HL 99: Electronic structure theory

Time: Thursday 15:00–17:00   Location: POT 151

HL 99.1 Thu 15:00 POT 151

Time-dependent density functional theory of magneto-optical response of periodic insulators — •IRINA V. LEBEDEVA[1], ILYA V. TOKATLY[1,2], and ANGEL RUBIO[1,3,4] — [1]Nano-bio Spectroscopy Group, Universidad del Pais Vasco, San Sebastian, Spain — [2]IKERBASQUE, Bilbao, Spain — [3]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [4]ETSF

Though the linear response theory has been successfully used for molecular systems for a long time, the extension of this theory to solids is not straightforward since the position operator is ill defined in extended periodic systems. The theoretical description of homogeneous static magnetic field in periodic systems is particularly challenging as the corresponding vector potential breaks the translational invariance of the Hamiltonian. We present a unified approach to calculation of all-order response to arbitrary electromagnetic fields both for periodic and molecular systems within the formalism of non-equilibrium Green functions. The approach is applied to derive the expression for the magneto-optical response of insulating solids in the approximation of non-interacting electrons. The formula obtained is completely identical to the expression for molecular systems if the proper position and orbital magnetization operators are chosen. The terms corresponding to changes in the optical response due to the orbital magnetization of Bloch states and due to the modified density of Bloch states in the magnetic field are identified. A computational scheme based on the density matrix-perturbation theory is developed for practical calculations of the magneto-optical response.

HL 99.2 Thu 15:15 POT 151

Predictive GW calculations with pseudopotentials and plane-waves — •JIRI KLIMES and GEORG KRESSE — Faculty of Physics, University of Vienna, Sensengasse 8/12, A-1090 Wien, Austria

The GW approximation is the standard approach to obtain quasiparticle (QP) energies in solid state physics. Despite its wide use, the agreement between values obtained by different implementations is often unsatisfactory, even for the simplest case of G_0W_0@LDA. This is often attributed to the use of pseudopotentials or to the limited size of local basis sets in all-electron codes. Moreover, little attention is usually paid to obtain results that are converged with respect to the size of the basis sets for orbitals and for the response function. Here we derive an analytic formula for the contribution of unoccupied states with high kinetic energies to the QP corrections. This clearly shows the necessity to converge with the number and basis set size for unoccupied states as well as with the basis set size for the response function. It also points to a problem in the current projector-augmented-wave (PAW) GW calculations that originates from the incompleteness of the on-site basis set of partial waves. We show that this issue can be avoided by using norm-conserving PAW partial-waves in the GW calculations. Our results are then in a very good agreement with the values obtained using all-electron FLAPW+lo method, even for the problematic case of ZnO [1].

[1] C. Friedrich, M. C. Müller, and S. Blügel, PRB **83**, 081101(R) (2011); **84**, 039906 (2011).

HL 99.3 Thu 15:30 POT 151

Eigenvalues from Density Functional Theory with exact exchange – chances and limitations — •TOBIAS SCHMIDT and STEPHAN KÜMMEL — University of Bayreuth, Germany

Density Functional Theory (DFT) has become one of the most widely used methods for electronic structure calculations, e.g., for predicting molecular geometries and binding energies. Also DFT eigenvalues are often used for physical predictions, e.g., for band structure studies. However, while functionals such as the Generalized Gradient Approximations can predict electronic binding reasonably, their limitations in band structure prediction are well known. On the other hand it has been reported that exact Kohn-Sham exchange (EXX) yields reasonable band structures, but its binding energy predictions are poor.

We here report a detailed investigation of so called Local Hybrid Functionals (LHFs), which strive to combine full, non-local Fock-exchange with a non-local, compatible correlation functional. We demonstrate that this functional class allows for an improved description of binding properties and an enhanced interpretability of the eigenvalues. However, we also point out that all presently available func-

tionals that incorporate EXX lead to a fundamental imbalance between their accuracy for eigenvalues and for binding energies.

To shed light on this issue we analyze the local multiplicative potential from LHFs, finding that it does not reach the correct form in the limit $|\mathbf{r}| \to \infty$. The potential is affected by the occurrence of nodal planes in the highest occupied KS orbital, and counterintuitively approaches different limits in different directions of space.

HL 99.4 Thu 15:45 POT 151

Energy Curvature of Solids with Fractional Charge in DFT — •VOJTECH VLCEK[1], HELEN EISENBERG[2], GERD STEINLE-NEUMANN[1], LEEOR KRONIK[3], and ROI BAER[2] — [1]Universitat Bayreuth, Germany — [2]Hebrew University, Jerusalem, Israel — [3]Weizmann Institute of Science, Rehovoth, Israel

DFT often does not perform well in terms of prediction of electron removal and addition energies. In exact DFT, the total energy of the system E versus number of electrons N upon addition/removal of a fraction of an electron is a series of linear segments between integer N. At these points the exchange-correlation potential can jump discontinuously by a derivative discontinuity (DD), which contributes to the change of the derivative of E and thus to the fundamental band gap. Without employing ensemble-DFT, commonly used approximations, however, do not satisfy the straight line condition and lack DD. In finite systems, this error is manifested by a curvature of the energy which has been studied extensively over the past decade.

The concept of energy curvature in infinite systems is still under debate. Competing concepts have emerged: 1) curvature was shown to approach zero in the infinite system size limit; 2) the energy per unit cell was shown to have curvature if the electron addition/removal per unit cell is considered. Here we analyze the missing DD by introducing a new measure for the curvature in an infinite periodic system. This allows us to compute the curvature in the thermodynamic limit when only an infinitesimal amount of electronic charge is removed or added to the system.

HL 99.5 Thu 16:00 POT 151

First-principles study of excitonic effects in Raman intensities — •YANNICK GILLET, MATTEO GIANTOMASSI, and XAVIER GONZE — Université catholique de Louvain, Louvain-la-Neuve (Belgium)

A resonance phenomenon appears in the Raman intensity when the exciting light has frequency close to electronic transitions. The theoretical prediction of the frequency-dependent Raman response of crystalline systems has received little attention.

Indeed, many Raman calculations are nowadays done in the static limit (vanishing light frequency), using Density-Functional Theory and Density-Functional Perturbation Theory, thus neglecting excitonic effects. In this work [1], a finite difference method is used to obtain the frequency-dependent Raman intensity of silicon within the Many-Body Perturbation Theory (excitonic effects are included by solving the Bethe-Salpeter equation). Since the convergence with the sampling of the Brillouin Zone is extremely slow, a double-grid technique needs to be used.

Two main conclusions can be drawn from our analysis. First, the double-grid technique permits to obtain well converged results without requiring huge memory and time requirements. Then, excitonic effects are of crucial importance in the resonance part of the Raman spectrum. The inclusion of these excitonic effects in the computations improves the agreement with the experimental data [2] with respect to analogous results obtained within the independent-particle approach.

[1] Y. Gillet, M. Giantomassi, X. Gonze, Phys. Rev. B 88, 094305 (2013). [2] A. Compaan and H. J. Trodahl, Phys. Rev. B 29, 793 (1984).

HL 99.6 Thu 16:15 POT 151

Zero-point motion effect on the bandgap of diamond: validation of codes — •SAMUEL PONCÉ[1], GABRIEL ANTONIUS[2], PAUL BOULANGER[3], ELENA CANNUCCIA[4], ANDREA MARINI[5], MICHEL CÔTÉ[2], and XAVIER GONZE[1] — [1]UCL, 1348 LLN, Belgium — [2]UMontréal, C.P. 6128, Montréal, Canada — [3]Institut Néel, BP 166, 38042 Grenoble, France — [4]ILL, BP 156 38042 Grenoble, France — [5]CNR, CP 10, Mont. Stazione, Italy

Verification and validation of codes, as well as new theoretical meth-

ods, are of utmost importance if one wants to provide reliable results.

In this work we present a rigorous and careful study of all the quantities that enters into the calculation of the zero-point motion renormalization of the direct band gap of diamond due to electron-phonon coupling. This study has been done within the Allen-Heine-Cardona (AHC) formalism as implemented into Abinit and Yambo on top of Quantum Espresso. In this work we aim at quantifying the agreement between the codes for the different quantities of interest. This study shows that one can get less than $10^{-5} Ha/at$ differences on the total energy, 0.07 cm^{-1} on the phonon frequencies, 0.5% on the electron-phonon matrix elements and less than 4 meV on the zero-point motion renormalization.

At the LDA level, the converged direct bandgap renormalization in diamond due to electron-phonon coupling in the AHC formalism is -409 meV (reduction of the bandgap)[1].

[1] S. Poncé *et al.*, arXiv:1309.0729 [cond-mat.mtrl-sci] and submitted for publication in Comput. Mat. Science (2013).

HL 99.7   Thu 16:30   POT 151

Wavefunction localisation and acceptor ionisation in Ga$_{1-x}$Mn$_x$As, an electronic structure perspective — ●Jerome Jackson and Gabriel Bester — Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany.

The Mn acceptor level in GaMnAs, although it has a binding energy well beyond that of a simple effective-mass impurity, is nevertheless weakly localized and has considerable valence band character. We discuss critically the ability of density functional theory methods to correctly reproduce the acceptor level localization, in direct contrast to clear experimental evidence (photoluminescence and tunneling experiments) for discrete Mn acceptor levels in the dilute limit. Using a non-selfconsistent wavefunction based approach, relying upon the essentially shortranged nature of the Mn defect potential, we are able to study the localization behavior of the acceptor wavefunction and apply corrections (in agreement with previous tight binding results) which improve upon the density functional description. We identify the principle problem with such calculations as being a poor description of the important $sp - d$ coupling, distinct from the problem of the deep Mn d state position. By calculating the screened Coulomb integrals between the defect states and the host bands and using a configuration-interaction method we are able to explicitly model the acceptor level ionization, illustrating the fundamentally many-body nature of such processes.

HL 99.8   Thu 16:45   POT 151

Origin of electronic subgap states in amorphous semiconductor oxides on the example of In-Ga-Zn-O (IGZO) — Wolfgang Körner, ●Daniel Urban, and Christian Elsässer — Fraunhofer IWM, Freiburg, Germany

A density-functional-theory study of amorphous In-Ga-Zn-O (IGZO) with focus on the use as transparent conducting oxide is presented [1]. We studied stoichiometric and oxygen-poor amorphous IGZO samples concerning their electronic properties and compared the results to those for crystalline IGZO. Subgap states in the electronic density of states of amorphous IGZO due to imperfections are calculated by means of the LDA and with a self-interaction-correction (SIC). In our study we relate the electronic subgap states, which were observed recently by Nomura et al. [2] to structural features of the amorphous samples. According to our analysis the valence band tail, caused by the disordered O 2p orbitals, is superimposed by deep defect states above the valence band which can be assigned to undercoordinated O atoms. Our interpretation is further supported by the observation that additional H suppresses these states by creating O-H bonds. This hydrogen doping improves the transparency and is consistent with experimental findings [2]. The deep levels below the conduction band arise mainly from miscoordinated metal atoms, mostly In–Zn pairs. By addition of O, i.e., by oxygen annealing, the frequency of such defect levels can be reduced.

[1] W. Körner, D. F. Urban and C. Elsässer, J. Appl. Phys. 114, 163704 (2013). [2] K. Nomura et al., J. Appl.Phys. 109, 073726 (2011).