Leveraging an open-subsystem formulation of Density Functional Theory (DFT) [1] we aim at describing periodic and molecular systems alike, including their electronic and nuclear dynamics. Subsystem DFT enables first principles simulations to approach realistic time- and length-scales, and most importantly sheds light on the dynamical behavior of complex systems. Taking subsystem DFT to the time domain allows us to inspect the electron dynamics of condensed-phase systems in real time. In liquids and interfaces, we observe all the relevant regimes proper of non-Markovian open quantum system dynamics, such as electronic energy transfer, and screening [2]. In addition, the ab-initio modeling of system-bath interactions brought us to observe and justify the holographic time-dependent electron density theorem. Contrary to interactions between molecular (finite) systems, when molecules interact with metal or semiconductor surfaces [3] the electron dynamics is strongly non-Markovian with dramatic repercussions to the molecule’s response to external perturbations. Metals and semiconductors typically have large polarizabilities, and even in a regime of low coupling their effect on impinging molecular species is significant – line broadening, peak shift, and intensity borrowing are observed, characterized, and explained in terms of inter-subsystem dynamical interactions and a many-body decomposition of the system’s density-density response function in a way that transcends the canons of Fermi Golden Rule.

References