DFT calculation of magnetic anisotropies for multinuclear complexes with antiferromagnetic coupling

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The density functional treatment of systems where the true many-electron wave function is multideterminantal faces a problem. This arises, for example, if one considers the low-energy manifold of states that arises from antiferromagnetic couplings between several open-shell transition metal centers. This low-energy manifold can faithfully be described by a phenomenological Heisenberg Spin Hamiltonian $\hat{H}_{iso} = \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$ where $\hat{S}_i$ is the spin operator representing the single-site (local) spin of a metal center. One can obtain a relation between the exchange coupling constants J_{ij} and energy expectation value differences of Ising-type configurations (where all local spins have either maximum or minimum spin projection). The latter are then identified with DFT energy differences from *broken symmetry* calculations. This way, DFT provides the parameters of $\hat{H}_{iso}$ whose diagonalization finally yiels the "true" energy differences.

The spin-orbit contribution to magnetic anisotropy (or zero-field splitting) can phenomenologically be described by adding single-site terms to the Spin Hamiltonian which then assumes the form

$$\hat{H} = \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j + \sum_i \hat{S}_i \cdot \mathbf{D}_i \cdot \hat{S}_i \tag{1}$$

The problem is now that all Ising configurations have the same magnetic anisotropy, and DFT calculations also show very similar magnetic anisotropies for all the different broken symmetry situations: not enough information is generated to get a hold on the magnetic anisotropies of the true many-electron states, which e.g. must be zero for singlets.

To generalize the broken symmetry approach to the calculation of zero field splittings or magnetic anisotropies, one must extract somehow the single-ion tensors $\mathbf{D}_i$ which can be done in numerical experiments by "switching on/off" the spin-orbit interaction at specific sites. Togehter with the J_{ij} calculated by the standard procedure, the Spin Hamiltonian can be set up and diagonalized which gives the "true" magnetic anisotropies for the individual spin states. Two-center contributions to the magnetic anisotropy have to be treated separately, but this can be well treated with a point-dipolar approximation.

This procedure is demonstrated for model complexes with two and three antiferromagnetically coupled Mn(III) centers, and large variations of the magnetic anisotropy is found across the low-energy spin states.

Literature:

C. van Wüllen, *J. Chem. Phys. A* **2009**, *113*, 11535–11530.