

Abstract Submitted
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Dependence of Localized Electronic Structure on Ligand Configuration in the [2Fe] Hydrogenase Catalytic Core* CHRISTOPHER H. CHANG, KWISEON KIM, National Renewable Energy Laboratory — The [FeFe] hydrogenase enzyme is found in a variety of organisms, including Archaea, Eubacteria, and green algae^{1,2}, and crystallographically determined atomic position data is available for two examples. The biologically unusual catalytic H-cluster, responsible for proton reduction to H₂ *in vivo*, is conserved in the known structures and includes two *bis*-thiolato bridged iron ions with extensive cyano- and carbonyl ligation. To address the configurational specificity of the diatomic ligand ligation, density functional theoretical calculations were done on [2Fe] core models of the active center, with varying CO and CN⁻ ligation patterns. Bonding in each complex has been characterized within the Natural Bond Orbital formalism. The effect of ligand configuration on bonding and charge distribution as well as Kohn-Sham orbital structure will be presented. [1] M. Forestier, P. King, L. Zhang, M. Posewitz, S. Schwarzer, T. Happe, M.L. Ghirardi, and M. Seibert, *Eur. J. Biochem.* **270**, 2750 (2003). [2] Posewitz, M.C., P.W. King, S.L. Smolinski, R.D. Smith, II, A.R. Ginley, M.L. Ghirardi, and M. Seibert, *Biochem. Soc. Trans.* **33**, 102 (2005).

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