# STM 2016- Relazione Scientifica Finale

## Equation of Motion for Drude-Lorentz solvent polarization coupled to time-dependent configuration interaction approaches

The program of this STM project was to extend previously developed ab initio real time methods for molecules hosted in a solvent to more complex dielectric environments, such as the neighbourhood of a metal nanoparticle (NP). This is important to enable the simulation of ultrafast spectroscopy of molecules close to NPs. To achieve this goal, it was necessary to derive and implement new time-dependent equations describing the time-dependent electromagnetic interactions between the molecule and the NP, described through apparent surfaces charges appropriated for a Drude-Lorentz dielectric function. In particular, the expected activity to be performed was:

i) Derive the proper equation of motion (EOM) for the Drude-Lorentz dielectric function based on the similar derivation for the Debye dielectric function.

ii) Implement in a Fortran module the required routines to numerically solve such equation of motions

iii) Interface such routines with the existing TD-CI code, already able to account for Debye dielectric functions EOM

During Dr. Pipolo's stay, such activities have been performed and completed. An article describing these developments has been very recently accepted by the ISI peer-reviewed Journal of Physical Chemistry C (STM program was duly acknowledged):

S. Pipolo, S. Corni, *Real-Time Description of the Electronic Dynamics for a Molecule Close to a Plasmonic Nanoparticle*. J. Phys. Chem. C in press DOI: 10.1021/acs.jpcc.6b11084

As documented in this manuscript:

i) The EOMs for the apparent surface charges $\mathbf{q}_{\mathbf{pol}}$ were derived, resulting in a damped forced harmonic oscillator form:

$$\ddot{\mathbf{q}}_{\mathrm{pol}}(t) \quad = \quad -\gamma\dot{\mathbf{q}}_{\mathrm{pol}}(t) - \mathbf{Q}_{\omega}\mathbf{q}_{\mathrm{pol}}(t) + \mathbf{Q}_{f}\mathbf{V}(t)$$

where $\gamma$ is the damping constant and $Q_{\omega}$ and $Q_{f}$ are proper PCM-like matrices.

ii) Proper Fortran routines were written for their numerical integrations, based on a specific implementation of the velocity-Verlet scheme [Vanden-Eijnden, E.; Ciccotti, G. Second-order integrators for langevin equations with holonomic constraints. Chem. Phys. Lett. 2006, 429, 310]

iii) They were interfaced with a code able to perform evolution of the time-dependent Schrödinger equation written on a basis of Configuration Interaction states.

The scheme was tested on LiCN subject to an impulsive electric field close to an elongated Drude-like Ag nanoparticles. The level of calculation was CIS/6-31G*. The resulting absorption spectrum for the molecule, as well as the nanoparticle, is shown in Fig. 1

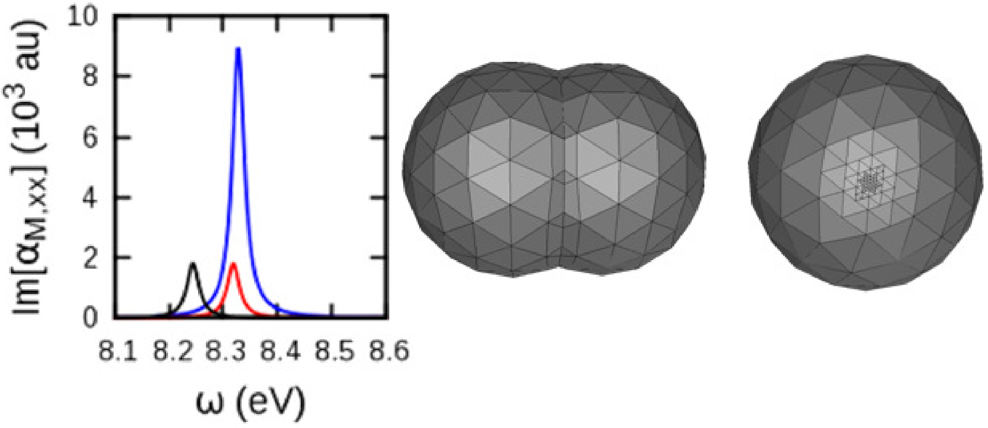

*Fig. 1 Left panel: Absorption spectrum of LiCN in the region 8.1-8.6 eV (black: no NP; red: with NP but its polarization is frozen; blue: with NP, time-dependent polarization). Right panel: Shape of the nanoparticle and of the tesselation used to define the position of the apparent surface charges.*

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Signature

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