Equation-of-Motion Coupled-Cluster Protocol for Computing Molecular Magnetic Properties

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A reliable *ab initio* description of molecular magnetic behavior is key to developing novel molecule-based quantum devices, with the potential to be more efficient and easily tunable. We present a new computational protocol for computing magnetic properties of transition-metal complexes, which complements experimental investigations on the design of improved molecular magnets. The approach follows a state-interaction scheme in which spin-orbit coupling (SOC) and the interaction with an applied magnetic field are treated as perturbations using equation-of-motion coupled-cluster (EOM-CC) wave functions. Temperature- and field-dependent magnetic properties are obtained by differentiation of the partition function computed using the energies of the perturbed EOM-CC eigenstates. The protocol is implemented within the *ezMagnet* software. We apply this protocol to a set of mononuclear Fe and Ni compounds, and show that the computed energy barriers for spin inversion, and magnetization and susceptibility data agree well with experiments. We complement our study by the analysis of spinless transition density matrices and related transition natural orbitals (NTOs), and explain the trends in magnetic anisotropy and barrier height in the Fe-based single-molecule magnets. Similarly, for a set of ring-substituted nickelocene ($NiCp_2$, Cp = cyclopentadienyl) derivatives and for a model system of the $NiCp_2$/MgO(001) adsorption complex, this NTO-analysis indicates that spin states and magnetic properties are retained upon modification of $NiCp_2$'s coordination environment and upon adsorption. Such resilience of the $NiCp_2$'s magnetic behavior supports using $NiCp_2$ as a spin-probe molecule by functionalization of the scanning tunneling microscope (STM)-tip.

References:

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2. M. Atanasov, J. M. Zadrozny, J. R. Long and F. Neese *Chem. Sci.* **4**, 139 (2013).
3. *ezMagnet* is available at: http://iopenshell.usc.edu/downloads/ezmagnet/.