

EXC!TING Symposium on Excited State Properties of Solids — Abstracts

Mannheim, Germany, May 16–19, 2005

I: Many-Body Perturbation Theory I-1 Tuesday 09:00–09:30

INVITED TALK

Many-Body Perturbation Theory using the Density-Functional concept: a successful combination!

— FABIEN BRUNEVAL,¹ FRANCESCO SOTTILE,¹ VALERIO OLEVANO,¹ RODOLFO DEL SOLE,² AND LUCIA REINING¹ — ¹Laboratoire des Solides Irradiés, École Polytechnique, 91128 Palaiseau, France, ²Istituto Nazionale per la Fisica della Materia e Dipartimento di Fisica dell'Università di Roma "Tor Vergata", Via della Ricerca Scientifica, 00133 Roma, Italy. ► Today, in the framework of solid state physics two main approaches are used to describe ground- and excited state properties of condensed matter: on one side, static ground state density functional theory (DFT) and its time-dependent extension (TDDFT) for the description of excited states; on the other side, Many-Body Perturbation Theory (MBPT), most often used in Hedin's GW approximation for the electron self-energy, or the Bethe-Salpeter equation for the calculation of response functions. Both approaches have led to breakthroughs, but suffer from different shortcomings: MBPT has a relative conceptual clarity, but calculations are in general numerically very demanding; in particular, it is prohibitive to go beyond the GW approximation. DFT-based approaches are in principle computationally more efficient, but, despite recent progress a generally reliable and at the same time very efficient description of exchange-correlation effects has still to be developed for TDDFT. We propose a way to overcome this dilemma, by introducing the density-functional concept into the MBPT equations. This combination leads to a new set of equations for response functions and self-energies that allows one to go straightforwardly beyond the standard approximations (namely GW for the self-energy and RPA or TDLDA for the density-density response). We show results for semiconductors and insulators, considering various types of spectroscopy.

I: Many-Body Perturbation Theory I-2 Tuesday 09:30–09:45

Variational approach to the calculation of the electron-electron (hole-hole) and electron-hole T-matrix

— I. A. NECHAEV (1) AND E. V. CHULKOV (1,2) — ¹Donostia International Physics Center (DIPC), P. de Manuel Lardizabal 4, 20018, San Sebastian, Basque Country, Spain ²Departamento de Física de Materiales, Facultad de Ciencias Químicas, UPV/EHU and Centro Mixto CSIC-UPV/EHU, Apdo. 1072, 20080 San Sebastian, Basque Country, Spain. ► We present a variational solution of the Bethe-Salpeter equation which determines the T-matrix describing multiple scattering both between two electrons or two holes and between an electron and a hole. The solution is obtained within a local approximation. The resulting expression for the T-matrix is similar to that in Hubbard models but contains the local interaction depending on momentum and frequency. By examining the ladder diagrams for irreducible polarizability, a connection between this interaction and the local-field factor is established. A new form of the T-matrix contribution to the electron self-energy is proposed. This form allows one to sum an infinite number of the electron-hole ladder diagrams for the electron self-energy without double counting.

I: Many-Body Perturbation Theory I-3 Tuesday 09:50–10:05

Orbital- and energy-dependent exchange-correlation functionals : molecular dissociation and band gap energy

— X. GONZE (1), M. FUCHS (1,2), Y.-M. NIQUET (1,3) — (1) UCL, Louvain-la-Neuve, Belgium (2) FHI, Berlin, Germany (3) CEA-Grenoble, France. ► Orbital- and energy- dependent functional have raises considerable interest recently, because they are potentially able to overcome limitations of commonly used approximations like the local-density approximation, the generalized-gradient approximation, or hybrid methods (B3LYP), especially in the description of Van der Waals forces, and dissociation of molecules. We show that Density Functional theory within the random-phase approximation (RPA) for the exchange-correlation energy provides a correct description of bond dissociation in H₂ in a spin-restricted Kohn-Sham formalism, i.e. without artificial symmetry breaking. However the RPA dissociation curve displays unphysical repulsion at larger but finite bond lengths. We also calculate the bandgap energy of a solid using the RPA, and find that it is similar to the one obtained from non-renormalized GW calculations, non-self-consistently, i.e. the G₀ W₀ approximation. This provides a well-defined and meaningful interpretation to G₀ W₀ quasiparticle bandgap calculations, but questions the physics behind the renormalization factors in the expression of the bandgap energy.

I: Many-Body Perturbation Theory I-4 Tuesday 10:10–10:25

The role of periodicity for GW calculations within the repeated-slab approach to surfaces

— CHRISTOPH FREYSOLDT (A), PHILIPP EGGERT (A), PATRICK RINKE (A), ARNO SCHINDLMAYR (B), MATTHIAS SCHEFFLER (A) — (a) Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

(b) Forschungszentrum Jülich. ► Many-body perturbation theory in the GW approximation has become a valuable tool for *ab-initio* band structure calculations that are typically in good agreement with photoelectron experiments. Surfaces are often treated in a repeated slab geometry for computational convenience. If no low-order electric multipole moments are present in the slab, the limit of the isolated slab is quickly reached when the slab separation is increased. Within GW, however, multipoles are induced even if the ground state exhibits no dipole which may lead to a slower convergence compared to DFT. We show that certain approximations that are commonly made in GW implementations must be carefully validated in order to capture the physical behaviour of the repeated slabs. Our numerical results give evidence that the periodic arrangement manifests itself noticeably in the bandstructure, which is in agreement with an electrostatic model that incorporates the induced dipole effects. Prospects for practical GW surface calculations are discussed.

II: Magnetism II-1 Tuesday 11:00–11:30

INVITED TALK

Calculation of photo-emission spectra on the basis of a combination of the KKR-method and the DMFT

— H. EBERT (A), J. MINAR (A), L. CHIONCEL (B), M.I. KATSNELSON (B), AND A.I. LICHTENSTEIN (C) — (a) Phys. Chem., University of Munich, Germany (b) University of Nijmegen, Netherlands (a) Phys. Chem., University of Munich, Germany (c) Institute for Theo. Physics, University of Hamburg, Germany. ► The Korringa-Kohn-Rostoker (KKR) or, equivalently, multiple scattering technique, is an extremely flexible band structure method because it gives direct access to the electronic Green's function. This feature is exploited for example when dealing with impurities, disordered alloys or surfaces. In addition this supplies a very reliable and sound basis when dealing with spectroscopic properties. In particular concerning photo-emission a straightforward implementation of the so-called one step model can be achieved. Corresponding calculations of photo-emission spectra have been done in general within the framework of local spin density functional theory (LSDA). Recently, a combination of the KKR-method with dynamical mean field theory (DMFT) has been presented by us, that allows an improved treatment of correlation effects compared with standard LSDA calculations. As it is shown, this development opens the way to corresponding photo-emission calculations. The most important technical aspects of the KKR+DMFT scheme will be presented together with applications to transition metal alloys. This is followed by a description of the KKR-based implementation of the one-step model of photo-emission. Results of corresponding calculations of various types of spectra (spin-resolved, angle-integrated and -resolved, respectively) will be presented and discussed. In addition it will be shown, that the investigation of spin-orbit induced effects as the Fano-effect and magnetic dichroism is possible by using a fully relativistic formulation of our scheme.

II: Magnetism II-2 Tuesday 11:30–11:45

Ab-initio density functional study of the Cr₈ antiferromagnetic ring

— V. BELLINI, A. OLIVIERI AND F. MANGHI — INFN-National Research Center on nanoStructures and bioSystems at Surfaces (S3) and Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via Campi 213/A, I-41100 Modena, Italy. ► Molecular nanomagnets, which show intriguing quantum and critical phenomena, like quantum tunneling of magnetization and coherence properties, have recently attracted much interest as next-generation nanoscale, monodisperse magnets for specialized applications. We are interested here in molecular rings, a subclass of nanomagnets with a cyclic shape and an antiferromagnetic exchange coupling between nearest neighbouring magnetic ions. We present the results obtained by first-principles DFT methods of the ground-state electronic and magnetic properties of the Cr₈ antiferromagnetic ring. By mapping the ab-initio total energies with interacting model Hamiltonians, we report the first ab-initio estimate of the exchange interaction parameters in this molecule, and compare with the ones extracted by thermodynamic and magnetization measurements.

II: Magnetism II-3 Tuesday 11:50–12:05

Second Harmonic Generation in NiO

— G. LEFKIDIS, O. NEY AND W. HÜBNER — Kaiserslautern University of Technology, PO Box 3049, 67653 Kaiserslautern, Germany. ► The discrete intragap states of both the bulk and (001) surface of NiO could be used with a four level ultrafast magnetic switching scenario. For this a tool is needed, both to detect the magnetic state of the sample, and to monitor the process. Second harmonic generation (SHG) is a very well suited tool, for it couples linearly to the antiferromagnetic order, is surface sensitive, and can detect all NiO domains. NiO is modelled as a cluster and its intragap and lowest charge transfer energy levels of the bulk and the (001) surface are obtained with two

ab-initio quantum chemistry methods. The one consists of the single excitation configuration-interaction technique with energy corrections from higher excitations [CIS(D)], and the other from the multiconfigurational complete active space method (MC-CAS). The symmetry analysis of the SHG tensors is made taking into account electric dipole (ED), magnetic dipole (MD) and electric quadrupole (EQ) transitions, both for the bulk and the (001) surface. The various tensor elements are calculated for the undistorted system, and within the frozen phonon approximation.

II: Magnetism II-4 Tuesday 12:10-12:25

Excitation content of one-particle spectral functions in strongly correlated 1D electronic systems — C. LAVALLE¹, M. ARIKAWA², AND A. MURAMATSU¹ — ¹*Institut fuer Theoretische Physik III, Universitaet Stuttgart*, ²*Bergische Universitaet Wuppertal, Fachbereich Physik*. ► Using a newly developed hybrid Monte Carlo algorithm for the nearest-neighbor t-J model in one dimension, we show that charge-spin separation takes place, including antiholons, that were first identified in the supersymmetric inverse squared t-J model. These new excitations with spin S=0 and charge Q=2e, where e is the charge of the electron, are shown to be present not only at the supersymmetric point (J=2t) but also for J = 0.5 t, a value of experimental relevance [1]. The numerically determined excitation content are corroborated at the supersymmetric point on the basis of the Bethe Ansatz solution.

[1] C. Lavallo, M. Arikawa, S. Capponi, F.F. Assaad and A. Muramatsu, Phys. Rev. Lett. 90, 216401 (2003).

III: Poster Session III-1 Tuesday 14:00-15:30

Ab initio nonlinear magneto-optics from a structurally optimized Fe/W(110) surface — TORSTEN ANDERSEN AND WOLFGANG HÜBNER — *Condensed Matter Theory Group, Kaiserslautern University of Technology, Box 3049, D-67653 Kaiserslautern, Germany*. ► The nonlinear magneto-optical response from a structurally optimized W(110) surface with a magnetic Fe overlayer is calculated from first principles. The electronic structure of the ground state is calculated using the full-potential LAPW method with first-order relativistic corrections, and the magneto-optical properties are obtained in the electric dipole approximation. We present results for the magnetic anisotropy energy as well as the nonlinear optical properties, including the susceptibility tensor, intensities in various optical configurations, angular dependences, and the nonlinear optical Kerr effect. We find that both the easy axis as well as the hard axis are in the surface plane, with the easy along the 1-10 direction and the hard axis along the 001 direction. We show how the direction of magnetization changes the magneto-optical properties, as well as how the addition of substrate layers influences the response.

III: Poster Session III-2 Tuesday 14:00-15:30

Excited States of Biphenyl - Consequences for Optical Spectra of Conjugated Polymers — WICHARD J. D. BEENKEN — *University of Vienna, Austria (in 2004, plan to move to Technische Universität Ilmenau, Prof. E. Runge)*. ► Conjugated polymers which contains phenyl or heterocyclic groups are important organic semiconductors mainly used for photo-electronic devices. Therefore, an understanding of their optically excited state is of high interest. However, the quantum-chemical calculation of the potential surfaces is already difficult for the simplest oligomer - biphenyl. We have studied this molecule comparatively by several quantum-chemical methods (ZINDO, TD-DFT, RI-CC2, and CASPT2). We found that the TD-DFT results fit best to the experimental data from IR and VIS spectroscopy, while those from the other methods even contradict them. Using TD-DFT for excited state optimization we could separate torsional and vibrational contributions to the Stokes shift. Based on our results for biphenyl, which demonstrate a strong dependence of the excitation energy on the torsion angle between phenyl rings, we state that it is not a dispersion of the conjugation length but the torsional disorder that determines the inhomogeneous broadening in this class of conjugated polymers. In particular our model may explain the solvent-dependence of the optical spectra.

III: Poster Session III-3 Tuesday 14:00-15:30

Bonds in Motion: The Time-Dependent Electron Localisation Function — T. BURNUS¹, M.A.L. MARQUES¹, M. ERDMANN², V. ENGEL², E.K.U. GROSS¹ — ¹*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*; ²*Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*.

► A time-dependent (TD) generalization of the so-called electron localization function (ELF) is presented. It is derived from the conditional probability of finding an electron in the vicinity of a point r if one knows with certainty that there is another electron with the same spin at r . Movies of the TDELFF allow the *time-resolved* observation of the formation, the modulation, and the breaking of chemical bonds, and can thus provide a visual understanding of the complex dynamics of excited electrons. We illustrate the usefulness of the TDELFF by two examples: A $\pi - \pi^*$ transition in acetylene induced by a laser field, and the destruction of bonds and the formation

of lone-pairs in scattering a high-energy proton from ethylene [1]. Finally, the TDELFF and its analogue for antiparallel spins are analysed in situations where the non-adiabatic coupling between electronic and nuclear motion are important [2].

[1] T. Burnus, M.A.L. Marques, E.K.U. Gross, Phys. Rev. A **71**, 010501 (2005).

[2] M. Erdmann, E.K.U. Gross, V. Engel, J. Chem. Phys. **121**, 9666 (2004).

III: Poster Session III-4 Tuesday 14:00-15:30

Optical and photoelectrical properties of Cd_{1-x}Mn_xTe crystals — IULIANA CARAMAN, GHEORGHE I. RUSU*, LIVIU LEONTIE* — *Bacau University, Calea Marasesti No.157, Bacau 600115, Romania*, **Al. I. Cuza University, Carol Bd No.11, Iasi 6600, Romania*. ► The absorption spectra at the edge of fundamental band and the kinetics of photo conductivity of Cd_{1-x}Mn_xTe (0 ≤ x ≤ 0,15 at 78–300 K have been studied. Mono crystals were grown by Bridgman method. The crystals of Cd_{1-x}Mn_xTe (0 ≤ x ≤ 0,15) have a good accentuate photo conductivity in the domain of fundamental absorption. The red edge of fundamental absorption band at 293 K in crystals with x ≥ 0,05 was obtained as a result of excitonic absorption. The line n = 1 strongly depend on temperature and at temperatures bigger than 160 K instead of this line we can observe just a threshold till room temperature. The edge of absorption band has the specific shape for the crystals with high density of impurity levels. The width of non-equilibrium charge carriers diffusion (~ 0,11 μm for x = 0,01) was calculated. The kinetics of photocurrent was studied at the excitation with light impulse with the life time 0,1 μs.

III: Poster Session III-5 Tuesday 14:00-15:30

Auger effect in atoms and solids: calculation of the auger decay characteristics in solids and the valence auger-spectra for molecules adsorbed on surface — ALEXANDER V. GLUSHKOV — *Head of Inst. Applied Mathematics and Atom.-Mol.-Laser Spectroscopy Centre, OEU Univ., P.O.Box 24A, Odessa-9, 65009, Ukraine*. ► Paper is devoted to calculation of characteristics of the Auger decay in the atoms and solids on the basis of S-matrix Gell-Mann and Low formalism. The cross sections of ionization of internal shells for number of atoms (Na, Si, Au) and energies of Auger electron transitions in solids (Na, Si, Ge, Ag) are calculated. It is carried out a quantum chemical studying the carbon and nitrogen KVV Auger-spectra obtained under adsorption of the CO and NO molecules on the transient metal (Mo, Pd) surfaces [1]. Calculation of the N(KVV) and O (KVV) spectra is carried out in the SCF approximation with using the cluster model and non-relativistic version of S-matrix formalism [1,2]. It is proposed the relativistic generalization of used theory. New approach to calculation of Auger electron energies adequately accounts the correlation, relativistic and solids effects.

[1] A. Glushkov, S. Malinovskaya, J. Phys. Chem. **68**, 1157 (1992); J. Struct. Chem. **36**, 3 (1995); Int. J. Quant. Chem. **99**, 889 (2004)

[2] A. V. Glushkov, L. N. Ivanov, J. Phys. B. **26**, L379 (1993); Phys. Lett. A **170**, 33 (1992); A. V. Glushkov, S. V. Ambrosov, Int. J. Quant. Chem. **99**, 936 (2004)

III: Poster Session III-6 Tuesday 14:00-15:30

Relativistic DFT calculation of carbon and alkali clusters. Quasi-particle time-dependent DFT theory for superconducting clusters — ALEXANDER V. GLUSHKOV — *Head of Inst. Applied Mathematics and Atom.-Mol.-Laser Spectroscopy Centre, OEU Univ., P.O.Box 24A, Odessa-9, 65009, Ukraine*. ► We present the results of the density-functional (DF) and relativistic perturbation theory (PT) [1,2] calculations for the electron structure of the carbon, alkali clusters. It is carried out the DFT calculation for single buckminsterfullerene (C60) system. The problem of the Coulomb barriers in dissociation of doubly charged clusters is also considered. A powerful motivation for cluster study is provided by known aspects relating with the high temperature superconductivity in the solid carbon clusters (K3C60 and Rb3C60). Early it was developed the Lagrange quasiparticle theory for superconducting multi-electron fermi-systems and time-dependent DF theory for superconductors [2]. We have presented the results of the numerical solution of the time-dependent Bogoliubov-de Gennes equations [3] for the K3C60 and Rb3C60 systems.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn, L. J. Sham, Phys. Rev **140**, A1133 (1965)

[2] A. V. Glushkov et al, Nucl. Phys. A **734**, e21 (2004); Int. J. Quant. Chem., **99**, 936 (2004); A. V. Glushkov, Sov. J. Ph. Chem. **68**, 1157 (1992); J. Struct. Chem. **36**, 3 (1995)

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III: Poster Session III-7 Tuesday 14:00-15:30

Theoretical study of electronic and magnetic properties of Diluted magnetic semiconductor Zincblende Al_{1-x}Cr_xN — S. GOURMI-SAÏD¹ AND M. B. KANOUN² — ¹*Department of Physics, Kaiserslautern University of*

Technology, Box 3049, D-67653, Kaiserslautern, Germany. ²Laboratoire d'Etude et Prédiction de Matériaux, URMER, Département de Physique, Faculté des Sciences, Université A. Belkaid, Tlemcen, B.P. 119, 13000 Tlemcen, Algeria. ▶ Using the full potential linearized augmented plane wave method plus local orbitals method, we have explored the structural, electronic and magnetic properties of the ordered ferromagnetic Al_{0.75}Cr_{0.25}N in zinc-blende phase. The analysis of the band structures, density of states, total energy, exchange interactions, and magnetic moments reveal that the alloy exhibits a half-metallic ferromagnetism character. Our calculations show that the valence band is ferromagnetically coupled to the Cr atoms, and the total magnetization of the cell is found equal approximatively to 3.0 μ_B . [Keywords: Diluted Magnetic Semiconductors, magnetic properties, electronic properties, FP-L/APW+lo method.]

III: Poster Session III-8 Tuesday 14:00-15:30

Lifetimes of electron-hole excitations at nanostructures on metal surfaces — T. HAKALA¹, M.J. PUSKA¹, N. ZABALA², AND E.V. CHULKOV² —

¹Helsinki University of Technology, Finland, ²University of the Basque Country and Donostia International Physics Center, Spain. ▶ The description of the evolution of electron-hole excitations on metal surfaces is of utmost importance for understanding phenomena as the dynamics of charge and energy transfer in catalytic reactions and the quantum interference and localization monitored by scanning tunneling spectroscopy. We calculate the lifetimes of electron-hole excitations at the nanostructures such as quantum corrals on the noble metal (111) surfaces. The substrate is described by a one-dimensional pseudopotential [1] and the nanostructure by the jellium model. The self-consistent electronic structures are obtained with a real-space method [2]. The lifetimes are calculated within the GW approximation of many-body theory [3].

[1] E. V. Chulkov, I. Sarria, V. M. Silkin, J. M. Pitarke, and P. M. Echenique, Phys. Rev. Lett. 80, 4947 (1998). E. Ogando, N. Zabala, E. V. Chulkov, and M. J. Puska, Phys. Rev. B 69, 153410 (2004).

[2] T. Torsti et al. Psi.k Newsletter, Highlight of the month, October 2004. <http://psi-k.dl.ac.uk/index.html?highlights>.

[3] I. Campillo et al. Phys. Rev. B 61, 13484 (2000).

III: Poster Session III-9 Tuesday 14:00-15:30

Interaction between conjugated organic molecules and small Au nanoparticles: A TDDFT study — GEORG HEIMEL, MATHIS GRUBER, JEAN-LUC BRÉDAS, AND EGBERT ZOJER —

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400; Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria. ▶ The synthesis and the characterization of small metal clusters, both neutral and charged, have been the focus of vast experimental and theoretical efforts. Recently, small noble-metal clusters coated with a shell of organic ligands have received a lot of attention in the context of nanotechnology and molecular electronics. By exploiting the techniques of molecular self-assembly, small noble-metal nanoparticles have also been successfully employed to achieve exceptionally high local concentrations of organic chromophores - systems which can be expected to exhibit novel and unusual optical properties. After careful assessment of their equilibrium structures, we employ time-dependent density-functional theory to evaluate the linear absorption spectra of small, magic-number gold clusters, coated with thiol-bound, π -conjugated organic chromophores. In addition to varying the aromatic backbone, particular emphasis is put onto the influence of coverage and of donor/acceptor substitutions on the ligands, as well as on the potential charge-transfer character (core to ligand or *vice versa*) of excited states.

III: Poster Session III-10 Tuesday 14:00-15:30

Electron-phonon coupling in metals — A. LEONARDO I. YU. SKLIADNEVA E.V.CHULKOV —

Donostia International Physics Center. ▶ We report first-principles pseudopotential study of electron-phonon interactions in bulk metals such as Mg, which is a free electron like metal and Pd, typical transition metal. The calculations are carried out using PWscf *ab-initio* code based on the DFPT. In addition to the Eliashberg spectral function averaged at the Fermi level and the corresponding e-ph coupling parameter we consider how k-selected electron states couple to phonons and how this coupling varies with electron energy and momentum. A detailed study of the phonon linewidth is presented in comparison with the experimental data. We also evaluate the electron-phonon contribution to the life-time broadening as a function of binding energy and temperature.

III: Poster Session III-11 Tuesday 14:00-15:30

Small rotational oscillations of the adsorbed chains and 2D molecular layers with quadrupolar interaction — V.A.LYKAH¹, E.S.SYRKIN² —

¹National Technic University "Kharkov Polytechnic Institute", 21 Frunze str., Kharkov, 61002, Ukraine. ▶ Molecular layers with rotational degrees of freedom and quadrupolar interaction between linear molecules are

investigated theoretically. Rotation of the molecules is considered to be in the plane of an adsorbing surface and centers of the molecules are pinned in the sites of rectangular lattice. It is found that alternative orientation of the molecules along and perpendicular to the axis of rectangular lattice is the preferable ordering. Equations of the rotational movement are derived and solved for linear oscillations of the molecules near the equilibrium positions. Dispersion relation for two branches of rotational excitations are obtained and analyzed. It is shown that the both branches are optic, their gaps and bandwidths are found. The normal coordinates of linear rotational waves are found to be strongly dependent on dispersion. In the long wave limit normal coordinates are symmetric (sum of the sublattices angles) and antisymmetric. The symmetric branch is harder than the antisymmetric one. The density of states is found analytically for the chain and 2D layer (several regions) of adsorbed molecules oscillation. Transition between square and chain limit pack is analyzed.

III: Poster Session III-12 Tuesday 14:00-15:30

Light diffraction on modulations of solid surface relief and low threshold IR multi-photon molecular dissociation on surface — DR. SVETLANA V. MALINOVSKAYA —

Dept.Quant. Opt. and Nucl.Phys., Odessa Univ., P.O.Box 24A, Odessa-9, 65009, Ukraine. ▶ The light diffraction on relief of surface changes a dynamics of laser induced reactions near the relief with spatial modulated profile [1]. We present new approach to modelling the low threshold IR multi-photon dissociation of molecules near surface with periodic relief. The system is molecular gas SiH₄ (SF₆, UF₆), that is resonantly excited by the CO₂ laser near surface of the periodic Cu lattice. A definition of the local electromagnetic fields and their increasing near surface, contribution of the surface relief parameters is accounted within non-linear theory of diffraction of the 2D, 3D light beams on surface with arbitrary discrete Fourier spectrum of relief [1]. New multi-level model for optimization of excitation of the molecular gas is based on equation of the Fokker-Plank type and optimal governing theory [2]. Numerical testing of optimized model for molecules of SiH₄, UF₆ is carried out. The obtained results are used for proposing a new laser isotope separation scheme.

[1] V. Bagratashvilli, V. Burimov, et al, Sov. Quant. Electr. 15, 2173 (1988)

[2] A. Glushkov, S. Malinovskaya, J. Techn. Phys. 38, 219 (1997); Int. Journ.Quant. Chem. 99, 936 (2004)

III: Poster Session III-13 Tuesday 14:00-15:30

Super intense laser field action on surface and forming the femto-second laser plasma in the porous materials — DR. SVETLANA V. MALINOVSKAYA —

Dept.Quant. Opt. and Nucl.Phys., Odessa Univ., P.O.Box 24A, Odessa-9, 65009, Ukraine. ▶ We study processes in the the femto-second laser plasma (FLP) in nano-structured porous materials (Si). Estimates show that a velocity of the plasma flying of the strongly porous samples Si is 10⁸ cm/s, that is to energy 21 MeV [1]. We carried out modelling FLP forming in the porous materials within the energy balance equations and Green's function method for non-ordered materials. Special attention is devoted to modelling material with clusters, on surface of which there is a number of bonds with H and OH groups. In a case of the D- and OD group's one can wait for realization of the cluster explosion process and reaction D+D- α +n (3,8 MeV). In the high density plasma there is possible an excitation of the low lying isomers. Atomic numerical code [2] is used for calculating the low lying isomers characteristics.

[1] Superstrong Fields in Plasmas. Eds. M.Lontano, AIP Proc. V.426, N.-Y. (1998)

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III: Poster Session III-14 Tuesday 14:00-15:30

Second Harmonic Generation on Transition Metal Oxides — O. NEY AND W. HÜBNER —

Department of Physics, Kaiserslautern University of Technology, Box 3049, 67653 Kaiserslautern, Germany. ▶ The second harmonic generation (SHG) allows to distinguish magneto-optically ferromagnetic from antiferromagnetic order of cubic (001) surfaces. A theoretical description of this processes within electric-dipole (ED) approximation for centrally symmetric media is limited to the interfaces only due to the symmetry properties of the nonlinear optical susceptibility tensor $\chi^{(2)}$. In this work we compute the ED-induced SHG from NiO(001) and CoO(001) surfaces from first principles using a high-level quantum-chemical *ab initio* approach to describe the electronic structure of these strongly correlated materials. We find that the intragap states of CoO(001), due to level bunching, are equally well suited for ultrafast manipulation of the antiferromagnetic state as those of NiO(001). Furthermore, we present the symmetry analysis of the tensor $\chi^{(2)}$ for the NiO(001) and CoO(001) surfaces, where we, besides the ED contributions include both magnetic-dipole and electric-quadrupole contributions giving an alternative explanation of the experimental results.

Collective electronic excitations of nanoparticles adjacent to metal surfaces — Y. PAVLYUKH AND W. HÜBNER — *Department of Physics, Kaiserslautern University of Technology, Box 3049, D-67653 Kaiserslautern.*

► Nanoclusters give us hope to produce a whole class of new materials. However, for each technological application they must be accommodated within a medium or supported on a surface. The inevitable coupling between the cluster and the environment modifies their electronic, magnetic, and chemical characteristics. Thus, the collective excitations of metal clusters approaching a metal surface are to be studied. Using a simple model for the frequency-dependent dielectric function $\epsilon(\omega)$ and the multiple scattering method we numerically investigate the shift in the plasmon resonance due to the coupling of the collective modes of the sphere with those of its mirror image. Results of the model calculation are verified by means of *ab initio* theory. As a prototypic system we study a Na_9^+ cluster on the Cu (100) surface. The representation of the solid surface by a cluster of several, typically 54 substrate atoms is used in the combination with a high level configuration interaction (CI) calculation.

Optimized Effective Potentials in Current-Density-Functional Theory

— S. PITTALIS, N. HELBIG, S. KURTH, E.K.U. GROSS — *Institut für theoretische Physik, Freie Universität Berlin.* ► The proper description of many-electron systems in the presence of magnetic fields within a density-functional framework requires the current density to be used as basic variable besides the electron density. Unlike in ordinary spin-density functional theory, where only the coupling of the magnetic field to the spin degrees of freedom is taken into account, in current-density-functional theory (CDFT) one also allows for the coupling to the orbital currents. Applications of this formalism have been limited because electron-gas-based (LDA-type) approximations of the CDFT exchange-correlation functional have serious pathologies which make them awkward or impossible to use in practical calculations. As an alternative we have developed a CDFT version of the optimized effective potential (OEP) method which allows for the use of explicitly orbital-dependent functionals in the context of CDFT. We present the derivation of these equations and show results for a quantum dot in external magnetic fields and open shell atoms exploiting a KLI-type approximation in both cases.

First-principle calculations of spin-orbit effects on energy bands gaps of In-based III-V semiconductors

— BENALI RERBAL AND GHOUTI MERAD — *Laboratory of Study and prediction of Materials, University of A. Belkaid, B.P. 119, Tlemcen, Algeria.* ► In this paper, the first-principles calculations, by means of the full-potential augmented plane waves method using the local density approximation, were carried out for the electronic properties of In-based III-V semiconductors. We have addressed in particular, the influence of the spin-orbit splitting on the electronic band structures of zinc blende InP, InAs and InSb compounds. The detailed information on the band structures obtained when we include or not the spin-orbit interaction for the three semiconductors is presented. Due to the fact that spin-orbit interaction is important in the description of the electronic properties of these materials, the different band structures are analysed with great details. The calculated values of the spin-orbit splitting, and the energy band gaps are compared to the available experimental and/or *ab-initio* data. (Key words: Electronic structure calculation methods, band structures, semiconductors, spin-orbit interaction).

Full potential calculation of structural, electronic and optical properties of KMgF3

— M. SAHNOUN, C. DAUL — *Chemistry department, University of Fribourg, Fribourg CH-1700 Switzerland.* ► A theoretical study of the structural, electronic and optical properties of KMgF3 is presented using the full-potential linearized augmented plane wave method (FP-LAPW). In this approach, the local density approximation was used for the exchange-correlation potentials. First, we present the main features of the structural and electronic properties of this compound, where the electronic band structure shows that the fundamental energy gap is indirect. The contribution of the different bands was analysed from the total and partial density of states curves. The different interband transitions have been determined from the imaginary part of the dielectric function. The results are compared with previous calculations and with experimental measurements.

Magnetism in metals and compounds using full potential exact exchange

— S. SHALLCROSS, S. SHARMA — *Physics Department, Theory & Modelling group, Linköping University, Institut für Physik, Karl-Franzens-Universität Graz, Austria.* ► Using a recently developed full potential exact exchange method we investigate the magnetism in a variety of metals

and compounds. We find that an exact exchange potential alone results in very bad agreement with experiment for 3d metals. However, as was noticed recently for the magnetic compounds Ni_3Al , Ni_3Ga , and FeAl the agreement with experiment appears to be excellent. We investigate the cause of this behaviour.

Dynamics of long-lived electronic states at noble metal surfaces with dielectric adlayers

— V.M. SILKIN, E.V. CHULKOV, P.M. ECHENIQUE — *Donostia International Physics Center, San Sebastian, Spain.* ► Electronic properties at surfaces and interfaces and their dependence on the interfacial structure are of fundamental interest to various research fields. The interaction of excited surface electronic states with the underlying substrate influences practically all electronically induced adsorbate reactions at metal surfaces. The dynamics of excited electrons at interfaces provides important information on electronic transport across device junctions, interaction of charges with metal-insulator interfaces, dielectrics in electronic circuits, etc. The adsorption of dielectric materials leads to significant modification of energy levels, wave functions and dynamics of the excited states at metal surfaces, as well as to the appearance of new classes of electronic states such as quantum well and buried interface states. Here we present the electron lifetimes in these states for rare gas adlayers of different thickness on noble metal surfaces calculated by using the GW method. These lifetimes are compared with recent time-resolved two-photon photoemission experimental data. We discuss the dependence of lifetimes on the thickness and composition of adlayers.

Electron-phonon coupling in the low-dimensional structures NaV_2O_5 and CaV_2O_5

— J. SPITALER[1], E. YA. SHERMAN[1,2], H. G. EVERTZ[2], AND C. AMBROSCH-DRAXL[1] — [1] *Institute for Physics, University of Graz, Universitaetsplatz 5, 8010 Graz - Austria,* [2] *Institute for Theoretical Physics, Graz University of Technology, Petersgasse 16, 8010 Graz - Austria.* ► NaV_2O_5 has attracted much attention after the discovery of a phase transition at $T_c=35$ K which was considered to be of spin-Peierls type. Further investigations showed that above T_c , NaV_2O_5 is the unique realization of a quarter filled ladder with one electron equivalently distributed over the two V atoms of one rung, while a complicated low-temperature crystal structure with charge ordering at the V sites for $T < T_c$ was revealed. Hence, spin, charge, and lattice degrees of freedom appear to be of similar importance. In this work, we investigate the role of lattice vibrations and their coupling to the electronic system by means of density functional theory. All Raman and IR active Γ point phonons of NaV_2O_5 are calculated and parameters of electron-phonon and spin-phonon coupling are extracted as a function of lattice distortions according to the eigenmodes. All results are compared to those of the isostructural CaV_2O_5 , where no such a phase transition is present. This way lattice deformations relevant for the phase transition can be identified. We also provide Raman scattering spectra which are a sensitive probe for electron-phonon coupling.

Dielectric Function and Electron-Energy-Loss Spectra Beyond GW

— H.-CH. WEISSKER¹, F. BRUNEVAL¹, F. SOTTILE², J. SERRANO³, L. REINING¹ — ¹*Laboratoires des Solides Irradies, Ecole Polytechnique, 91128 Palaiseau, France,* ²*Donostia International Physics Center (DIPC), Apdo 1072, 20018 Donostia / San Sebastian, Spain,* ³*E.S.R.F., 6 rue Jules Horowitz, B.P. 220, F-38043 Grenoble Cedex, France.* ► We report calculations of both the dielectric function and the electron energy loss spectrum within RPA, TDLDA, GW, and beyond, including the electron-hole interaction [1,2]. The obtained spectra are discussed in view of previous [3] and ongoing experiments. We analyze not only the overall shape and position of the plasmon peak but also secondary structures on the plasmon. Possible implications for the application of the GW approximation are discussed. [1] Francesco Sottile, Valerio Olevano, and Lucia Reining, Phys. Rev. Lett. 91, 056402 (2003). [2] Lucia Reining, Valerio Olevano, Angel Rubio, and Giovanni Onida, Phys. Rev. Lett. 88, 066404 (2002). [3] W. Schlke, J. R. Schmitz, H. Schulte-Schrepping, and A. Kaprolat, Phys. Rev. B 52, 11721 (1995).

Electron density partitioning calculations of the splitting energies of lanthanide cations in chloroelpasolite crystals

— MOHAMED ZBIRI, TOMASZ A. WESOLOWSKI, CLAUDE DAUL — *University of Fribourg.* ► Ligand field splitting energies of lanthanides Ln^{3+} ($\text{Ln} =$ from Ce to Yb) in octahedral environment are calculated using the first-principles based embedding formalism [Wesolowski and Warshel, *J. Phys. Chem.* 97 (1993) 8050]. In this formalism, the lanthanide is described at orbital level whereas its environment is represented by means of an additional term (*effective em-*

bedding potential) in the Kohn-Sham-like one-electron equations. This term is expressed as an explicit functional of two electron densities: that of the cation ρ_1 and that of the ligands ρ_2 . It is shown that the formalism and the applied relevant approximate functionals, developed and used previously for embedded subsystems comprising only for s-, p-, and d-elements, is also an adequate method for embedded f-elements. The calculated splitting energies in the studied systems are attributed to two main factors *i*) polarization of the electron density of the ligands and *ii*) ion-ligand Pauli repulsion.

[1] Mohamed Zbiri, Mihail Atanasov, Claude Daul, Juan Lastra and Tomasz A. Wesolowski, Chem. Phys. Lett., **397** (2004) 441.

IV: Code Development IV-1 Tuesday 16:00-16:15

Linear-Response TDDFT in Frequency-Reciprocal space on a Plane-Waves basis: the DP (Dielectric Properties) code — VALERIO OLEVANO, LUCIA REINING AND FRANCESCO SOTTILE — *Laboratoire des Solides Irradies, CNRS - CEA, Ecole Polytechnique.* ► We will illustrate Linear-Response TDDFT in Frequency-Reciprocal space on a Plane-Waves (PW) basis as it is implemented in the DP (Dielectric Properties) code (<http://theory.lsi.polytechnique.fr/codes/dp/>). This scheme is particularly convenient for infinite periodic systems, e.g. bulk solids. By using supercells, the code could also be used for semi-infinite systems, like surfaces, wires and tubes. As every other PW scheme, its limits are represented by the largest elementary cells which is possible to simulate on an actual computer. Being natively in frequency space, this scheme is suited for the calculation of Optical or, more generally, Dielectric spectra. Thanks to the latest developments concerning the search for good approximations to the linear-response exchange-correlation kernel, this scheme has been proven successful both in reproducing Energy-Loss but also Optical spectra. The accuracy of the results is good. In some cases, a quantitative agreement with the experiment is found. Some examples of the results obtained using the DP code will be presented. Finally there will be a discussion on the future and the licence of the code.

IV: Code Development IV-2 Tuesday 16:20-16:35

The ABINIT package — X. GONZE — *UCL, Louvain-la-Neuve, Belgium.* ► A brief introduction to the ABINIT software package is given. Available under a Free Software license, it allows to compute directly a large set of properties useful for solid states or nanoscience studies, including structural and elastic properties, electronic properties, phonon spectra, prediction of phase (meta) stability, piezoelectricity, dielectric properties, etc. A special emphasis will be set on the computation of excitation energies, based on the TDDFT and the GW approximation. ABINIT is especially easy to use, with extensive documentation, allowing newcomers to quickly step in.

IV: Code Development IV-3 Tuesday 16:40-16:55

Exact cutoff techniques in supercell calculations — C.A. ROZZI (1), A. RUBIO (2), E.K.U. GROSS (1) — *1) Institut für Theoretische Physik, Freie Universität Berlin, 2) Donostia International Physics Center (DIPC).* ► TDDFT has been shown to be an excellent approach to correctly and efficiently describe excited states in atoms and molecules. Yet, when applied to infinite periodic systems, both conceptual and implementational problems arise. We focus on systems that are periodic in less than three dimensions, like polymers and nanotubes, or surfaces and thin films. Such systems are usually treated in a supercell approach, as a three dimensional array of chains or slabs, and the computational cost for the simulations dramatically increases with the cell size. Moreover, due to the long range character of the Coulomb interaction, the equivalent isolated system (i.e. the single chain or film) is exactly described only in the limit of an infinite supercell. This has led to the request for efficient techniques to cut off the Coulomb interaction in systems with reduced periodic dimensionality. We will show how to calculate exact analytical cutoffs to properly screen at a desired extent the long range Coulomb interaction in both 1D and 2D systems. This allows one to compute most efficiently the properties of the infinite system alone to compare them with those of the system plus its periodic images.

IV: Code Development IV-4 Tuesday 17:00-17:15

Overview of the EXCITING code capabilities — J. K. DEWHURST, S. SHARMA AND C. AMBROSCH-DRAXL — *Institut für Physik, Karl-Franzens-Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria.* ► Motivated by the need for an all-electron code to study excited state properties, the EXCITING code has been written from scratch for the Network. This full-potential linearised augmented plane wave code is both clearly written and fully documented so that new methods in the field can be incorporated easily and efficiently. We present an overview of its current capabilities, with examples from exact exchange, phonons, optics and non-collinear magnetism.

IV: Code Development IV-5 Tuesday 17:20-19:00

Hands-on demonstrations of excited-state codes: ABINIT, EXCITING, OCTOPUS, DP.

V: Lifetimes, Transport V-1 Wednesday 09:00-09:30

INVITED TALK

TDDFT-based formalism for the response of solids, nanostructures and biomolecules — ANGEL RUBIO — *Dpto. Física de Materiales, Facultad de Químicas, U. Pais Vasco, Centro Mixto CSIC-UPV/EHU and Donostia International Physics Center (DIPC), Apdo. 1072, 20018 San Sebastian/Donostia, Spain.* ► We will review the recent implementations of TDDFT to study the optical absorption of biological chromophores, one-dimensional polymers and layered materials. In particular we will show the effect of electron-hole attraction in those systems. We will follow two routes: one based on solving the Bethe-Salpeter equation and the other on an orbital-dependent OEP method on top of the GW approximation from the self-energy. Virtues and deficiencies of both methods will be illustrated. [Work done in collaboration with A. Castro, M. Marques, A. Marini, M. Gruning, L. Wirtz and D. Varsano and supported by the NANOQUANTA network of excellence]

V: Lifetimes, Transport V-2 Wednesday 09:30-09:45

A Practical Scheme for Quantum Transport using Time-Dependent Density Functional Theory — S. KURTH¹, G. STEFANUCCI², C.-O. ALMBLADH², A. RUBIO³, E.K.U. GROSS¹ — *¹Institute for Theoretical Physics, Free University Berlin, Berlin, Germany. ²Solid State Theory, Lund University, Lund, Sweden. ³Donostia International Physics Center, San Sebastian/Donostia, Spain.* ► The Landauer formalism is a popular method to calculate the current of non-interacting electrons through a nanoscopic system connected to two (or more) macroscopic electrodes in the steady-state. Here we present a *time-dependent* description of transport based on the time evolution of the non-interacting Schrödinger equation. We develop a numerical algorithm for the time propagation of extended states. For simple model systems, the scheme is used to compute the time-dependent current in response to an external dc or ac bias. As expected, for a dc bias the system evolves to the steady state predicted by the Landauer formula. Using the algorithm in the framework of time-dependent density functional theory allows for the description of transport of *interacting* electrons beyond the Landauer formalism.

V: Lifetimes, Transport V-3 Wednesday 09:50-10:05

Theoretical description of correlated transport through atomic nanowires — ANDREA FERRETTI, ARRIGO CALZOLARI, ROSA DI FELICE AND FRANCA MANGHI — *INFN National Research Center on nanoStructures and bioSystems at Surfaces (S3) and University of Modena and Reggio Emilia, Physics Department, Modena (Italy).* ► Large interest is focused on the field of molecular electronics as an opportunity of reverting the usual top-down approach to device fabrication. In this scenario a large effort is being devoted to develop theoretical and computational tools able to describe transport properties in nanostructures. While many properties and phenomena such as electron-electron interactions, electron-phonon interactions, electric field structural effects and others, assume more and more importance due to the very nature of the bridging unit, at the moment no standard approach exists to deal with them. In this work we present an atomistic first principles framework to describe quantum transport in such systems adopting the three-body scattering approximation in order to account for strong short range electron-electron interactions, and Wannier functions as basis set to implement a reliable and efficient transport calculation in a Landauer-like approach. We applied the above-described theoretical approach to the case of transition-metal atomic chains. We describe our results for transport properties and discuss the implications of introducing a fully interacting model.

V: Lifetimes, Transport V-4 Wednesday 10:10-10:25

First-principle GW+T approach to the inelastic lifetimes and mean free path's of excited electrons in metals — V.P. ZHUKOV, E.V. CHULKOV, P.M. ECHENIQUE — *Donostia International Physics Center, San Sebastian, Spain.* ► We develop an ab initio method for calculations of inelastic lifetimes and mean free path's (IMFP) of excited electrons in metals. The lifetimes calculations are based on many-body series expansion of the electron self-energy in terms of dynamically screened potential. The lowest term is calculated within the GW approximation whereas the high terms are evaluated by means of the T-matrix approach. We calculate direct T-matrix terms with multiple electron-hole and electron-electron scattering; the scattering between quasi-particle with equal and opposite spin is included. We performed the lifetimes calculations for paramagnetic Pd, Ta and Al, lifetime and IMFP calculations for ferromagnetic Fe, Ni and Ni₈₀Fe₂₀. We discuss the role of various T-matrix terms, analyze the IMFP's in terms of group velocities and convolutions of densities of states.

VI: New DFT Developments VI-1 Wednesday 11:00-11:15

Combining quasiparticle energy calculations with exact-exchange

density-functional theory — PATRICK RINKE⁽¹⁾, ABDALLAH QTEISH^(1,2), JÖRG NEUGEBAUER⁽³⁾ CHRISTOPH FREYSOLDT⁽¹⁾ AND MATTHIAS SCHEFFLER⁽¹⁾ — ⁽¹⁾*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin*, ⁽²⁾*Yarmouk University, Irbid - Jordan*, ⁽³⁾*University of Paderborn, Germany*. ► We present a systematic *ab initio* study of the electronic structure for selected II-VI compounds and group III nitrides in the zinc-blende structure with special emphasis on analysing the role played by the semicore *d*-electrons. We show that applying density-functional theory (DFT) in the exact-exchange (EXX) approach [1] leads to an improved description of the *d*-electron hybridisation compared to the local-density approximation (LDA). Moreover we find that it is essential to use the newly developed EXX pseudopotentials [2] in order to treat core-valence exchange consistently. In combination with quasiparticle energy calculations in the *GW* approximation we achieve very good agreement with available photoemission data. Since the DFT energies and wavefunctions serve as input for the *GW* calculation we conclude that for these materials EXX constitutes the better starting point.

[1] M. Städele *et al*, Phys. Rev. Lett. **79** 2089 (1997).

[2] M. Moukara *et al*, J. Phys.: Condens. Matter **12** 6783 (2000).

VI: New DFT Developments VI-2 Wednesday 11:20–11:35

Importance of Core-valence Interaction and Asymmetry in the Exact Exchange Potential — S. SHARMA, J. K. DEWHURST AND C. AMBROSCH-DRAXL — *Institut für Physik, Karl-Franzens-Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria*. ► We have implemented the exact exchange (EXX) potential within the all-electron full-potential (FP) linearised augmented-plane-wave method (the EXCITING code), including core-valence interactions. Two classes of extended solids are studied using this FP-EXX method. 1. In semiconductors and insulators we find that unlike pseudopotential (PP) there does not exist an excellent agreement of the KS gaps with experiments and that EXX is consistent in its treatment of both materials. Furthermore, unlike PP-EXX results we find that the *d*-band positions calculated using FP-EXX are in excellent agreement with experiments. We attribute this behaviour to the presence of core-valence interaction. 2. The magnetic properties of FeAl, Ni3Al and Ni3Ga are determined. The correct ground state for these materials is obtained in all cases: non-magnetic for FeAl and Ni3Ga and ferromagnetic in Ni3Al with a magnetic moment of 0.20 μ_B per formula unit, which is in excellent agreement with experiments. We attribute the success of exact exchange to the strong asymmetry in the exchange potential. This should be a desirable feature of next generation of approximate functionals.

VI: New DFT Developments VI-3 Wednesday 11:40–11:55

Understanding the dissociation of diatomic molecules in the DFT-ACFD formalism — Y. POUILLON, F. TOURNUS, Y.-M. NIQUET, M. FUCHS, X. GONZE — *Unité PCPM - Université Catholique de Louvain - 1348 Louvain-la-Neuve - Belgium*. ► There is a growing need for exchange-correlation functionals going beyond LDA and GGA, in particular in systems where van der Waals interactions play a crucial role. These can only be taken into account by means of fully non-local XC functionals. One way to build such a functional is to resort to the Adiabatic-Connection Fluctuation-Dissipation (ACFD) theorem in conjunction with the Random-Phase Approximation (RPA). However, a spurious maximum in the dissociation curve was evidenced for the N_2 and H_2 molecules. It may result from either (a) H_2 and N_2 being pathological cases, or (b) the lack of self-consistency, as well as (c) the RPA being insufficient to describe the dissociation regime. We are examining the dissociation of several diatomic molecules, such as LiH, Be_2 , Mg_2 and Ca_2 , both within the LDA/GGA and ACFD frameworks. The calculations already carried out on Be_2 using ABINIT default pseudopotentials show a huge bump at intermediate range too. We are now exploring thoroughly the influence of several parameters, such as cell size, number of bands, and pseudopotential on both the quality of the final results and the characteristics of the bump.

VI: New DFT Developments VI-4 Wednesday 12:00–12:15

Ab-initio calculations of the electron excitation by phonons in SrTiO3 — WILFRIED WUNDERLICH, HIROMICHI OHTA, KUNNIHITO KOUMOTO — *Nagoya University, Dept. Molecular Design, JST-CREST, 464-8603 Nagoya, Japan*. ► The ab-initio prediction of the electron excitation by phonons is still a challenge and would make the design of thermoelectric material possible. Highly doped SrTiO3 is known as a kind of model material because of its fairly large Seebeck-coefficient [1] especially in SrO-containing superlattices. In spite of its large optical band-gap of 3.2eV, SrTiO3 shows semi-conducting behavior with electric conduction up to 1000K, where the phonon energy is still smaller than the bandgap. Ab-initio calculations using the Vasp-code [2] were performed on modified SrTiO3 supercells, considering the properties of the phonon spectra of perovskites [3]. The results show a remarkable narrowing of the band-gap for certain vibration modes, especially when Ti-atoms are shifted. As expected from the electron-gas theory, also the

effective mass of the excited electrons are reduced in these cases and lead to further improvement of thermoelectric materials is discussed.

[1] S. Ohta, T.Nomura, H. Ohta, K.Koumoto, J. Appl. Phys. (2005) accepted.

[2] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558, ibid 49 (1994) 14251.

[3] K.Parlinski and Y.Kawazoe, J.Chem.Phys. 114 (2001) 2395.

VI: New DFT Developments VI-5 Wednesday 12:20–12:35

Density functional theory for superconductors: Applications to MgB₂ and solids under pressure — A. FLORIS¹, N. LATHIOTAKIS¹, C. FRANCHINI², G. PROFETA³, M. LÜDERS⁴, M. A. L. MARQUES¹, A. CONTINENZA³, S. MASSIDDA² AND E.K.U. GROSS¹ — ¹*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*, ²*Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari, Italy*, ³*Dipartimento di Fisica, Università degli studi dell'Aquila, I-67010 Coppito (L'Aquila) Italy*, ⁴*Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*. ► Understanding and predicting the properties of superconductors is of both fundamental and technological importance. The discovery of superconductivity in MgB₂, with its rather high critical temperature ($T_c = 39.5K$) and the presence of multiple gaps, has renewed the interest for conventional superconductors. We present several applications of a novel approach to superconductivity that allows one to calculate material-specific properties, such as the gap and the T_c , in a truly ab-initio fashion without using any adjustable parameter, such as the Coulomb pseudopotential μ^* . Within this approach, we obtained the T_c and the two gaps of MgB₂ in good agreement with experiment, taking into account the strong anisotropy of this material. As a further application, we have studied the behaviour of T_c in Li and Al as a function of pressure. Despite their simple metal structure, these two materials show a different behaviour upon pressure. While Li undergoes several transitions favouring superconductivity, in Al the electron-phonon coupling decreases with pressure, leading to a complete suppression of superconductivity around 8GPa.

VII: Technological Applications VII-1 Wednesday 14:00–14:30

INVITED TALK

Ultrafast Generation of Ferromagnetic Order via Laser-induced Antiferromagnetic-Ferromagnetic Phase Transformation — GANPING JU,¹ JULIUS HOHLFELD,¹ BASTIAAN BERGMAN,^{1,2} RENÉ J.M. VAN DE VEERDONK,¹ OLEG N. MRYASOV,¹ JAI-YOUNG KIM,¹ XIAOWEI WU,¹ DIETER WELLER,¹ AND BERT KOOPMANS² — ¹*Seagate Research, 1251 Waterfront Place, Pittsburgh, PA 15222, USA*, ²*Eindhoven University of Technology, Department of Applied Physics, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands*. ► The ultrafast spin/magnetization dynamics has recently attracted strong scientific interest. Modulation of ferromagnetism has been shown on sub-picosecond time scales upon ultrafast photoexcitation, resulting in moment reduction and precession [1]. Another area of scientific interest and potential applications is the generation of ferromagnetic order on an ultrashort timescale. Here we present [2] an optically induced antiferromagnetic-ferromagnetic phase transformation in chemically ordered FeRh films. We demonstrate that ferromagnetism can be induced on the sub-ps timescale by driving the transformation with femtosecond optical pulses. A sub-ps onset of induced ferromagnetism is followed by a slower increase over 10-30 ps when FeRh is excited above threshold. The observation of a ferromagnetic signal before the lattice has time to expand, in conjunction with a microscopic model based on first principles calculations, indicates that the underlying AFM-FM transformation is accompanied, but not driven by, a lattice expansion. The mechanism for such ultra-fast magnetic transformation is identified to be the strong ferromagnetic exchange mediated via Rh moments induced by Fe spin fluctuations. The application of such phenomena and other magnetization dynamics in magnetic recording will be also discussed. [1] E. Beaurepaire *et al.*, Phys. Rev. Lett. **76**, 4250 (1996), and many other [2] G. Ju, *et al.*, Phys. Rev. Lett. **197403** (2004)

VII: Technological Applications VII-2 Wednesday 14:30–14:45

LiNH₂-MgH₂ as a Potential Hydrogen Storage Material: a Density Functional Theory Study — RALPH H. SCHEICHER (1), C. MOYSES ARAUJO (1), RAJEEV AHUJA (1,2) — (1) *Uppsala University, Sweden*; (2) *KTH, Stockholm, Sweden*. ► LiNH₂ possesses high capacity for hydrogen storage [1], but its large hydride formation enthalpy leads to operating temperatures and pressures that lie outside the practicable range for vehicular applications. Partial substitution of Li by Mg can destabilize the system and thus improve the hydrogen de-sorption characteristics, as it has been shown in recent experimental studies [2]. We present and discuss results from our density functional theory investigations of the LiNH₂-MgH₂ system. The main aim of this study is to understand the bonding characteristics, the Mg-induced destabilization mechanism, and the thermodynamics of hydrogen de-sorption from an electronic structure viewpoint.

[1] P. Chen *et al.*, J. Phys. Chem. B **107**, 10967 (2003).

[2] W. Luo, J. Alloys Compd. **381**, 284 (2004).

Lifetimes of quasiparticle excitations in 4d transition metals Mo and Rh — A. MÖNNICH, D. BAYER, M. BAUER, M. AESCHLIMANN — *Dep. of Physics, Kaiserslautern University of Technology.* ► The dynamics of excited electrons in metals are crucial for a detailed understanding of various chemical and physical phenomena on metal surfaces. It is already known that noble metals show a longer lifetime of quasiparticle excitations than transition metals due to the higher density-of-states around the Fermi level. But also the electron dynamics between different transition metals can exhibit significant divergences. With the time resolved two-photon photoelectron spectroscopy (TR-2PPE) method we investigated the electron dynamics of Mo and Rh in an energy range up to 3eV above the Fermi level. LMTO-RPG-GW calculations predict a surprising large difference between the averaged lifetimes of electron quasiparticles in the 4d transition metals Mo and Rh [1] that were confirmed in our experiment. The characteristics of electronic structure responsible for energy dissipation processes of hot electrons will be discussed.

[1] V. P. Zhukov, F. Aryasetiawan, E. V. Chulkov, P. M. Enchenique PRB 65 115116 (2002).

What is the driving force in a ferroelectric material, LiTaO₃ — H. MI-ZOTA, D. HORIGUCHI, K. YOKOI, H. OOHASHI, Y. ITO, T. TOCHIO¹, A. M. VLAICU², H. YOSHIKAWA², S. FUKUSHIMA², H. NAKAZAWA², S. TAKEKAWA², K. KITAMURA², S. YOS³ — *Laboratory of Atomic & Molecular Physics, Institute for Chemical Research, Kyoto University, ¹Keihanna, Seika-cho, Gakkenn-toshi, Kyoto 619-0237 Japan ²NIMS, 1-1 Namiki, Tsukuba-shi, Ibaraki, Tsukuba 305-0044 Japan ³Department of Engineering, Doshisha University, 1-3 tatara, Kyoutanabe-shi, Kyoto 610-0394 Japan.* ► X-ray emission in LiTaO₃ has been confirmed by thermal treatment in a vacuum system. Detailed single crystal high-temperature x-ray structure analyses were carried out far below the phase transition. The unit cell dimensions, *a* and *V* show a linear increase with temperature, however, the lattice parameter, *c* is almost constant. Moreover, the electronic state in Ta was investigated using a high resolution double-crystal spectrometer. Based on the results, X-ray emission induced by the charged particles including electrons can be considered in the compound.

Self-defects and oxygen self-diffusion on a silica glass by first-principles — L. MARTIN-SAMOS — *INFMS-3.* ► We present a complete and statistical first principles study of self-defects in an amorphous 108 atoms SiO₂ super-cell. The ab-initio calculations were performed using independently the VASP, SIESTA and PWSCF first principles codes based on density functional theory (DFT) within the local density approximation (LDA). As expected, at variance with SiO₂ crystalline phases, the defects formation energies are distributed. In fact, we have proved that the formation energy dispersion is correlated to the local stress before the defect formation. Having the statistic of oxygen defect formation energies and having performed some calculations on migration energies, we will present a preliminary study on the main oxygen diffusion mechanism as a function of the oxygen partial pressure and its activation energy.

INVITED TALK

Exotic excitations in interacting systems with strong geometric frustration — ERICH RUNGE — *Technische Universität Ilmenau, Fakultät für Mathematik und Naturwissenschaften, FG Theoretische Physik I, 98693 Ilmenau, Germany.* ► The possibility of elementary excitations (quasiparticles) with very unusual properties such as half-integer charge $e/2$ in strongly interacting many-particle systems with geometric frustration is discussed using a model of spinless fermions. On various frustrated lattices, strong nearest-neighbor repulsion leads to a macroscopic ground-state degeneracy in the absence of a hopping term (kinetic energy). Based on exact diagonalization cluster results, we predict for finite hopping and certain commensurate filling fractions a finite number of liquid-like, i.e., translationally invariant, degenerate ground states. An additional electron is expected to decay into two excitations, each carrying charge $e/2$. We will comment on the connection of ground-state degeneracy, fractional charges, topological order, and the statics under permutation. Future challenges are to develop approximate analytical theories and to explore how well the excited-state properties are described within, e.g., DFT. The unusual low-temperature behavior of the *d*-metal heavy-fermion compound LiV₂O₄ may indicate experimental evidence for such exotic low-energy excitations.

Ab initio calculations of bound excitons in GaN — ROBERT LASKOWSKI,¹ NIELS EGEDE CHRISTENSEN,¹ GILLES SANTI,¹ AND

CLAUDIA AMBROSCH-DRAXL² — ¹*Dept. of Physics and Astronomy, University of Århus, DK-8000 Århus C, Denmark,* ²*Institute of Physics, University of Graz, Universitätsplatz 5, A-8010 Graz, Austria.* ► The optical absorption and excitonic properties of wurtzite GaN are investigated by means of an *ab initio* approach taking into account electron-hole correlations. This is done by solving the Bethe-Salpeter equation, using the results of density functional theory calculations as a starting point. Our main focus is the calculation of the binding energies of bound excitons, as well as their dependence on structural parameters and details of the electronic structure. Spin-orbit coupling was neglected in all our BSE calculations, but fully relativistic electronic structure calculations have shown that its effect at the valence band maximum is particularly small in wurtzite GaN (about 5 meV). The lowest excitations have been associated with the ground states of three bound excitons, labeled A, B and C. The A, B excitons are degenerate when spin-orbit coupling is neglected and are mainly composed of Ga-*N*-*s* and N-(*p*_{*x,y*}) states. The C exciton originates mainly from Ga-*N*-*s* and N-*p*_{*z*} states. In the absence of spin-orbit coupling, the oscillator strengths of the A, B excitons are non-zero only for perpendicularly polarized light, whereas the C exciton is active only for parallelly polarized light (with respect to the *c*-direction). The excitonic binding energy is defined as a difference between the excitation energy and the separation of the (quasiparticle) conduction and valence bands contributing to that exciton. For the experimental unit cell parameters, the calculated binding energies of the degenerate A, B excitons are 37 meV and 35 meV for exciton C. These were found to be mostly insensitive to changing the shape of the unit cell (*c/a* ratio and Ga-N distance in the *c*-direction, *u*) and to be slightly increasing with increasing pressure for volume changes of up to 4% in agreement with experimental findings. We estimate that the inclusion of spin-orbit coupling in the BSE Hamiltonian would result in splitting the A, B exciton binding energies by only a few meV and would therefore not affect our main conclusions. Nevertheless, SOC affects the symmetry of the valence states so that both the B and C excitons become active (non-zero oscillator strengths) for both polarizations. This and the fact that the crystal field splitting is of the same order of magnitude as the excitonic binding energies make the interpretation of experimental results particularly delicate.

Ab-initio simulation of optical spectroscopies in carbon nanotubes — A. RUINI, E. CHANG, G. BUSSI, AND E. MOLINARI — *INFMS-3 and Dipartimento di Fisica, Università di Modena e Reggio E., Italy.* ► A theoretical, many-body formalism based on the GW approximation and the Bethe-Salpeter equation is developed to study optical properties in carbon nanotubes by exploiting symmetry effects. In particular, we address the absorption spectrum and the resonant Raman profile for the radial breathing mode phonon in a carbon (4, 2) nanotube. The approach used takes into account the electron-hole interaction and excitonic effects, which are crucial in one-dimensional systems.

Excitonic Effects in Phenylenes and Thiophenes — S. SAGMEISTER, K. HUMMER, P. PUSCHNIG AND C. AMBROSCH-DRAXL — *Institute of Physics Division of Theoretical Physics, University of Graz, A-8010 Graz, Austria; Institute of Thermal Engineering, Graz University of Technology, A-8010 Graz, Austria.* ► In plastic electronics research, poly(paraphenylene) (PPP) and polythiophene (PT) has been thoroughly investigated by means of experiments as well as theoretical models. E.g., among the variety of organic semiconducting polymers, PPP is a very promising candidate for opto-electronic devices. In comparison to polymers, molecular crystals built by short oligomers can be synthesized with higher crystallinity and hence may be more important for applications. They form well defined crystals with a herringbone arrangement of molecules, governed by intermolecular interactions. One possibility to enhance these interactions is to apply hydrostatic pressure. One goal of this work is to investigate the effect of the intermolecular interactions on the electronic and optical properties of biphenyl as a function of pressure. Second, the dependence of these properties on the oligomer length is studied by comparing the oligomers to their corresponding polymers. In particular, we apply density functional theory as a starting point for the computation of the dielectric tensor by solving the Bethe-Salpeter equation, which accounts for the Coulomb interaction between the electron and the hole.

Surface excitons and site-selective desorption of insulators using laser excitation — PAOLO TREVISANUTTO, PETER SUSHKO, AND ALEXANDER SHLUGER — *Department of Physics and Astronomy, University College London, London, UK.* ► Photo-excitation of insulators with photons with specially tuned energies is accompanied by the hyper-thermal desorption of atoms induced by exciton localization and decomposition. We determined energies of surface excitons in several alkali halides by a sensitive detection technique and using embedded cluster calculations. Recently, laser-induced

desorption of oxygen atoms with hyperthermal velocities and formation of O-species has also been observed on MgO films. Using ab initio embedded cluster method we created a unified theoretical model of these complex processes. The results suggest that photons at ca. 3.5 - 4.5 eV create charge transfer excitons at O and Mg corners at the MgO surface. We demonstrate that surface excitons relax via radiative and non-radiative processes and predict the luminescence energies and barriers for their thermal quenching. These excitons can be further excited creating bi-excitons, where the oxygen species becomes effectively neutral and prefer to leave the surface with kinetic energies of several tenths on an eV. We demonstrate a large degree of site and energy selectivity in a wide range of photo-induced processes at the MgO surface.

IX: Localized Excitations IX-2 Thursday 11:20-11:35

Theory of Photoinduced absorption in poly(diphenyl)-polyacetylenes — PRIYA SONY AND ALOK SHUKLA — *Physics Department, Indian Institute of Technology, Powai, Mumbai 400 076 India.* ► Recently discovered conjugated polymers poly(diphenyl)-polyacetylenes (PDPAs) [1] can be considered as close cousins of trans-polyacetylene (t-PA). However, their linear optical properties are significantly different from those of t-PA, in that PDPAs exhibit strong photoluminescence (PL) with large quantum efficiency, while t-PA does not exhibit any PL. First, we will briefly review that work in the present talk [2]. Next, we will present a theoretical study of $1B_u$ and $2A_g$ PA spectra of oligo-PDPA's using correlated-electron Pariser-Parr-Pople (P-P-P) model and various configuration interaction (CI) methodologies [3], and compare them to the recent experimental results of the Korovyanko *et al.*

- [1] I. Gontia *et al.*, Phys. Rev. Lett. **82**, 4058 (1999).
 [2] A. Shukla and S. Mazumdar, Phys. Rev. Lett. **83**, 3944 (1999); H. Ghosh, A. Shukla, and S. Mazumdar, Phys. Rev. B **62**, 12763 (2000).
 [3] P. Sony and A. Shukla, submitted for publication (2004).

IX: Localized Excitations IX-3 Thursday 11:40-11:55

Theoretical Investigation of Photochemical Reactions on Surfaces: A first principles approach — PROF. DR. THORSTEN KLÜNER — *Carl von Ossietzky University Oldenburg, Institute of Pure and Applied Chemistry.* ► Surface photochemistry occurs in many instances, including photocatalysis, laser induced desorption, and solar energy conversion. Despite its ubiquitous nature, a microscopic understanding of the underlying basic processes and elementary reactions remains a great challenge. In this talk, I will focus on the theoretical description of the simplest photochemical phenomenon on surfaces: the laser-induced desorption of small molecules. Ab initio calculations of high dimensional potential energy surfaces (PES) for ground and excited states of the systems NO/NiO(100) and CO/Cr2O3(0001) will be presented. The surface model consists of a small cluster embedded in

an array of point charges to simulate the electrostatic field above the surface. Based on Configuration Interaction (CI) calculations a reliable construction of global potential energy surfaces for the electronic ground state as well as for excited states of the adsorbate substrate system becomes feasible. Subsequent high-dimensional time-dependent wave packet studies using the calculated potential surfaces enable us to simulate almost all details of quantum state resolved experiments without using empirical information.

IX: Localized Excitations IX-4 Thursday 12:00-12:15

Optimal control theory of time-dependent targets — J. WERSCHNIK, I. SERBAN, E.K.U. GROSS — *Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.* ► The control of quantum mechanical systems by laser interaction has witnessed tremendous progress in the last 15 years. On the experimental side this progress was due to the development of pulse shaping techniques and on the theoretical side, the prediction of laser pulses has been pushed forward by the introduction of rapidly, monotonically convergent algorithms. So far, theory and experiment have concentrated on the control of time-independent targets, e.g., a specified final state should be maximally populated at the end of the laser pulse. In this talk we demonstrate the feasibility of computational quantum control for time-dependent targets [1]. In particular, we show that the time-dependent density can be driven along a given trajectory in real space and we control the time-dependent occupation numbers of a two-level system and a 1D model for hydrogen. The employed algorithm converges monotonically and is computationally not more expensive than algorithms for the optimization of time-independent targets.

- [1] I. Serban, J. Werschnik, E.K.U. Gross, arXiv: quant-ph/0409124.

IX: Localized Excitations IX-5 Thursday 12:20-12:35

Localized excited states in condensed phase derived from electron density partitioning — TOMASZ A. WESOLOWSKI — *Department of Physical Chemistry, University of Geneva, Switzerland.* ► New type of applications of the one-electron equations for embedded systems (Eqs. 19-20 in Ref.[1]) concerning excited states will be presented. Such applications became possible owing to the recent developments concerning: their efficient computer implementation and their incorporation into the general framework of linear-response time-dependent density-functional-theory[2]. We will discuss in detail: interaction-induced shifts in the electronic excitation energies [3], f-orbital levels for lanthanide centers in crystals [4], impurities in perovskites, and solvatochromic shifts will be presented.

- [1] T.A. Wesolowski and A. Warshel, *J.Phys.Chem.*, **97** (1993) 8050.
 [2] M.E. Casida and T.A. Wesolowski, *Intl. J. Quant. Chem.*, **96** (2004) 577.
 [3] T.A. Wesolowski, *J. Am. Chem. Soc.*, **126**, (2004) 11444.
 [4] M. Zbiri, *at al.*, *Chem. Phys. Lett.*, **397**, (2004) 441.