Magnetic Exchange Couplings in High-Nuclearity Transition Metal Complexes from Density Functional Theory Methods

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The magnetic characterization of molecular complexes containing dozens or even hundreds of magnetic centers is key to understanding many biological processes, future technology developments, and the discovery of novel quantum materials. In most cases, magnetic exchange couplings are the most elusive among the basic parameters involved in spin model Hamiltonians used for this purpose. The reason is that experimental methods cannot provide a detailed breakdown of the individual exchange couplings between all magnetic centers due to the multiple couplings present. In some cases, one may rely on magneto-structural correlations, provided that a consistent training set exists. For other cases, density functional theory (DFT) methods are the only option, considering the size of the molecular complexes of interest. Traditional methods to extract exchange couplings from DFT rely upon mapping the broken-symmetry DFT solutions to Ising-like spin model energies. These methods need many energy evaluations and quickly become impractical for large, high-nuclearity complexes. Other methods involve a mapping based on single spin-flip energies. In contrast to energy differences methods, an approach based on local spin rotations that rely on approximate Green's function perturbation theory and yields a simple Alder-Wiser style sum-over-states expression is popular in the solid state physics community. In this talk, I will review existing methods to extract magnetic exchange couplings from DFT, and show that the two families of methods yield the same exchange couplings, provided that the local spin rotations include the proper spin-density variational relaxation. The approximate Green's function method is very attractive for the particular case of high-nuclearity complexes since it can be very fast and automated to systematically screen multiple and diverse complexes. I will introduce some of our new developments based on local rotations of the magnetization in different flavors and show some examples such as Fe_{22}, Fe_{24} , and Fe_{36} complexes.

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