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In the following a brief summary report on the progress in a number of areas explored in the project is given:

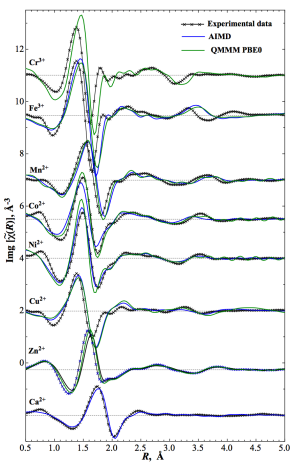


Figure 1: 1st principle based XAFS calculations for transition metal ions.

High resolution EXAFS studies of the hydration shell structure of ions in solution: The local water structure surrounding ions in aqueous solutions greatly affects their chemical properties such as reaction rates, ion association, and proton and electron transport. These properties result in the behavior of ions in natural aqueous environments. For example ore transport is facilitated by chloride ion pair formation and the reaction of ions in an interface is strongly dependent on the dehydration of the ion hydration shell. We are developing the use of high-resolution XAFS observations and 1st principles based MD-XAFS analysis (spectra simulated using 1st principle methods with no adjustable parameters, AIMD) to interpret the solution properties of strongly interacting aqueous solutes under arbitrary pressure and temperature conditions. In the 1st principle MD-XAFS method density functional theory (DFT) based MD simulations(Car and Parrinello, 1985) are used to generate a large ensemble of structural snap shots of the hydration region. These are then used to generate scattering intensities. I emphasize three points about this novel approach to analyzing XAFS data. 1st: As illustrated in Figure 1, the level of agreement between the calculated and observed intensities is considerably higher than has been obtained by any XAFS analysis to date (note 2nd shell region, R> 2 Å). 2nd: This result was obtained from a parameter free simulation with no fitting of the interaction potentials to any data. This supports the use of these methods for more difficult environments and more complex solutes (polyions). 3rd: New information about the shell structure (Figure 1) is now available because of this more detailed agreement. We note also that both multiple scattering and second shell features are well represented in the analysis. As far as we know this is the 1st analysis of second shell structure and multiple scattering. Excellent agreement has been obtained for most of the third row metal ions: Ca^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}. Calculations on these systems are demanding because of their open electronic shells, and high ionic charge. **Key Result: The extraordinary agreement between the data and theory suggests that 1st – principle MD XAFS may be further developed into a high resolution spectroscopy for**

the study of geochemical processes in aqueous environments under arbitrary conditions.

Al^{3+}-Cl^- ion pair formation: Knowledge of ion-associated species and hydrolysis products is essential to the formation of reliable thermodynamic models and interpretation of species transport. In this program *Ab initio* molecular dynamics (AIMD) was used to investigate the ion pairing behavior between chloride and the Al^{3+} ions in an aqueous $AlCl_3$ solution (Figure 2). The calculated potential of mean force (PMF, free energy) of the aluminum-chloride ion pair shows a pronounced minimum at a distance $r_{Al\text{-}Cl}$ = 2.3 Å leading to the formation of a contact ion pair (CIP). When moving the Cl^- ion from 2.3 Å to 3.6 Å (when the Cl^- ion is in the 2nd hydration shell of the Al^{3+} ion), a free energy barrier of 9.6 kcal/mol is observed. Two less pronounced local minima assigned as solvent separated ion pairs (SSIP) are identified at distances $r_{Al\text{-}Cl}$= 4.4 and 6.0 Å. **Key Result: We can now calculate solution structural properties and species from 1st principles (no parameters). However, the results require a large computation commitment (20 AIMD ps per force evaluation). Better sampling approaches will be necessary to find reliable free energy structures.**

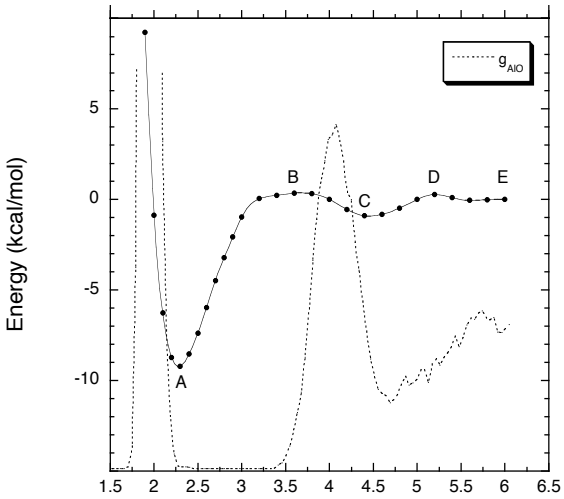


Figure 2. Al^{3+}-Cl^- Ion pair free energy as a function of Al-Cl separation. Dashed line $g_{Al\text{-}O}(r)$.

The continued development of hybrid DFT, Parallel Implementation of exchange: The most computationally practical approximation to the electronic Schrödinger equations used for AIMD is local DFT based on an efficient approximations to the exact exchange-correlation functional (e.g. GGA). While DFT+GGA type calculations seem to predict structures quite well it is becoming clear that augmentation with some fraction of exact exchange (hybrid-DFT, e.g. PBE0) is needed for many systems. Examples of interest include charge localization in transition elements with tightly bound *d* electrons in oxide materials(Cora et al., 2004; Di Valentin et al., 2006) (e.g. Fe_2O_3, TiO_2), the underestimation of reaction barriers and band gaps in solids (Marsman et al., 2008; Stadele et al., 1997; Stadele et al., 1999) and accurate predictions of spin structure of solids and nanoparticles (Cinquini et al., 2006). The drawback of hybrid-DFT is that it adds a significant amount of expense to an already expensive AIMD simulation. However, as we approach the Petaflop milestone, we can cope with the high computational costs through vastly increased parallelism. Our present exact exchange algorithm scales to nearly 100k processors as illustrated in Figure 3. **Key result: We have developed methods of calculating exact**

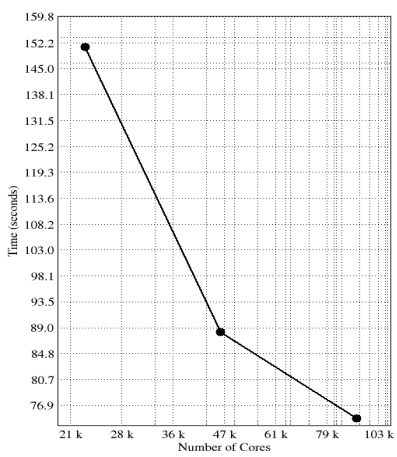


Figure 3. Timings for exact exchange showing scaling to 100k processors (560 atom cell).

exchange in condensed matter systems that scale to 100k processors and are efficient enough for some dynamical simulation.

Forward in time parallel algorithms: In molecular dynamics the Newton force equations are integrated forward in time. Since this is a sequential calculation (must know prior positions and momentum before a new forward in time step can be taken) it is not straightforward to develop a parallelization strategy. Recently we have been developing a class of algorithms that is based on domain decomposition in the time dimension (see Figure 4). Some recent and very preliminary results using this algorithm are shown in Figure 5. This is the 1st calculation using a parallel in time algorithm for a serious molecular dynamics problem. This algorithm provides a quite good speed up for this stage of the investigation. **Key Result: We have shown that a significant parallel speed up can be obtained with "parallel in time algorithms" thus providing a means to explore longer time domains via highly parallel and distributed (cloud) computing. This algorithm supports the application of higher level electronic structure dynamics calculations (e.g., MP2, CCSD) to complex geochemical environments.**

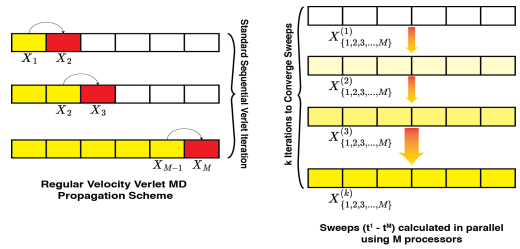


Figure 4: Illustration of the parallel in time simulation convergence (right side)

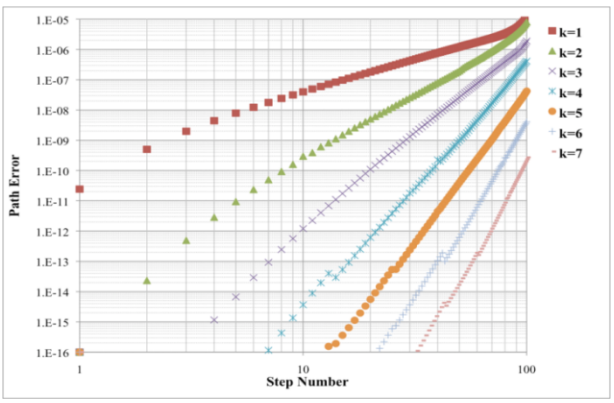


Figure 5: Accuracy versus step number for a parallel in time simulation of 1000 atoms interacting via a Stillinger Weber potential. Speed up approximately 15.

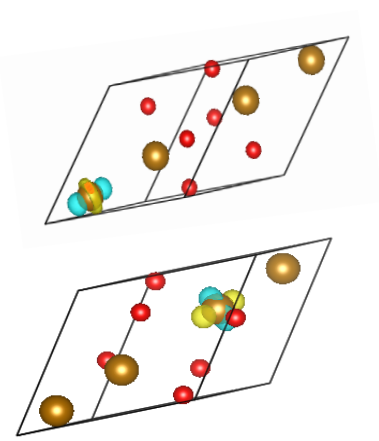


Figure 6: Localization of reducing electron in hematite lattice. Top: before lattice relaxation. Bottom: with small polaron formation. (our calculations)

Electron Localization in Iron Oxide Surfaces: Iron oxides contain partially filled, very localized 3d atomic orbitals. While for these systems the usual application of density function methods leads to reasonable structural properties, the prediction of other properties such as band gaps and position of the d band are very poor. Even more important to the oxidation/reduction processes(Katz et al., 2010; Yanina and Rosso, 2008) that we are interested in, electron localization and spin polarization prediction are qualitatively incorrect. The inclusion of exact exchange in the DFT calculations methods provide a more realistic description of electron correlation and are still efficient enough to allow dynamical simulation. To carry out these types of calculation required the development of a fast and scalable exchange algorithm. Results of these calculations illustrating charge localization in a hematite lattice (single

electron reduction) are given in Figure 6. In the upper panel (hybrid exchange calculation) the electron is localized in the periodic lattice as Fe^{2+} (electron on a single Fe^{3+}ion). In the lower panel the reduced Fe^{3+} site is allowed to relax forming a small polaron with increased localization. If DFT (with no exchange) was used in these calculations no localization would have occurred (extra electron delocalized over whole lattice in either figure). **Key Result: To predict electronic properties of metal oxide, inclusion of exact exchange is necessary for even qualitative accuracy. Inclusion of "exact exchange" provides at least qualitative agreement.**

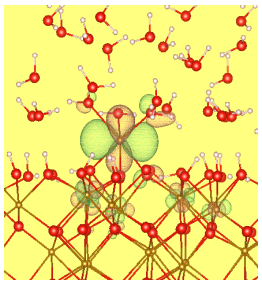
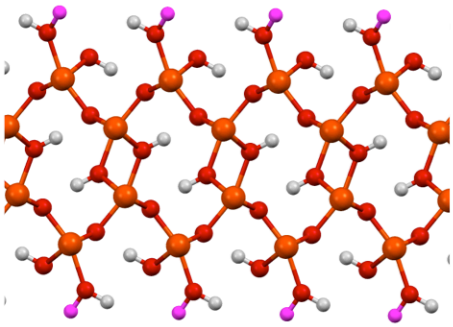


Figure 7: Fully solvated Fe^{2+} ion reacting with the 001 surface of Hematite. The system is thermally equilibrated.

Electronic structure calculations of reactions at Transition Metal Surface/Aqueous Fluid Interface of Hematite: Many chemical processes in materials and environmental chemistry occur in the interface region formed by solid transition metal oxides and oxihydroxides (e.g., hematite, goethite) surfaces and their coexisting fluid phases. Theoretical analysis of this region poses a difficult problem since: the properties of these materials are heavily dependent on the behavior of strongly localized transition metal d electrons making the electronic structure calculations extremely difficult; the disorder of a mineral interface is difficult to model; the interaction of the solution phase with the highly charged and structured mineral surface can strongly change the interatomic forces in the fluid phase; and the highly fluxional nature of the liquid region requires dynamic analysis.

We are developing parallel 1st principle based electronic structure methods and using them to simulate the surface structure and reactions of mineral surfaces with absorbed layers (see Figure 7). To obtain agreement with spin localization in these systems it is necessary to include some level of exchange while still retaining the efficiency to allow sampling of large numbers of configurations (e.g., DFT +GGA+ U or DFT+GGA+exact exchange). **Key Result: The fully equilibrated bonding interaction and charge transfer between a solvated Fe^{2+} ion on the (001) hematite surface show a strong interaction and considerable charge transfer. The interaction of Fe^{2+} ions with the (012) surface of hematite is much weaker.**



(c)

Figure 8: Structure of the lowest energy (100) geothite surface. Magenta atom is capping proton to form weakly interacting water with long bond.

Weakly bound water structure, bond valence saturation and water dynamics at the Geothite 100 surface/aqueous interface: Ab initio molecular dynamics simulations

Many important geochemical and biogeochemical reactions occur in the mineral/formation water interface of the highly abundant mineral, goethite (α-Fe(OOH). We have done *Ab-initio* molecular dynamics (AIMD) simulations of the goethite α-FeOOH (100) surface and the structure, water bond formation and dynamics of water molecules in this region. Several exchange correlation functionals with and without dispersion corrections were employed (PBE96, PBE96+Grimme, and PBE0) in the simulations of a (3x2) surface with 65 absorbed water molecules in a 3D-periodic supercell (a=30 Å, FeOOH slab ~12 Å thick, solvation layer ~18 Å thick).

The lowest energy goethite (100) surface termination model was determined to have an exposed surface Fe^{3+} that was loosely capped by a water molecule and a hydroxide shared with a neighboring surface Fe^{3+}. Each surface Fe^{3+} was coordinated with only 5 neighbors molecules. The nearest water molecules capping these ions were loosely bound at all DFT levels with and without the Grimme corrections leading to long bonds. These long bonds were supported by bond valence theory calculations. In these calculations the bond valence of the surface Fe^{3+} ion was saturated and surface had a neutral charge. The polarization of the water layer adjacent to the surface was found to be small and affected only the nearest water. Analysis by density difference plots and localized Boys orbitals identified 3 types of water molecules: those loosely bound to the surface Fe^{3+}; those hydrogen bound to the surface hydroxyl, and those with bulk tetrahedral coordination. Boys orbital analysis also showed that the spin down lone pair orbital of the weakly absorbed water interacted more strongly with the spin up orbitals of the Fe^{3+} ion.1st layer loosely bound water molecules were also found to rapidly exchange with the second water layer (~0.025 exchanges/ps) using a dissociative mechanism.

Key Result: The water molecules nearest to the goethite surface are very weakly bound to the surface. As a result these molecules readily exchanged with the bulk water. The large surface Fe-OH_2 distances in the DFT suggest that the surface Fe^{3+} atoms have their bond valence fully satisfied with only 5 neighbors, and are therefore under-coordinated relative to the bulk Fe^{3+} ions.

High-level treatment of condensed matter electron correlation; surface bonds

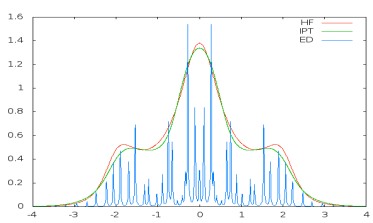


Figure 9: Spectral density for the 3d Hubbard tight binding model as a function of the Hubbard model Coulomb interaction U=2.

The valance d atomic orbitals in transition metal atoms are highly localized near atom centers. When these elements are components of condensed systems this localization results in very weak d orbital interactions between neighboring atoms. This combined with the very strong Coulomb interactions (for doubly occupied d atoms) on the atom sites leads properties such as superconductivity and magnetism found in these materials. However, the need to represent the electronic correlation (e.g., on site Coulomb electron-electron repulsion) results in a very difficult electronic structure problem.

We are interested in the electronic structure of the surface region of highly correlated transition metal oxides. Since these are condensed materials we must consider semi-infinite systems. The traditional methods of quantum chemistry (e.g., CCSD(T), Quantum Monte Carlo) can't be used because of the large size of the system. Model calculations based on 2nd quantization can be used. But even these problems cannot be solved exactly. One approach that seems to have promise is Dynamic Meal Field Theory (DMFT). In this method a much over simplified model of electron-electron interaction is introduced. The "bulk" problem is "solved" by imbedding a self-consistent impurity model (Anderson Model) into a lattice mean field solution. This solution can be shown to be "exact" in some limits. This is difficult calculation. However, we are making progress. In Figure 3 we show some preliminary results for three different methods of solution of the DMFT problem (for the Bethe lattice). In this figure we show the spectral density, which is related to the density of excited state within an infinitesimal frequency range and is calculated from the many-body green's function for the system. **Key Result: We are working to imbed these solvers into our existing NWChem software to provide tools to calculate the electronic structure of real highly correlated materials (e.g., Hematite surfaces).**

Spin Localization in Density Functional Theory: Typically in the application of Density Functional Theory (DFT) to systems in which spin ordering is important (e.g., for my group,

transition metal oxides) the possibility of spin localization is supported (still in a local density context) by using a single spin-orbital filling basis (SDFT). This allows for the symmetry of the spatial part of the spin orbitals to be broken and the formation of spin ordered mean field solutions. Although subject to the usual problems with DFT approaches, this method can be useful particularly when used with some higher exchange approximation (e.g., spin ordered DFT+U). However, the understanding of the mathematics of the formation of broken symmetry SDFT is very incomplete and the use of SDFT can lead to peculiar and unwanted results, for example the lack of spin localization using SDFT for systems that must have spin ordered ground states.

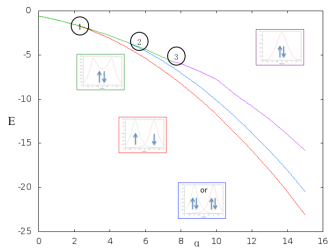


Figure 10: The bifurcation diagram for the SDFT Hamiltonian. The H_2 bond

In this project we are exploring the dependence of the formation of localized spin as a function of the exchange parameters (strength of the Dirac exchange potential) in SDFT Hamiltonians. Our calculations are presently only for the simple 2 electron mean field states of the H_2 molecule (still a difficult Hamiltonian to rigorously analyze). In Figure 10 the nature of the ground state and first excited state after bifurcation as a function of the Dirac exchange contribution, multiplied by α, is plotted. On far left hand side of this figure there is only one solution (same orbital solution for both electrons). This is consistent with the lack of spin localization in the H_2 molecule in SDFT. However at higher exchange contributions (as from the lengthening of the diatomic bond) there is a bifurcation in the solution (point 1 in Figure 3) and two separate functions appear (the total density is still a symmetric function). One of these is the USDFT solution. The second of these is the continuation of the doubly occupied RDFT solution that was the ground state before bifurcation. **Key Result: The 1st excited state retains orbital symmetry. However, in the SDFT case there are other bifurcations, as illustrated on the Figure (upper lines). The symmetric orbital solution (the 1st excited state) persists beyond the bifurcation 1. This solution bifurcates again at point (2) to form two new solutions. One of these solutions does not have a symmetric density.**