Analysis of spin-spin interactions in transition metal clusters of biochemical interst

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I will give an overview of our applications of density functional theory to explore aspects of electronic stuctures of active site of metalloproteins. The focus will be on open-shell transition metal systems, espeically with more than one metal site. This will include a discussion of spin-unrestricted theories, and a look at "broken symmetry" and other approaches to spin coupling among metal sites, including ways of estimating exchange interaction energies and the spectroscopic properties of coupled sites. The principal spectroscopic probes of interest here are ligand and metal hyperfine interactions, and vibrational spectroscopies (especially as monitored by nuclear resonance vibrational spectroscopy or NRVS).

A second area will discuss practical methods of estimating the effects of the the protein and solvent environment. The subjects described above are essentially on "model compounds" -- fragments that mimic some aspects of the active sites of metalloproteins. Some important progress has been made in making more direct representations of active sites within their protein/solvent environment. This makes possible estimates of redox potentials and pKa values.

For each area, examples will largely be drawn from work (in collaboration with Lou Noodleman, Tim Lovell, and Rhonda Torres) on iron-sulfur clusters, with a focus on ferredoxins the MoFe protein of nitrogenase. [1-3]

[1] L. Noodleman, T. Lovell, W. Han, J. Li, F. Himo, *Chem. Rev.* 2004, **104**, 459.
[2] R.A. Torres, T. Lovell, L. Noodleman, D.A. Case, *J. Am. Chem. Soc.* 2003, **125**, 1923.
[3] T. Lovell, T. Liu, D.A. Case, L. Noodleman, *J. Am. Chem. Soc.* 2003,**125**, 8377.