Comparing non-periodic and periodic TD-DFT calculations for inorganic minerals

R. Rullan[1], S. N. Steinmann[1], T. le Bahers[1,2]

[1]ENSL, CNRS, Laboratoire de Chimie UMR 5182, 46 allée d'Italie, 69364 Lyon France
[2]Institut Universitaire de France, 103 boulevard Saint-Michel, 75005, Paris, France

The simulation of excited states in condensed phase is a long-standing challenge due to the large number of atoms and bands to compute. Two approaches can be considered: 1) a **cluster approach** that seeks to divide the system into a cluster treated at a quantum chemical level and its environment that can be treated at different levels [1] and 2) a computationally costly **periodic approach** using **periodic boundary condition (PBC)** where the whole unit cell simulating the system is treated at the quantum chemical level. While the cluster approach has the strength to rely on strongly developed molecular quantum chemical codes and methodologies including post-HF treatments of excited states, this approach comes at the cost of extracting a cluster which might not be relevant for all systems, and finding the appropriate description of the environment. Hence resorting to periodic codes seem to be a tempting solution but comes with the drawback of a less developed community, i.e. codes are rare and technical issues common. Still, the last few years have seen the development of efficient periodic TD-DFT schemes in widespread codes like CP2K that complement the more traditional periodic GW and emerging periodic post-HF schemes which are limited to relatively small systems.

We here compare cluster and periodic TD-DFT computations of experimentally well-characterized solids. Our benchmarks are excited states involved in the photochromism observed in aluminosilicates, having the advantage of providing both localized and charge transfer excited states, singlet-to-triplet transitions all with experimental reference values [2]. After presenting technical aspects (such as the choice of the truncation cutoff radius in periodic exact-exchange computations), we compare periodic and non-periodic TD-DFT results with experimental transition energies and with post-HF non-periodic CIS(D) calculations. The influence of the nature of the functionals (GGA, global hybrid, range-separated hybrids) will be discussed. The results show that the periodic and non-periodic TD-DFT follow the same trends but with the advantage for the former to avoid the delicate choice of the cluster size and the embedding technics.

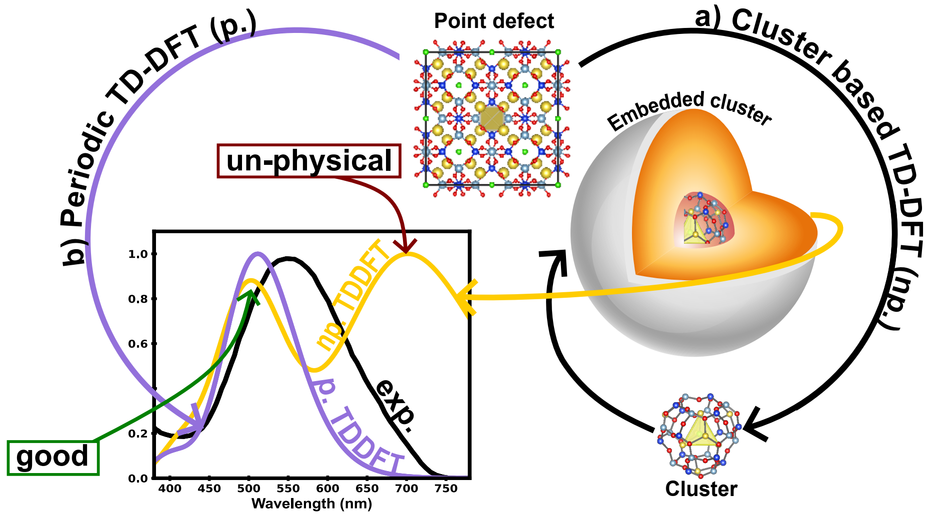

Figure 1: Comparison of a) Cluster-based approach and b) periodic approach for the computation of spectroscopic properties.

References:

[1] R. B. Rullan, S. N. Steinmann, T. Le Bahers, Assessing Nonperiodic and Periodic TD-DFT: The Case of Photochromism in Aluminosilicates, J. Phys. Chem. C, **129**, 13051-13063 (2025)

[2] P. Colinet, H. Byron, S. Vuori, J.-P. Lehtiö, P. Laukkanen, L. Van Goethem, M. Lastusaari, T. Le Bahers, The Structural Origin of the Efficient Photochromsim in Natual Minerals, Proc. Natl. Acad. Sci. USA PNAS, **119**, 23 (2022)