O 74: Focussed session: Theory and computation of electronic structure: new frontiers VI (jointly with HL, DS)

Time: Thursday 15:00–16:30 Location: TRE Phy

O 74.1 Thu 15:00 TRE Phy

Excited States from *GW*: the role of self-consistency — •Fabio Caruso[1], Xinguo Ren[1], Patrick Rinke[1], Angel Rubio[1,2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut, Faradayweg 4-6, Berlin, Germany — [2]Universidad del Pais Vasco, San Sebastian, Spain

The *GW* approximation offers an accurate framework to study *ab-initio* electronic excitations in molecules and solids. However, due to its numerical cost, *GW* is mostly introduced perturbatively following a density-functional theory (DFT) calculation (G_0W_0). We have implemented a fully self-consistent *GW* scheme based on the iterative solultion of Dyson's equation in the all-electron localized basis set code FHI-*aims* [*http://www.fhi-berlin.mpg.de/aims*]. The self-consistent treatment corrects several pathologies of the G_0W_0 scheme, such as the violation of particle number conservation and the dependence on the starting point. Our self-consistent *GW* total energies are in good agreement with available literature values [Stan *et al*, JCP **130**, 114105 (2009)]. From the *GW* spectral function we extracted the ionization energies of a set of small molecules. The values are close to experimental results, but exhibit a slight tendency to underestimate. Building on this we apply self-consistent *GW* to charge-transfer systems. At large separation between the molecular fragments time-dependent DFT in (semi-)local approximations underestimates the charge-transfer energy. This error can be traced back to the wrong description of the HOMO-LUMO gap and its evolution with intermolecular distance. This error is capture by *GW* as it properly accounts for the difference between the donor ionization potential and acceptor electron affinity.

O 74.2 Thu 15:15 TRE Phy

Electronic excitations from a perturbative LDA+*GdW* approach — •Michael Rohlfing — Fachbereich Physik, Universität Osnabrück, Germany

We discuss an efficient approach to excited electronic states within ab-initio many-body perturbation theory (MBPT). Quasiparticle corrections to density-functional theory result from the difference between metallic and non-metallic dielectric screening. They are evaluated as a small perturbation to the DFT-LDA band structure, rather than fully calculating the self energy and evaluating its difference from the exchange-correlation potential. The dielectric screening is desribed by a model, which applies to bulk crystals, as well as, to systems of reduced dimension, like molecules, surfaces, interfaces, and more. The approach also describes electron-hole interaction. The resulting electronic and optical spectra are slightly less accurate but much faster to calculate than a full MBPT calculation. We discuss results for bulk silicon and argon, for the Si(111)-(2×1) surface, the SiH_4 molecule, an argon-aluminum interface, and liquid argon.

[1] M. Rohlfing, Phys. Rev. B 82, 205127 (2010).

O 74.3 Thu 15:30 TRE Phy

First-principles study (GW+PAW) on new phosphors for white LED — •Bruno Bertrand[1,2], Masayoshi Mikami[3], Martin Stankovski[1], and Xavier Gonze[1] — [1]European theoretical spectroscopy facility (ETSF), Université Catholique de Louvain, Louvain-la-Neuve, Belgium — [2]CERDECAM, Institut Supérieur Industriel ECAM, Bruxelles, Belgium — [3]Mitsubishi Chemical Group Science and Technology (S&T) Research Center, Inc., Yokohama, Japan

White-LEDs will be one of the major actor involved in the future generations of eco-friendly light sources. For novel types of white LEDs, an optimal combination of two green- and red-emitting phosphors absorbing partly the blue light from the InGaN LED is mandatory to obtain a white light source by post recombination of the light.

We have theoretically studied two oxynitride phosphors, one is an efficient green phosphor $Ba_3Si_6O_{12}N_2$:Eu developed at the Mitsubishi Chemical Group (S&T) Research Center, and the other is a bluish-green phosphor $Ba_3Si_6O_9N_4$:Eu that exhibits little luminescence at room temperature. Our results rely on many body perturbation approach (GW+PAW) applied to the two hosts : $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$. The calculation shows a slightly narrower energy gap for $Ba_3Si_6O_9N_4$, that is 0.33 eV. Yet such a result provides keys to understand the thermal quenching mechanism, by comparing materials with a similar chemical composition, but different thermal behaviour. Then a deeper analysis with Eu-doped models sheds new light onto the relationship between emission/excitation colors from the Europium luminescent centers, and the properties of their complex ligands.

O 74.4 Thu 15:45 TRE Phy

First principle calculation on the Fermi contact shift of lithium ion in paramagnetic battery materials — •Yuesheng Zhang[1], Florent Boucher[1], Aurore Castets[2], Dany Carlier[2], and Michel Ménétrier[2] — [1]IMN, Nantes, France — [2]ICMCB, Pessac, France

Solid state NMR in materials for lithium-ion batteries is considerably developing. In paramagnetic materials, the NMR shift of lithium is mainly contributed by the Fermi contact that can be qualitatively interpreted using chemical intuition and the concept of delocalization or polarization mechanisms. In this paper, with accurate first principle methods implemented into WIEN2k, we have obtained the spin density at the nucleus of lithium ions, and then calculated the contact shifts of lithium in several selected transition metal oxides or phosphates. The results show that the calculated values are sensitive to the exchange/correlation potential used in calculation. GGA or LDA generally overestimate the shifts, the calculated values being always shifted along positive direction comparing to the experimental ones. Adding orbital potential "U" or exact exchange on transitional metal ions can improve the results, but still some differences are found with experiments for some cases. The best agreement can be obtained when partial exact exchange potential is applied to both transitional metal and oxygen ions. This means that appropriate exchange correlation potential for transitional metals and oxygen ions is really crucial to calculate the contact shift of lithium ions. This work is funded by Agence Nationale de la Recherche (ANR-09-BLAN-0186-01)

O 74.5 Thu 16:00 TRE Phy

First-principle approach to the temperature dependence of electronic energies. — Paul Boulanger[1,2], Michel Cote[2], and •Xavier Gonze[1] — [1]ETSF / IMCN, Université Catholique de Louvain, 1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium — [2]Département de physique, Université de Montréal, C.P. 6128, succ. Centre-ville, Montréal (Québec) H3C 3J7, Canada

The energy bands of semiconductors exhibit significant shifts with temperature, due to electron-phonon interactions. In search of an efficient first-principle approach to this effect, we have found that formulas derived by Allen, Heine and Cardona in a semi-empirical context cannot be transposed to Density-Functional Theory or to Many-Body Perturbation Theory without critical reexamination. For these theories, the correct formulation includes a extra term, the non-site-diagonal Debye-Waller term, which is dependent on second-order derivatives of the self-consistent electron-lattice potential with respects to atomic displacements. We have studied the importance of this extra term for diatomic molecules and found that it partially cancels the standard Debye-Waller and Fan terms leading a decrease by 52% for H2, 10% for N2 and 37% for LiF. For CO it adds about 15% to the temperature dependence. The lack of this term might explain the discrepancy found between previous theory and experiment for solids. Furthermore, the slow convergence of the sum-over-states approach of Allen-Heine-Cardona approach can be avoided in a new formalism proposed here, based on Density-Functional Perturbation Theory, leading to a dramatic decrease of calculation times.

O 74.6 Thu 16:15 TRE Phy

Quasiparticle calculations of core levels — •Arno Schindlmayr and Dominik Biffart — Department Physik, Universität Paderborn, 33095 Paderborn, Germany

Electrons that occupy core orbitals are tightly bound to the atomic nucleus and do not participate in chemical bonding. Nevertheless, their binding energies are sensitive to the chemical environment, because the redistribution of the valence electrons due to bond formation strongly influences the interaction with the nucleus. For this reason, core-level spectroscopy is an important tool to clarify the atomic structure of materials, such as the geometry of surfaces, interfaces or defects, which can be used even when direct imaging techniques are not applicable. Theoretical calculations of core levels are typically based on density-functional theory. Although these often show the correct

trends, they are plagued by the well known deficiencies of common exchange-correlation functionals as well as technical difficulties, especially in the prevalent pseudopotential approximation. As an alternative, we employ many-body perturbation theory, where the quasiparticle correction to the Kohn-Sham eigenvalues provides a formally exact description of dynamical screening around the core hole in the final state. Our implementation is based on the full-potential linearized augmented-plane-wave (FLAPW) method and employs the GW approximation for the electronic self-energy. The calculated core levels of selected systems, such as silicon in various crystalline materials with differing local environments, are in very good quantitative agreement with experimental data from X-ray photoemission measurements.