

Computational Modeling of Spin-Crossover Systems using Density Functional Methods

Jordi Cirera

Departament de Química Inorgànica I Orgànica and Institut de Química Teòrica i Computacional (IQTC-UB), Universitat de Barcelona

Spin-Crossover (SCO) molecules have two alternative electronic states close in energy that can be accessed using an external perturbation, most commonly, the temperature. Such behavior makes those systems quite appealing for nanotechnological applications as molecular switches. The temperature with equal populations of both spin-states is known as transition temperature ($T_{1/2}$), and it would be highly desirable to be able to preselect its value in order to make such systems operational in given conditions. However, the study of such problem with computational tools is difficult, due to the fact that accurate spin-state energy differences must be computed.

In this presentation, a robust computational strategy based on Density Functional Theory (DFT) methods to accurately compute spin-state energy gaps in transition metal complexes with SCO behavior will be introduced.[1] With such methodology, it is possible to quantitatively compute $T_{1/2}$ and explain the observed experimental trends for families of SCO systems in terms of the underlying electronic structure, using the relevant d-based molecular orbitals.[2,3] The presented methodology not only allows us to explain the observed trends, but also to make predictions on the behavior of systems yet to be reported, with particular emphasis in systems for which not enough experimental data is available.[4] Finally, we will show how our methodology can be expanded to study systems in the condensed phase, allowing for the inclusion of crystal packing and counterion effects.[5] The computational strategy presented opens the door for the *in silico* design of new SCO materials with tailored properties.

- [1] *Inorg. Chem.* 57(22), 14097-14105 (2018)
- [2] *J. Am. Chem. Soc.* 142(47), 20170-20181 (2020)
- [3] *Dalton Trans.* 50, 8704-8710 (2021)
- [4] *Inorg. Chem. Front.*, (2023), Advance Article
- [5] *Phys. Chem. Chem. Phys.* 22(9), 4938-4945 (2020)