HL 26: Focus Session: Frontiers of Electronic-Structure Theory IV (joint session O/HL)

Time: Wednesday 10:30–13:00 Location: TRE Ma

HL 26.1 Wed 10:30 TRE Ma

A systematic DFT+U and Quantum Monte Carlo benchmark of magnetic two-dimensional (2D) CrX_3 (X = I, Br, Cl, F) — •Daniel Wines, Kamal Choudhary, and Francesca Tavazza — Materials Science and Engineering Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA

The search for two-dimensional (2D) magnetic materials has attracted a great deal of attention because of the experimental synthesis of 2D CrI_3, which has a measured Curie temperature of 45 K. Often times, these monolayers have a higher degree of electron correlation and require more sophisticated methods beyond density functional theory (DFT). Diffusion Monte Carlo (DMC) is a correlated electronic structure method that has been demonstrated successful for a wide variety of systems, since it has a weaker dependence on the Hubbard parameter (U) and density functional. In this study we designed a workflow that combines DFT+U and DMC in order to treat 2D correlated magnetic systems. We chose monolayer CrX_3 (X = I, Br, Cl, F), with a stronger focus on CrI_3 and $CrBr_3$, as a case study due to the fact that they have been experimentally realized and have a finite critical temperature. With this DFT+U and DMC workflow and the analytical method of Torelli and Olsen, we estimated an upper bound of 43.56 K for the T_c of CrI_3 and 20.78 K for the T_c of $CrBr_3$, in addition to analyzing the spin densities and magnetic properties with DMC and DFT+U. We expect that running this workflow for a well-known material class will aid in the future discovery and characterization of lesser known and more complex correlated 2D magnetic materials.

Topical Talk HL 26.2 Wed 10:45 TRE Ma

TREX: an integrated HPC software platform for quantum Monte Carlo calculations — •Claudia Filippi — University of Twente, Enschede, The Netherlands

I will present the software development strategy and current achievements of the European Center of Excellence TREX "Targeting Real chemical accuracy at the EXascale" [1]. TREX focuses on methods at the high-end in the accuracy ladder of electronic structure approaches and, in particular, on quantum Monte Carlo methods which are uniquely positioned to fully exploit the massive parallelism of upcoming architectures. The main objective of TREX is the development of a user-friendly and open-source software suite, which integrates quantum Monte Carlo codes within an interoperable, high-performance platform. Core of our software efforts is the creation of the following two libraries:

- TREXIO: A common I/O library and file format for easily exchanging data between applications, facilitating high-throughput computing workflows [2];

- QMCkl: A library of computational kernels, written together by quantum Monte Carlo and HPC experts, to perform common CPU-intensive quantum Monte Carlo tasks [3].

[1] https://trex-coe.eu
[2] https://github.com/trex-coe/trexio
[3] https://trex-coe.github.io/qmckl

HL 26.3 Wed 11:15 TRE Ma

Exciton-phonon coupling in luminescence of indirect band-gap materials — Matteo Zanfrognini[1,2], Fulvio Paleari[1], Daniele Varsano[1], and •Ludger Wirtz[3] — [1]Centro S3, CNR-Istituto Nanoscienze, Modena, Italy — [2]Università di Modena e Reggio Emilia, Modena, Italy — [3]Department of Physics and Materials Science, University of Luxembourg, Luxembourg

Layered, quasi-2D materials, such as hexagonal boron nitride (hBN) are known to display very strong excitonic effects due to the concentration of excitons in two dimensions and due to the relatively weak dielectric screening. If the band-gap of the material is indirect, the dispersion of the lowest lying exciton can have a minimum at a finite wave vector q. Upon absorption of a photon and excitation to a vertical (q=0) exciton, the system will relax to the finite-q exciton. Luminescence then entails the absorption/emission of a phonon with wave vector q. We present a computational approach for phonon-assisted luminescence in the presence of strong excitonic effects using two approaches: (i) a finite-displacement approach for the exciton-phonon coupling and (ii) a diagrammatic approach, calculating the q-

dependent exciton-phonon coupling from the exciton eigenvectors and electron/hole-phonon scattering matrix elements. We show that the methodology quantitatively explains recent measurements of different stackings of BN layers. [1]

[1] A. Plaud, I. Stenger, F. Fossard, L. Sponza, L. Schué, F. Ducastelle, A. Loiseau, J. Barjon, to be published.

HL 26.4 Wed 11:30 TRE Ma

A combined G_0W_0/BSE scheme of characterizing photoexcitations in hydroxylated rutile $TiO_2(110)$ — •Savio Laricchia, Andrea Ferretti, Daniele Varsano, and Claudia Cardoso — Centro S3, CNR-Istituto Nanoscienze, 41125 Modena, Italy

In reduced TiO_2, electronic transitions originating from polaronic excess electrons in surface-localized band-gap states (BGS) are known to contribute to the photoabsorption and to the photocatalytic response of TiO_2 in the visible region. Recent state-selective studies using two-photon photoemission (2PPE) spectroscopy have also identified an alternative photoexcitation mechanism contributing to the photoabsorption of the reduced surface (110) of rutile TiO_2. This process involves d-d excitations from BGS arising from surface and subsurface defects, including bridging hydroxyls and oxygen vacancies. Density Functional Theory (DFT) has been used to determine the character of the electronic excited states involved in a $d_{t_{2g}}$-$d_{t_{2g}}$ transitions, but its accuracy is questioned by its theoretical framework: DFT is in principle exact for ground state systems and does not describe interacting photogenerated electron-hole pairs, i.e. the excitons. This has highlighted the need to move beyond the DFT formalism, by working within a many-body perturbation theory (MBPT) framework. It will be shown how a G_0W_0 method, combined with the solution of the Bethe-Salpeter equation (BSE), provides a powerful tool for characterizing from first principles the optical excitations from BGS identified by 2PPE experiments on hydroxylated $TiO_2(110)$.

15 min. break

HL 26.5 Wed 12:00 TRE Ma

Scaling the Way for All-Electron XPS Simulations to CalculateAbsolute Binding Energies of Surface Superstructures — •Dylan Morgan[1], Sam Hall[1], Benedikt Klein[1,2], Matthew Stoodley[1,2], and Reinhard Maurer[1] — [1]Department of Chemistry, University of Warwick, United Kingdom — [2]Diamond Light Source, Harwell Science and Innovation Campus, United Kingdom

First principles simulations of x-ray photoemission spectroscopy (XPS) and near-edge x-ray absorption fine-structure (NEXAFS) crucially support the assignment of surface spectra composed of many overlapping signatures. Core-level constrained Density Functional Theory calculations based on the Δ-SCF method are commonly used to predict relative XPS binding energy (BE) shifts but often fail to predict absolute BEs. The all-electron numeric atomic orbital code FHI-aims enables an accurate prediction of absolute BEs, but the legacy code lacked computational scalability to address large systems and robustness with respect to localisation of the core hole. We present a redesign of the core-hole constrained code in FHI-aims that delivers improvements to the scalability and robustness of core-hole constrained calculations in FHI-aims. We demonstrate the improved scaling behaviour and employ the new code to simulate core-level spectroscopic fingerprints of graphene moire superstructures. The code refactorisation forms the basis to expand the code towards improved core hole localisation methods and the rigorous treatment of relativistic effects for core-level spectra beyond the 1s shell.

HL 26.6 Wed 12:15 TRE Ma

Efficient diagonalization of BSE electron-hole Hamiltonian using group theory — •Jörn Stöhler[1,2], Dmitrii Nabok[1], Stefan Blügel[1], and Christoph Friedrich[1] — [1]Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich, Germany — [2]RWTH Aachen University, Germany

The Bethe-Salpeter equation (BSE) is the state-of-the-art method for the calculation of optical absorption and electron-energy loss spectra including excitonic effects. We solve the BSE by diagonalizing an effective electron-hole Hamiltonian. Often, a high number of **k**-points is needed to converge the BSE spectra, which leads to a large size of

the Hamiltonian matrix and makes its diagonalization very expensive. In this work [1], we use the full spatial symmetry group to transform the electron-hole product basis into a symmetry-adapted product basis, which brings the Hamiltonian into a block-diagonal form and speeds up the subsequent diagonalization. The basis transformation is sparse and causes little overhead. We provide an implementation of our method in the FLAPW code `Spex` and demonstrate speedups of 36, 52, 12 for Si, BN, and monolayer MoS_2, respectively.

[1] J. Stöhler, C. Friedrich, *Unpublished*

HL 26.7   Wed 12:30   TRE Ma

Excitonic effects on quadratic optical photoresponse tensors of semiconductors — ●Peio Garcia-Goricelaya[1] and Julen Ibañez-Azpiroz[1,2] — [1]Centro de Física de Materiales, University of the Basque Country UPV/EHU, Spain — [2]IKERBASQUE Basque Foundation for Science, Spain

We present a general ab initio scheme for including many-body excitonic effects in the non-linear optical photoresponse up to second order. Our practical implementation starts from the length-gauge formulation of the single-particle non-interacting optical photoresponse tensors [1] that are efficiently calculated using Wannier interpolation [2]. Subsequently, excitonic corrections are included in the many-body interacting current-density response tensors by means of Dyson-like equations derived within TD-CDFT. These equations allow a natural connection with the formalism of the single-particle picture and the Wannier-interpolation scheme respecting the tensorial character of the response. We employ this scheme to assess the impact of excitonic effects on several quadratic optical processes as the second-harmonic generation and the shift-current bulk photovoltaic effect in technologically appealing semiconductors.

[1] J. E. Sipe and A. I. Shkrebtii, Phys. Rev. B 61, 5337 (2000).
[2] G. Pizzi et al., J. Phys. Cond.Matt. 32, 165902 (2020)

HL 26.8   Wed 12:45   TRE Ma

Electronic and optical properties of $CoFe_2O_4$ from density functional theory calculations, including many-body effects — ●Shohreh Rafiezadeh[1], Vijaya Begum-Hudde[1,2], and Rossitza Pentcheva[1] — [1]Department of Physics University of Duisburg-Essen, Germany — [2]University of Illinois at Urbana-Champaign, USA

$CoFe_2O_4$ is a ferrimagnetic semiconductor that finds application as an anode material in photocatalytic water splitting. We present a comprehensive study of the electronic and optical properties of bulk $CoFe_2O_4$ using density functional theory calculations and many-body perturbation theory to clarify the broad range of reported band gaps both experimentally (0.55-4.1 eV)[1] and theoretically (0.9-1.90 eV). Starting with different exchange-correlation functionals, we obtain a direct band gap of 1.38 [PBE+(U=4 eV)], 1.69 eV [SCAN+(U=3 eV)], and an indirect gap of 2.02 eV (HSE06). Including quasiparticle corrections within G_0W_0 enhances and renders indirect band gaps for all functionals of 1.78, 1.95 and 2.17 eV, respectively. Excitonic effects are accounted for by solving the Bethe Salpeter equation and result in the lowest threshold for optical transitions at 1.50 eV (SCAN) and 1.61 eV (HSE06), followed by peaks at ~ 2.0, 3.5 and 5.0 eV, in agreement with experiment highlighting the importance of electron-hole interactions. Support by DFG- within CRC/TRR 247, project B04, and computational time at MagnitUDE is gratefully acknowledged. [1] S. Singh and N. Khare, Sci. Rep. **8**, 6522 (2018).