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Insights on spin density delocalization/polarization mechanisms through the source function

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The Source Function (SF) tool [1] is applied to the analysis of the ab-initio spin density in two azido Cu(II) dinuclear complexes, where the azido group, acting as a coupler between the copper atoms, is linked to the metal centers either in an End-On or in an End-End fashion. The SF for the spin density [2] highlights to which extent the magnetic centers contribute to determine the local spin delocalization and polarization at any point in the two systems and whether an atom or group of atoms of the ligands acts in favour or against a given local spin delocalization/polarization. Analogies and differences between the two systems have been quantitatively established. Ball-and-stick atomic SF percentage representations allow for an immediate visualisation of the magnetic pathways and of the specific role played by each atom along these paths, at given reference points. Decomposition of SF contributions in terms of a magnetic and of a relaxation component provides further insight.

Reconstruction of partial spin densities by means of the Source Function is introduced [3]. At variance with the standard SF percentage representations, such reconstructions offer a simultaneous view of the sources originating from specific subsets of contributing atoms, in a selected molecular plane or in the whole space and are therefore particularly informative. The SF tool is also used to evaluate the accuracy of the analysed spin densities. It is found that those obtained at the unrestricted B3LYP DFT level, relative to those computed at the CASSCF(6,6) level, greatly overestimate spin delocalization to the ligands, while comparatively underestimate magnetic connection (spin transmission) among atoms, along the magnetic pathways. As a consequence of its excessive spin delocalization, the UB3LYP method also overestimates spin polarization mechanisms between the paramagnetic centers and the ligands. Spin delocalization measures derived from the refinement of Polarised Neutron Diffraction data seem in general superior to those obtained through the DFT UB3LYP approach and closer to the far more accurate CASSCF results. It is also shown that a visual perfect accord on the spin resolved electron densities rho-alpha and rho-beta derived from different approaches does not warrant a corresponding agreement between their associated spin densities.

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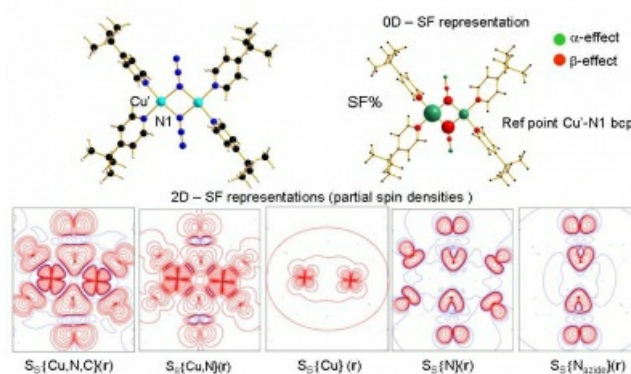
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