# Electron and Electron-Nuclear Dynamics of Open Quantum Subsystems

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## Abstract

Leveraging an open-subsystem formulation of Density Functional Theory (DFT) 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. 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 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 [1,3,6].

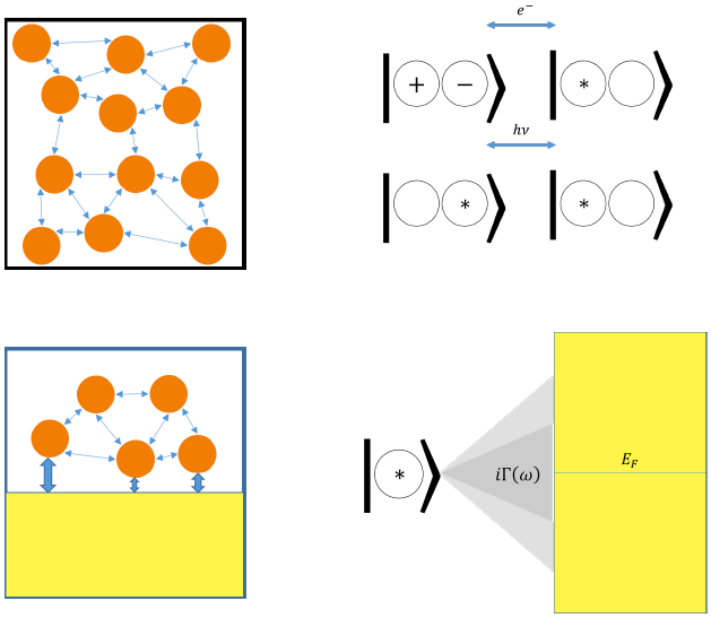


**Figure 1: Open subsystems and their interactions. Upper left: collection of molecular subsystems; upper right: typical avenues of exchange of energy and electrons between open subsystems; lower left: interface between a set of molecular subsystems and an extended subsystem; lower right: depiction of the coupling between a finite subsystem having a discrete energy spectrum and an extended system having a dense energy spectrum.**

To approach the nonadiabatic dynamics of condensed-phase systems, we set on finding methods for computing excited states that are "balanced" with ground state calculations and that can be seamlessly extended to a subsystem formulation. Exploiting the machinery of Constrained DFT, we proposed [3] a variational method for calculating low-lying excited states of molecular systems which we dub eXcited Constrained DFT (XCDFT). Excited states are obtained by self-consistently constraining a user-defined population of electrons, $N_c$, in the virtual space of a reference set of occupied orbitals. By imposing this population to be $N_c = 1$, we compute the first excited state. Our results show that XCDFT achieves accurate excitation energies without incurring into problems of variational collapse typical of the more commonly adopted ΔSCF method, even for certain multireference excited states [7]. XCDFT is capable of reproducing energy surfaces featuring conical intersections (azobenzene and $H_3$) with correct topology and correct overall energetics also away from the intersection. Venturing to condensed-phase systems, XCDFT reproduces the TDDFT solvatochromic shift of benzaldehyde when it is embedded by a cluster of water molecules. We also implemented nonadiabatic couplings for XCDFT which are quantitative against MR-CI for a select set of molecular systems and excited states [8].

In the cost-extension year of the grant (2020-2022), we implemented of Ehrenfest dynamics in a subsystem real-time TDDFT software which is available in a TDDFT simulation in the QEpy software [10] and for a Subsystem TDDFT simulation, in the eDFTpy software [11]. In addition to the Ehrenfest dynamics, we have developed a robust software for subsystem TDDFT in Python called eDFTpy [11] which we have applied to determine the many-body dispersion effects among water molecules while they solvate a surface comprised by monolayer $MoS_2$ [12]. As we have also developed an embedding method capable of combining orbital-free DFT and TDDFT as well as Kohn-Sham DFT and TDDFT in a single electronic structure method [13]. While the code for now has only been applied to describe the ground electronic states of interface systems, we plan to explore way of coupling subsystem TDDFT with time-dependent Thomas-Fermi theory for metal surfaces. We expect the latter to yield fast and still accurate models of the dynamics of molecule-metal interfaces which is still largely uncharted due to the large computational cost of modeling the metallic system. This is subject of ongoing research.

In order to employ orbital-free TDDFT as a reliable alternative to TDDFT for metals and large-sized nanoparticles, we developed a fully nonadiabatic Thomas-Fermi method (time-dependent orbital-free DFT) capable of recovering the large majority of the nonadiabaticity in the Pauli kernel [9,14]. which will be useful when nonstandard embedding schemes (such as the one mentioned above) are implemented. We implemented a new orbital-free DFT code [5] where we collect all of the latest methods.

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**Publications Acknowledging the Grant**

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**Other publications not mentioned in this report but still supported by the DOE grant – and directly resulting from the implementations and method development resulting from the DOE grant project:**

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