

Self-consistent self-interaction corrected DFT studies of annite

ERIC J. BYLASKA¹, KIRIL TSEMEKHMAN²,
EUGENE S. ILTON¹ AND KEVIN M. ROSSO¹

¹Pacific Northwest Laboratories, Richland, WA, 99352, USA
(eric.bylaska@pnl.gov, eugene.ilton@pnl.gov,
kevin.rosso@pnl.gov)

²University of Washington, Seattle, WA, 98195, USA
(kirilt@ikazki01.chem.washington.edu)

One of the more persistent failures of standard DFT methods has been their failure to yield localized charge states such as polarons, excitons and solitons in solid-state and extended systems. It has been suggested that standard DFT functionals which are not self-interaction free tend to favor delocalized electronic states since self-interaction creates a Coulomb barrier to charge localization. Pragmatic approaches in which the exchange correlation functionals are augmented with small amount of exact exchange have shown promise (i.e. B3LYP and PBE0) in localizing charge states. However, a large amount of exact exchange must be added in order for these methods to yield localized charge states, which results in band-gaps and reaction barriers being overestimated. We have recently developed a framework for implementing self-consistent self-interaction corrections (SIC) into pseudopotential plane-wave density functional theory (PSPW). This technique has shown great promise predicting localized charge states as well as accurate band-gaps and reaction barriers. Furthermore, this technique is applicable to both confined and extended systems, as well as to Car-Parrinello ab initio molecular dynamic simulations. We present here results from a recent study of the oxidation of annite in air. Some evidence exists that oxidation of annite will result in a charge states inside the single-particle band gap, associated with localized Fe^{3+} ion state. Such a state is typically the result of local distortion of the lattice leading to localization of the electronic wave function. So far, only small cluster models within Hartree-Fock approximation have yielded such a localized Fe^{3+} state. It is well known that the Hartree-Fock approximation unnecessarily favors localized states. In contrast, large-scale periodic DFT calculations using standard DFT functionals do not localize these types of states. Using our newly developed DFT+SIC method we have been able to obtain a significant degree of charge localization. Various aspects of this application and implications of the DFT+SIC theory to modeling charge transfer in extended systems will be discussed.

Siderophore-metal interactions on oxide surfaces

SAMUEL J. TRAINA¹ AND CHIA-CHEN CHEN²

¹Sierra Nevada Research Institute, University of California,
Merced, California 95344, USA

²University of Texas, Austin, Texas 78712, USA

Desferoxamine B (DFB) is a representative oxamic acid siderophore. These natural chelates are produced by a number of microorganisms and play a significant role in Fe-availability to these organisms. Siderophores have recently received considerable attention because of their potential to react with lanthanides, actinides and an array of other toxic metals. Indeed, the fate and transport of a number of metals in soils and sediments may be greatly influenced by reactions with siderophores. The present study examines the effects of on DFB of Eu, Nd, Pb and Zn desorption from hematite and maghemite. Macroscopic measurements show that siderophore-induced metal desorption is incomplete removing only a fraction of the surface bound sorptive. Dissolution of the mineral substrate (indicated by release of Fe to solution) appears to be subsequent, rather than simultaneous to the release of Eu, Nd, Zn and Pb. In all cases, DFB-induced release of Fe is less in the presence of adsorbed Eu, Nd, Zn and Pb than their absence. Europium-, Nd-, Pb- and Zn-EXFAS collected prior to reaction of the mineral-sorptive adducts with DFB indicate a prevalence of mono-dentate surface species at the mineral/water interface. In contrast EXAFS spectra collected after reaction of DFB with these same mineral-metal complexes shows a prevalence of bidentate surface bound metals, suggesting that these species are less reactive and therefore less susceptible to removal by the complexing ligand. The implications of this work to contaminant chemistry and elemental cycling will be discussed.