Double resonant Raman in graphene

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Vibrational Raman spectroscopy is the most widely used experimental technique to characterize carbon materials such as graphene and carbon nanotubes. Raman lines such as the defect-induced D and D', their overtones and the D'+D", are usually interpreted within the double resonance mechanism. These lines are very well studied since they are an experimental probe of the defects but also can be used to count the number of layers in graphene. Several excellent theoretical works already appeared on the topic providing an overall good understanding of the situation. However, the many different approximations used by different authors (e.g. constant electron-phonon matrix elements, resonant phonons are assumed to be on some high symmetry line, in some cases the electronic dispersion is conic, the electronic life-time is a parameter, etc.) and the several debates still going on leave with the unpleasant sensation that something is missing. Besides, some fundamental questions are basically untouched: Which kind of defects are probed by measuring different lines? Does Raman spectroscopy probe the defects which mostly influence electronic transport?

We determined the DR Raman spectra of graphene by using the most precise available electronic bands, phonon dispersions, and electron-phonon coupling matrix elements (obtained by combining ab-initio density functional theory and many-body GW methods). Three different model defects are considered. The method results in a consistent framework to determine the position, the shape, the width and the intensity of the Raman lines as a function of the laser energy and of the defect concentration. Moreover it allows to treat at the same level defect-induced lines and two-phonon lines. The overall agreement with available experimental data is very good.

Tuning the Kohn Anomaly in the Phonon Dispersion of Graphene by Interaction with the Substrate and by Doping

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The phonon dispersion of graphene displays two strong Kohn Anomalies (kinks) in the highest optical branch (HOB) at the high-symmetry points Γ and K [1]. The slope of the HOB around K is a measure of the electron-phonon coupling (EPC) and determines the dispersion of the Raman D and 2D lines as a function of the laser energy. We show that the EPC can be strongly modified both due to interaction with the substrate (in particular, if the substrate is metallic) and due to doping.

For graphene grown on a Ni(111) surface, a total suppression of the Kohn anomaly occurs: the HOB around K becomes completely flat. This is due to the strong hybridization of the graphene π-bands with the Nickel d-bands which lifts the linear crossing of the π-bands at K. For other metallic substrates, where the distance between the graphene sheet and the substrate is larger, hybridization is much less pronounced and the Kohn anomaly is only weakly perturbed. From experimental phonon dispersions one can therefore draw conclusions about the interaction strength between graphene and its different substrates [2].

Furthermore, we present a new way to tune the EPC in graphene through electron/hole doping. Calculations of EPC on the level of density-functional theory with a (semi-)local exchange-correlation functional (like LDA or GGA) predict that the EPC is almost independent of the charge state. Taking electron-electron correlation into account on the level of the GW-approximation [3], we show that for the highest optical branch at K, the EPC is strongly dependent on the doping level. This dependency influences the dispersion of the Raman D and 2D lines and makes it possible to measure the charge state of graphene via resonant Raman spectroscopy. Moreover, in multi-layer graphene it will affect the splitting of the 2D peak. Finally, this doping dependence opens the possibility to construct tunable electron devices through the external control of the electron-phonon coupling.

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Ab initio study of bilayer graphene: from electronic structure properties to Raman spectra

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The recent discovery that the application of an external electric field induces a band gap opening in bilayer graphene attracted a lot of interest on this system, due to important applications in nanoelectronics. Most of the theoretical studies on this system are performed using a Tight Binding (TB) model. In the first part of this talk I will present ab initio results on the electronic structure properties of gated bilayer graphene compared to TB results, which allowed us to identify important différences between the two methods. Then, I will focus on the vibrational properties of bilayer graphene. In particular, I will show how information on the band gap can be obtained by comparing experimental Raman spectra and our theoretical Raman spectra, computed using TB model fitted on ab initio calculations.

As resonant Raman spectroscopy is one of the main experimental techniques for the characterization of few-layers metallic systems, the development of a fully ab initio technique to calculate double resonant raman spectra is highly desirable.This is particularly relevant in systems where a simple tight binding parametrization of the electronic structure and of the electron-phonon interaction is not available.

In the second part of the talk, I will discuss this recently developed methodology and I will present preliminary results on monolayer and bilayer graphene.

Ultrafast quantum dynamics of exciton dissociation at organic semiconductor junctions

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The photophysics of extended systems like conjugated polymers or molecular aggregates is characterized on the one hand by the properties of the molecular building blocks and on the other hand by the delocalized nature of the electronic excitations, i.e., the formation of excitonic states. The dynamical phenomena induced by photoexcitation therefore involve an interplay of site-site interactions entailing excitation energy transfer (EET), and vibronic (electron-phonon) coupling which typically leads to ultrafast internal conversion and charge transfer processes. We propose here a molecular-level, quantum-dynamical approach as exemplified by our recent study of exciton dissociation at interfaces of semiconducting polymer phases (so-called heterojunctions) [1]. This study combines a vibronic coupling model parametrized for several relevant electronic states and 20-30 phonon modes, with accurate quantum dynamics simulations using the multiconfiguration time-dependent Hartree (MCTDH) method and a Gaussian-based variant thereof (G-MCTDH) [2]. In addition, we employ transformation techniques [1,3] by which a relevant set of effective modes is constructed which account for the short-time dynamics in high-dimensional systems involving conical intersection topologies. This approach has recently been extended to more general system-bath type models, in conjunction with a hierarchical approximation scheme for the spectral density that is tailored to non-Markovian situations [4]. Applications to EET in conjugated polymer chains involve both site-local and site-correlated electron-phonon coupling, and shed some light on recent observations of unexpectedly long-lived coherences in such systems [5]. A perspective is given on the role of static and dynamic conformational disorder.

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Dynamics of electrons and phonons out of equilibrium

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The ultrafast dynamics of a photoexcited system is directly connected to the scattering mechanisms between electrons and the nuclear lattice. As a consequence, the average coupling strength of superconductors can be extracted from the rate of phonon emission during the electronic cooling. We will revise the employment of this technique in order to measure the electron-phonon coupling of an high temperature superconductor. Interestingly, the energy relaxation mechanism gives rise to the generation of non-equilibrium optical phonons. Such non equilibrium phonons may be incoherently or coherently excited. In the latter case, a periodic modulation of the lattice displacement has been observed. An experiment on a charge density wave material, shows that the amplitude of such modulations is proportional to the electron-phonon coupling of a specific mode with a a specific electronic Bloch-function of the solid.

Polaronic effects in semiconductor quantum dots

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The study of the electronic states of self-assembled quantum dots has deserved a lot of interest. Energy levels calculations predict that their electronic states, namely, their low-lying electron, hole and electron/hole (excitons, for brevity) states are organized in a series of discrete levels. This result has almost naturally lead to the description of such structures as isolated entities : the so-called macro-atom scheme. This image, very often invoked in the literature, has gained some support from the observations of a sequence of lines in PLE experiments of either an ensemble of dots or on single dots. The macro-atom scheme is nevertheless completely unsatisfactory to explain the energy relaxation of electrons photoexcited by a far-infrared excitation and of excitons photocreated in an excited dot state. This is due to the fact that the usual image of carriers interacting weakly with optical phonons (like in bulk materials and quantum wells) does not apply in quantum dots.

It is nowadays well established that carriers confined in a quantum dot are in a strong coupling with longitudinal optical phonons and the correct excitations of the system are the polarons. This strong coupling has been clearly evidenced in optical experiments done in doped quantum dots. Additionally, the framework of polarons, other than describing properly the energetics of the dot states, also provides a natural scheme to treat the energy relaxation problem. Indeed, since polaron states are intrications of electronic and phonon states, the bulk-like instability of the phonons modes entering in the formation of the quantum dots polarons plays a fundamental role in their relaxation. These different aspects will be reviewed in this talk.

Phonon scattering in silicon nanowires

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We model the scattering of electrons by phonons in ultimate [110]-oriented silicon nanowires with an atomistic valence force field and tight-binding approach. All electron-phonons interactions are included in the calculations. Using a full resolution of the Boltzmann transport equation, the low-field mobility is calculated and its dependence on the temperature, density of electrons, and size of the nanowires is investigated. We show that, as a result of strong confinement, i) electrons couple to a wide and complex distribution of phonon modes, and ii) the mobility has a non-monotonic variation with wire diameter and is strongly reduced with respect to bulk. Comparing with the effect of charged impurities on the transport, we obtain that, while acceptor- and phonon-limited mobilities can be comparable at room temperature, the electron-phonon coupling is the main source of scattering in n-doped nanowires.

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Ab initio and semi-empirical calculations of electron-phonon interaction in semiconductors and superlattices

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In recent papers [1-3] the ab initio methods are developed to calculate electron - shortwave phonon scattering processes in semiconductors. The perturbation of a crystal potential due to the lattice vibrations is calculated self-consistently within the density functional perturbation theory (DFPT [4]). Intervalley Γ-X and Γ-L phonon-assisted scattering in A^3B^5 semiconductors were investigated. The characteristics of the phonon-induced decay processes of excitons in GaP , GaAs [1,2], Ge and excited states of shallow donors in Si [3] were calculated having a good agreement with experiment. Electron-phonon scattering probabilities are calculated through matrix elements of this perturbation between the Kohn-Sham electronic states.

The comparison with alternative approaches is of interest. We attempted an investigation of electron - shortwave phonon scattering processes basing on a method of empirical pseudopotential. Parameters of atomic pseudopotentials are fitted to reproduce the experimental energies of interband transitions so the single-electron wave-functions should be considered as the reliable approximation to the genuine ones. The phonon-induced perturbation of a crystal potential was approximated by a rigid shift of a pseudopotential formfactor which follows the ions' displacement. Despite the principal difference the two approaches agree well at least for the processes which are actually important in the device applications. It concerns to the scattering between the lowest Γ,X, L valleys of conduction bands in binary semiconductors A^3B^5 [5] as well as for ultrathin ($n+m\leq10$) superlattices $(GaAs)_n(AlAs)_m$ (001) [6].

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Theoretical approaches to the temperature and zero-point motion effects on the electronic band structure of semiconductors

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State of the art *ab initio* calculations of band gaps have attained a level of accuracy at which the discrepancy with respect to experiment is dominated by the neglect of the zero-point motion of the atoms. The thermal and zero-point corrections to the optical spectra of many bulk semiconductors and insulators are calculated at the level of the adiabatic perturbation theory.

A new ab initio formalism based on DFPT is developed and implemented in the ABINIT package. In this new formulation of the theory of the electron-phonon coupling, the first-order wave functions are determined by the Sternheimer equation and are thus not constructed using the unperturbed wave functions as in the sum-over-states approach developped in the litterature by Allen-Heine and Cardona (AHC). In the AHC theory a slow convergence on the number of included states his observed : one must include 2000 states for the correct treatment of H2 and 400 states for silicon. Using the DFPT formalism with only 10 bands yields a decrease in calculation times by a factor of 40 in silicon. This new implementation of the DFPT formalism was tested using the cases studies of diatomic molecules and a wide range of semiconductors and insulators. The results obtained for the diatomic molecules reproduce finite difference calculations up to the numerical error present in the finite difference approach. The procedure reproduces the result of previous semi-empirical studies for silicon but underestimates drastically the electron-phonon coupling in diamond. This is shown to originate from the LDA.

Finally, the finite difference method used in the diatomic molecules permitted the direct evaluation of the validity of the rigid-ion approximation, used in AHC theory and the DFPT formalism developped here, by evaluating the non-site-diagonal Debye-Waller term (NDDW). It was found that this term partially cancels the sum of the site-diagonal Debye-Waller and Fan term. It contributes from 11 % of this sum for CO to 60 % for LiF and is by no means negligible in any of the diatomic molecules considered.

Superconductivity in doped clathrates, diamond, and silicon

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We will review in this presentation some of the experimental and theoretical aspects related to the superconducting transition in column IV doped semiconductors and insulators [1-2], with emphasis on the case of silicon clathrates [3-4], diamond [5-8], and silicon [6,9-10]. Upon sufficient doping, and beyond the so-called insulator-metal transition, doped semiconductors turn into degenerate systems with the Fermi level entering the valence band (in the case of hole-doping). As such, they present metallic properties and the superconducting transition at low temperature is made possible. Beyond existing experimental results, we will present recent predictions [11-13] suggesting that these “covalent metals” may present superconducting transition temperatures equivalent or larger than that of MgB_2.

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Electron-phonon interaction in Fe-based superconductors: what can we learn from DFT?

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In this talk, I will address the problem of the electron-phonon interaction in the recently-discovered Fe-based superconductors,[1] using first-principles calculations. In these systems, obtaining a reliable estimate of the electron-phonon coupling constant is complicated by the proximity of a (mostly) itinerant magnetic phase.[2,3]. In this talk, I will first show and explain early results, based on standard, non-magnetic linear response calculations, which yield extremely low values of the electron-phonon coupling constant, similarly to the cuprates[4]. I will then present more recent results, which explicitely calculate the effect of static magnetic moments and doping.[5]

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Phonons and electron-phonon from Wannier functions

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We present a first-principles approach for the calculation of phonon frequencies and electron-phonon interaction in metals based on a Wannier interpolation scheme. The method relies on the variational properties of the force-constant functional with respect to the first-order perturbation of the electronic charge density and on the localization property of the deformation potential in the Wannier function basis. This new theoretical and computational approach allows the calculation of dynamical properties on ultra-dense mesh of electron and phonon momenta, with negligible computational time/memory with respect to state-of-the-art methods.

We demonstrate the accuracy of the method calculating the phonon dispersions and electron-phonon coupling of MgB2 and CaC6, two of the most important and studied BCS superconductors.
In both compounds we demonstrate the occurrence of several Kohn anomalies, absent in previous calculations, that are manifest only after careful electron and phonon momentum integration and that improve the agreement with the available experiments.