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Watching Excitons Move: Real-Time and Linear-Response TDDFT for Periodic Systems in TURBOMOLE

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The optical response of materials, from excitons in atomically thin semiconductors to laser-driven currents behind petahertz electronics, unfolds on femto- to attosecond timescales. Plane-wave codes dominate this field, yet local Gaussian bases offer a compelling alternative: all-electron accuracy, natural treatment of core excitations, seamless transition from molecules to crystals, and no artificial replication of low-dimensional systems. This talk presents the extension of TURBOMOLE's riper module into a full time-dependent spectroscopy engine for periodic systems of any dimensionality.

At its core is k-resolved real-time TDDFT: the time-dependent Kohn–Sham equations are propagated at every point of the Brillouin zone mesh using unitary Magnus and enforced-time-reversal-symmetry schemes, with the absorption spectrum extracted from the induced macroscopic current. Velocity and hybrid gauges are available, and gauge invariance is verified through the Thomas–Reiche–Kuhn sum rule. Crucially, the propagation now includes exact exchange, so global hybrid and range-separated functionals capture the excitonic effects that semilocal functionals miss, at the moderate cost enabled by density fitting and continuous fast multipole methods. Periodic linear-response TDDFT within the same framework provides an independent cross-check, and agreement between the two routes is demonstrated for chains, monolayers, and bulk crystals, culminating in the excitonic absorption of two-dimensional hexagonal boron nitride and bulk silicon.

Because real materials are rarely perfect crystals, the framework connects to embedding: real-time TDDFT embedding theory evolves a molecular region inside a frozen periodic environment, giving access to chromophores at surfaces and in explicit periodic solvent boxes at near-molecular cost, with solvatochromic shifts reproduced to within 0.1 eV of full-system references.

One code and one input thus carry a simulation from an isolated dye to a dye embedded in a crystal to the crystal itself. The talk concludes with the road ahead: strong-field dynamics and high-harmonic generation in solids with hybrid functionals, toward predictive attosecond materials science.