# O 2: Focus Session: Frontiers of Electronic-Structure Theory – Advances in Time-Dependent and Nonequilibrium Ab Initio Methods I

Time-dependent and non-equilibrium phenomena in condensed matter involve a wide and diverse landscape of excitations (excitons, polarons, magnons, polaritons, etc.) and fundamental interaction mechanisms spanning different time and length scales as well as different levels of complexity. There has been enormous progress in the experimental probes of a variety of time-resolved phenomena with high precision, motivating further advancements in the ab initio description of ultrafast phenomena with electronic-structure calculations, explicit quantum dynamics, mixed quantum-classical dynamics methods, and many-body theories. This interdisciplinary Focus Session will cover recent progress in this area, with a primary focus on novel theoretical and computational paradigms for the description of time-dependent and nonequilibrium phenomena in quantum materials.

Organizers: Fabio Caruso (U Kiel), Claudia Draxl (HU Berlin), Reinhard Maurer (U Warwick)

Time: Monday 10:30–13:00 Location: HE 101

O 2.1 Mon 10:30 HE 101

**Electron-phonon coupling in photoexcited graphene** — •Nina Girotto and Dino Novko — Institute of Physics, Zagreb, Croatia

Understanding the out-of-equilibrium interactions and how they evolve in time is one of the main goals of ultrafast experiments. Here, we present an extensive study of the phonon spectrum and electron-phonon coupling in pristine and doped graphene during a strong optical excitation, calculated from first principles density-functional perturbation theory with adjusted occupations of the electronic states. By promoting a substantial number of electrons from the valence to the conduction band with a laser pulse, the thermalization process of photoexcited carriers includes three distinct electron distributions; photoexcited state is achieved exactly after the laser pulse and is followed by the photo-inverted state (cca 100 fs), and finally at timescales at the order of the electron thermalization time, the electrons follow a hot Fermi-Dirac distribution. In the three time regimes, we find renormalizations of the real and imaginary parts of the phonon self-energy, resulting from the interplay between ultrafast scatterings between nonequilibrium electrons and strongly coupled optical phonons and changes in the electron-phonon coupling matrix elements. Some of the compelling features are the photo-induced negative phonon linewidth, or 'phonon gain', found for some wave vectors, as well as anomalous phonon frequency shifts of strongly-coupled modes. Our results shed light on the intricate effects of photoexcitation on electron-phonon coupling, and track their changes in time.

O 2.2 Mon 10:45 HE 101

***Ab initio* theory of coherent phonons in semimetals** — •Christoph Emeis, Yiming Pan, and Fabio Caruso — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24118 Kiel, Germany

The spectral signatures of coherent phonons in pump-probe experiments can disclose novel insight into electron-phonon interaction and its influence on ultrafast phenomena. We developed an ab initio framework to describe the coherent phonon dynamics in photo-excited semimetals based on the time-dependent Boltzmann equation and its extension [1]. To illustrate the predictive capability of this approach, we investigate the displacive excitation of coherent phonons in Sb and $MoTe_2$ and discuss its fingerprints in frequency-domain ARPES, a powerful experimental technique to probe coherent phonons and electron-phonon coupling in semimetals [2]. [1] F. Caruso and D. Novko. Adv. Phys. X **7**, 2095925 (2022). [2] P. Hein et al. Nat. Commun. **11**, 2613 (2020).

O 2.3 Mon 11:00 HE 101

**First-principles light-driven molecular dynamics through equivariant neural networks** — •Elia Stocco[1], Christian Carbogno[2], and Mariana Rossi[1] — [1]MPI for the Structure and Dynamics of Matter, Hamburg, Germany — [2]Fritz Haber Institute of the MPS, Berlin, Germany

Recent experiments have shown a rich phenomenology in solids, liquids and molecules when driven by ultra-fast THz pulses. However, simulation techniques that can describe the nuclear dynamics of these processes for all material classes, without relying on dimensionality reduction, and going beyond perturbation theory, are very challenging. Here we propose an ab initio molecular dynamics (MD) method within the electric dipole approximation that allows a single machine-learning model to describe the coupling at diverse field strengths and with time dependence. Our requirement is that the system remains near the electronic ground state. We train an equivariant differentiable neural network to learn the dipole of isolated and periodic systems. Atomic tensor derivatives w.r.t. the nuclear coordinates are obtained through autodifferentiation. We present applications of this machine-learning-assisted MD protocol on water and LiNbO3. We show full-dimensional ab initio simulations of the excitation of vibrational modes at an ultrafast time scale and highlight the different nonlinearities of these dynamics.

O 2.4 Mon 11:15 HE 101

**Anharmonic fingerprints from THz modes of naphtalene crystals enabled by machine-learning** — •Paolo Lazzaroni, Shubham Sharma, and Mariana Rossi — Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

Organic molecular crystals exhibit strong lattice anharmonicity, especially in the collective motions that are governed by intermolecular interactions and lie in the low-frequency THz range [1]. Inspired by recent observations that the polarization-orientation (PO) Raman spectra can give exquisite insight into the anharmonic couplings between modes [2], we devise a first-principles framework that aims at reproducing, explaining and give quantitative insight into the type and strengths of mode coupling. This framework is based on machine-learned potentials and polarizability tensors trained on ab-initio molecular dynamics trajectories [3]. We obtain results, even for large system supercells, through the time-correlation formalism for PO Raman signals, retaining the full anharmonic nature of the potential. In order to do this, a procedure has been developed that allows us to isolate the Γ-point Raman signal from our real-space molecular dynamics simulations. [1] M. Asher et al., Adv. Mater. 32, 1908028 (2020) [2] N. Benshalom et al., J. Phys. Chem. C 127, 36 (2023) [3] N. Raimbault et al., New J. Phys. 21 105001 (2019)

O 2.5 Mon 11:30 HE 101

**Electron-phonon interaction in silicon and diamond using Gaussian orbitals** — •Gerrit Johannes Mann, Thorsten Deilmann, and Michael Rohlfing — Institute of Solid State Theory, University of Münster, Germany

Electron-phonon interaction is a crucial mechanism in solid state physics that is responsible for a multitude of phenomena. However, in electronic structure calculations it is often neglected. We developed an ab-initio implementation on top of density functional theory that combines finite differences calculations with the perturbative Allen-Heine-Cardona framework in order to calculate the temperature-dependent renormalization of the electronic bandstructure due to electron-phonon interaction using a basis set of localized Gaussian orbitals.

Our implementation circumvents the limiting problems of previous implementations while maintaining a good agreement with the literature. For the direct band gaps of silicon and diamond we find a zero-point renormalization of $-43\,\mathrm{meV}$ and $-411\,\mathrm{meV}$, respectively. In addition, the approach allows to evaluate Debye-Waller contributions beyond the rigid-ion approximation.

O 2.6 Mon 11:45 HE 101

**Electron-phonon interactions in hybrid inorganic-organic systems from first-principles calculations** — •Ignacio Gonzalez Oliva[1], Sebastian Tillack[1], Fabio Caruso[1,2], Pasquale

Pavone[1], and Claudia Draxl[1] — [1]Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — [2]Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24118 Kiel, Germany

Hybrid materials composed of organic molecules and two dimensional (2D) transition metal dychalcogenides (TMDCs) exhibit interesting physical processes happening at the interface. By means of full-potential all-electron density-functional theory and many-body perturbation theory, we investigate the electronic properties and electron-phonon interactions of a prototypical system, comprising of a MoS$_2$ monolayer and a physisorbed molecule, pyrene. $G_0W_0$ calculations show that the electronic levels of both components are renormalized due to dynamical screening effects. Temperature renormalization of the electronic bands are computed with the electron-phonon self-energy in the Fan-Migdal approximation. The calculated spectra reveal discernible features attributable to electron-phonon coupling within this system. Notably, distinctive signatures emerge, suggesting the manifestation of polaronic effects attributed to the presence of pyrene.

O 2.7 Mon 12:00 HE 101

**Phonon mediated superconductivity obtained by combining `elphbolt` and `exciting`** — •Marten Pretorius, Sebastian Tillack, Ignacio Gonzalez Oliva, Pasquale Pavone, Nakib Haider Protik, and Claudia Draxl — Humboldt-Universität zu Berlin

We present an *ab initio* study of superconductors within the Migdal-Eliashberg formalism. Using the implementation of the full-potential all-electron density-functional theory package `exciting` [1], we construct compact real-space representations of the dynamical matrix, Hamiltonian, and the electron-phonon interaction matrix using density-functional perturbation theory and maximally-localized Wannier functions. These generated quantities are passed to the `superconda` app of the `elphbolt` [2] package, which solves the coupled Migdal-Eliashberg equations for the superconducting gap and the mass renormalization. We apply this workflow to selected materials.

[1] A. Gulans, *et al.*, J. Phys.: Condens. Matter **26**, 363202 (2014).

[2] N.H. Protik, *et al.*, npj Comput. Mater. **8**, 28 (2022).

O 2.8 Mon 12:15 HE 101

**Phonons in FLEUR employing Density Functional Perturbation Theory: Towards 2D** — •Thomas Bornhake[1,2], Alexander Neukirchen[1,2], Gregor Michalicek[1], Daniel Wortmann[1], Gustav Bihlmayer[1], and Stefan Blügel[1,2] — [1]Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich GmbH and JARA, 52425 Jülich, Germany — [2]RWTH Aachen University, 52062 Aachen, Germany

Phonons are important excitations in solids. The investigation of phonon properties by density functional theory of magnetic systems is underrepresented in the literature. Recently, we completed successfully the implementation of the phonon dispersion using the density functional perturbation (DFPT) method in the all-electron full-potential linearized augmented plane-wave (FLAPW) method FLEUR [1,2]. In this talk, we present recent advancements for phonon calculations within FLEUR. We discuss calculations in magnetic bulk systems and compare these to phonon dispersions obtained with the finite displacement method for which the FLEUR code has been combined with the phonopy tool [3]. Motivated by the physics of 2D materials, we extended our methodology to 2D films in semi-infinite vacuum [4].

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[1] D. Wortmann *et al.*, 10.5281/ZENODO.7891361; www.flapw.de

[2] C.-R. Gerhorst *et al.*, arXiv:2309.14799v2 (2023).

[3] http://www.phonopy.github.io/phonopy/

[4] H. Krakauer *et al.*, Phys. Rev. B **19**, 1706 (1979)

O 2.9 Mon 12:30 HE 101

**Light-matter dynamics in full minimal coupling Maxwell-TDDFT for beyond-dipole interactions** — •Franco P. Bonafe, Esra Ilke Albar, Heiko Appel, and Angel Rubio — MPI for Structure and Dynamics of Matter, Hamburg, Germany

The electric dipole approximation (EDA) has been by far the most extensively used treatment of light-matter interaction in molecular and nanoscopic systems, owing to the typically long wavelength of the incoming field compared to the size of these systems. However, for the deep understanding of novel spectroscopy techniques and phenomena where the interplay between electric and magnetic fields is relevant, a description beyond the EDA is sometimes mandatory.

In this talk, we show an efficient fully ab initio approach to couple electrons, nuclei and photons, by self-consistently coupling Maxwell's equations with time-dependent density functional theory (TDDFT) using the Pauli full minimal coupling Hamiltonian [1]. This method is based on a rigorous density-functional reformulation of the non-relativistic Pauli-Fierz Hamiltonian of quantum electrodynamics, and has been implemented in the Octopus package [2]. The effects of the non-uniform transverse fields in the dynamics will be exemplified with several systems, including the Cherenkov radiation from an electronic wavepacket, core-level photoabsorption, and chiroptical activity.

[1] R. Jestädt, M. Ruggenthaler, M.J.T. Oliveira, A. Rubio, and H. Appel. Adv. Phys. 68:4, 225 (2019)

[2] N. Tancogne-Dejean, M.J.T. Oliveira, et al. J. Chem. Phys. 152, 124119 (2020)

O 2.10 Mon 12:45 HE 101

**Path-integral generalized Langevin dynamics: quantum nuclei with position-dependent friction** — •George Trenins[1], Paolo Lazzaroni[1], Yair Litman[2], and Mariana Rossi[1] — [1]MPI for the Structure and Dynamics of Matter, Hamburg, Germany — [2]Yusuf Hamied Department of Chemistry, University of Cambridge, UK

Dissipative dynamics model large-scale problems by treating a few degrees of freedom explicitly and describing the rest statistically. For example, in the study of nuclear dynamics at metal interfaces, nonadiabatic coupling to the electrons can be modelled as "electronic friction" [1]. Such systems with no clear separation of timescales are a computational challenge, due to the dependence of the dissipative forces on position and time. To address this, our group has developed an instanton rate theory that accounts both for the friction and for nuclear quantum effects [2]. However, since this theory cannot describe reactions taking place in liquid environments, we explore an alternative approach, explicitly introducing friction into ring-polymer molecular dynamics [3]. This framework uncovers the unexpected interplay between position-dependent friction and quantum dynamics in a model potential. We show practical approaches to propagating the underlying equations of motion and solutions to simulating multidimensional quantum dissipative systems. [1] W. Dou, J. E. Subotnik, JCP **148**, 230901 (2018). [2] Y. Litman et al. JCP **156**, 194106 (2022). [3] S. Habershon et al. Annu. Rev. Phys. Chem. **64**, 387–413 (2013).