O 37: Electronic structure theory I

Time: Tuesday 10:30–12:30 Location: TRE/PHYS

Invited Talk O 37.1 Tue 10:30 TRE/PHYS

Calculations of excited electronic states by converging on saddle points on the electronic energy surface — •Hannes Jonsson — University of Iceland, Reykjavik, Iceland

Calculations of excited electronic states are important in various contexts, e.g. photocatalysis and molecular motors. They are challenging as commonly used optimization methods are based on minimization and thereby converge on the ground state. A time-dependent formulation of density functional theory (TD-DFT), especially within the linear response and adiabatic approximations, is therefore often used to estimate excited states, but can fail especially when significant charge transfer occurs and when states are close in energy. Alternatively, by converging on a saddle point on the electronic energy surface, the orbitals can be optimised for an excited state to provide a solution of the underlying Kohn-Sham equations with higher energy than the ground state. This turns out to a give more robust estimate of the excitation energy than TD-DFT with computational effort similar to that of a ground state calculation. Several applications of this approach with commonly used density functionals will be presented, as well as calculations using a self-interaction corrected functional giving improved results. In particular, excited states involving twisting of a C=C bond, e.g. in molecular motors, and Rydberg states have been analysed. As a solid state application, the various states involved in the optical preparation of a pure spin state in nitrogen/vacancy defect in diamond will be presented. The results show close agreement with more computationally demanding calculations as well as experiments.

O 37.2 Tue 11:00 TRE/PHYS

Probing quantum coherence with free electrons — •Hebrew Crispin and Nahid Talebi — Christian-Albrechts-Universität, Kiel, Germany

Advances in ultrafast electron microscopy have enabled the study of coherent interactions between free electrons and quantum systems with high spatial resolution. Recent works have examined the coupling of free electrons to two-level systems, including the use of coherently shaped electron wavefunctions to probe coherence in individual or collective quantum emitters. Coherence can also be accessed through sequential time-resolved cathodoluminescence spectroscopy, which has demonstrated the ability to measure ultrafast radiative decay and dephasing in single emitters with femtosecond resolution. In addition, there is increasing interest in time-resolved electron energy-loss spectroscopy (EELS) techniques capable of tracking system dynamics.

Here, we present a general theoretical framework for coherent interactions between free electrons and quantum emitters prepared in arbitrary initial superposition states. We employ a fully quantum, time-dependent description of both the propagating electron wavepacket and the emitter. Quantum coherence manifests as transient oscillations in both the emitter populations and in the zero-loss peak of the spectral energy-loss probability density, even for an unmodulated electron wavepacket. Our work reveals novel coherent dynamics in the interactions between free electrons and quantum systems.

O 37.3 Tue 11:15 TRE/PHYS

Phonons in polar materials: a DFPT extension in the FLAPW method *FLEUR* — •Friedrich Hanrath[1,2], Thomas Bornhake[1,2], Gustav Bihlmayer[1], Gregor Michalicek[1], Daniel Wortmann[1], and Stefan Blügel[1,2] — [1]Peter Grünberg Institut, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany — [2]Institute for Theoretical Physics, RWTH Aachen University, D-52074 Aachen, Germany

Phonons play a pivotal role in determining many essential properties of solids. Using Density Functional Perturbation Theory (DFPT), a state-of-the-art approach for computing fundamental physical response properties from first principles, phonon calculations have previously been realized [1] within the full-potential linearized augmented plane-wave (FLAPW) method *FLEUR* [2]. In polar materials, zone-center vibrations are altered by their interaction with long-range electric fields, giving rise to the characteristic LO-TO splitting in the long-wavelength limit. In this talk, we present the extension of the DFPT framework in *FLEUR* to a macroscopic electric-field perturbation, enabling the calculation of high-frequency dielectric tensors and Born effective charges, quantities required to describe LO-TO splitting, and compare our results with experiments.

This work was supported by the CoE-MaX (EuroHPC Joint Undertaking, Grant 101093374) and DFG through CRC 1238 (Project C01).

[1] C.-R. Gerhorst *et al.*, Electron. Struct. **6**, 017001 (2024).
[2] D. Wortmann *et al.*, 10.5281/zenodo.7576163; www.flapw.de

Invited Talk O 37.4 Tue 11:30 TRE/PHYS

Many-Body Theory meets Electrochemistry: Electronic Structure of Cathode Materials — •Silke Biermann — Centre de Physique Théorique, UMR7644, Ecole Polytechnique, Institut Polytechnique de Paris, 91128 Palaiseau, France

Progress in dynamical mean field-based electronic structure methods over the last years has provided us with precious tools allowing for a microscopic understanding of electronic mechanisms at work in correlated materials, including functional materials. In this talk, we will focus on layered transition metal compounds studied for battery applications. Analysing the electronic structure, energetics and intercalation voltage, we find that Hund's exchange coupling plays a crucial role for the electrochemistry of these compounds. We identify the battery charging process as a transition from a high-spin Mott insulator to a low-spin correlated metal. We argue that a deeper understanding of the microscopic mechanisms at work in such materials might contribute to paving the way to better battery materials in the future.

O 37.5 Tue 12:00 TRE/PHYS

Massively parallel and GPU-accelerated evaluation of three-center integrals for numerical atomic orbitals (NAOs) — •Moritz Leucke, Antonio F. Delesma, and Dorothea Golze — Julius-Maximilians-Universität Würzburg, Germany

Four-center electron repulsion integrals appear in many electronic structure methods, such as many-body perturbation methods like the Random-Phase-Approximation or GW and others. To reduce their computational cost, the resolution-of-the-identity (RI) approximation is commonly employed. RI refactors the four-center integrals into three- and two-center integrals, among which the three-center integrals remain a computational bottleneck, particularly when using NAOs.

We present a global RI scheme combined with a local metric (attenuated Coulomb) within an all-electron NAO framework, treating molecules and solids on equal footing. Central to the approach is a novel GPU-accelerated algorithm for computing 3-center integrals that relies on domain decomposition to improve load balancing and strong scaling.

We demonstrate that our RI implementation achieves linear scaling with system size and maintains meV-level accuracy for GW energies. Performance benchmarks show scalability across thousands of CPU cores and substantial speedups with GPU support.

[1] Delesma et al., NIC Symposium Proceedings, 52(2025), 113-123.

O 37.6 Tue 12:15 TRE/PHYS

Efficient all-electron implementation of the Bethe-Salpeter method using crystal symmetries — Jörn Stöhler, Stefan Blügel, and •Christoph Friedrich — Peter Grünberg Institut, Forschungszentrum Jülich, 52425 Jülich, Germany

We describe an implementation of the Bethe-Salpeter equation (BSE) method in the full-potential linearized augmented-plane-wave (FLAPW) method. As in most implementations, the BSE is solved by the diagonalization of a two-particle Hamiltonian matrix, whose dimension is proportional to the number of **k** points. Due to the large number of **k** points required to converge the spectra, the resulting matrix becomes large even for small unit cells. We describe a method that exploits the crystal symmetries to accelerate the construction and diagonalization of the two-particle Hamiltonian. In particular, we employ group theoretical tools to bring the Hamiltonian into block-diagonal form. It is shown that, in many cases, only one of the blocks needs to be taken into account, which leads to a considerable speedup of the diagonalization step. In the case of Si, for example, the dimension of the Hamiltonian is reduced by a factor of five, giving rise to a speedup factor of 125 in its diagonalization. The optical absorption spectrum calculated with a 60×60×60 **k** mesh is very close to the experimental spectrum. The code allows for the inclusion of spin-orbit coupling and is parallelized with the possibility of storing the Hamiltonian in distributed memory over many nodes. We also show results for LiF and the MoS_2 monolayer.