(TD)DFT - Dirty secrets under the hood

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Density Functional Theory (DFT) and the time-dependent (TD-) DFT calculations are widely used for predicting ground state energies and spectral features due to their attractive combination of accuracy with relatively low computational cost. Recent implementations [1] on real time propagation TD-DFT allow applications at nanoscale, such as noble metal nanoparticles. In order to go beyond the spectral properties, excitations can be analyzed further, for example in order to understand the nature of d-band screened plasmonic excitations in noble metals [2]. In first part of the talks, I will introduce time-propagation methods in TD-DFT, including our recently developed Kohn-Sham decomposition method. I will discuss the nature of TD-DFT excitations by presenting them as an analogous classical Hamiltonian with symplectic structure, and apply this point of view to understand plasmonic excitations. Natural transition orbitals and natural transition currents will be introduced as tools for understanding nanoscale transitions. In second part, I will concentrate on non-equilibrium transport properties, such as electron energy transfer (EET). I will formulate diabatic presentation, which will be applied with real time TD-DFT to study ab initio EET compared to experimental measurements on KU Orange 2 (dye) and Au_{102}(p-MBA)$_{44}$ ligand protected nanoparticle. All of the demonstrations are done with GPAW electronic structure code on tools which will be made available on open source.

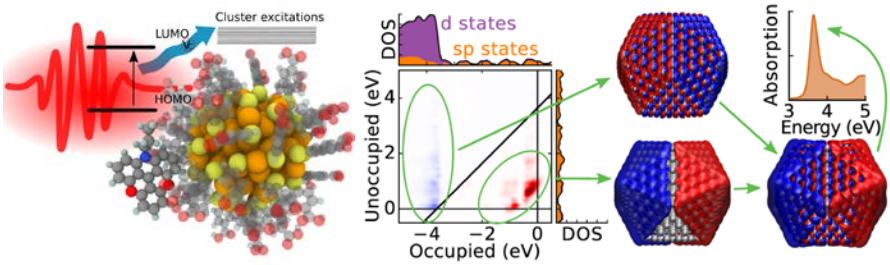

Figure 1. (left) Schematic representation on EET process with KU Orange 2 and Au_{102}(p-MBA)$_{44}$. (right) Kohn-Sham decomposition analysis on Ag_{561} nanocluster, showing the nature of plasmon resonance in noble-metal nanoparticles.

References

[1] Phys. Rev. B, **91**, *115431* (2015)
[2] J. Chem. Theory Comput. just accepted *10.1021/acs.jctc.7b00589* (2017)