

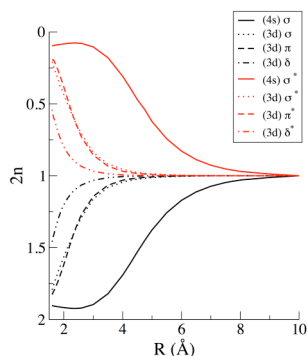
Structure and bonding in transition metal containing systems: natural orbital functional and wavefunction-based calculations

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The research performed in small transition metal clusters is essential nowadays in science and technology because of their wide range of applications in optics, biomedicine and catalysis, among others. The use of metal dimers allows a detailed study of molecular properties without the presence of ligands that may complicate the interpretation of experiments and relieves the computational effort as well.

The Cr₂ dimer sets a big challenge from a theoretical point of view since shows one of the most complicated electronic structures that can be found among metal dimers. The ¹Σ_g⁺ electronic ground state is highly multiconfigurational, with the following dominant configuration: 4sσ_g²3dσ_g²3dπ_u⁴3dδ_g⁴, which weights only a 47% of the total wavefunction. Besides, the experimental potential energy surface shows a shelf-like region at about 2.5 Å, where the interaction between the 4s orbitals is dominant. Finally, the dimer dissociates into two Cr atoms in their high-spin electronic configuration 3d⁵4s¹ (⁷S), which means that the electron correlation is dramatically important along the potential energy surface. In this work we have explored several methods to study the potential energy surface of Cr₂, namely, the CASSCF/CASPT2 method and the Piris Natural Orbital Functional in its 5th version (PNOF5)^[1], which is presented as an alternative to both DFT and wavefunction-based methods.



Occupation of the Cr₂ PNOF5 natural orbitals along the potential energy surface

Another aspect of the role of transition metals in biological systems is the enzymatic function of metal clusters. Clusters involving Fe and inorganic sulphide are ubiquitous in biological systems and can be found at the active sites of wide-variety metalloproteins and metalloenzymes that are involved in biological electron transfer processes, small molecule activation, radical based catalytic transformations, DNA repair and signal transduction. The most common types of clusters involve [Fe₂S₂], [Fe₃S₄] and [Fe₄S₄] cores, and their primary function lies in mediating one-electron redox processes, being integral components of respiratory and photosynthetic electron transfer chains and a host of redox enzymes. In these polymetallic systems, the iron ions have variable oxidation states and the unpaired electrons on the metal can couple by magnetic interactions and define a manifold of ferromagnetic and antiferromagnetic electronic states, which can be separated by small energy differences. Thus, a detailed comprehension of intracuster valence delocalization in terms of Fe – Fe interactions is crucial for understanding the ground and excited states properties. In order to do that, we will employ, again, the CASSCF/CASPT2 and PNOF5 methods. In this seminar, only preliminary CASPT2 results of [Fe₂S₂] will be presented.

[1] M. Piris, J. M. Matxain, F. Ruipérez, X. Lopez and J. M. Ugalde, *J. Chem. Phys.* **2011**, 134, 164102.