ACCURATE PREDICTION OF ^{57}FE MöSSBAUER PARAMETERS VIA DENSITY FUNCTIONAL THEORY: PREDICTION OF REACTION INTERMEDIATES AND CATALYTIC CYCLES OF IRON ENZYMES

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Computational methods of electronic structure can predict the electron density, $\rho(\mathbf{r})$, at the site of ^{57}Fe nuclei ($\mathbf{r}$ = 0) and, therefore, Mössbauer isomer shifts (δ_{Fe}). In addition, one can predict electric field gradient tensors and quadrupole splittings (Δ_{EQ}). We report the implementation of a computational methodology for the accurate prediction of Mössbauer spectral parameters via spin density functional theory (SDFT). Given the crystallographic structure, the method can be applied to any molecular or biomolecular system and, in addition to predicting spectral parameters, allows the microscopic interpretation of experimental spectra. Herein, we use SDFT to predict and elucidate complex spectra (Figure 1) of antiferromagnetic binuclear iron proteins (Figure 2). We also describe the phenomenological simulation of spectra of antiferromagnetic diiron centers based on the use of spin Hamiltonians with a leading Heisenberg term, $J\mathbf{S}_1\bullet\mathbf{S}_2$, where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the intrinsic spin operators of each iron site.[1-3]

Mössbauer spectra of spin-coupled diiron proteins, recorded as a function of applied magnetic field (Figure 1) and temperature, are highly informative but difficult to interpret. We have combined the use of phenomenological spin Hamiltonians and spin density functional theory [2] to predict and interpret spectroscopic parameters of several antiferromagnetic binuclear iron proteins. In particular, we have predicted Mössbauer parameters of methane monooxygenase hydroxilase (MMOH), an enzyme that catalyzes the conversion of methane to methanol.[4] In addition, by incorporating the effects of spin-orbit coupling (SOC) via perturbation theory (PT) on top of conventional SDFT calculations, we predict with a high degree of accuracy the zero-field splittings (ZFS) of the iron centers. This SDFT-PT methodology allows us to establish a direct relationship between electronic structure, geometric structure, and ZFS parameters. Finally, we describe the prediction of geometric structures of reaction intermediates in catalytic cycles of iron enzymes using Mössbauer parameters as a reference.[4]

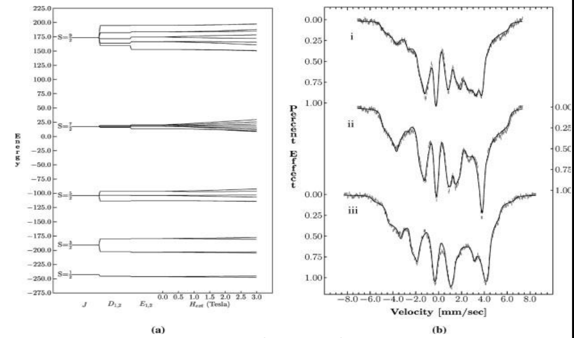

Figure 1. (a) Energy levels of the antiferromagnetic diiron protein uteroferrin (Ufr) obtained from diagonalization of a spin Hamiltonian. [1] The ground doublet (S = 1/2) and higher spin multiplets are shown as the Heisenberg exchange, zero field splitting (ZFS), and Zeeman interactions are turned on. (b) Spectra recorded at 4.2K under variable external fileds.[1]

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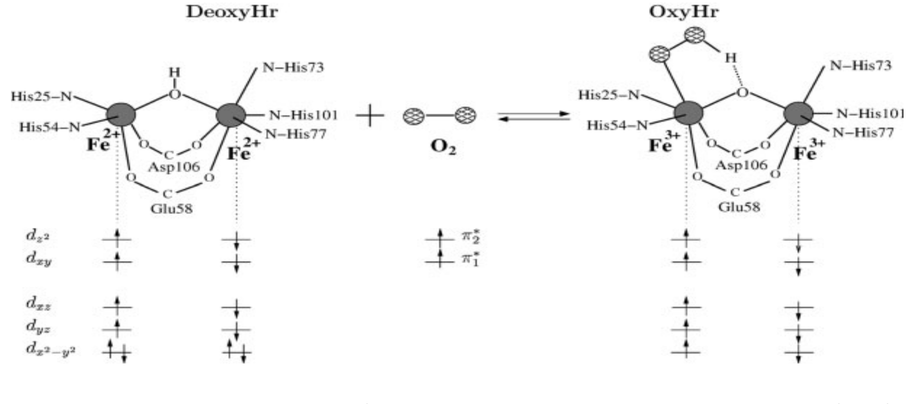

Figure 2. DeoxyHr, an oxygen transporting protein, has an antiferromagnetic binuclear where the unpaired electrons of one ferrous ion are antiparallel to those of the other. This gives rise to an open-shell singlet ground state. Upon binding to the triplet ground state of O_2 the protein cycles to the oxidized state (OxyHr), where the unpaired electrons of one ferric ion are antiparallel to those of the other, also giving rise to an open-shell singlet.[1] The antiferromagnetic interaction between the irons is described by the Heisenberg operator $J\mathbf{S}_1\bullet\mathbf{S}_2$.[1,2,3]