee break
17:00 - 17:30	L. Urquiza Pseudopotential Bethe-Salpeter calculations for	Vun Binh Theoretical studies of novel graphene based nanostructures	Y. Pan Non-equilibrium dynamics of chiral valley phonons from the	What is the ETSF? Alberto Castro
	spectra		nanostructures	Boltzmann equation
17:30 - 18:00	Y. Schmerwitz Calculations of excited electronic states by converging on saddle points using generalized mode following	Social event and Social dinner		Industry session:
18:00 - 18:30	E. Selenius Improving density functional calculations of intramolecular charge transfer excited states		Poster session	Calcavecchia
18:00 - 19:30				
20:00				

### Is there any recipe for using RPA?

#### M. Rodríguez-Mayorga, P. Besalú-Sala, J. C. Sancho-Garcuía, A. J. Pérez-Jiménez

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The random phase approximation (RPA) used in the adiabatic connection fluctuation theorem is known to be a reliable and cost-effective method to render electronic correlation effects when combined with the density-fitting techniques and the integration over imaginary frequencies.<sup>1-3</sup> The RPA energy functional is usually evaluated using orbitals  $\{\Phi\}$  and orbital energies  $\{\epsilon\}$  obtained from a Kohn-Sham (KS) Density Functional Theory (DFT) calculation (normally) performed with the PBE functional.<sup>4</sup> The performance of the RPA energy functional to predict weakinteractions,<sup>5</sup> lattice parameters,<sup>6</sup> is well documented in the literature. Nevertheless, when DFT calculations are performed with hybrid functionals, which are known to mix some DFT exchange with the exact exchange, the  $\{\Phi\}$  and  $\{\epsilon\}$  change w.r.t. the ones obtained with the PBE functional. Hence, in this talk I will discuss the effect of the amount of exact exchange employed at the KS DFT level (to obtain the  $\{\Phi\}$  and  $\{\epsilon\}$ ) on the final value of the RPA energy for some molecular systems<sup>7</sup> and extended Our results indicate that large amounts of exact should be systems.<sup>8</sup> preferred to compare well w.r.t. reference values. Finally, we introduce the **RPA@PBEh(0.85)** approximation that uses 85% of exact exchange at the KS DFT level and is shown to be an excellent approach for the computation of non-linear optical properties.<sup>9</sup>



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9 P. Besalú-Sala, F. Bruneval, J. A. Pérez-Jiménez, J.C. Sancho-García, and M. Rodríguez-Mayorga RPA, an accurate and fast method for the computation of non-linear optical properties *arxiv* arxiv:2306.04418

## Beyond GW: non-unique method and diversity of choices

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The search for good approximations to the electron self-energy is still of high interest. The standard and most widely used approximation is Hedin's GW expression, which has become the state-of-the-art for the band structure calculations of solids. However, the validity of the GW approximation is limited to a range of materials where correlations are weak to moderate, and to describe more correlated materials remains a challenge. Going beyond GW is not straightforward, and there is no unique and wellestablished method. Moreover, even once an expression has been chosen, there are many possible choices of ingredients that make the situation ambiguous. For instance, if one stays at the GW level or if one adds second order diagrams in terms of the screened Coulomb interaction W to go beyond GW, it still remains to be defined which W is to be used. This question is still waiting for an answer, and there is no consensus in the Many-Body Perturbation Theory (MBPT) community. Recently, the combination of Time Dependent Density Functional Theory (TDDFT) and MBPT has become a popular way to add approximate vertex corrections beyond GW, using the exchangecorrelation kernel (fxc) from TDDFT. My talk will address some of the open questions, and in particular, those linked to the use of fxc. I will discuss both the use of exact TDDFT ingredients and of approximations to them. Our goal is to improve total energy calculations for a large range of materials using the one-body Green's function. For illustrations, we use the symmetric Hubbard dimer model at half-filling (two-electrons).

Keywords: Green's function, GW and beyond, vertex corrections, total energy.

### References

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## Charge density as a functional of the potential: Connector Theory approach

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The first widely successful formulation of the exchange-correlation effects within Density Functional Theory in real materials was based on the Local Density Approximation (LDA) which uses the results of the homogeneous electron gas model to describe the real material at hand. Motivated by this idea, we present results of a general and in principle exact theory called the connector theory (COT) which formulates a systematic way to simulate a real system for a given model by making use of the "connector" which is a mathematical object bridging the model and real system. We show that by using a connector we are able to create accurate functionals for describing certain observables, without diagonalizing the Hamiltonian. Further, we recall that the connector theory provides a spectrum between locality and non-locality in which the connector acts as a tuning parameter, and LDA is just one special case of this theory (Vanzini et al., 2022). We focus our study on calculating the charge density as a functional of a given mean-field potential within the framework of COT. Our results successfully capture the correct behavior of the charge density in cubic He with almost no computational cost. We further compare local and bilocal connector results, and propose new systematic ways to implement these ideas in other materials.

# Many-body GW approximation approach toward the calculation of X-ray absorption spectra of Cu<sup>0</sup>, Cu<sup>+</sup>, Cu<sup>2+</sup>, and Cu<sup>3+</sup> structures

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Pulsed laser irradiation of suspended nanoparticles, introduced as a promising technique for the fabrication of heterostructures [1], has been used for the synthesis of heterostructures of copper and its oxides. Although thermodynamic approaches predict the formation of Cu-CuO-Cu<sub>2</sub>O heterostructures by nano-pulsed laser irradiation of Cu-ethanol suspensions, the kinetic aspect of the process regarding the alternative, fast, high-temperature nature of the process suspects the formation of the Cu<sup>3+</sup> oxidation state mainly on the surface of the particles [2]. Here, we have attempted to use many-body GW approximations to accurately calculate the X-ray absorption spectra (XAS) of various oxidation states of copper for linear combination fitting of extended X-ray absorption fine structure (EXAFS) spectra and Gaussian fitting of X-ray absorption near edge structure (XANES) spectra of consistent species. Quantum Espresso and jfeff software were used to relax the 2\*2\*2 supercells of Cu, CuO, Cu<sub>2</sub>O, Cu<sub>2</sub>O<sub>3</sub>, CuCO<sub>3</sub>, and Cu(OH)<sub>2</sub> as probable phases that could have crystallized in the system (Figure 1). The results show that although the characteristic peaks in the XAS spectra of the different oxidation states of copper are detected in a small range of X-ray energy, there are still differences between the spectra that can be used in both linear combination and Gaussian fitting to predict the more accurate composition of the final heterostructure. Based on the results of this study, we confirmed the presence of catalytically enriched  $Cu^{3+}$  on the surface of Cu-CuO-Cu<sub>2</sub>O heterostructure particles, with remarkable electrocatalyst behavior for ethanol oxidation fuel cells. This work is supported by the Polish National Science Center under programs No. 2018/31/B/ST8/03043 and 2022/06/X/ST3/01743. The calculations were also performed in the Prometheus Cluster, Cyfronet, under grant number PLG/2022/015573. We thank the Polish National Synchrotron Center (SOLARIS) for its efforts in the XAS experiments and for providing the jfeff license.

<u>Keywords</u>: DFT calculation; many-body GW approximation; X-ray absorption spectroscopy; Pulsed laser irradiation; Cu-based heterostructure

### References

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[2] Mohammad Sadegh Shakeri et al. "Alternative local melting-solidification of suspended nanoparticles for heterostructure formation". Submitted In: Advanced Materials, under review.



**Figure 1.** Calculated XAS spectra of copper compounds that can be thermodynamically or kinetically crystallized during the PLIS process. The spectra were calculated using the jfeff10 software. For the calculation of Cu K-edge, we used the parameters, RPATH: 5.5, SCF: 10, Exchange: Dirac-Hara+HL and FMS: 25. These parameters were set to obtain the best correlation between calculated and measured spectra. CuCO<sub>3</sub>, Cu(OH)<sub>2</sub> and Cu<sub>2</sub>O<sub>3</sub> models without measured references were calculated with the same set of parameters. The yellow, red, black and white colors in the atomic models represent Cu, O, C and H atoms, respectively.

## Investigation of atomic core levels with *ab initio* many body theory.

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X-ray photoelectron spectroscopy (XPS) measures electron removal energies, providing direct access to core electrons binding energies, hence probing the electronic structure. In this meeting, I will present the benchmark of *ab initio* many-body *GW* approximation on the complete electron binding energies of noble gas atoms (He-Rn), which spans 100 keV. Our results demonstrate that *GW* achieves an accuracy within 1.2% in XPS binding energies, by systematically restoring the underestimation from density-functional theory (DFT, error of 14%) or the overestimation from Hartree-Fock (HF, error of 4.7%). Such results also imply the correlations of d electrons are very well described by *GW*[1].

However, absolute binding energy is not the single quantity identified by XPS, also shift of binding energies (known as chemical shift) gives an information about chemical composition and structures. Thus, I will also present the study of chemical shift with described above methods (DFT). We benchmarked the accuracy of the chemical shift of carbon 1s electron in a set of molecules against experiments. Besides, our study reveals the physical origin of the chemical shift [2].

Keywords:

Core-electrons, XPS, chemical shift, DFT, GW

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## **Transcorrelated Selected Configuration Interaction**

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Selected Configuration Interaction (SCI) methods offer a way to achieve near Full Configuration Interaction (FCI) accuracy within a given set of one-electron basis functions (B). These methods select the most relevant Slater determinants from the exponentially scaling FCI space, which depends on the system size. However, despite their effectiveness, traditional SCI approaches often exhibit slow convergence in terms of B, making them computationally challenging for larger systems.

One effective technique to enhance convergence in terms of basis functions B is to incorporate an explicit correlation factor in the wavefunction. However, this approach significantly complicates the evaluation of integrals.

In this study, we introduce an extension of the SCI methods that enables selection in the presence of an explicit correlation factor. This extension is made possible by the Transcorrelated (TC) theory, which provides a non-Hermitian framework for incorporating the correlation factor directly into the Hamiltonian. Our findings demonstrate that the SCI expansion within the TC framework exhibits significantly faster convergence compared to the traditional SCI approach, particularly in terms of the basis B.

## Pseudopotential Bethe-Salpeter calculations for shallow-core spectra: Excitonic effects and Resonant Inelastic X-Ray Scattering in α-Al2O3.

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Resonant inelastic X-ray scattering (RIXS) is a powerful technique for studying elementary excitations due to its element and orbital specificity, as well as its access to a wide range of energies and momenta. The theoretical description of the RIXS double differential cross-section is typically carried out using all-electron calculations. Here, we present a study of shallow-core excitations at the L-edges of aluminum in  $\alpha$ -Al2O3 using a pseudopotential plane-wave framework. Since strong excitonic effects have been observed in the optical [1] and core [2] absorption spectra of alumina, we perform the calculations using the Bethe-Salpeter equation (BSE), which is the state-of-the-art technique for describing electron-hole interactions.

In our work, we address the question of the validity of the pseudopotential approximation for X-ray absorption near-edge structures (XANES) and RIXS spectra of shallow-core edges. We investigate the limits of the pseudization of the wave functions in many-body BSE calculations and the advantages of treating all the valence and shallow-core electrons on the same footing.

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## Calculations of Excited Electronic States by Converging on Saddle Points Using Generalized Mode Following

Yorick L. A. Schmerwitz<sup>1</sup>

6<sup>th</sup>-order (a) Symmetry-broken GS, PBE saddle point Symmetry-pure GS, PBE (c)(b) MRCISD Second electronic Hessian eigenvalue V E DO-GMF/L-BFGS inergy Charge transfer excitation 0 DO-MOM/L-SR1 θ

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Figure 1: Examples of DO-GMF calculations with PBE functional: (a) Doubly excited state of ethene as a function of twisting angle. (b) Conical intersection in ethene. (c) Charge transfer excitation in N-phenylpyrrole.

Variational density functional calculations [1] provide an improved description of excited electronic states with large change of the electron density compared to the frequently used adiabatic linearresponse density functional theory (TDDFT) as well as correct avoided crossing and conical intersection topologies, as the orbitals are variationally optimized for the excited state. However, there are some challenges: (1) Excited states are typically saddle points on the surface describing the variation of the energy of the system as a function of the electronic degrees of freedom, requiring identification of the directions along which the energy has to be maximized, and (2) common selfconsistent field algorithms are prone to convergence failures near degeneracies. We introduce a novel direct optimization generalized mode following approach (DO-GMF) [2] that converges on an n<sup>th</sup>-order saddle point by inverting the components of the gradient in the direction of the eigenvectors of the n lowest eigenvalues of the electronic Hessian matrix. This approach has the distinct advantages of inherently avoiding variational collapse to the ground state without additional methods and following a chosen excited state by its saddle point order through molecular configurations where the symmetry of the single determinant wave function is broken and thereby makes it possible to calculate challenging charge transfer excitations, avoided crossings and conical intersections where other state-specific methods tend to fail [3]. These advantages are demonstrated in calculations of potential energy curves for the ethene and dihydrogen molecules (panels (a) and (b) in the figure). Results of calculations are presented for challenging charge transfer excitations in nitrobenzene and N-phenylpyrrole (panel (c) in the figure), involving calculations of 4<sup>th</sup>- and 6<sup>th</sup>-order saddle points, respectively.

Keywords: Excited state, saddle point, mode following, charge transfer, conical intersection

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## IMPROVING DENSITY FUNCTIONAL CALCULATIONS OF INTRAMOLECULAR CHARGE TRANSFER EXCITED STATES

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Intramolecular charge transfer excitations in organic molecules have an important role in several processes in nature, such as photosynthesis and vision, and in various applications, such as solar cells. Reliable and efficient modeling of charge transfer excitations in organic dyes is crucial for the understanding and utilization of such processes. Since charge transfer excitations lead to large electronic rearrangements, they are challenging to describe for methods that neglect orbital relaxation in the excited state, such as the commonly used linear-response time-dependent density functional theory (TD-DFT), which tends to significantly underestimate the excitation energy, especially for long-range charge transfer [1]. Time-independent methods involving variational optimization of the excited state orbitals can provide a better approximation, but often face convergence issues.

To address these challenges, we present a strategy for robustly converging variational calculations of charge transfer states, based on stepwise direct optimization of the orbitals [2-4]. The approach is shown to successfully converge challenging charge transfer states where the commonly used maximum overlap method fails, and it is further used to assess variational density functional calculations of charge transfer excitations in organic molecules from the benchmark set of Loos et al. [1] (see figure below). The variational method is found to improve the estimate of the excitation energy over TD-DFT for long-range charge transfer excitations when using a semilocal exchange correlation functional, such as PBE, providing an accuracy comparable to TD-DFT with a hybrid functional, but at a significantly lower computational cost.



**Figure 1: a**, An example of a charge transfer excitation in an organic molecule (DMABN), showing the orbitals involved in the excitation. **b**, The mean absolute error (MAE) of the excitation energy for 26 excitations and a subset of 14 long-range charge transfer excitations obtained with TD-DFT and variational direct optimization calculations using the semilocal PBE functional. The error is calculated with respect to theoretical best estimates [1].

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Keywords: DFT, excited states, charge transfer excitations, orbital optimization

### Calculations of absorption tail in mixed halide perovskite

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Bandgap tunability of lead mixed-halide perovskites makes them promising candidates for various applications in optoelectronics since they exhibit sharp optical absorption onsets despite the presence of disorder from halide alloying. Here I will present our work to use localization landscape theory and Wigner-Weyl approximation to reveal that the static disorder due to compositional alloying for lodide:Bromide perovskite contributes at most 3 meV to the Urbach energy. Our modelling reveals that the reason for this small contribution is due to the small effective masses in perovskites, resulting in a natural length scale of around 20nm for the "effective confining potential" for electrons and holes, with short range potential fluctuations smoothed out. The increase in Urbach energy across the compositional range agrees well with our optical absorption measurements. We model systems of sizes up to 80 nm in three dimensions, allowing us to explore halide segregation, accurately reproducing the experimentally observed absorption spectra and demonstrating the scope of our method to model electronic structures on large length scales. Our results suggest that we should look beyond static contribution and focus on the dynamic temperature dependent contribution to the Urbach energy.

## CALCULATION OF OPTICAL SIGNATURES OF DEFECTS: COMPARING DIFFERENT METHODS

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Defects play a major role in many relevant technologies such as transistors, quantum computers and solar cells. Understanding the optical properties of defects is particularly important, but from a computational point of view they remain difficult to calculate. The necessity of supercells for defect calculations to reduce spurious defect-defect interaction with its periodic neighbors, often does not allow us to use many-body perturbation theory. This limits us to comparing total energies, which is a reliable quantity within density functional theory. Our aim is to analyze the difference between charge transition levels, optical transition levels, the position of defect related Kohn-Sham states, and optical excitation energies as obtained by the difference between ground and excited states.

Keywords: defects, DFT, electronic properties, optical properties, tight-binding, machine learning

## Plasmon-assisted electron dynamics in photocatalysis: hydrogen production from formic acid

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Modeling complex light-driven dynamics occurring in composite systems of chemical interest, such as light-harvesting complexes or metal nanostructures (NSs) interacting with molecules, is a challenging task for theoreticians. An accurate and rigorous theoretical modeling is necessary in order to interpret and analyze the experimental data, and to suggest novel routes. Describing systems with millions of atoms at full quantum (QM) level of theory is impractical or impossible. This is the reason why a multiscale approach, based on the application of less expensive classical methods to study effectively large portions of the overall systems and of more accurate QM approaches for a small subregion, is a proper choice for this kind of systems [1]. We applied the developed methodology to plasmon-assisted photocatalysis [2,3]. Light exposure at a certain wavelength in metal NSs (antenna) generates a plasmon excitation. The plasmon is transferred to a catalytic reactor, in which hot carriers are generated whereas the molecular species involved in the reaction are adsorbed on the reactor surface. The antenna is described classically using a time-dependent formulation of the polarisable continuum model [3], while the molecule+reactor system is characterized by a QM treatment, such as DFT and TDDFT [7]. We investigated the H<sub>2</sub> generation from formic acid on Au-Pd and Au-Pt heterodimers, inspired by experimental works [4, 5]. The goal is to achieve a microscopic understanding of the factors affecting the electron dynamics of the rate determining step of the reaction, by looking at the charge generation and injection [6] to the formiate moiety adsorbed on Pd or Pt, in presence of Au nanorod.

Keywords: photocatalysis, TDDFT, multiscale methods, plasmonic excitations, electron dynamics

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## Ab initio study of Fe-phthalocyanine adsorption on the antiferromagnetic NiO(001) surface

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Antiferromagnetic materials are relevant in the production of spintronics (i.e. spin-electronics) devices [1], being able to transport high-frequency (THz) coherent spin excitations [2], and to avoid dissipative coupling with external magnetic stimuli. The adsorption of organic molecules on these substrates [3], forming so-called spinterfaces, modifies the dispersion of the spin excitations through charge transfer and crystal deformations [4], and offers the possibility to produce them through light excitations. In the case of magnetic organic molecules, the spin-crossover effect can enable the change the magnetic state of the molecules, which consequently will induce magnetic changes in the substrate.

We study the properties of a spinterface, formed by Fe-phthalocyanine [5] magnetic molecules and transition-metal NiO [6]. We are particularly interested in the ground-state and excited-state properties, looking for mechanisms to produce spin-excitations.

Transition metals are often\_improperly described in a standard density functional theory (DFT) approach with semi-local exchange-correlation functionals; here we employ an Hubbard correction as a practical method for handling moderately large simulation models with a better accuracy in the description of the magnetic properties. We study individual FePc molecules on NiO(001), determining the adsorption conformation: we find that the central Fe atom couples with the surface through O atoms and this reflects in the electronic and magnetic properties of the molecule. We further investigate the optical spectra of adsorbed molecules in a time-dependent DFT approach, identifying changes in the Fe spin-state as a result of excitations.

This work is performed within the SINFONIA project (EU grant No. 964396).

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### NON-TRIVIAL EXCITONIC FINGERPRINTS AND OPTICAL ANISOTROPY OF 2D TELLURIUM



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Tellurene is an emerging 2D anisotropic semiconductor, with fascinating electronic and optical properties that differ dramatically from its bulk counterpart, which has come to us owing to its unique chained structures. Tellurene is the 2D form of Tellurium and it was proposed by theoretical calculations – and then verified by experiments – in 2017 [1]. In this work, we investigate the electronic and optical properties of three different allotropic forms of few-layer Tellurene by means of ab initio calculations based on Density Functional Theory (DFT) and Many-Body Perturbation Theory (MBPT), using the Quantum ESPRESSO suite [2] and the YAMBO code [3]. Following our previous work [4], we focus our attention on the most stable and interesting  $\beta$ - and  $\gamma$ -phase – concerning the monolayer (1L) configuration –, also including bilayer (2L)  $\alpha$ -phase, since 1L  $\alpha$ -phase is unstable and can be transformed into  $\beta$ -phase without barriers. These three very diverse structures are semiconductors with both direct ( $\gamma$ ) and indirect ( $\alpha$ ,  $\beta$ ) electronic (quasiparticle) bandgap, ranging from about 1 to 2 eV. Each system shows its characteristic optical fingerprint and absorbs light mainly in the far-infrared range, showing very high photon absorptions for in-plane light polarization, superior to that of other previously studied 2D materials. Moreover, due to their orthorhombic crystal structure and very peculiar chemical bonding,  $\alpha$ - and  $\beta$ -phase exhibit strong optical anisotropy which is hardly to be found in the 2D world. Lastly, we propose a comparison of the (GW) bands alignments with that of different 2D materials for possible type-2 heterostructures involving Tellurene.

Keywords: ab initio, DFT, MBPT, BSE, optical absorption, Tellurene

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### Molecular systems probed by near-field spectroscopy

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Spectroscopy coupled to scanning tunneling microscopy technique (STM) is a powerful tool to analyze molecular properties at a single molecule level with atomic resolution. This is made possible by the interaction between the molecular sample and the plasmonic nanocavity formed between the metallic STM tip and a metal sample, which amplifies the molecular emission signal by orders of magnitude (near-field spectroscopy). In this way, some intrinsic limitations and selection rules of conventional far-field spectroscopy of molecules in solution are overcome. This aspect, together with the high resolution of the signal and the precise control over the sample, allows to obtain information otherwise not accessible in conventional spectroscopy. On the other hand, to fully unpack and rationalize such information, a theoretical interpretative framework should accompany the experimental findings. Therefore, a crucial aspect is the capability of modelling the molecular spectroscopic response in the near-field and the availability of high-level quantum-chemical calculations on the molecular systems. In this presentation, some examples of STM-induced luminescence (STML) of conjugated molecules will be shown. Results obtained on single molecules and small aggregates will be discussed [1,2]. Particular focus will be put on the modeling aspects and the interesting molecular properties that become accessible when experiments and theory complement, such as for example the structural arrangement of the molecule, the electronic structure of its ground or excited electronic state, or its response to stimuli.

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### THEORETICAL STUDIES OF NOVEL GRAPHENE BASED NANOSTRUCTURES

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Some very appealing methods to open a sizable bandgap in graphene consist in reducing nanoscale dimensions or in forming an ordered array of holes in its honeycomb lattice. Indeed, the reduction of one dimension of graphene leads to graphene nanoribbons (GNRs) [1] while the reduction of the two dimensions leads to graphene quantum dots (GQDs) [2]. As forementioned, a gap can be opened via ordering an array of holes in a graphene lattice as shown in a first theoretical study in 2008. It is called a Graphene Nanomesh (GNM) or a Graphene Anti-dot Lattice (GAL) [3]. First, experimental realizations of GNMs started in 2010 at UCLA [4] and LBNL [5] using a combination of di-block copolymer organization or nanoprinting and selective etching (top-down approach). In this presentation, we will explore the electronic, optics and transport properties of C96 GQDs and its GNM. In Fig. 1a it is possible to obtain C96 GQDs on the gold surface from C96H24(C12H25)6 by physical vapor deposition after heating over 100°C and observed in the experiment. We will show our TB and ab initio calculated results on its electronic structures. Its optical spectra will be performed within an Independant particle picture, with TB as appeared in Fig. 1b. The transport properties will be simulated by ab initio simulated Scanning tunneling microscopy (STM) images (as shown in Fig. (f-g)) as well as tunnel current spectroscopies (STS) and then compared with experimental results (Fig. (c-e)).



**Figure 1: a**, C96 GQDs's physical vapor deposition conditions and procedures on gold surface. **b**, Photoluminescence spectra of C96C12 and IP-TB spectra of C96's GQD. **c-e**, The height profile, STM and STS experiment results of C96's GQD on Au(111) surface. **f-g**, Projected density of states and STM simulation results of C96's GQD on Au(111) surface.

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Keywords: DFT, electronic properties, optical properties, tight-binding, graphene quantum dots.

## Insights from vibrational properties in determining structural prototypes of ferroelectrics

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In this seminar I will present a microscopic picture of paraelectric and ferroelectric phases based on a symmetry-based methodology we recently introduced, designed to identify meaningful structural prototypes for local disorder. These prototypes can then serve as minimal structural models used to faithfully represent these phases in calculations. Importantly, these are local minima of the potential-energy landscape and therefore do not display any structural instability. I will show how one can construct prototypes of paraelectric and ferroelectric phases through a group-subgroup analysis refined with density-functional-theory calculations, first using barium titanate as a test case. The methodology allows us to systematically explore and identify structural prototypes for the paraelectric phase which accommodate the strong chemical drive towards [111] titanium displacements while maintaining a cubic point symmetry. Furthermore, we show how these could be inferred from symmetry-constrained phonon instabilities of the 5-atom-primitive cell [PRR 4, L012042 (2022)]. I will then show how these results extend across all the perovskite titanates, niobates and zirconates, as well as the extension to the lower-symmetry ferroelectric phases.

### Mode-coupling theory of anharmonic lattice dynamics

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The theory of lattice dynamics describes the collective motion of atoms in a crystal as a gas of phonons. This problem is usually addressed by separating the vibrational energy into an exactly solvable harmonic contribution and an anharmonic one, which is usually treated as a small perturbation. Unfortunately, this perturbative approach is not always a valid approximation.

In this presentation, we introduce the mode-coupling theory of anharmonic lattice dynamics [1] that can alleviate the main drawbacks of standard perturbation theory by partitioning the motion in an exact way that ensures a valid perturbation expansion, even for very anharmonic systems. The theory is based on the Mori-Zwanzig projection operator formalism [2,3], which allows to build of an exact generalized Langevin equation for renormalized phonon quasiparticles were dissipative contributions are introduced in a memory kernel. Using mode-coupling theory [4], introduced originally to describe glass-forming liquids, we obtain a perturbation theory where each order must be smaller than the previous ones. The theory provides an accurate description of the vibrational properties of strongly anharmonic systems in a systematic manner and can be applied for classical as well as quantum systems.

Our works lays the foundations of a complete formalism of anharmonic lattice dynamics, with which it will be possible to accurately predict technologically important properties such as thermal conductivities, phase transition temperatures or vibrational spectroscopy.

Keywords: Anharmonicity, phonon spectral function

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## MACHINE LEARNING ASSISTED CALCULATION OF PHONON PROPERTIES IN LAYERED hBN

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The calculation of finite temperature properties of solids is a topic under heavy discussion in recent years. There are mainly three predominant approaches to the problem: harmonic theory [1], effective harmonic models (e.g. the sSCHA [2] or sTDEP [3,4]) which renormalize the phonons to account for temperature dependent effects using stochastic sampling, and ab initio molecular dynamics (aiMD) simulations ([5]) which samples the classical distributions exactly. The latter two overcome the clear faults of the first in dealing with anharmonicity, resulting in the correct prediction of quantities like thermal expansion and the shift of the potential energy surface minima.

These approaches all do, however, suffer from the same problem of needing large amounts of DFT calculations in order to obtain converged results. This is especially the case for aiMD, where some systems reach prohibitive calculation times to obtain relevant properties.

In this work we show how taking advantage of Machine Learning (ML) assisted canonical sampling (MLACS) and interatomic potentials (MLIP) [6] as a general accelerating method allows for the usage of MD and TDEP as an easy approach for predicting accurate temperature dependent quantities. We exemplify this with the case of monolayer hexagonal boron-nitride (hBN) by calculating the temperature evolution of their phonon band-structures, Raman shifts and thermal conductivities.



Figure 1: Temperature dependent phonon band structure of monolayer hBN

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Keywords: Phonons, thermal transport, Machine Learning, anharmonicity.

### NITROGEN-VACANCY CENTER: UNDERSTANDING THE ELECTRONIC STRUCTURE FROM AB-INITIO CALCULATIONS

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A good platform for quantum computing and communication requires high-quality qubits. There are several ways to create and manipulate quantum bits, such as quantum dots, trapped ions, superconducting qubits, topological qubits, and photonic qubits - each with its advantages and drawbacks. One of the most promising types of qubits is based on the nitrogen-vacancy (NV) center in diamonds. With a very long coherence time and the ability to work at a wide range of temperatures (even room temperature), this negatively charged defect in diamond also emerges as a very promising way of mapping the magnetic response in high-pressure superconductors. Therefore, understanding the electronic structure and exited states of the defect is fundamental for the fast advance of its quantum technological applications. In this work, we applied first principle calculations in combination with the extended Hubbard model to describe the full excitation spectra of the negatively charged NV center. Using the HSE06 exchange-correlation potential, we calculated the ground state and excited triplet states of the NV center, which we used as input to fit our Hubbard model to obtain the correlated singlet-singlet transitions. Our results show the importance of the electronic correlations in the description of the optical and non-radiative excitations, along with the spin interactions which are crucial in the protocol for qubit preparation and read-out.

Keywords: Point Defects, DFT, Hubbard model, Nitrogen-Vacancy Center, Diamond

## Phonon anharmonicity in quantum paraelectrics beyond densityfunctional theory

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Accurately calculating phonons in materials, even in the presence of strong quantum anharmonicity, is key to describing many of their temperature-dependent physical properties. In SrTiO3 and KTaO3, the strongly anharmonic lattice dynamics lead to a quantum paraelectric behavior at low temperatures, whereby the ferroelectric instability is suppressed due to anharmonic quantum fluctuations. A detailed quantitative understanding of the phonon anharmonicity underpins the study of emergent properties in this class of materials, but poses significant challenges. In this talk, I will discuss an approach for calculating the temperature-dependent anharmonic properties of these materials with beyond density-functional theory accuracy. Specifically, we employ machine-learned potentials in combination with the stochastic self-consistent harmonic approximation. I will show that this method seamlessly allows to fully capture strong anharmonicities while retaining first-principles accuracy, and furthermore opens up the possibility to perform manybody calculations beyond DFT via Δ-machine learning. I will show that the paraelectric phase in KTaO3 and SrTiO3 is stabilized by anharmonic quantum fluctuations down to 0 K. In the case of SrTiO3, we further characterize the cubic to tetragonal transition by the softening of the antiferrodistortive instability. I will discuss how a quantitative description of the quantum paraelectric behavior requires a higher-level treatment of electronic correlation effects via the random phase approximation.

## Non-equilibrium dynamics of chiral valley phonons from the time-dependent Boltzmann equation

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Charge carriers in transition-metal dichalcogenide (TMD) monolayers are characterized by a valley degree of freedom, which can be exploited to realize properties and functions absent in other 2D material families. Under non-equilibrium conditions, an anisotropic carrier population can be established across different valleys leading. e.g., to valley polarization [1] and chiral valley excitons [2]. In this work, we demonstrate that ultrafast electron-phonon scattering in photoexcited  $MoS_2$  can lead to the excitation of chiral valley phonons – vibrational states characterized by a well-defined valley index.

To investigate the non-equilibrium properties of TMD monolayers, we implemented the time-dependent Boltzmann equation (TDBE) – an ab-initio approach to the ultrafast dynamics of electrons and phonons in presence of electron-phonon and phonon-phonon scattering. Numerical solution of the TDBE [3] indicates that a population imbalance between phonons at the K and -K high-symmetry points can be established following photoexcitation with circularly-polarized light, leading to valley polarized phonons and vibrational dichroism persisting for several picoseconds. To guide the experimental observation of these phenomena, we simulate the dynamical structure factor, which can be measured via ultrafast electron diffuse scattering (UEDS) experiments [4]. Our findings suggest that these phenomena constitute a viable route to excite chiral valley phonons in TMD monolayers [5], – thereby extending the paradigm of valleytronics to the domain of vibrational excitations.

Keywords: Ab-initio calculation, non-equilibrium, electron-phonon interaction, ultrafast dynamics, time-dependent boltzmann equation

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## Metal-insulator transitions in the Hubbard model: local vs non-local correlation effects

### Maria Chatzieleftheriou

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The Hubbard model exhibits different kinds of metal-insulator transitions that are driven by fluctuations, interactions, or temperature. The system's rich phase diagram has been extensively studied using a huge collection of advanced computational methods. However, a clear identification of the effects behind each transition is missing. In this talk I will introduce the main techniques used in the field and I will discuss important advances that have been made within the last years. I will finally present a recent work, where we self-consistently combine a state-of-the-art dynamical mean-field theory description of an interaction-driven Mott transition with a diagrammatic description of the non-local collective electronic fluctuations, and revisit in detail the phase diagram of the Hubbard model. This approach allows us to identify the role the local magnetic moment plays in the metal-insulator transitions in different regimes of electronic interaction.

I had an exchange with Changming Yue (the other speaker on the strongly correlated session) in order to avoid overlap in our presentations with respect to the introduction to the field. Considering the things he wants to present compared to mine, he suggested that we ask you to switch our order in the day. I agree with him, indeed it makes more sense that I go first since my work is more method and model oriented, while his is related to application to realistic materials.

### GROUND STATE SYMMETRIES AND COLLECTIVE MODES IN TA2NISE5 – AN EXCITONIC INSULATOR CANDIDATE

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The origin of phase-transition from a high temperature orthorhombic phase to a low temperature monoclinic phase in Ta2NiSe5 is debatable. There are two competing scenarios, namely, a structural instability with a B2g zone center optical phonon and electronic order parameter of excitonic nature breaking the discrete set of lattice symmetries due to a sponteneous interband hybridization between Ta and Ni mediated by Coulomb many-body interactions [1-4]. We further explore the ground state symmetries and nature of collective excitations in the excitonic ordered phase of this compound. We perform a realistic modeling using Density Functional Theory as a starting point to construct a tight-binding Hamiltonian and describe the electronic correlations on a Hartree Fock level. The collective modes or excitonic susceptibilities in the ordered phase are computed within the linear response regime [5]. We see the breaking of discreet lattice symmetries due to the Ta-Ni hybridization makes the phase mode massive. The frequency of this phase mode scales with the strength of Ta-Ni hybridization. An amplitude mode appears at the gap edge and the intensity of it is less than the phase mode (cf Fig. 1). The frequency of modes also show a systematic dependence with temperature. We further discuss the need for inclusion of the electron phonon coupling to provide a complete picture of this phase transition.



**Figure 1: a-b** Variation in the amplitude and phase mode of the order parameter with time in the excitonic phase. **c**, Bandstructure of Ta2NiSe5 with the Ni band-character shown in red and the Ta band-character shown in blue. **d**, Collective modes in the excitonic susceptibilities with a massive phase mode and an amplitude mode at the gap edge.

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Keywords: DFT+ Hartree Fock, excitonic properties, phase-transition, tight-binding, Ta2NiSe5.

Charge ordering as the driving mechanism for superconductivity in rareearth nickel oxides

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Superconductivity is a peculiar property of materials characterized by zero resistance to direct current and the expulsion of magnetic flux. It is explained by the formation of bound electrons called Cooper pairs. The most widely studied superconductors are the perovskite cuprates which have the highest critical temperature ( $T_c$ ) at ambient conditions. In the search for compounds analogous to cuprates, nickel oxides were long proposed to host superconductivity [1,2]. This research crystallized in 2019 with its discovery in infinite layer nickelates  $R_{1-x}Sr_xNiO_2$  [3] and lately in a reduced Ruddlesden-Popper Nd<sub>6</sub>Ni<sub>5</sub>O<sub>12</sub> [4] with similar critical temperatures ( $T_c = 9-15$  K), albeit without clarifying the pairing mechanism.

Here we use Density Functional Theory (DFT) to show that superconductivity is tightly related to a charge and a bond ordered state that produce a significant electron-phonon coupling. We reveal the existence of an intrinsic instability of Ni<sup>1.5+</sup> cations ( $3d^{8.5}$ ) in the half-doped case that prefers to transform to more stable Ni<sup>+</sup> ( $3d^9$ ) and Ni<sup>2+</sup> ( $3d^8$ ) cations in the ground state. It results in a bond disproportionation of NiO<sub>2</sub> square complexes, a charge ordering and an insulating state. Starting from this half doped situation, doping is shown to suppress disproportionation effects, ultimately resulting in a metallic regime. Once this charge ordered state is suppressed, the related bond disproportionation mode is still highly coupled to the electronic structure and the resulting electron-phonon coupling is sufficient to explain the T<sub>c</sub> dome versus doping content observed experimentally. It suggests that the vicinity of a charge ordered state is a prerequisite for superconductivity in the nickelates. Hence, these compounds appear similar to non-magnetic bismuthates [5].

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## Understanding borophene: From the atomic structure to the electronic response.

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In the last decades, 2D materials such as graphene have gained attention for all sort of applications. Among these materials, borophene has gained popularity for applications that go from transparent conductors to superconductivity[1,2]. Given its polymorphism and anisotropy, it constitutes an ideal prototype for the study of 2D materials. It is therefore interesting to investigate how the atomic structure influences its electronic structure, and how these changes affect the properties of the material: optical absorption, loss function, and charge density evolution with respect to an external perturbation in the linear regime.

In this work we have selected a set of borophene polymorphs structurally different to each other and we have compared them in commensurable unit cells . We have found out striking similarities among the structures, but we have also noted how the slight differences change the properties from polymorph to polymorph. Our calculations were performed with Abinit (ground-state), with DP (full polarizability), and with SRden (density evolution) [3-5].

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## Analysis and comparison of optimal-continuum Gaussian basis sets for High-Harmonic Generation spectra of atoms and molecules.

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The increasing interest for the simulation of high-energy optical processes (such high harmonic generation (HHG) or photoionization) leaded to the necessity to improve the theoretical representation of continuum states [1,2].

Several solution have been proposed for the description of continuum states, such as grid-based calculations[3], B-splines[4] and Gaussian functions[5,6]. The aim of our work is to underline the flexibility and efficiency of continuum Gaussian functions, that can be added to standard Gaussian basis set in order to improve the description of continuum states. We have selected from literature four different types of Gaussian continuum functions [7,8,9,10,11] and we have tested their efficacy in representing continuum performing HHG spectra of hydrogen atom, comparing them with grid representation and exact solutions [12]. Also, we have presented an application of the efficiency of the use of continuum Gaussian function in the basis set for performing HHG spectra for complex biological molecules[13,14].

<u>Keywords</u>: Strong-field electron dynamics, quantum chemistry, wavepacket propagation, HHG, Gaussian basis sets

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## Strong Correlation and Unconventional Superconductivity in Bulk and Trilayer Alkali-Doped Fullerides

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The alkali-doped fullerides A3C60 (A = K, Rb, Cs) exhibit strong correlation and unconventional superconductivity (SC) in both bulk and thin films. In the first part of the seminar [1], the speaker will investigate the unconventional pairing mechanism in bulk A3C60 using dynamical mean-field theory (DMFT) in the Nambu formalism. He will show that the local orbital fluctuations are substantially enhanced in the superconducting state and provide the pairing glue in A3C60. A lock-in phenomenon between the SC gap (fermionic) and the local orbital fluctuation energy (bosonic) is found, which is consistent with an experimentally observed universal linear relationship.

Epitaxially grown K3+xC60 thin films exhibit a Mott insulating state in the monolayer and a strong electron-hole doping asymmetry in the superconducting state in the trilayer [2], which asymmetry is absent in the three-dimensional bulk limit. In the second part of the seminar [3], using DFT+DMFT, the speaker will show that this doping asymmetry results from a substantial charge reshuffling from the top layer to the middle layer. The interlayer charge transfer and layer-selective metal-insulator transition result from the interplay between crystal field splittings, strong Coulomb interactions, and an effectively negative Hund coupling.

If the time is allowed, the speaker would like to report the recent progress in the analytic continuation of anomalous self-energy and its application in K3C60. This method paves the way for the theoretical study of momentum resolved spectra in the SC phase using quantum Monte-Carlo method [4].

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### Quantum computers: why should I (and you) care?

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In the first part of this talk I will answer some of the W-questions (What, How, When, and Why) about quantum computers to describe the "state-of-the-union" and (hopefully) convince you to be "quantum-ready" to use quantum computers in your research because they might come earlier than we expect.

I will devote the second part to introduce you to the fascinating world of noisy intermediate-scale quantum (NISQ) computers: past, present and future, to finish up with a call for help!

## Electron-plasmon satellites in the spectral function of highly-doped hafnium disulfide (HfS<sub>2</sub>)

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Collective charge-density oscillations (plasmons) can thoroughly influence the electronic properties of doped semiconductors and manifest themselves via distinct spectroscopic fingerprints in experiments [1,2]. In this work, we combine *ab-initio* calculations (based on many-body perturbation theory and the cumulant expansion) with angle-resolved photoemission spectroscopy (ARPES) to understand and quantify the electron-plasmon interaction in the transition metal dichalcogenide HfS<sub>2</sub> [3,4]. ARPES reveals the emergence of satellite features suggesting strong coupling to ~ 200 meV plasmons, which are well reproduced by our *ab-initio* calculations. Based on a simple surface model of the dielectric function, we further show that reduced screening at the surface underpins an enhancement of the electron-plasmon interaction, resulting in the formation of plasmonic polarons [5].

Keywords: TMD, spectral function, MBPT, cumulant expansion, ARPES, plasmonic polarons

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### Encapsulated BN nanocages and nanocapsules as anode materials for Magnesium-Ion Batteries: A DFT Study

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We present an ab-initio study in the Density Functional Theory (DFT) framework, performed using the DMol3 package [1] from the Materials Studio environment [2], of the effect of encapsulation of halogens (Cl, Br) and chalcogens (O, S, Se) in the interaction of the B<sub>12</sub>N<sub>12</sub> nanocages with the Mg<sup>2+</sup> cation; and of encapsulation of homonuclear diatomic halogens (Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>) and chalcogens (S<sub>2</sub>, Se<sub>2</sub>) in the interaction of the B<sub>24</sub>N<sub>24</sub> nanocapsules with the Mg<sup>2+</sup> cation. Our aim is to predict whether these functionalized BN nanomaterials could be suitable anode materials for Magnesium-Ion Batteries (MIBs), which are considered a cheap, sustainable, and safe substitute to Lithium-Ion Batteries (LIBs) [3]. To assess their potentiality as negative electrodes, the formation energy, the interaction energy, and the cell voltage have been calculated for each geometrically optimized system. Remarkable cell voltages have been obtained for B<sub>12</sub>N<sub>12</sub> nanocapsules encapsulated with selenium, reaching a cell voltage of 3.50 V; and for B<sub>24</sub>N<sub>24</sub> nanocapsules encapsulated with a diatomic iodine molecule, reaching a cell voltage of 3.61 V.

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### Electron-phonon coupling in warm dense transition metals

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In metallic samples illuminated with ultrashort laser pulses, the electrons are rapidly heated to temperatures ranging in the tens of thousands of Kelvin within a timescale that is comparable to the duration of the pulse, while the ions remain at a much lower temperature. The process of equilibration between the two temperatures occurs over several picoseconds and is determined by the electron-ion coupling factor. In this study, we have employed methods based on Density-Functional Theory and Density-Functional Perturbation Theory to investigate the thermal relaxation of warm dense gold and molybdenum and to calculate the electron-ion coupling factor for extreme values of electronic temperature. Our approach involves revisiting the formulations presented in existing literature and improving the accuracy of the calculations by eliminating most of the approximations used in other studies. Our results provide valuable insights into the non-equilibrium dynamics of transition metals in the warm dense matter regime.

### Ab-initio study of the effects of Pb intercalation in Graphene/SiC heterostructures

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Graphene has paved the way to a widespread interest in two dimensional materials. Due to its peculiar electronic, mechanical, and electron-transport properties it is regarded as a promising material for nanoelectronic and spintronic applications. Many efforts have thus been made to find proper substrates and efficient processes for high quality graphene growth, and SiC has been found to be one of the leading solutions. However, the absence of a tunable band gap in graphene is a crucial barrier for nanoelectronics applications. Moreover, the strong covalent interactions with the SiC in graphene/SiC heterostructures results in a high electron doping in graphene, which affects the charge carrier mobility [1]. Finding an efficient way to open a band gap and decouple graphene from the substrates is thus essential. A solution to overcome these obstacles, which has attracted much interest in recent years, is the intercalation of atomic species into the graphene/substrate interface. In fact, two key factors in the opening and tuning a band gap in graphene are the symmetry breaking of the sublattice and the presence of strong spin-orbit (SO) interaction. Intercalated metals have become promising to engineer a large band gap in graphene via spin-orbit coupling. Several species have been found to be able to intercalate in the graphene layer like H, Au, Pt, Li, Na, F, Mn, Si, Ge. Among them, intercalation of heavy atoms like Pb with large SO coupling was used to modify the energy spectra and density of states of graphene in order to make it equivalent to the energy levels of a 2D electron gas in a constant magnetic field [2][3]. It has been experimentally observed that twisted Plumbene is able to open a gap of 30 meV at the Fermi energy [4]. Moreover, it has been found that intercalating atoms under epitaxial graphene can efficiently decouple it from the substrate. The aim of this work is to investigate, via DFT calculations, the intercalation of a 2D plumbene layer in graphene on a SiC substrate. Calculation of DOS and band structure projection onto atomic states highlight the effect of Pb intercalation in altering the dispersion of the states near the Dirac cones due to energy levels hybridization. Analysis of the vacuum level, work function as well as investigation of charge transfer in the designed Van der Waals heterostructure, before and after intercalation, are included in this study. Starting from the choice of a proper coincidence lattice, calculations also reveal, after the intercalation, the formation of a disordered Pb monolayer covalently bonded to the SiC substrate.

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Keywords: Van der Waals heterostructure, lead intercalation, band structure, graphene

## IMPROVING THE NUMERICAL DESCRIPTION OF HIGH-PRESSURE SOLID HYDROGEN PHASES

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A variety of molecular solid hydrogen phases can be synthesized with diamond anvil cells between 100 and 400 GPa [1]. Raman and Infrared spectroscopy measurements have allowed the determination of the hydrogen phase diagram in this pressure range [2]. However, structural information on these phases is currently missing because of the low scattering efficiency of the hydrogen atom in X-ray diffraction experiments [3]. As such, numerical calculations are extremely valuable. Unfortunately, most Density Functional Theory (DFT) methods employed so far poorly describe the high-pressure molecular solid hydrogen phases [4]. Our objective has thus been to identify and use other methods presenting a better accuracy/computational cost ratio on these systems. We studied for this purpose the II-III phase transition occurring around 150 GPa experimentally. We found the Random Phase Approximation (RPA) to be in good agreement with reference calculations provided by quantum Monte Carlo methods [5,6]. We also found the hybrid DFT functional PBE0 containing 48% of Hartree-Fock exchange to be an accurate alternative. The relatively low computational cost of RPA and hybrid functionals, coupled with their enhanced accuracy, make them interesting tools for further improving the description of solid hydrogen phases by including effects currently missing in the numerical treatment, such as lattice vibrations and quantum nuclear effects.

Keywords: DFT, RPA, solid hydrogen, phase transition, electronic properties

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## CALCULATION OF OPTICAL SIGNATURES OF DEFECTS: COMPARING DIFFERENT METHODS

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Defects play a major role in many relevant technologies such as transistors, quantum computers and solar cells. Understanding the optical properties of defects is particularly important, but from a computational point of view they remain difficult to calculate. The necessity of supercells for defect calculations to reduce spurious defect-defect interaction with its periodic neighbors, often does not allow us to use many-body perturbation theory. This limits us to comparing total energies, which is a reliable quantity within density functional theory. Our aim is to analyze the difference between charge transition levels, optical transition levels, the position of defect related Kohn-Sham states, and optical excitation energies as obtained by the difference between ground and excited states.

Keywords: defects, DFT, electronic properties, optical properties, tight-binding, machine learning

## Prediction of high-*T<sub>c</sub>* superconductivity in ternary actinium beryllium hydrides at low pressure

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Hydrogen-rich superconductors are promising candidates to achieve room-temperature superconductivity. However, the extreme pressures needed to stabilize these structures significantly limit their practical applications. An effective strategy to reduce the external pressure is to add a light element M that binds with H to form MH, units, acting as a chemical precompressor. We exemplify this idea by performing ab initio calculations of the Ac-Be-H phase diagram, proving that the metallization pressure of Ac-H binaries, for which critical temperatures as high as 200 K were predicted at 200 GPa, can be significantly reduced via beryllium incorporation. We identify three thermodynamically stable (AcBe<sub>2</sub>H<sub>10</sub>, AcBeH<sub>8</sub>, and AcBe<sub>2</sub>H<sub>14</sub>) and four metastable compounds (fcc AcBeH<sub>8</sub>, AcBeH<sub>10</sub>, AcBeH<sub>12</sub> and AcBe<sub>2</sub>H<sub>16</sub>). All of them are superconductors. In particular, fcc AcBeH<sub>8</sub> remains dynamically stable down to 10 GPa, where it exhibits a superconducting-transition temperature  $T_c$  of 181 K. The Be–H bonds are responsible for the exceptional properties of these ternary compounds and allow them to remain dynamically stable close to ambient pressure. Our results suggest that high- $T_c$ superconductivity in hydrides is achievable at low pressure and may stimulate experimental synthesis of ternary hydrides.



FIG. 1. Thermodynamical stability. Ternary convex hull of Ac–Be–H at 200 GPa. The stable and metastable phases are depicted as hexagons (green) and circles (pink and gray), respectively.

Keywords: DFT, crystal prediction, hydrogen-rich superconductor, electronic properties

## MACHINE LEARNING ON TOPOLOGICAL ELECTRONIC MATERIALS

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Topological electronic materials are highly concerned because of their robust surface states and unconventional electromagnetic activity. [1] With high throughput calculation, thousands of topological materials were detected and several databases were compiled. [1, 2, 3] However, this method is limited to crystal structures with well-defined symmetry, and in the experimental field, essential factors that may affect the topological properties are still unclear. The machine learning (ML) technique, a method that has developed rapidly in recent years, provides a novel view to overcoming the above shortcomings.

A topological electronic materials dataset that combined 'Materiae' [2] and 'topological quantum chemistry' [1] is compiled in our work. We first benchmark several algorithms with data from 'Materiae', the multiclassification method of gradient boosted trees (GBTs) algorithm [4] achieved the highest accuracy 85,2%, which is chosen for further analysis. At last, we analyzed some basic features that are important to the topological materials and compared the result for distinguishing trivial insulators and topological nontrivial materials.

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Keywords: Machine Learning, topological materials

## Phonon angular momentum from broken inversion symmetry

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Phonons are quanta of vibrations in crystals, and carry energy and linear momentum. They can also carry angular momentum (AM) which originates from circular motion of the atoms [Zha14]. It has first been indirectly observed experimentally by Zhu et al. in monolayer WSe2 [Zhu18] and directly observed by inelastic X-ray scattering in bulk WC and quartz [Cai21, Ued23]. Their applications range from energy-efficient information processing [Zhu18, Lee11] to fast magnetic data storage [Tau22]. Phonon angular momentum is central to a variety of phenomena such as the phonon angular momentum Hall effect and phonon angular momentum magnetic Hall effect [Par20], and the chiral phonon diode effect [Chen22]. It is also deeply involved in ultra-fast demagnetization processes [Tau22, Mün19].

Phonon angular momentum originates from the breaking of inversion and time reversal (PT) symmetry. In this poster, I will focus on materials with broken inversion symmetry: WC and AlAs which are hexagonal and cubic respectively. In WC, only the z-component of the angular momentum is allowed to take a non-zero value: this condition is verified by my ab initio calculations. Degenerate acoustic and optical transverse modes are present along the [001] direction and can be linearly combined to have arbitrary AM. A difference should be drawn between the intrinsic AM of non-degenerate modes and the arbitrary AM of degenerate modes. The degenerate optical modes could be excited by circularly polarized light to carry angular momentum through the material. For AlAs, the phonon AM exhibits cubic symmetry, and show the presence of intrinsic as well as degenerate phonon angular momentum.



Keywords: phonons, angular momentum, transport, ab initio

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## Tuning the Schottky Contacts of graphene/phosphorene heterostructure: a DFT study

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We present a comprehensive study of the structural and electronic properties of graphene/phosphorene (G/P) heterostructure in the framework of density functional theory (DFT). We have investigated several supercells, ranging from G(4x1)/P(3x1) to G(4x13)/P(3x12), considering the high mechanical anisotropy of the phosphorene [1].

At odd with what reported in the literature [2,3], we demonstrate that the G(4x1)/P(3x1) is subject to a strain as high as 7%. The strain is drastically reduced under 1% using instead a G(4x13)/P(3x12) heterostructure. After finding the equilibrium configuration of the phosphorene layer relative to the graphene one in the xy plane, we have calculated the equilibrium interlayer distance and the binding energy between the layers. We obtain an equilibrium distance of 3.5 Å between the layers and a binding energy per carbon atom of -38.02 meV, confirming the presence of weak van der Waals (vdW) interactions between the graphene layer and the phosphorene one in the heterostructure [2]. Then, we have evaluated the electronic properties of the heterostructure under different conditions of strain, interlayer distance and applied electric field. We demonstrate that G/P heterostructures form a p-type Schottky contact which could be transformed into an n-type Schottky contact under different external conditions. This feature, together with the possibility to control the barrier height, suggests that G/P is promising for novel applications in electronics and could open a new avenue for the realization of innovative optoelectronic devices.

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Keywords: van der Waals heterostructure, Schottky contact, band structure, graphene, phosphorene

### The study of magnon and heat transport in topological materials

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A popular thing to do in physics is to merge known physical concepts with new mathematical ideas and see what happens. One of such merger is between topology and insulating materials which are better known as topological insulators (TIs). TIs have the interesting behavior that they are insulating on the inside (the crystal bulk) and conducting on their edges. The edge states are protected by their topology against many forms of perturbations. Applications for TIs vary from quantum computing or ultraprecise sensors to magneto/opto-electronic devices. An important subclass of topological materials are magnetic Weyl semi metals, which present Fermi surfaces reduced to isolated points in reciprocal space, and recently several groups have found magnetic Weyl semi metals with exotic transport properties [1]. My PhD research goal is to study and predict the behavior of magnons (quantized spin waves) and heat transport in these topological materials. This will be done with the use of density functional theory, Wannier functions and spin dynamics calculations. Our predictions will then be tested and compared with the experimental data obtained from the 'CONNECT' EOS project. The goal up to now was to use these theoretical tools on Cobalt (Co), which is a well-studied metal, as a first step towards a topological material like Co<sub>3</sub>Sn<sub>2</sub>S<sub>2</sub>.



Excitation of magnons in a 2D magnet [2].

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## A study on SrO formation in $La_{1-x}Sr_xFe_yO_3$ electrode using DFT calculations

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Solid oxide cell (SOC) is a high temperature electrochemical device that exhibits a very high efficiency compared to other technologies [1]. Thanks to its reversibility, the same system can alternatively be used in both electrolysis mode for hydrogen production and fuel cell mode for electricity production. The SOC is composed of a dense electrolyte typically in Yttria Stabilized Zirconia (YSZ) sandwiched between two porous electrodes. The hydrogen electrode is a cermet made of Ni and YSZ (Ni-YSZ) while the oxygen electrode is a mixed ionic electronic conductor (MIEC) made of La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3</sub> (LSCF) or La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (LSF). A thin barrier layer of Gadolinium doped Ceria (GDC) is usually added to limit the reactivity between the oxygen electrode and the electrolyte. Despite its advantages and the recent progress, the technology has not yet been commercialized on a large scale because the degradation rates are too high [2]. The loss of performances has been mainly attributed to microstructural evolutions [3] and material decompositions in the electrodes [4]–[6]. Among the many physical phenomena that contribute to the degradation, decomposition of the LSCF or LSF oxygen electrode has been identified to be one of the most detrimental [7].

Despite its capital importance, the underlying mechanisms controlling the LSCF or LSF demixing is still not precisely understood. It has been observed that the strontium atoms tend to migrate to the electrode surface during operation forming SrO, leading to the passivation of the electrode surface [4], [5]. SrO is an insulating phase which hinders the oxygen exchange between the electrode and the atmosphere, thereby reducing the overall electrochemical performance of the cell. In particular, the origin of the oxygen atoms for the formation of SrO is yet unclear. It was proposed previously that the oxygen atoms could come from the LSCF or LSF bulk rather than the oxygen species from the atmosphere [8]. To tackle this question, the following model reactions in which two mechanisms, differing by the origin of the oxygen species used for the formation of SrO in LSF, are considered: (i) oxygen coming from the LSF bulk and (ii) oxygen from the atmosphere.

(i)  $La_{1-x}Sr_{x}FeO_{3} \rightarrow y SrO + La_{1-x}Sr_{x-y}FeO_{3-y}$ 

(ii)  $La_{1-x}Sr_xFeO_3 + y \frac{1}{2}O_2 \rightarrow ySrO + La_{1-x}Sr_{x-y}FeO_3$ 

The reaction enthalpies of these two reactions are calculated using Density Functional Theory (DFT) calculations. Energetically favorable mechanism between the two will be identified in comparing the reaction enthalpies.

The model reactions will also enable us to analyze the effect of Co elements on the overall energetics of the SrO formation in a subsequent study that will be carried out with LSCF. The aforementioned calculations will also serve as a basis to investigate the mechanism of Sr migration from the LSCF bulk to the surface. A deep understanding of this mechanism is crucial to identify mitigating solutions to enhance the electrode stability.

Keywords: Sr segregation, Density Functional Theory, LSF

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### DEFECT INDUCED 3D TOPOLOGICAL INSULATORS FROM FRIST-PRINCIPLES

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In the past few years, it has been realized that 3D systems exhibit topological phases supported by topologically protected states appearing at their surfaces in the absence of an external magnetic field. The topological phases occur only in certain materials with a bulk bandgap and a band inversion generated by strong spin-orbit coupling (SOC). These materials are known as non-trivial topological insulators (TIs). In the present work, we have studied two classes of TIs classified based on their band inversion:  $\alpha$ -Ag<sub>2</sub>Te (s-p type) and Bi<sub>2</sub>Se<sub>3</sub> (p-p type) [1]. These materials have many intriguing technological applications in spintronics [2], quantum computing [3], magnetic and optoelectronic devices [4], etc. Since defects are inevitable during their preparation process, it is important for us to study how their electronic properties as well as topological properties get affected when defects are induced in the pristine systems. From first-principles calculations under Density functional theory (DFT) and using Wanniertools based on the tight-binding model, we presented the evidence of conducting surface states forming 2D Dirac cones at time-reversal invariant momenta (TRIM). We observed that Ag-site and Se-site are favorable for defects in  $\alpha$ -Ag<sub>2</sub>Te and Bi<sub>2</sub>Se<sub>3</sub> respectively. Moreover, among two types of TI,  $\alpha$ -Ag<sub>2</sub>Te having vacancy at Ag-site fulfills the three non-trivial topological criteria. In Bi<sub>2</sub>Se<sub>3</sub>, only two calculations show topological behavior when we create a vacancy at Se-site. In addition to that, we have also shown that both pristine and Ag-site defected  $\alpha$ -Ag<sub>2</sub>Te systems are dynamically stable through Phonopy calculations. Thus,  $\alpha$ -Ag<sub>2</sub>Te (s-p type) is a more promising candidate for TI than Bi<sub>2</sub>Se<sub>3</sub> (p-p type) under defects.

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Keywords: Topological insulators (TIs), Spin-orbit coupling (SOC), First-principles, Defects, Surface states.

## SolarUP: Advanced Strategies for Development of Sustainable Semiconductors for Scalable Solar Cell Applications

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The call for clean and sustainable energy sources has never been louder. Meeting the everincreasing global energy demands, while at the same time drastically reducing carbon emissions from the over reliance on and usage of fossil fuels remains one of the most critical challenges for humankind in the 21st century. The market needs an innovative alternative, one that is not only commercially competitive, but also in line with social values of sustainability, circularity, and responsibility. *SolarUp* aims to demonstrate an ultra-thin nano-structured solar cell based on zinc phosphide (Zn2P3) with unprecedented conversion efficiencies [1,2]. Zinc phosphide is an earthabundant, direct bandgap semiconductor with the potential to bridge the gap between efficiency, scalability, and recyclability, providing a breakthrough technological solution that can revolutionize modern PV [3]. The *SolarUp* project brings together researchers from all over Europe to tackle this problem from various perspectives, including Prof. Silvana Botti's group in Bochum to run extensive, high-throughput computations based on Density Functional Theory and Machine Learning Models to understand not only the fundamental properties of zinc phosphide, but to further identify promising dopants, interfaces, and solar cell architectures.

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Keywords: earth-abundant semiconductors, ab initio, zinc phosphide thin films, photovoltaics