

First-principle Studies for Actinide Materials

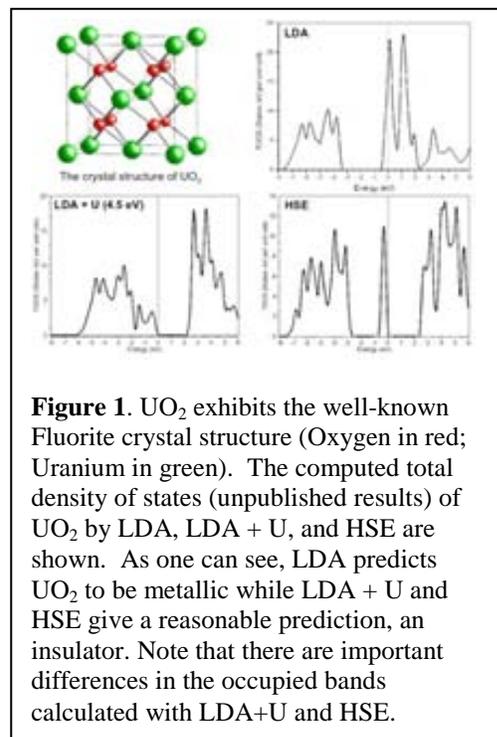
Specific Aims:

We propose to utilize the Chinook super-computer to characterize the ground state electronic structure of actinide oxides (AnO , AnO_2), actinide carbides (AnC , AnC_2) and actinide nitrides (AnN , AnN_2) where $\text{An} = \text{U}$, Np and Pu using a “standard” generalized gradient approximation functional (PBE), and two modifications based upon it: the PBE+U approach, and the screened hybrid functional HSE. The research will not only offer theoretical data to aid interpretation of experiments, but also provide benchmarks to develop new theoretical tools. In addition, success in this work will deepen our fundamental understanding of the nuclear energy materials.

Background:

The actinide (U, Np, Pu) oxides, nitrides, and carbides are of both fundamental and applied interest. Fundamental interest stems from the fact that they are members of the class of strongly correlated materials – the oxides being Mott insulators, and the nitrides and carbides strongly correlated metals. The practical interest stems from their use or possible use as advanced nuclear fuels. However, their physical and chemical complexity make them challenging systems to characterize both experimentally and theoretically. A number of basic properties associated with their electronic structure are still not known; this includes magnetic ordering, optical gaps, and resistivity.

Density functional theory (DFT) has proven to be a very powerful tool for the quantitative prediction of material properties in the field of solid-state physics as well as in chemistry. However, a first principles predictive capability for actinide materials has long been problematic and is one of the grand challenges of electronic structure. The computational studies of solid-state properties in actinide materials are few and far between in part due to the complexity of the problem and also due to the large computational resources needed to run these calculations. Both these limitations make this problem a good candidate to be tackled by large supercomputing facilities such as Chinook, which are intended for computational problems that cannot be carried out at local computing clusters with more modest resources. Developing a tool that can accurately predict the solid-state properties of actinide materials would have a strong impact in a number of important fields of interest to DOE including the development of materials for future-generation nuclear power reactors, as well as for accurate simulations of the interactions of disposed materials, from spent nuclear fuel and from the rest of the nuclear industry, into the environment. As an example of the problems of standard DFT applied to actinide materials, the local density approximation (LDA) predicts UO_2 to be a ferromagnetic metal (see **Figure 1**). It is, in fact, an antiferromagnetic Mott insulator. This prediction is not improved by subsequent generations of density functional approximations (GGA, meta-GGA). Significant progress has been made by applying models with ad hoc parameters, such as LDA/GGA+U¹ (which is an on-site coulomb interaction) and dynamical mean-field theory (DMFT). Parameter-free models, such as hybrid-DFT² and the GW approximation,³ have met with some success in the Mott insulators (AnO_2), but are largely untested for



¹ V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *J. Phys.: Condens. Matter* 1997, 9, 767.

² J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* 2003, 118, 8207

³ L. Hedin, *Phys. Rev.* 1965, 139, A796

correlated metals (AnN, AnC), in good part due to the computational cost. We propose to explore that void here.

We have recently initiated a joint collaboration between theory and experiment to study the electronic structure of these materials. This project, funded by the LDRD program at LANL and the BES Heavy Element Chemistry Division of DOE, combines novel synthesis techniques with state-of-the-art experimental characterizations targeted to reveal the most pertinent aspects of the electronic structure. These experiments on high quality samples allow us to benchmark the most commonly used and most promising theoretical approaches, and we hope will lead us to improved theories capable of providing a true first principles predictive capability for this important class of materials. The experimental effort has so far produced the first single-crystal quality films of NpO_2 , PuO_2 , U_3O_8 , UN_2 , and UC_2 , and is measuring a variety of parameters: structural parameters, optical properties including the resistivity, angle-resolved photoelectron spectroscopy, and x-ray absorption spectroscopy. The theoretical effort has been characterizing various approximations for comparison with experiment. Progress would be much more rapid if larger computing resources were available to us.

Approach

To optimize the structures and compute densities of states (total and local) and band structures we will use the VASP code for *ab-initio* electronic structure simulations. We have a license for VASP 5 that includes functionals with Hartree-Fock exchange. For classification sake we divide the studies into three classes: GGA, GGA+U, and screened hybrid DFT (HSE). Because the goal of our program is not only to obtain the electronic structure but also to benchmark the pros and cons of the various functionals we propose to run all the systems with all the functionals, including the pertinent magnetic states. This leads to a rather large request in order to be thorough, but we believe it is an important project and worthy of adequate support to do the job.

(a) GGA functionals on Actinide Materials: We will investigate the performance of PBE on the actinide oxides, nitrides and carbides mentioned above. If (people) time permits we will complement this with LDA results as well. Though it is well known that these “standard” functionals fail to predict the ground states and electronic properties for the oxides, the predictions for the metallic species are rather sparse, and we wish to thoroughly document their performance. Indeed some preliminary studies indicate that for UN the GGA functionals may give a better description of the valence bands than hybrid functionals. This may be coincidental or indicate that there is more to be learned from the pure functionals.

(b) GGA+U on Actinide Materials: The LDA/GGA +U formalism has been extensively studied for Mott insulators, such as transition metal oxides (FeO , CoO , NiO) and actinide oxides (UO_2 , PuO_2). In this work, we will extend these studies to the correlated metals (UN, UC), for comparison with other approximations.

(c) Screened Hybrid DFT on Actinide Materials: The screened hybrid density functional by Heyd, Scuseria, and Enzerhof (HSE) allows hybrid DFT to be applied to metallic systems. The trick used here is range-separation, in which the interelectronic repulsion operator is separated into short-range and long-range contributions. The upshot is a functional which appears to be a standard hybrid at short-range, and a simple PBE functional at long-range. A parameter m , determined in previous studies, defines the screening length. HSE has shown excellent performance in semiconductors and Mott insulators, but its performance in strongly correlated metallic systems is not known. In a few studies we plan to adjust the screening parameter (m) in order to see how the more effective screening anticipated in a metal affects the results. This should teach us something about the different length scales that may need to be built into future functionals. All these computational studies will be compared and contrasted against the measurements of the experimental team at LANL (J. Joyce, T. Durakiewicz, S. Kozimor, and S. Conradson).

Justification for Computational Resources

As stated above, the requested resources are for running VASP for the actinide oxide, carbide, and nitride systems detailed: actinide oxides (AnO, AnO₂), actinide carbides (AnC, AnC₂) and actinide nitrides (AnN, AnN₂) where An = U, Np and Pu. In our group we use an opteron-based cluster with processors very much like those in Chinook although the interconnection is much slower. Therefore, our timings are based on single 8-processor node runs and we will assume that VASP scales well to 64 processors, which may end up being an under-estimation of about 20%.

We will perform spin-polarized VASP calculations with spin orbital coupling to optimize the geometries. Three magnetic states need to be simulated, antiferromagnetic (AFM), ferromagnetic (FM), and non-magnetic (NM). In order to build these magnetic orderings fairly large super-cells are needed. We estimate that we will need super-cells of 10x10x10Å³ containing between 48 and 96 atoms (roughly 800 electrons). In order to correct the density of states for inter-band dispersion a few of the band structure diagrams will need to be scanned at high resolution but for standard band diagrams we use between 100 and 200 points along the main k-space axis. Such calculations in VASP routinely exceed 1000 CPU-hours per structure with very large memory requirement. These states will be simulated with the following functionals: GGA, GGA+U, and HSE. Once again, the LDA and LDA+U approximation may be addressed for completeness in a few cases. The “+U” functionals take roughly 3 times more than the standard ones and HSE takes between 20 and 40 times more. The table below summarizes the resources requested:

Table 1. Summary of resources requested

Functional	SU per structure ¹	# structures ²	Ground states ³	Sum ⁴	Properties calculation ⁵	Total SU
PBE	200	20	3	12,000	x 2	24,000
PBE+U	600	20	3	36,000	x 2.5	90,000
HSE	4000	20	3	240,000	x 11	2,640,000
Total SU for the proposal						2,754,000
Total node hours requested						344,250

1. The SU is based on one node with 8-cpu benchmark runs on opteron 2.2GHz proc. With 4 GB of memory per processor.
2. The 18 structures are AnO, AnO₂, AnC, AnC₂, AnN, AnN₂ where An=U, Np, and PU. Note for AnO, AnC, and AnN. There are two kinds of phases (rock salt and hcp phase)
3. Three types of magnetic states, AFM, FM, and NM will be considered;
4. The sum is only for optimization calculations on these structures.
5. The property-calculation multipliers reflect a complete study of the system: electronic properties, optical properties, and thermal conductivities. The scale is based on the optimization calculation.