Developping methods to model excited states in condensed phase: application to oxide minerals

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ABSTRACT

The large growth of photonic systems (OLED, photovoltaic, photocatalysis...) and the need of quantum chemical tools to understand them have urged the development of quantum chemical methods for spectroscopic properties in the condensed phase. However, the simulation of such properties is still a challenging task and often requires the use of different computational approaches. Until recently, very few codes were able to combine periodicity and excited state calculations and, most of the time, at prohibitive computational costs. One widely used solution to this problem is based on the embedded cluster approximation. This method implies to divide the system between a cluster and its environment, which can be straightforward for molecular solids but not as easy for inorganic materials. We will present our work dedicated to the study of the polychromism in oxide minerals, namely alexandrite and cordierite, using the aforementioned embedded cluster approach. The cluster is treated at the Time Dependent Density Functional Theory (TDDFT) level and the environment is modelled with point charges fitted to reproduce the electrostatic potential of the infinite crystal [1]. Depending on the functional used, this method showed results in qualitative agreement with the experiment, especially for the reproduction of the photochromism phenomenon in the cordierite mineral which has a blue-purple color (see Fig. 1) in one direction and is colorless in another direction [1]. However, in the case of the alexandrite minerals, the results are less satisfactory. Even if we reproduced the two different colors observed with two different light sources, the anisotropy of light absorption is not captured, pinpointing the difficulties of TDDFT to describe the anisotropy of the electric dipole moment [1]. Finally, we will discuss our on-going developments for new embedding methods to go beyond the point charge approach.

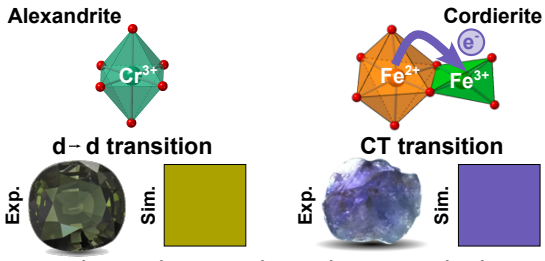

Figure 1: Alexandrite and Cordierite polychromism

References

[1] Rullan, R.; Colinet, P.; Desdion, Q.; Steinmann, S.; Le Bahers, T. Modeling the polychromism of oxide minerals: The case of alexandrite and cordierite. *J Comput Chem*, **2023**, DOI: 10.1002/jcc.27288