

Workshop on electron-phonon interaction and its effects in condensed matter and reduced dimensionality systems

22-24 May 2018 – Louvain-la-Neuve, Belgium

ETSF - electron-phonon collaboration team



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Program

Tuesday 22 nd May	Wednesday 23 rd May	Thursday 24 th May
	8.30 Welcome	8.30 Welcome
	Theory / Methods	Spectroscopy
	9.00 Walter Lambrecht	9.00 Xavier Gonze
	9.30 Marios Zacharias	9.20 Pedro Melo
	9.50 Sven Reichardt	9.40 Henrique Miranda
	10.10 Yaroslav Pavlyukh	10.00 Discussion
	10.30 Coffee break	10.30 Coffee break
	11.00 Gabriel Antonius	11.00 Carla Verdi
	11.30 Hardy Gross	11.20 Fulvio Paleari
	11.50 Discussion	11.40 Discussion
13.30 Welcome	12.30 Lunch	
Materials	Phonon interactions	
14.00 Matteo Calandra	14.00 Francesco Mauri	
14.30 Anna Miglio	14.30 Matthieu Verstraete	
14.50 Jean-Paul Nery	Software	
15.10 Discussion	14.50 Christian Carbogno	
15.30 Coffee break	15.10 Matteo Giantomassi	
16.00 Pasquale Pavone	15.30 Discussion	
16.20 Michel Côté	15.50 Coffee break	
16.40 Fabio Caruso	Transport	
17.00 Discussion	16.20 Nicola Bonini	
17.20 Discussion : Open issues ?	16.40 Alejandro Molina	
	17.00 Samuel Poncé	
	17.20 Discussion	
	18.30 Social dinner	

(Tuesday PM)

Exchange Enhancement of the Electron-Phonon Interaction in low dimensional systems

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The effect of the exchange interaction on the vibrational properties and on the electron-phonon coupling were investigated in several recent works. In most of the case, exchange tends to enhance the electron-phonon interaction, although the motivations for such behaviour are not completely understood. In this talk I will consider the class of weakly doped two-dimensional multivalley semiconductors and I will show that in these systems, at low enough doping, even a moderate electron-electron interaction enhances the response to any perturbation inducing a valley polarization. If the valley polarization is due to the electron-phonon coupling, the electron-electron interaction results in an enhancement of the superconducting critical temperature. I will demonstrate the applicability of the theory by performing random phase approximation and first principles calculations in transition metal chloronitrides. I will show that exchange is responsible for the enhancement of the superconducting critical temperature in Li_xZrNCl and that much larger T_c s could be obtained in intercalated HfNCl if the synthesis of cleaner samples could remove the Anderson insulating state competing with superconductivity[1, 2, 3, 4]. Finally, I will show that in the low dimensional transition-metal dichalcogenide TiSe_2 , the inclusion of the exchange interaction is the key to achieve a simultaneous description of the electronic structure and of the vibrational properties in the charge density wave phase[5].

Coworkers: B. Pamuk, M. Hellgren, J. Baima, F. Mauri and L. Wirtz

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(Tuesday PM)

Temperature dependence and zero-point renormalization in a test set of binary oxides

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Vibrational effects and electron-phonon coupling have a significant impact on the properties of materials, in particular for those containing light atoms. Nowadays, these effects can be computed from first-principles.

Among the various approaches, we used density-functional perturbation theory (DFPT) and the Allen-Heine-Cardona (AHC) approach in the non-adiabatic harmonic approximation [1, 2]. We consider a dozen of binary oxides. We compute the zero-point renormalization and temperature dependence of the band gap, valence and conduction band extrema within the AHC theory and compare the results with those obtained with a model based on the Fröhlich Hamiltonian.

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(Tuesday PM)

ETSF Workshop May 2018

Temperature-dependence of the (222) X-ray forbidden reflection in silicon

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May, 2018

Abstract

Crystals with an *fcc* lattice like silicon have Bragg scattering at $\mathbf{K} = 2\pi(h, k, l)/a$ for integers hkl all even or all odd. The two-atom basis of the diamond structure causes destructive interference whenever $h + k + l$ is an odd multiple of 2; for example, the (222) reflection is nominally forbidden. However, there is not total interference because of tetrahedral rather than spherical scattering symmetry. Such asymmetry arises from anharmonic vibrations and from bonding. Therefore, the weakly allowed (222) X-ray reflection in silicon is useful for studying bond charge. Temperature variation of the (222) X-ray intensity has been measured [1] and studied [1,2] beyond that expected from anharmonicity. Previous theories have been somewhat ad hoc, not dealing fully with electron-phonon induced valence charge density thermal shifts. Namely, the valence charge was assumed to vibrate rigidly around the mid-point of the ions, and Debye-Waller (DW) factors were used. Here we obtain a full second-order perturbation theory expression for the change of the charge density with temperature, and use it to study the forbidden reflection in silicon. An acoustic sum rule is used to express the DW-type term in terms of Fan-type terms to simplify numerical calculations.

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*Jean Paul Nery acknowledges support of the European Union by the core2 phase of the graphene flagship. Philip B. Allen acknowledges support from DOE grant number DE-FG-02-08ER46550.

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(Tuesday PM)

***Ab-initio* lattice dynamics of Ga₂O₃ polymorphs
with an emphasis on polar phonon modes**

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Germany

Gallium oxide is a promising material for novel electronic devices, due to its large band gap and its remarkable high carrier mobilities. Understanding electron-phonon interaction is essential for describing its transport properties. In this work, we perform a comparative study of the lattice dynamics of the two most stable polymorphs of Ga₂O₃, the α and β phase, using density-functional theory and density-functional perturbation theory. We include non-analytical contributions to the dynamical matrix which allow for the full description of polar phonon modes. For these modes at the zone-center we give a detailed discussion of the atomic displacements and analyze their IR-response and LO/TO-splitting. We calculate the Born effective charges, high frequency dielectric tensors as well as the full phonon dispersions and, the corresponding phonon projected density of states. Furthermore, we investigate which modes have the strongest impact on the electronic structure by calculating mode effective charges and average long-range coupling constants.

Influence of electron-phonon coupling on the pressure-induced topological phase transition in BiTeI

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Topological phase transitions are closely related to the bulk electronic bandstructure, which varies with temperature. This variation is a consequence of electron-phonon interactions, which induce a shift in the electronic band energies that may promote or suppress the topologically non-trivial phase.[1, 2] When studying tunable topological phase transitions in real materials, the value of the critical parameter may therefore change with temperature.[3] Understanding the effect of temperature on these phase transitions is thus crucial in designing real devices intended to work in various conditions. We investigate the temperature dependence of the pressure-induced topological phase transition in three-dimensional crystalline BiTeI[4] through first principles methods. We compute the electron-phonon coupling and the electronic bandstructure using density functional perturbation theory (DFPT). We also study the behavior of the narrow intermediate Weyl semimetal phase that has been theoretically predicted for this material, to evaluate if it could be observed experimentally.

References

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(Tuesday PM)

Temperature-dependent effective-mass renormalization in SnSe.

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Based on the many-body theory of the electron-phonon interaction, we investigate the influence of temperature on the electronic structure of SnSe, a promising thermoelectric material. First-principles calculations of the angle-resolved photoemission spectrum reveal a pronounced dependence on temperature, which results from the thermal excitation of soft polar modes and manifests itself through a fivefold increase in the electron linewidths in range between 0 and 600 K. Our study further suggests that the interplay of lattice anharmonicity and electron-phonon coupling underpins a highly-anisotropic renormalization of the hole effective mass by up to 20%.

LATTICE POLARIZATION EFFECTS ON W IN THE GW APPROXIMATION

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The macroscopic dielectric constant enters the screened Coulomb interaction W of the GW theory in the limit $\mathbf{q} \rightarrow 0$ which provides an integrable divergent term to the self-energy. One may thus include the effects of the lattice relaxation on this term by replacing the electronic-only dielectric function by the one including the lattice polarization effects. This leads to a lattice-polarization correction to GW first introduced by Botti and Marques.[1] However, the question of how to take the limit $\mathbf{q} \rightarrow 0$ remained unclear as well as how this approach fits into the more general approaches to the electron-phonon coupling renormalization of the gap. Recognizing that it amounts to the long-range Fröhlich coupling term, we show that the \mathbf{q} -region over which the correction applies is set by the polaron length-scale. We apply the approach to strongly ionic materials, MgO, NaCl, etc.[2] as well as SrTiO₃ [3] and show that consistent results are obtained in the simple polaronic model and the thus renormalized Botti-Marques approach. Finally, we discuss how these corrections compare with those due to missing electron-hole interactions in the screening.

References

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(Wednesday AM)

Temperature-dependent optical spectra and band structures using the special configuration method

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The calculation of the electronic and optical properties of solids is usually performed by describing the nuclei as classical particles clamped to their equilibrium positions. This approximation inevitably misses the dependence of electronic and optical properties on temperature, quantum zero-point effects, and phonon-assisted optical processes [1]. Recently we introduced a new methodology to incorporate these effects in electronic structure calculations by describing the nuclear thermal motion via a single atomistic configuration in a supercell geometry [2]. Using this method, a single calculation is able to capture the temperature-dependent band-gap renormalization including quantum nuclear effects in direct-gap and indirect-gap semiconductors, as well as phonon-assisted optical absorption in indirect-gap semiconductors. In this talk I will develop the theory of this ‘one-shot’ method, I will show how it can be derived rigorously from the Williams-Lax theory of temperature-dependent electronic transitions [3], and I will prove that the method becomes exact in the thermodynamic limit of an extended system. I will discuss a few recent examples of calculations that have been performed using this new technique, including phonon-assisted optical absorption and complete temperature-dependent band structures. I will also discuss how our special configuration represents a classical analogue of the quantum nuclear wavefunction, and is closely related to the quantum-classical analogy in the path-integral formalism. Since this method is agnostic to the underlying electronic structure method, it might represent an ideal tool for calculating temperature-dependent optical properties using high-level theories such as GW and Bethe-Salpeter approaches, and it holds promise for high-throughput calculations of electronic and optical properties at finite temperature.

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(Wednesday AM)

Many-Body Perturbation Theory Approach to Raman Spectroscopy, Phonons, and Electron-Phonon Interaction

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We present a novel and general, correlation function-based approach for the calculation of Raman scattering rates that can potentially also be applied to ultra-fast Raman spectroscopy out of equilibrium. [1] Besides these theoretical developments, we present concrete computational recipes for the calculation of Raman intensities that allow the inclusion of both excitonic effects and non-adiabatic effects of lattice vibrations, which is not possible with current state-of-the-art methods. Additionally, we present a novel theoretical approach for the calculation of phonon frequencies and the screened electron-phonon coupling based on electronic correlation functions only. [1] Our method has the potential to pave the way for the efficient computation of phonon-related quantities in systems with strong correlation effects such as Kohn anomalies (e.g., graphene) or Peierls instabilities. To illustrate the power and flexibility of our approach we also present results of calculations of the laser- and Fermi-energy dependence of the one-phonon Raman intensity of graphene [2], which also illustrate the importance of non-resonant electronic transitions in Raman scattering and quantum interference effects. The latter have also recently been shown to be important in other two-dimensional materials of current interest. [3]

References

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Nonlinear electron-boson coupling

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(Wednesday AM)

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Electron-boson (e-b) Hamiltonians are ubiquitous in particle, condensed matter physics and optics [1, 2]. The interaction between electrons and bosons is typically treated linearly in electronic density and bosonic displacement. However, there are cases where nonlinear coupling is comparable in strength or even dominate the first-order e-b interaction (e. g., flexural phonons in graphene [3]). We present a formal derivation of the many-body perturbation theory for a system of electrons and bosons subject to a nonlinear e-b coupling [4] with arbitrary number of bosons scattered. We focus here on a self-consistent theory in terms of *dressed propagators* and generalize the Hedin's equations using the Schwinger technique of functional derivatives. The method leads to an exact derivation of the electronic and bosonic self-energies, expressed in terms of a new family of vertex functions, high order correlators and bosonic and electronic mean-field potentials (Figure 1).

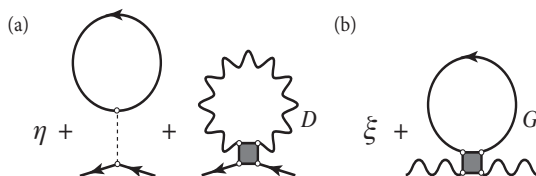


Figure 1: In theories with quadratic e-b interaction, the vertex enters the electronic (a), and the bosonic (b) mean-field potentials. The latter is also known as the Debye-Waller self-energy.

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Interplay between electron-phonon, electron-electron, and electron-hole interactions

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The electron-phonon coupling strength generally gets renormalized by the many-body interactions among electrons, and eventually among electron and holes. While density functional theory accounts for the static screening of the bare electron-phonon coupling potential, it may not describe accurately the effect of exchange and correlation and tends to over-screen the perturbation. The GW formalism, however, is known to enhance the electron-phonon coupling strength due to exchange and correlation effects, in better agreement with experiments [1, 2, 3]. So far, its application to electron-phonon interactions has been limited to frozen-phonon calculations. We present a linear-response implementation of the GW formalism designed to correct electron-phonon coupling matrix elements, and show its equivalence to the frozen-phonon approach.

In the second part of this talk, we discuss the effect of electron-hole interactions on the electron-phonon coupling for bound excitonic states. We show that the coupling strengths must be computed in the exciton basis and that the exciton binding energies must be accounted for, in order to describe the phonon scattering time of the excitons [4].

References

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(Wednesday AM)

**Nuclear velocity perturbation theory within the exact factorization:
A new way of treating non-adiabatic effects**

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The starting point of essentially all modern electronic-structure techniques is the Born-Oppenheimer (BO) approximation. It not only makes calculations feasible, the motion of nuclear wave packets on the lowest BO potential energy surface often provides us with an intuitive picture of chemical reactions. To go beyond this limit is notoriously difficult. Here we present a novel approach to non-adiabatic effects that is based on the exact factorization [1] of the full electron-nuclear wave function into a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The variational principle leads to two equations of motion., one for the nuclear wave function and one for the electronic conditional amplitude. The equation for the nuclear factor is a standard Schrödinger equation which describes the molecular motion – formally exactly- on a single time-dependent potential energy surface. When there is a splitting of the nuclear wave packet in the vicinity of an avoided crossing of BO surfaces, this exact time-dependent surface shows a nearly discontinuous step [2] connecting different BO surfaces, thus incorporating the influence of multiple adiabatic surfaces. The electronic equation of motion is not a standard Schrödinger equation: In addition to the usual BO Hamiltonian it contains terms which are non-linear, non-local and non-Hermitian. These terms are responsible for the proper description of decoherence [3,4]. Here we treat these additional terms by perturbation theory, the small parameter turns out to be the nuclear velocity (in the classical limit). This provides a successful description of electronic flux densities [5] and vibrational circular dichroism [6]. Furthermore, we use the approach to deduce an ab-initio electron-phonon interaction, and we explore the possibility of describing non-adiabatic effects in, e.g., proton transfer by R-dependent nuclear masses [7].

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(Wednesday PM)

Anharmonic phonons and second-order phase-transitions by the stochastic self-consistent harmonic approximation

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Anharmonic effects can generally be treated within perturbation theory. Such an approach breaks down when the harmonic solution is dynamically unstable or when the anharmonic corrections of the phonon energies are larger than the harmonic frequencies themselves. This situation occurs near lattice-related second-order phase-transitions such as charge-density-wave (CDW) or ferroelectric instabilities or in H-containing materials, where the large zero-point motion of the protons results in a violation of the harmonic approximation. Interestingly, even in these cases, phonons can be observed, measured, and used to model transport properties. In order to treat such cases, we developed a stochastic implementation of the self-consistent harmonic approximation valid to treat anharmonicity in the nonperturbative regime and to obtain, from first-principles, the structural, thermodynamic and vibrational properties of strongly anharmonic systems [1, 2, 3]. I will present applications to the ferroelectric transitions in SnTe, to the CDW transitions in NbS₂ and NbSe₂ (in bulk and monolayer) and to the hydrogen-bond symmetrization transition in the superconducting hydrogen sulfide system [4, 5, 6], that exhibits the highest T_c reported for any superconductor so far. In all cases we are able to predict the transition temperature (pressure) and the evolution of phonons with temperature (pressure). FM acknowledges support from the European graphene flagship.

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(Wednesday PM)

Competition of lattice and spin excitations in the temperature dependence of spin-wave properties

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The interplay of magnons and phonons can induce strong temperature variations in the magnetic exchange interactions leading to changes in the magnetothermal response. This is a central mechanism in many magnetic phenomena, and in the new field of Spin Caloritronics, which focuses on the combination of heat and spin currents. Boson model systems have previously been developed to describe the magnon-phonon coupling, but almost all reported studies rely on empirical parameters. In this work we propose a first principles approach to describe the dependence of the magnetic exchange integrals on phonon renormalization, leading to changes in the magnon dispersion as a function of temperature. The temperature enters into the spin dynamics (by introducing fluctuations) as well as in the magnetic exchange itself. Depending on the strength of the coupling, these two temperatures may or may not be equilibrated, yielding different regimes. We test our approach in typical and well known ferromagnetic materials: Ni, Fe, and Permalloy. We compare our results to recent experiments on the spin-wave stiffness, and discuss departures from Bloch's law and parabolic dispersion.

(Wednesday PM)

All-Electron, Real-Space Perturbation Theory: Theory, Implementation, and Application within DFT

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Despite the massive progress achieved in the computation of electron-phonon interactions over the last decade [1], two challenges remain: First, applying existing formalisms to large systems is challenging, since achieving the necessary accuracy in Brillouin zone integrals is difficult [2]. Second, *anharmonic* effects are not accounted for in *harmonic* perturbational approaches. To overcome these limitations, we have developed a real-space formulation of perturbation theory within the all-electron, numeric atomic orbitals based code FHI-aims [3, 4]. We discuss the fundamental theoretical framework and the details of the implementation that give us access to *all* responses within the *full* Brillouin zone at once. Furthermore, we demonstrate how this approach can be combined with *ab initio* molecular dynamics simulations so to fully account for *anharmonic* effects. By this means, we are able to obtain accurate anharmonic Raman spectra for two polymorphs of the paracetamol crystal [4]. Eventually, we discuss how this strategy can be applied to phonon-phonon couplings to obtain accurate thermal conductivities for strongly anharmonic materials [5].

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(Wednesday PM)

Automating electron-phonon calculations: challenges and perspectives

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The field of high-throughput ab-initio materials modeling has been raising considerable interest in the last decade. Nowadays high-throughput techniques are routinely used to screen and optimize for desired properties as well as create large databases for data mining applications.

High-throughput computations including electron-phonon (EPH) interaction are still challenging due to the much larger computational cost compared to standard DFT calculations. Still EPH coupling plays a key role for many physical phenomena in solids and nanostructures. Automatized algorithms for setting up the calculations and determining convergence parameters would be highly beneficial to guide both experiments and further calculations.

In this talk I will discuss some of the challenges associated with ab initio calculations in a high-throughput framework as well as the techniques employed in our recent works to automate DFPT [1] and *GW* calculations [2].

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(Wednesday PM)

Magneto-transport coefficients in p-doped diamond from the solution of the Boltzmann transport equation

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We present a first-principles study of the magneto-transport coefficients in p-doped diamond via the exact solution of the linearised Boltzmann transport equation. The electronic and vibrational properties of diamond, including electron-phonon and phonon-phonon interactions, are obtained from density functional theory and density functional perturbation theory, and carriers scattering rates are computed using standard perturbation theory. We also exploit Wannier interpolation (both for electronic bands and electron-phonon matrix elements) for an efficient sampling of the Brillouin zone. This approach gives results in good agreement with the experimental data for the Hall and drift mobilities, the low- and high-field magnetoresistance and the Seebeck coefficient, including the phonon drag effect. In particular, our results provide a detailed characterisation of the exceptionally high values for both the mobility and the Seebeck coefficient, and predict to what extent these properties can be affected by doping, temperature, and magnetic fields.

(Wednesday PM)

Ultrafast carrier dynamics in 2D materials driven by electron-phonon interaction

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Single-layer transition metal dichalcogenides such as MoS₂, MoSe₂, WS₂ and WSe₂ are highly attractive 2D materials due to their interesting optical properties. Recent experiments have shown that a circularly polarized laser field can excite electronic transitions in one of the inequivalent K and K' valleys. Such selective valley population corresponds to a pseudospin polarization and can serve as a degree of freedom in a valleytronic device provided that the timescale for its depolarization is sufficiently large. The understanding of the photo-generation and the relaxation mechanisms is thus crucial for the use of these materials in future applications. We have developed an atomistic ab-initio methodology to simulate the valley and spin dynamics in semiconducting 2D materials. We are able to calculate the photogeneration and the subsequent relaxation of the valley polarization by several scattering mechanisms. We focus on the influence of the electron-phonon interaction on the carrier and spin dynamics, and in particular on the intravalley and intervalley scattering of electrons and holes. Finally, we compare with ultrafast spectroscopy techniques such as time-dependent Kerr rotation and circularly polarized pump-probe experiments [1].

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(Wednesday PM)

Predictive calculations of phonon-limited carrier mobilities in semiconductors

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In this talk, we will probe the accuracy limit of *ab initio* calculations of carrier mobilities in silicon, within the framework of the Boltzmann transport equation [1]. In particular, we will show that predictive calculations of electron and hole mobilities require many-body quasiparticle corrections to band structures and electron-phonon matrix elements, the inclusion of spin-orbit coupling, and an extremely fine sampling of inelastic scattering processes in momentum space [2].

Such fine sampling calculation is made possible at an affordable computational cost through the use of efficient Fourier-Wannier interpolation of the electron-phonon matrix elements as implemented in the EPW code [3].

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(Thursday AM)

Quasiparticles and phonon satellites in spectral functions of semiconductors and insulators: Cumulants applied to full first principles theory and Fröhlich polaron.

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The electron-phonon interaction causes thermal and zero-point motion shifts of electron quasiparticle (QP) energies $\epsilon_k(T)$. Other consequences, visible in ARPES experiments, are broadening of QP peaks and appearance of sidebands, contained in the electron spectral function $A(k, \omega)$. Electronic structure codes start to address the shift, broadening and sideband computations.

We consider MgO and LiF, and determine their nonadiabatic Migdal self energy [1]. The spectral function obtained from the Dyson equation makes errors in the weight and energy of the QP peak and the phonon-induced sidebands. Only one phonon satellite appears, with an unphysically large energy difference (larger than the highest phonon energy) with respect to the QP peak. By contrast, the spectral function from a cumulant treatment of the same self energy gives a quite accurate QP energy and several satellites approximately spaced by the LO phonon energy. In particular, the positions of the QP peak and first satellite agree closely with those found for the Fröhlich Hamiltonian by Mishchenko *et al.* [2] using diagrammatic Monte Carlo. We provide a detailed comparison between the first-principles MgO and LiF results and those of the Fröhlich Hamiltonian [1]. Such an analysis applies widely to materials with infrared(IR)-active phonons.

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(Thursday AM)

Electron-phonon interaction effects on photoluminescence and Kerr rotation signals of TMDs

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The interest in properties of TMDs has increased due to the discovery of the coupling between spin and valley degrees of freedom and bright photoluminescence (PL). The theoretical study of the latter has been hindered due to lack of predictive ab initio numerical techniques [1,2,4]. We present a complete theoretical framework for the computation of PL where electrons, nuclei, and photons are quantised. The intrinsic non-equilibrium nature of the process is fully taken into account [3]. Starting from the Keldysh contour, we arrive at a set of equations for the Green's functions of electrons, phonons, and photons. These equations are then simplified by using the generalised Baym-Kadanoff ansatz and the completed collision approximation [3]. This reduces the problem to a set of decoupled equations for the density matrix that describe all kinds of static and dynamical correlations. We show how the micro-macro connection relates the observable spectrum with the time-dependent microscopic dynamics, via the Bethe-Salpeter equation. Finally, we present the results of our numerical studies on 2D materials, such as WS₂ and MoSe₂, where we relate the evolution of the carrier populations due to electron-phonon interaction in the Brillouin zone with the changes in the PL spectrum and Kerr rotation signals of the material.

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(Thursday AM)

First-order resonant Raman intensities of MoS₂ from first-principles

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We investigate the laser-energy dependent Raman intensities of MoS₂ using two different approaches. In the first approach, we calculate the Raman intensities from finite differences of the dielectric susceptibility according to the phonon displacements. In the second, we formulate the Raman tensor in terms of time-dependent perturbation theory and calculate it using electron-photon and electron-phonon coupling matrix elements obtained from density functional theory. We demonstrate that the two approaches are formally and numerically equivalent in the adiabatic limit. The second approach allows to include the phonon dynamical effects and captures the Stokes and anti-Stokes shift with respect to the adiabatic case. This method, which is computationally more efficient, is also extended to include temperature effects with electronic lifetimes calculated from many-body perturbation theory.

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(Thursday AM)

ARPES spectra of doped oxides from first principles: coupling to phonons and plasmons.

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The coupling of electrons to bosonic excitations in solids, such as infrared-active phonons and carrier plasmons, can lead to the formation of polarons, i.e. electrons dressed by a boson cloud. Conducting oxides represent an ideal playground to investigate this phenomenon. In angle-resolved photoemission spectroscopy (ARPES) the signature of polarons is the appearance of spectral satellites below the conduction band. Here we calculate ARPES spectra from first principles by combining *ab initio* calculations of the electron-phonon and electron-plasmon coupling with the cumulant expansion method [1, 2]. For the paradigmatic example anatase TiO₂, we show that the transition from polarons to a weakly-coupled Fermi liquid with increasing doping observed in experiments [3] originates from nonadiabatic polar electron-phonon coupling. We show that a similar mechanism also applies to the ferromagnetic semiconductor EuO, and that this material can host tunable plasmonic polarons.

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(Thursday AM)

Phonon-assisted optical transitions in bulk hexagonal boron nitride from first principles

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The optical response of layered materials such as hexagonal boron nitride (hBN) is usually dominated by the presence of strongly bound excitons. Recent photoluminescence experiments [1, 2], have displayed a low-lying fine structure in the emission spectrum of hBN that is convincingly explained in terms of phonon replicas arising from the recombination of indirect bound electron-hole pairs. Here, we present a finite-difference approach to the computation of the phonon-assisted optical spectrum of bulk hBN. We demonstrate the existence of a Davydov pair of indirect excitons lying 0.1 eV below the direct one. These excitons are dark for the equilibrium geometry of the lattice. However, these states may become optically visible when coupled with the phonon modes with momentum q corresponding to the indirect band gap. In order to quantify this, we compute the second derivative of the dielectric function (including excitonic effects) via a finite-difference method, displacing the atoms within a BN supercell according to the eigenvectors of the corresponding phonon modes of momentum q . Our adiabatic calculations are then corrected by incorporating the phonon frequencies needed to describe single-phonon emission and absorption response functions. We obtain an *ab initio* phonon-assisted optical spectrum with excitonic effects that compares favorably with experimental results. We find that the fine structure seen in experiments results from the contributions of the transverse acoustic mode and all transverse and longitudinal optical modes, which couple with various strengths to the two indirect excitonic states.

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