O 46: Density functional theory and beyond for real materials I

Time: Wednesday 10:30–13:15   Location: H34

O 46.1   Wed 10:30   H34

Structure and magnetism of clean and decorated grain boundaries in nickel — MONIKA VŠIANSKÁ[1,2] and •MOJMÍR ŠOB[1,2] — [1]Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic — [2]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic

With the help of density-functional theory, we have studied the structure and magnetism of the $\Sigma 5(210)$ grain boundary (GB) in nickel as well as segregation and embrittling potency of sp-elements in the 3rd, 4th and 5th period (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) at this GB. For comparison, segregation of these impurities at the (210) free surface (FS) has also been investigated. Full relaxation of the geometric configuration of the GB and FS without and with impurities has been performed and the effect of impurities on the distribution of magnetic moments has been analysed. We determined the embrittling potency energy from the difference between the GB and FS binding energies on the basis of the Rice-Wang model; here a positive/negative value of this quantity means that the solute atom has the embrittling/strengthening effect on the GB. It turns out that all substitutionally segregated impurities studied are GB embrittlers in Ni.

O 46.2   Wed 10:45   H34

Electron Correlation and the Ferromagnetic Behaviour of Chromium Oxide — •MALLIA GIUSEPPE[1], JOHN DRAIN[1], and NICHOLAS M. HARRISON[1,2] — [1]Imperial College London - Thomas Young Centre - Chemistry Department, London UK — [2]STFC, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

One might expect that the half-metallic ferromagnet CrO2 would provide an excellent spin injection material for use in spintronics applications. In practice this is not the case. CrO2 was first predicted to be a half-metallic ferromagnet on the basis of density functional theory calculations (Schwarz 1986). In the current work a more reliable treatment of electronic correlation that includes strong on-site Coulomb interactions is used to reexamine the bulk and surface electronic structure. It is demonstrated that strong electron correlation significantly reduces the density of states at the Fermi edge in the bulk phase and is sufficient to open an energy gap at the (110), (100) and (001) surfaces. This data is used to rationalise recent ultraviolet photoemission spectra and point contact Andreev spectroscopy measurements.
K. Schwarz J. Phys: F-Metal Physics 16(9):L211-L215 (1986)

O 46.3   Wed 11:00   H34

Theory of angular resolved X-ray photoelectron spectroscopy in correlated magnetic solids — •JAN MINAR, J. BRAUN, and H. EBERT — Dept. Chemie und Physik, LMU University of Munich, Germany

The combination of local spin density approximation (LSDA) and the dynamical mean field theory (DMFT) provide a powerful basis to treat correlations beyond plain LSDA. The KKR or multiple scattering approach implemented on this basis allows among others to deal with surface systems as well as to study spectroscopic properties [1]. The latter feature is particularly interesting as a direct comparison with experiment reveals the impact of correlation effects unambiguously as matrix element effects are treated on the same level. This is demonstrated by results for the angle-integrated as well as angle-resolved photo emission of transition metal ferromagnets [2]. Special emphasis will be put on the spin-polarised relativistic mode allowing to deal with the spin-orbit coupling induced properties like orbital magnetic moment and magnetic dichroism. Applications of this formalism on the 3d-transition metal surfaces, Heusler alloys and transition metal oxides will be presented.
1. J. Minár et al., Phys. Rev. B 72, 0415125 (2005); S. Chadov et al., Europhys. Lett. 82, 37001 (2008)
2. J. Minar et al., Phys. Rev. Lett. 95, 166401 (2005); J. Braun et al., Phys. Rev. Lett. 97, 227601 (2006); M. Pickel et al., Phys. Rev. Lett. 101, 066402 (2008); J. Sanchez-Barriga et al., arXiv:0910.4360v1 (2009).

O 46.4   Wed 11:15   H34

LDA+DMFT calculations of x-ray absorption and x-ray circular dichroism spectra: Role of valence-band correlations — •ONDREJ SIPR[1], JAN MINAR[2], ANTONIN SIMUNEK[1], and HUBERT EBERT[2] — [1]Institute of Physics AS CR, Cukrovarnicka 10, Prague, Czech Republic — [2]Universitat Munchen, Butenandtstr. 5-13, Munchen, Germany

$L_{2,3}$-edge XAS and XMCD spectra of 3d elements are calculated via a self-consistent LDA+DMFT method (including thus valence-band correlations). It is found that the asymetry of the calculated XAS white lines increases upon inclusion of the correlations for Fe and Co but not for Ni. The change in the height of the L_3 and L_2 peaks in the XMCD spectra is in a good agreement with the change of the orbital magnetic moment caused by adding the valence-band correlations. As a whole, adding valence-band correlations improves the agreement between the theory and experiment but visible differences still remain. Therefore, a core hole is additionally accounted for via the final state approximation and the impact of such a procedure is assessed.

O 46.5   Wed 11:30   H34

A strong correlation study: the paradigmatic case of V_2O_3 — •FEDERICO IORI — Lsi - Ecole Polytechnique,Cnrs -Cea-Iramis Palaiseau, France

Aim of our work is to study through an ab initio theoretical approach the paramagnetic metallic (PM) and insulating (PI) phase of V_2O_3 in order to understand better the metal-insulator phase transition of this system. It has been shown that at DFT level it's not possible to describe properly the insulating paramagnetic phase because of a poor treatment of the strong electronic correlation for such systems with d- or f- incomplete shell within including many body effect such the ones arising from a direct photoemission spectroscopy. Hard x-ray inelastic x-ray scattering in the non resonant regime has indeed proven highly effective to measure low energy losses, especially dd excitations, when operating at high momentum transfer. The dynamical structure factor for PM and PI phase of the V_2O_3 has been thus evaluated through *ab initio* calculations of the loss function for large transferred momenta parallel and perpendicular to the xy plane. Experimental evindence shown in the energy region between 2-3 eV, non dipolar transitions which favor intraband excitations become increasingly allowed while the probing length q^{-1} approaches typical d orbital spatial extension.

O 46.6   Wed 11:45   H34

The calculations of the XANES L edges 3d compounds — •ROBERT LASKOWSKI and PETER BLAHA — Vienna University of Technology, Institute of Materials Chemistry, Vienna, Austria

We report on the calculations of the x-ray absorption near-edge structure spectra focusing on the transition metals L edges. In our approach we solve Bethe-Salpeter equation (BSE) formulated in a basis of single particle states calculated within DFT. The presented method goes beyond the commonly used DFT electron-hole calculations and is an alternative to a relativistic Hartree-Fock configuration interaction method. The DFT core-hole method, cannot reproduce some features of the L edge spectra, usually interpreted as multiplet effects. For example in the single particle approximation, the branching ratio should be proportional to the occupancy of the corresponding core levels, for p3/2 and p1/2 branches it should be close to 2:1. However the measured branching ratio may be quite different, for example for 3d0 cations like K+, Ca 2+, Ti 4+ the p1/2 branch is enhanced such that a ratio closer to 1:1 is observed. We show that this is related to the interaction between elementary excitations from p3/2 and p1/2 core states in the BSE approach. Independent calculations performed for p3/2 and p1/2 branches result in a ratio close to 2:1 and only when the interaction between the p3/2 and p1/2 excitation is included the correct ratio is obtained.

O 46.7   Wed 12:00   H34

Optical Absorption and Bound Excitons in MnO, FeO, CoO, and NiO — •CLAUDIA RÖDL, FRANK FUCHS, and FRIEDHELM BECHSTEDT — Institut für Festkörpertheorie und -optik and European Theoretical Spectroscopy Facility (ETSF), Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

Since magnetic materials gain more and more importance also for technological applications, we calculate the optical properties of the row of antiferromagnetic oxides from MnO to NiO from first principles.
We present optical absorption spectra solving the Bethe-Salpeter

equation (BSE), thus including excitonic and local-field effects (LFE). It turns out that the main absorption peaks are due to d-d excitations which are dipole forbidden at the Γ point. It is shown that the influence of LFE is almost vanishing for the materials under investigation, while the electron-hole attraction leads to a significant redistribution of spectral weight to lower energies.

Besides the dipole allowed excitations which contribute to the absorption spectra, also optically forbidden excitations within the fundamental gap occur. The latter are related to Frenkel-like bound excitonic states. These excitons have their origin in transitions between the occupied and empty d states of the transition-metal cations. Due to the separation of the excitonic Hamiltonian into the independent subspaces of spin-allowed and spin-forbidden transitions, they can be split into two groups: excitons which involve a flip of the one-particle spin between valence and conduction bands and excitons without spin flip.

O 46.8 Wed 12:15 H34

CO adsorption on transition metal surfaces applying the random phase approximation — •Laurids Schimka[1], Judith Harl[1], Alessandro Stroppa[2], Andreas Grüneis[1], Martijn Marsman[1], Florian Mittendorfer[1], and Georg Kresse[1] — [1]Faculty of Physics, University of Vienna, Austria — [2]CNR-INFM-CASTI Regional Laboratory, University of L'Aquila, Italy

Most gradient corrected density functionals predict surfaces to be more stable than they are experimentally. This observation would suggest that adsorption energies on surfaces are too small, but the contrary is often found: chemisorption energies are usually overestimated within the generalized gradient approximation. By modifying the gradient correction either the adsorption or the surface energy can be improved, but never both at the same time [1]. We show that a computationally fairly efficient approach, the random phase approximation (RPA) [2] to the correlation energy, yields both: accurate surface and accurate adsorption energies for carbon monoxide (CO) on transition metal surfaces ((111)-Cu,Ru,Rh,Pd,Ag and Pt). In addition and contrary to most semi-local functionals, the RPA predicts in every single case the correct adsorption site of the CO molecule on the surface.

References

[1] Stroppa, A. & Kresse, G. New Journal of Physics 10, 063020 (2008).

[2] Nozieres, P. & Pines, D. Phys. Rev. 111, 442-454 (1958).

O 46.9 Wed 12:30 H34

Time-dependent Kohn-Sham self-interaction correction — •Dirk Hofmann, Thomas Körzdörfer, and Stephan Kümmel — Department of Physics, University of Bayreuth, 95440 Bayreuth

The self-interaction error of commonly used density functionals leads to a number of well-known problems in density functional theory (DFT). A particularly pronounced and practically important one is the serious overestimation of charge transfer in extended molecular systems.

Perdew and Zunger proposed an energy functional to overcome the selfinteraction problem (SIC), but their approach is not unitarily invariant and thus difficult to straightforwardly incorporate into Kohn-Sham theory. It has recently been shown, though, that the unitary invariance problem can systmatically be overcome by employing the generalized optimized effective potential (GOEP) formalism. However, in a time-dependent Kohn-Sham framework self-interaction correction is even more involved. The time-dependent optimized effective potential (TDOEP) equation is very demanding to solve and approximations to the TDOEP are not necessarily reliable.

Here, we extended the GOEP approach to the time-dependent case for a proper treatment of the unitary invariance problem. Furthermore, we implemented and tested this time-dependent Kohn-Sham SIC (TD-SIC) scheme in a real-time Kohn-Sham propagation code. First results indicate that orbital localization improves the stability of the TDSIC scheme, making it a possible candidate for dealing with the problem of charge-transfer excitations.

O 46.10 Wed 12:45 H34

Electronic excitations in nanostructures: an empirical pseudopotential based approach — •Gabriel Bester — Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

In this contribution we will outline the framework, based on empirical pseudopotentials and configuration interaction [1], to obtain quantitative predictions of the excited state properties of semiconductor nanostructures using their experimental sizes, compositions and shapes. The methodology can be used to describe colloidal nanostructure of few hundred atoms all the way to epitaxial structures requiring millions of atoms. The aim is to fill the gap existing between *ab initio* approaches and continuum descriptions. Based on the pseudopotential idea and the developments of empirical pseudopotentials for bulk materials in the early 60's, the method has evolved into a powerful tool, where the pseudopotential construction has lost some of its empirical character and is now based on density functional theory. We will present the construction of these potentials and the way the ensuing wave functions are used in a subsequent configuration interaction treatment of the excitation. We will illustrate the available capabilities by recent applications of the methodology to unveil new effects in the optics of nanostructures. We will close by an outlook on some envisionned improvements of the method.

[1] G. Bester, J. Phys.: Condens. Matter.**21** 023202 (2009).

O 46.11 Wed 13:00 H34

Time dependent hybrid density functional calculations on semiconductor nanocrystallites — Marton Voros and •Adam Gali — Budapest University of Technology and Economics

Recent technological developments allow the preparation of nanometer sized semiconductor nanocrystals [1-2]. Due to the small size, these nanocrystals exhibit several special features [2-4], therefore understanding the electronic and optical properties at the molecular level is crucial for applications. We show that by using a hybrid functional based TDDFT approach the calculated absorption spectrum of small diamond nanocrystals (diamondoids) near quantitatively agrees with recent experiments [5-6]. We show that Rydberg transititions rule the low energy part of the absorption spectra even in relatively large diamondoids [6] which is not common in other group IV type semiconductor nanocrystals. This property makes it computationally hard to get a well-converged result using supercell based methods. Applying the same technique we show that the low energy part of the absorption spectrum of biologically inert silicon carbide nanocrystals strongly depends on the actual type of surface reconstruction. This would allow the identification of surface reconstruction by comparing the experimental and calculated absorption spectra.

[1] J. E. Dahl et al., Science 299, 96 (2003) [2] X. L. Wu et al., Phys. Rev. Lett. 94, 026102 (2005) [3] Jiyang Fan et al., Small 4, No. 8, 1058 (2008) [4] W. L. Yang et al., Science 316, 1460 (2007) [5] Lasse Landt et al., Phys. Rev. Lett. 103, 047402 (2009) [6] Márton Vörös and Adam Gali, Phys. Rev. B 80, 161411(R)(2009)