

O - 17 Getting more physical and chemical insight into electron spin density distributions and their accuracies

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Modelling magnetic properties of crystalline compounds by experiments is truly challenging^[1]. New methodological routes are now available to ease this task. By combining the information obtained by different techniques such as X-ray and polarized neutron diffraction (PND)^[2,3], or PND and X-ray magnetic diffraction^[4], the limitation of the scarce number and resolution of experimental data is partly overcome. More precise wavefunction-based models or electron spin densities (SDs) are so obtained and comparison with *exact* wavefunctions or densities becomes clearly advisable to test their accuracy. *Ab-initio* electron SDs can be easily calculated but they are usually far from being reliable. Systematic studies demonstrated that DFT is often unable to treat open-shell systems properly, leading to non-accurate electron SDs^[5,6]. *Ab-initio* electron correlation methods or density-matrix renormalization group approaches^[6], have to be called for. Yet, they are often computationally too demanding and unsuited for large systems.

On top of all this, extraction of chemical information from the SD is not a trivial task as it is for the electron density (ED), even for very simple molecular systems^[7]. We thus purposely extended the concept of Source Function (SF)^[8] to SD distributions and used such tool to analyze the magnetic patterns in organic systems^[9] and in metal complexes molecular crystals^[10,11]. The SF SD serves as an useful tool for discussing the SD accuracy and for disclosing the origin of the SD discrepancies when approaches of increasing quality are used. It is here applied to analyze and compare the theoretical SD in two azido di-copper complexes, one weakly and one strongly ferromagnetically coupled.^[10,11] The SF enables to highlight the origin of the SD differences between the two di-copper complexes and among the adopted computational approaches (CASSCF, UDFT, UHF). Further insight is provided by *partial* Source Function SD reconstructions using subsets of atoms. DFT methods exaggerate electron sharing between Cu and the ligands, leading to spin delocalization towards them and to an overestimation of the metal-ligand spin polarization. At the same time, DFT underestimates the spin information transmission between atoms, relative to the CASSCF method. PND SD is closer to CASSCF SD than to DFT SD. We also discuss whether it is DFT overdelocalizing spins, or is it a consequence of DFT overdelocalizing the charge, exploring ways, if any, to untangle the two effects.

The SF is a quite general concept and a powerful interpretive tool, whether applied to the SD or, as it is more usual, to the experimental or theoretically derived ED^[12-13], like in recent studies aimed at probing cyclic π -electron delocalization in N-heterocyclic carbenes^[12] or at revealing the locality extent of the hydrogen bonds of the DNA base pairs in their neutral and ionized ground states^[13]. Suitably extended to the electrostatic potential (EP) reconstruction, the SF concept has also recently enabled to interpret^[14] the group atomic contributions to the EP maxima associated with chalcogen bonds, which were found to act as stereoselective secondary interactions in HPLC enantioseparations.

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