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Chemical bond descriptors from multiconfigurational wavefunctions in lanthanide and actinide compounds

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Chemical bonds are fundamental in chemistry, serving as the foundation for understanding molecular properties. Some of the most renowned approaches for analyzing chemical bonds can be broadly categorized into two groups. The first group includes energy-based and its derivative decomposition descriptors like the Local Vibrational Mode (LVM) theory. The second group comprises methods based on wavefunction or electron density analysis, such as the Quantum Theory of Atoms in Molecules (QTAIM). A new set of density-based decomposition chemical bond descriptors, the Chemical Bond Overlap (OP) model, was recently introduced and expanded[1]. This abstract reports on the recent extension[2] of the overlap density and its topological descriptors (OP/TOP) using Multiconfigurational Self-Consistent Field (MCSCF) wavefunctions. We present a comparative analysis of OP/TOP descriptors CASSCF wavefunctions for a diverse range of lanthanide and actinide compounds, including LnX_3 (Ln = Eu, X=F, Cl, Br), UN_2, UO_2, UO_2^{2+}, UO_2Cl_4, UO_2F_4, and $UO_2(CO)_4$. Full-electron relativistic (2nd Order Douglas-Kroll-Hess) CAS(6,7) and CAS(8,7) calculations challenge the MCSCF-based OP/TOP bond descriptors, with comparisons to QTAIM and LVM descriptors. The selected compounds serve as models for larger coordination compounds and as test targets benchmarking relativistic methodologies. Despite their popularity, there are still open questions regarding their structure, bonding, and molecular properties. Figure 1a-d exhibits the obtained overlap density maps for selected systems, where it is possible to observe that the increase in the electronegativity of X in EuX_3 shifts the overlap density toward X. Chemical bonds in uranium compounds are known to be more covalent than in their lanthanide counterparts. Figures 1e-g clearly show that the overlap densities in uranium compounds are more spread along the bonds, due to the effective participation of 5f electrons, with U–N (Fig. 1f) bonds sharing more electrons than U–O counterpart (Fig. 1e).

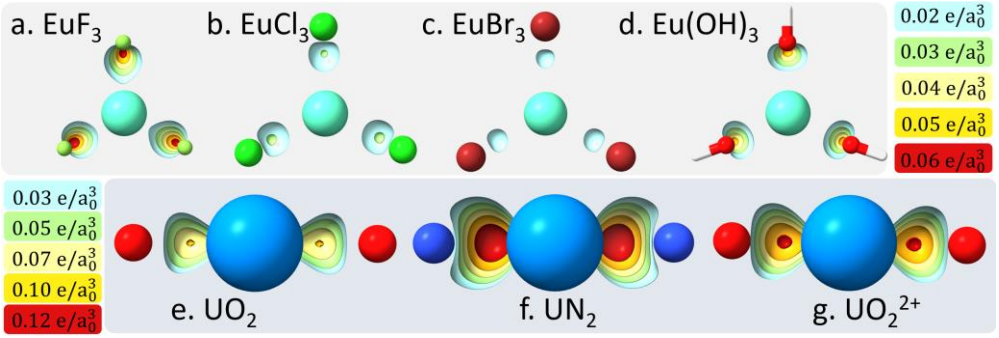

Figure 1. Electron density maps for selected studied systems. Isovalues are indicated in the figure.

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References

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