Multiscale Methods for Computational Spectroscopy

Tommaso Giovannini

Department of Physics, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133, Rome, Italy

The theoretical description of large systems in the condensed phase at a high level of accuracy is particularly challenging due to the large number of degrees of freedom (both electronic and nuclear) that need to be treated. However, for systems embedded in an external environment, such complexity can be drastically reduced by partitioning the total system into smaller, interacting subsystems, with a special focus on a specific portion [1-3]. The theoretical approaches developed within this framework belong to the family of multiscale focused models [1-3] and are valuable tools used to bridge the gap between theory and experiment. In the most accurate multiscale focused models, the target moiety is treated at the quantum mechanical (QM) level, while the environment is atomistically described at a lower level of sophistication either classically (QM/Molecular Mechanics – QM/MM [2,3]) or at the QM level (quantum embedding [4]).

I will present novel multiscale methods for describing the light-matter interaction of molecular systems embedded in external environments, ranging from solvents to nanostructured plasmonic materials. In the first part of the talk, I will focus on molecular systems in solution, by showcasing the recent developments in the context of QM/MM [3] and quantum embedding approcheas [5,6], specifically designed for computational spectroscopy of solutions characterized by specific solute-solvent interactions, such as hydrogen bonding.

In the second part of the talk, I will address plasmonics and molecular plasmonics, by discussing a novel approach to predict the plasmonic properties of nanostructures of complex shapes, general enough to describe, at the same level of accuracy, metal nanoparticles [7,8] and graphene-based nanoaggregates [9]. Finally, the coupling with a QM description of an adsorbed molecular system is presented and extended to predict Surface-enhanced Raman scattering (SERS) signals [10].

References

[1] J. Tomasi, B. Mennucci, R. Cammi. *Chem. Rev.* **2005**, *105*, 2999.

[2] H. M. Senn, W. Thiel. *Angew. Chem., Int. Ed.* **2009**, *48*, 1198.

[3] T. Giovannini, F. Egidi, C. Cappeli. *Chem. Soc. Rev.* **2020**, *49*, 5664.

[4] T. A. Wesolowski, S. Shedge, X. Zhou. *Chem. Rev.* **2015**, *115*, 5891–5928.

[5] G. Marrazzini, T. Giovannini et al. *J. Chem. Theory Comput.* **2021**, *17*, 791.

[6] T. Giovannini et al. *J. Chem. Theory Comput.* **2023**, *19*, 1446.

[7] T. Giovannini et al. *Nanoscale* **2019**, *11*, 6004.

[8] T. Giovannini et al. *ACS Photonics* **2022**, *9*, 3025.

[9] T. Giovannini et al. *J. Phys. Chem. Lett.* **2020**, *11*, 7595.

[10] P. Lafiosca, et al. *J. Chem. Theory Comput.* **2023**, *19*, 3616.