Final Report: DOE-UNT-15508
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"Towards a Predictive Thermodynamic Model of Oxidation States of Uranium Incorporated in Fe (hydr) oxides"

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I. Summary and Overview of Activities

The theoretical research in this project has been directed toward the interpretation of core-level spectroscopies for systems relevant to the project. For the initial efforts, the focus of our theoretical simulations has been the interpretation of laboratory and synchrotron X-Ray Photoemission Spectra, XPS. In more recent efforts, an increasing emphasis has been placed on developing transparent understandings of X-Ray Adsorption Spectra, XAS . For the XAS, the principle concern is for the near-edge features, either just below or just above, an ionization limit or edge, which are described as Near-Edge X-Ray Adsorption Fine Structure, NEXAFS. In particular, a priority has involved the analysis and interpretation of XPS and NEXAFS spectra measured by our PNNL collaborators. Prior efforts of others in the theory for the interpretation of NEXAFS, in particular for the metal edges of high spin compounds and complexes, have relied heavily on the complex mathematical formulations of angular momentum coupling based on Clebsch-Gordon algebra. An unfortunate consequence of the use of complex mathematical formulations is that the NEXAFS analyses are accessible to a limited audience and the connections of the NEXAFS spectral features to the chemical interactions and the physical environment are difficult to make. In the approach used in our work, as demonstrated by our earlier and our recent publications, we avoid the complex mathematics and we interpret the theoretical results in terms of chemical interactions and chemical bonding. In particular, we have shown how the U L_3, or 2p, edge of different oxidation states of UO_x provides direct evidence of the covalent character of the U-O interaction and how the width of the unresolved states contained in this edge are directly related to the U-O distance in the different oxides; see paper X in Sec. IV.

The overall objective of our theoretical studies is to establish connections between features of the spectra and their origin in the electronic structure of the materials. The efforts for the analysis of XPS have been reviewed in a paper by the PI, C. J. Nelin, and E. S. Ilton from PNNL on "The interpretation of XPS spectra: Insights into materials properties", Surf. Sci. Reports, **68**, 273 (2013). Two materials properties of special interest have been the degree of ionicity and the character of the covalent bonding in a range of oxides formed with transition metal, lanthanide, and actinide cations. Since, the systems treated have electrons in open shells, it has been necessary to determine the energetic and character of the angular momentum coupling of the open shell electrons. In particular, we have established methods for the treatment of the "intermediate coupling" which arises when the system is between the limit of Russell-Saunders multiplets, and the limit of j-j coupling where the spin-orbit splittings of single electrons dominate. A recent paper by the PI, M. J. Sassi, and K. M. Rosso, "Intermediate Coupling For Core-Level Excited States: Consequences For X-Ray Absorption Spectroscopy", *J. Elec. Spectros. and Related Phenom.*, **200**, 174 (2015) describes our first application of these methods.

As well as applications to problems and materials of direct interest for our PNNL colleagues, we have pursued applications of fundamental theoretical significance for the

analysis and interpretation of XPS and XAS spectra. These studies are important for the development of the fields of core-level spectroscopies as well as to advance our capabilities for applications of interest to our PNNL colleagues. An excellent example is our study of the surface core-level shifts, SCLS, for the surface and bulk atoms of an oxide reported in a paper by C. J. Nelin *et al.* on "Surface Core Level Binding Energy Shifts for MgO(100)", Phys. Chem. Chem. Phys. **16**, 21953 (2014). This paper provides a new approach to understanding how the surface electronic of oxides differs from that in the bulk of the material and may provide a new key to understanding the reactivity of oxide surfaces. A second example concerns our clarification of the separation XPS effects due to initial state and final state effects as given within Density Functional Theory, DFT, through the use of Kohn-Sham, KS, eigenvalues. This work involved a study of the initial final state separation for a wide range of molecules comparing Hartree-Fock, HF, theory with DFT using several different exchange-correlation functionals. The work was reported in two papers: N. P. Bellafont, F. Illas, and P. S. Bagus, "Validation of Koopmans' Theorem For Density Functional Theory Binding Energies", *Phys. Chem. Chem. Phys.* **17**, 4015 (2015) and N. P. Bellafont, P. S. Bagus, and F. Illas, "Prediction of core level binding energies in density functional theory: rigorous definition of initial and final state contributions and implications on the physical meaning of Kohn-Sham energies", *J. Chem. Phys.* **142**, 214102 (2015). This work showed the limitations of the KS orbital energies for predicting absolute initial state contributions to XPS binding energies, BE's, but it established their validity for determining, within acceptable uncertainties, the initial stae contribution to BE shifts. As such, it validates the body of prior work using the KS orbital energies to analyze XPS BE's and represents a major advance in our theoretical understanding.

Our theoretical studies use cluster models with finite numbers of atoms to describe the properties of condensed phases and crystals. This approach has allowed us to focus on the local atomistic, chemical interactions. For these clusters, we obtain orbitals and spinors through the solution of the Hartree-Fock, HF, and the fully relativistic Dirac HF equations. These orbitals are used to form configuration mixing wavefunctions which treat the many-body effects responsible for the open shell angular momentum coupling and for the satellites of the core-level spectra. Our efforts have been in two complimentary directions. As well as the applications described above, we have placed major emphasis on the enhancement and extension of our theoretical and computational capabilities so that we can treat complex systems with a greater range of many-body effects. Noteworthy accomplishments in terms of computational enhancement and development have included: (1) An improvement in our treatment of the large matrices that must be handled when many body effects are treated. (2) Improvements and extensions of our capabilities for the calculation of the intensities of XPS and XAS transitions. And, (3) ongoing development of flexible programs for the visualization of the theoretical spectra so that they can be compared with experiment.
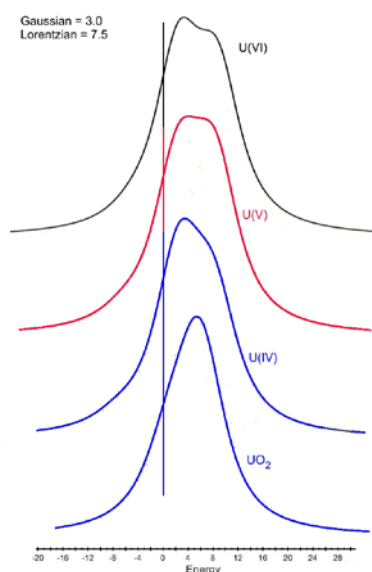
Our efforts and advances have received significant external recognition. In particular our paper in the journal *Surface Science Reports*, Volume 68, pages 273-304 (2013) continues to be highly downloaded and cited. We are regularly invited to present seminar at major international meetings and at major Research Institutes and Universities. In this context, the PI have received the 2016 AVS Geade-Langmuir Award for his contributions to the understanding of XPS at surfaces.

Our efforts on these and related topics will continue under a sub-contract to PNNL.

This report contains three following sections: Section II describes our progress on several scientific issues during the period of the current award, 01/01/13 to 12/31/15. Section III presents information about major advances in our theoretical and computational capabilities. Finally, Section IV contains a list of publications acknowledging DOE support that appeared in the award period noted above.
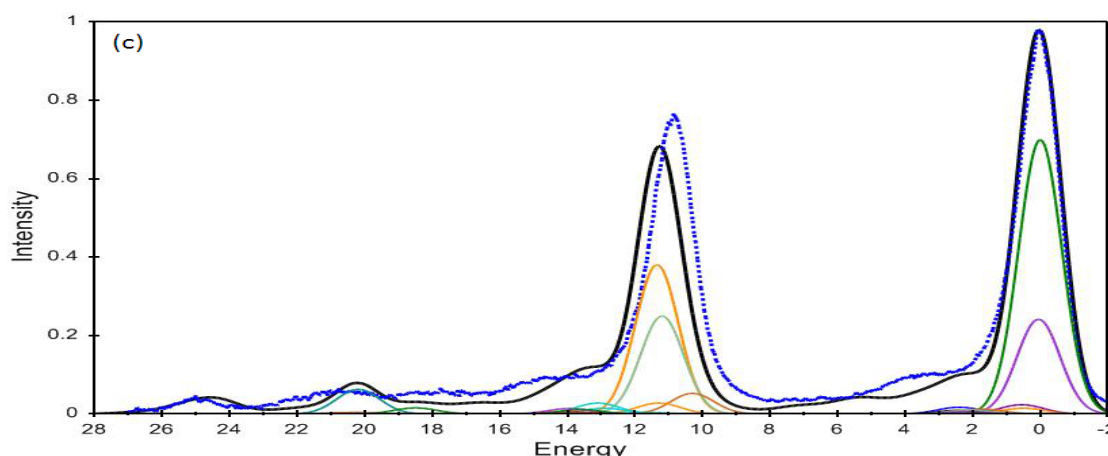
II. Scientific Accomplishments

A. U L_3-Edge NEXAFS IN U Oxides. Rigorous theoretical studies of the electronic structure to describe the Uranium L_3 near edge X-ray adsorption fine structure of different oxidation states of U in UO_x have been made. Key features of the spectra are related to the ligand field splitting of the excited state orbitals. Furthermore, the ligand field splitting is related to the different extents of covalent mixing that occur at different U-O distances for the different oxidation states. The theoretical relative energies and intensities are based on electronic wavefunctions for cluster models of the oxides, which allow, for the first time, direct relationships between cation and anion interaction and covalent mixing to be established. In addition, correlations are established between the width of the L_3 NEXAFS and the U-O distance. The figure below shows how the NEXAFS features for octahedral U(VI), U(V), and U(IV) and for flourite UO_2 clearly distinguish the different oxidation states

B. Theoretical Modelling of the U 4f XPS for U(VI) and U(IV) Oxides. A rigorous study has been made of the physical processes related to the 4f XPS of U oxides, which, as well as being of physical interest in themselves, are representative of XPS in heavy metal oxides. In particular, we present compelling evidence for a new view of the screening of core-holes that extends prior understandings. Our analysis of the screening focuses on the covalent mixing of high lying U and O orbitals as opposed to the, more common, use of orbitals that are nominally pure U or pure O. It is shown that this covalent mixing is quite different for the initial and final, core-hole, configurations and that this difference is directly related to the XPS satellite intensity. Furthermore, we show that the high-lying U d orbitals as well as the U(5f) orbital may both contribute to the core-hole screening, in contrast with previous work
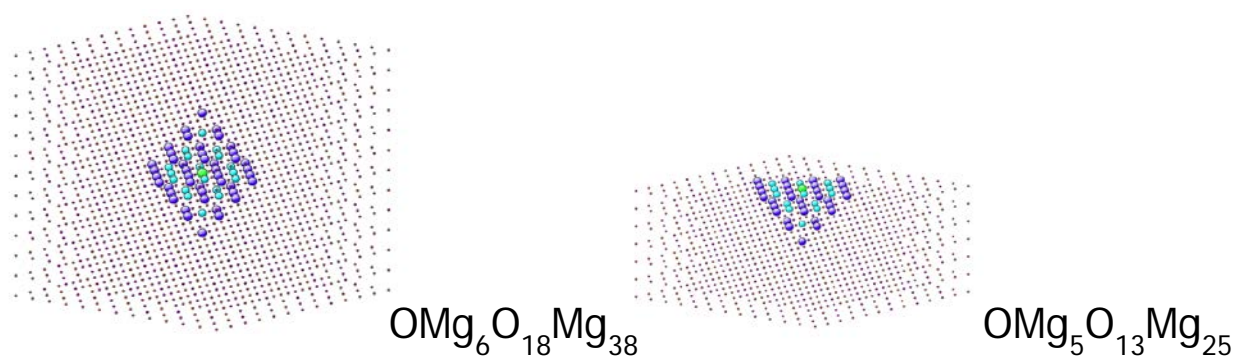
that has only considered screening through the U(5f) shell. The role of modifying the U-O interaction by changing the U-O distance has been investigated and an unexpected correlation between U-O distance and XPS satellite intensity has been discovered. The role of flourite and octahedral crystal structures for U(IV) oxides has been examined and relationships established between XPS features and the covalent interactions in the different structures. The physical views of XPS satellites as arising from shake processes or as arising from ligand to metal charge transfers are contrasted; our analysis provides strong support that shake processes give a more fundamental physical understanding than charge transfer. Our theoretical studies are based on rigorous, strictly *ab initio* determinations of the electronic structure of embedded cluster models of U oxides with formal U(VI) and U(IV) oxidation states. Our results provide a foundation that makes it possible to establish quantitative relationships between features of the XPS spectra and materials properties. The figure below for the 4f XPS of UO_3 compares the experimental spectra, dotted curves, with theory, solid dark curve. It shows that with a proper selection of the active space for shake excitations the fine details of the shake satellites, especially those at relative energies of 20 and 25 eV can be correctly described. This is the first time that a theoretical analysis has accounted for these high energy satellites.

C. Covalent Interactions In Oxides. The covalent character of ionic metal compounds, in particular oxides, may lead to substantial departures from nominal oxidation states. Since this covalent character changes the effective charge of the cation, it contributes to the chemical and physical properties of these compounds. A novel method of determining the degree of the covalent mixing by projection has been developed. In this method, cation and ligand orbitals determined for the isolated species are projected on the total wavefunctions for clusters used to model the electronic structure of these compounds. An important advantage of this method is that it can be used to obtain estimates of the uncertainties in the assignments of effective charges to the cations and anions. Such estimates of the uncertainty directly reflect the overlap of cation and anion orbitals and, hence, their potential for chemical bonding. These kinds of estimates are not generally given when assignments of charge are made. The core-hole states created in X-Ray photoemission spectroscopy, XPS, have a very different covalent character than the initial states where the core shells are filled. It is shown that the increase of the covalent character in the core-hole configurations provides insight into a major aspect of the core-hole screening.
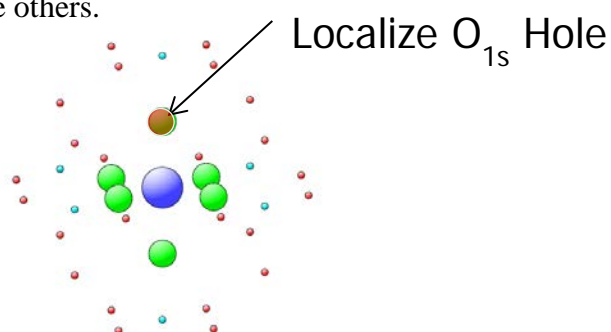
D. Surface Core Level Shifts, SCLS, For Oxide Surfaces. The SCLS has been studied extensively for metal surfaces but has not been reported for oxide surfaces prior to our paper in the journal Physical Chemistry Chemical Physics, Volume 16. An important aspect of this work is that we used very large clusters containing several shells of explicitly treated atoms

around the central atom whose binding energies were modeled. A schematic of representative clusters modelling bulk, left, and surface, right, indicating the atoms explicitly treated and the embedding point charges is shown below.

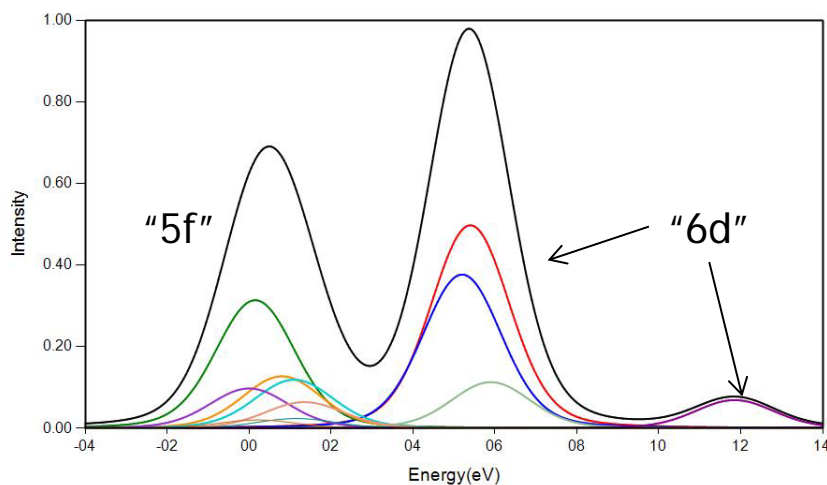$OMg_6O_{18}Mg_{38}$ $OMg_5O_{13}Mg_{25}$

For our applications to cluster models of heavier metal compounds, we are now in a position to treat clusters of this size with larger calculations and using pseudo-potentials to treat the deep core electrons of the outer shells of atoms. We have tested the pseudopotential treatment for a UF_6 molecule and determined that we obtain comparable results to a full electron treatment. Thus, we are in a position to apply the information gained for the model compound MgO to the surfaces of various UO_x systems. The important physics and chemistry learned for the SCLS of MgO is that while the cation SCLS had a value expected from electrostatic arguments, The anion SCLS was reduced to almost zero because of a cancellation of contributions to the SCLS. The electrostatics would lead to a negative SCLS while the pull back of the surface O charge below the surface acted to raise the SCLS leading to an almost zero anion SCLS. For the UO_x systems where the bond distances are larger and the cation charge is also larger; the cancellation may be such as to lead to U and O SCLS of the same sign and comparable magnitude. This would be useful information about the chemical activity of the surfaces of heavy metal oxides, an important goal in this project.
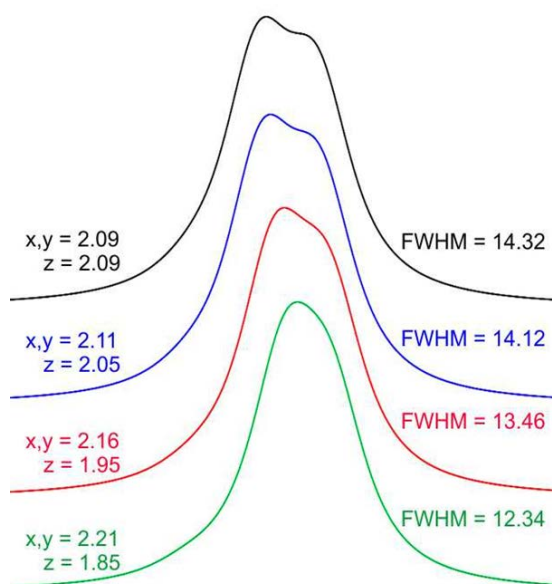
E. O K-Edge NEXAFS For U(IV) Oxides. In order to excite a localized O electron into an unoccupied valence level, it was necessary to drop the symmetry of the UO_6 cluster model of the octahedral UO_x systems as shown schematically in the figure below where one O atom is distinguished from the others.

Localize O_{1s} Hole

With this choice of localized O K-edge excitation, we are able to predict the NEXAFS for δ-UO$_3$: see below.
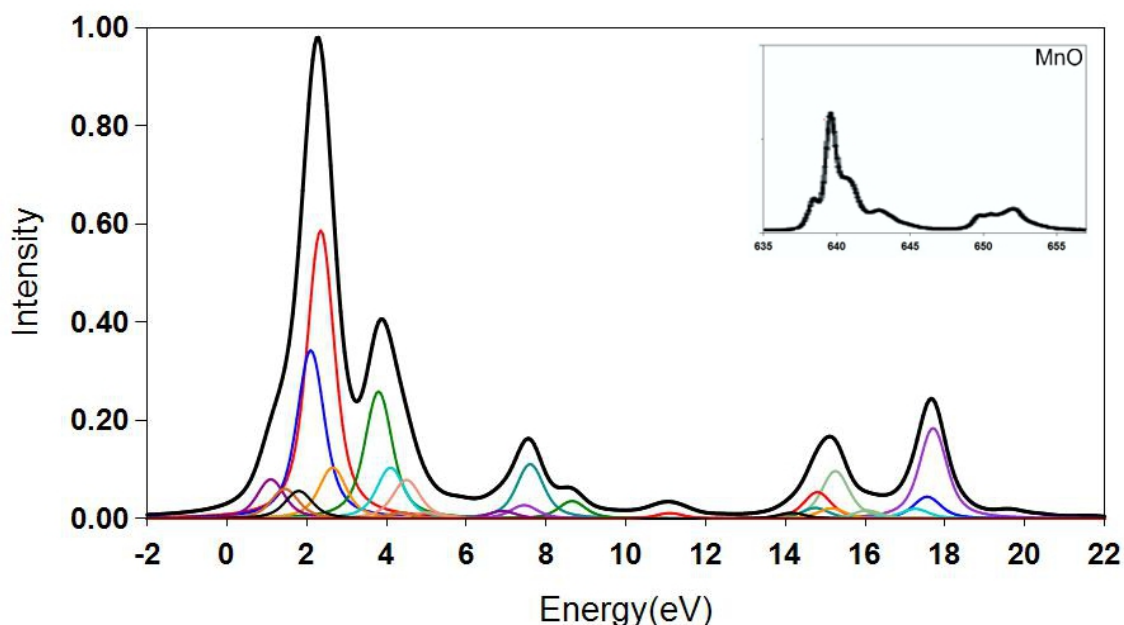

There is also work in progress on the use of "squashed" models of U(VI) oxides for the L$_3$ edge NEXAFS in order to better understand the influence of crystal structure. Initial results show that the distortion of the crystal leads to a narrowing of the spectra; see below..
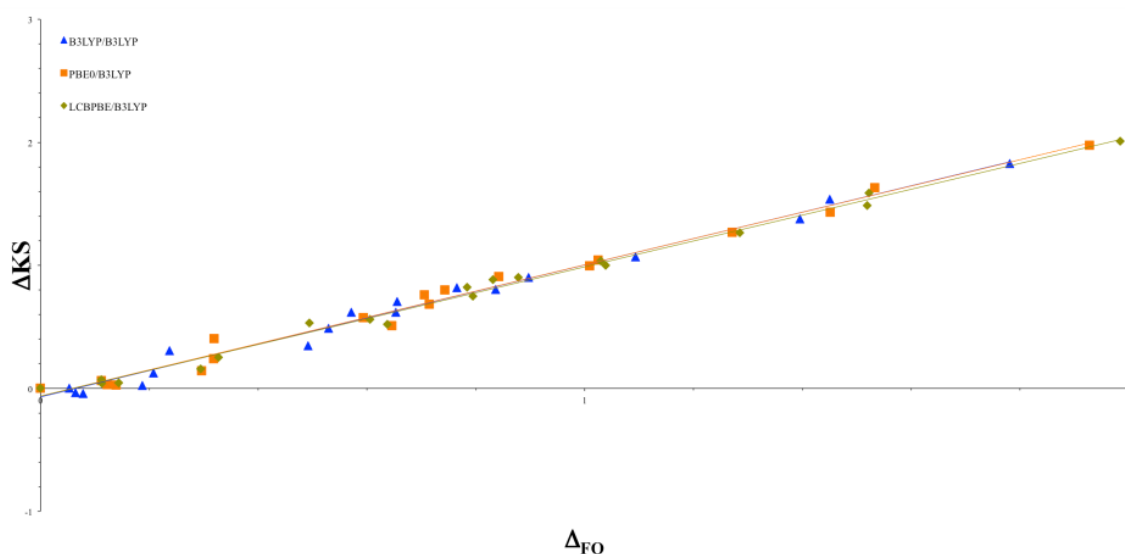

F. Intermediate Coupling For Core-Excited States. In early work published in 2008, in collaboration with colleagues at the Fritz-Haber institute and with Eugene Ilton at PNNL, the selection rules and the branching ratios of different core-level edges were analyzed in terms of the angular momentum coupling of the core and valence open shell electrons; see, P. S. Bagus, H-J. Freund, H. Kuhlenbeck, and E. S. Ilton, "A New Analysis of X-Ray Adsorption Branching Ratios: Use of Russell-Saunders Coupling", *Chem. Phys. Lett.*, **455**, 331(2008). This work was substantially extended in recent work with M.Sassi and K. Rosso at PNNL to study the intermediate coupling in the Fe(III) cation for the initial and final states of the L$_{2,3}$ edge NEXAFS spectra; see P. S. Bagus, M. J. Sassi, and K. M. Rosso, "Intermediate Coupling For Core-Level Excited States: Consequences For X-Ray Absorption Spectroscopy", *J. Elec. Spectros. and Related Phenom.*, **200**, 174 (2015). In this work, correlations between the intensities of the NEXAFS features and the extent of the dipole

allowed Russell-Saunders multiplet in the intermediate coupling for the relativistic wavefunctions of the $L_{2,3}$ edge final states were established. In particular, the origin of the complex NEXAFS features of X-Ray Absorption, XAS, spectra in transition metal complexes was analyzed and interpreted in terms of the angular momentum coupling of the open shell electrons. Especially for excited configurations where a core-electron is promoted to an open valence shell, the angular momentum coupling is intermediate between the two limits of Russell-Saunders, RS, coupling where spin-orbit splitting of the electron shells is neglected and j-j coupling where this splitting is taken as dominant. The XAS intensities can be understood in terms of two factors: (1) The dipole selection rules that give the allowed excited RS multiplets and (2) The contributions of these allowed multiplets to the wavefunctions of the intermediate coupled levels. It is shown that the origin of the complex XAS spectra is due to the distribution of the RS allowed multiplets over several different intermediate coupled excited levels. The specific case that is analyzed is the $L_{2,3}$ edge XAS of an Fe^{3+} cation, because this cation allows a focus on the angular momentum coupling to the exclusion of other effects; e.g., chemical bonding. Arguments are made that the properties identified for this atomic case are relevant for more complex materials. The analysis is based on the properties of fully relativistic, ab initio, many-body wavefunctions for the initial and final states of the XAS process. The wavefunction properties considered include the composition of the wavefunctions in terms of RS multiplets and the occupations of the spin-orbit split open shells; the latter vividly show whether the coupling is j-j or not. The complex NEXAFS spectrum is shown in the figure below where the broadened intensity to individual finals states, light colored traces, and their sum, bold trace, are compared with experiment for a closely related $3d^5$ oxide, MnO. For the individual traces only those with the largest intensities are plotted but it is clear that there are many final states contributing to the total $L_{2,3}$ edge NEXAFS spectra. The agreement between theory and the experiment, shown in the inset, is impressive and this good agreement lends considerable support to the assignments that our theory has made for the individual and total peaks.
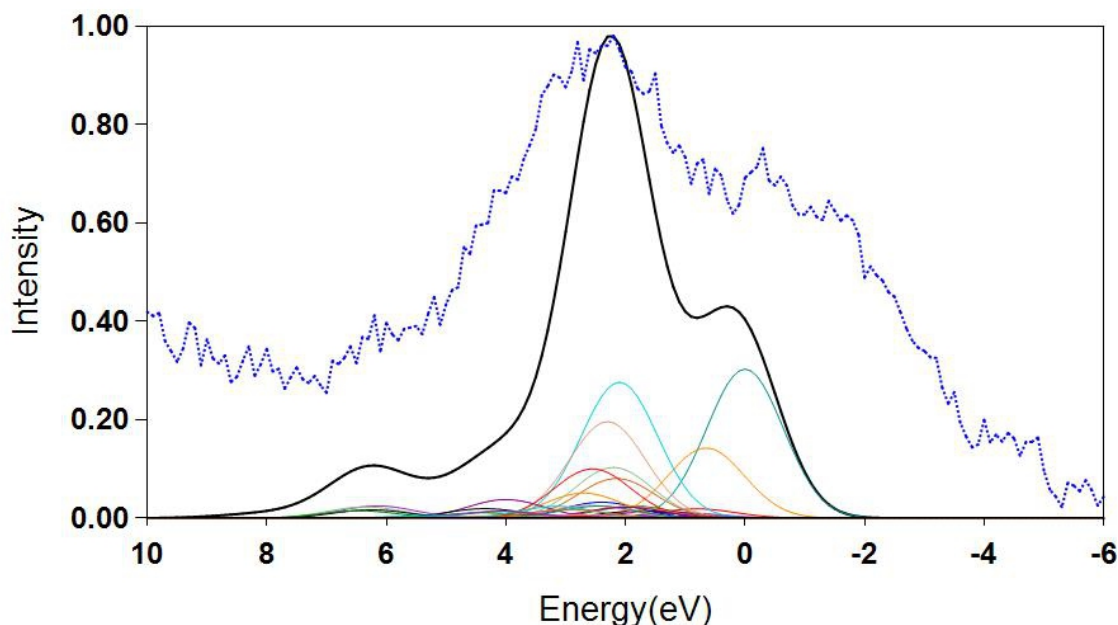

G. Separation of the Origin of XPS Binding Energies into Initial and Final State Contributions: Use of Kohn-Sham Orbital Energies in the Framework of Koopmans' Theorem. The PI and his collaborators at the University of Barcelona have made a systematic

study of the N(1s) core level binding energies (BE's) in a broad series of molecules employing Hartree-Fock (HF) and the B3LYP, PBE0 and LC-BPBE density functional theory (DFT) based methods with a near HF basis set. The results show that all these methods give reasonably accurate BE's with B3LYP being slightly better than HF but with both PBE0 and LCBPBE being poorer than HF. A rigorous and general decomposition of core level binding energy values into initial and final state contributions to the BE's is proposed that can be used within either HF or DFT methods. The results show that Koopman's theorem does not hold for the Kohn-Sham eigenvalues. Consequently, Kohn-Sham orbital energies of core orbitals do not provide estimates of the initial state contribution to core level BE's; hence they cannot be used to decompose initial and final state contributions to BE's. However, when the initial state contribution to DFT BE's is properly defined, the decompositions of initial and final state contributions given by DFT, with several different functionals, are very similar to those obtained with HF. Furthermore, it is shown that the differences of Kohn-Sham orbital energies taken with respect to a common reference do follow the trend of the properly calculated initial state contributions. These conclusions are especially important for condensed phase systems where our results validate the use of band structure calculations to determine initial state contributions to BE shifts. The correlation between the different BE shifts determined from the Kohn-Sham orbital energies compared to the rigorous calculation of frozen-orbital BE shifts clearly validates the use of KS orbital energies to obtain the initial state contribution to BE shifts. Specifically, it validates the use of Koopmans' Theorem for the initial state contribution to BE shifts/
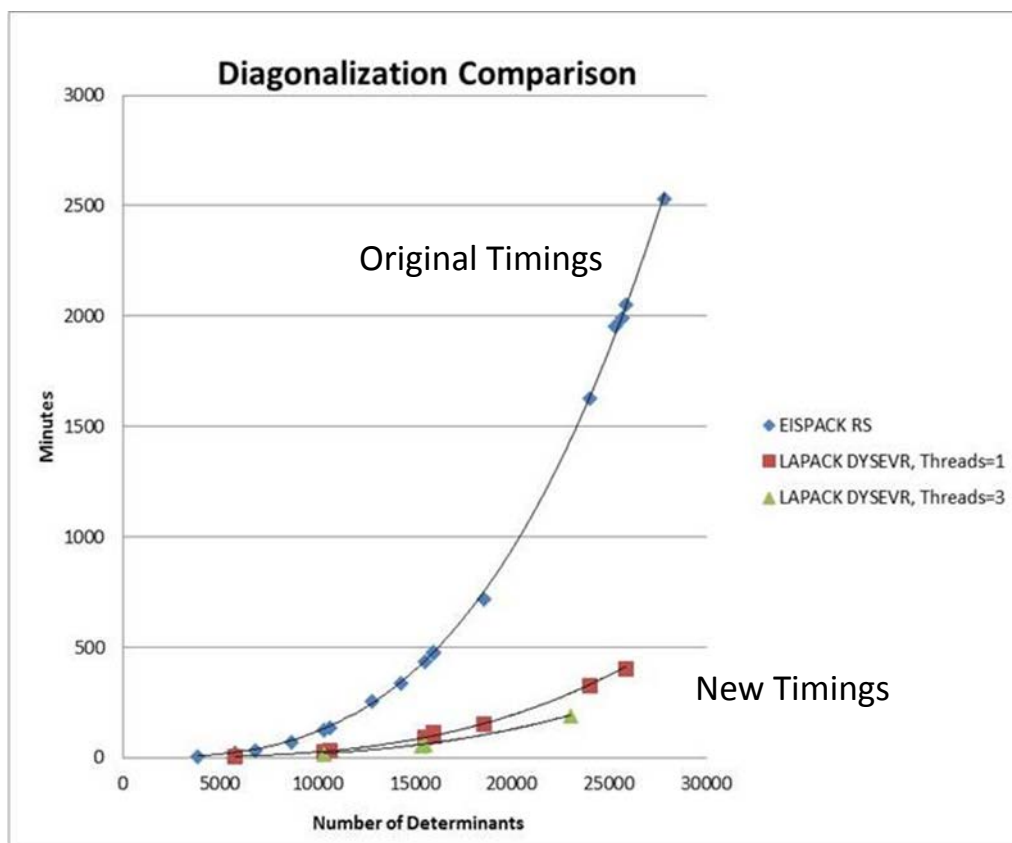

H. Dependence of XPS Multiplet Splittings on Oxidation State for Heavy Elements. The multiplet splittings in XPS are a means of distinguishing different open shell occupations, or different oxidation states, in the material being studied. Indeed, especially for 3d transition metal complexes, these multiplet splittings have provided fingerprints of the metal oxidation state. The present work provides theoretical and experimental evidence that it may also be possible to use multiplets to characterize the oxidation state of heavy metal, lanthanide and actinide, cations in complexes. This effort was carried out in collaboration with colleagues at SABIC, H. Idriss and Y. M. Al-salik, and at PNNL, E. S. Ilton. The potential to use multiplets to characterize cation oxidation states is new information since standardly taken and published XPS for these materials do not display multiplet splittings and it is possible that they are too small to be resolved. However, our work has demonstrated that it is important to make a proper choice of the XPS region to study in order to obtain large

multiplet splittings. We identify a low binding energy, BE, peak that had been observed for Ce(III) in CeO_x as a high spin coupled multiplet. Furthermore, we show that a low BE feature with reasonable intensity is characteristic of other XPS regions and of other metals. This feature arises from a high spin multiplet and serves as a fingerprint to distinguish closed shell from open shell cations. Evidence is presented that it may also be possible to distinguish different open shell occupations. In the figure below, the theoretical U $5p_{3/2}$ XPS for a UO_8 cluster model of UO_2 is compared with the measured $5p_{3/2}$ XPS for UO_2. In the figure, the maxima of the main experimental and theoretical peaks are aligned. It is clear that the theoretically predicted multiplets are present in the experimental data.
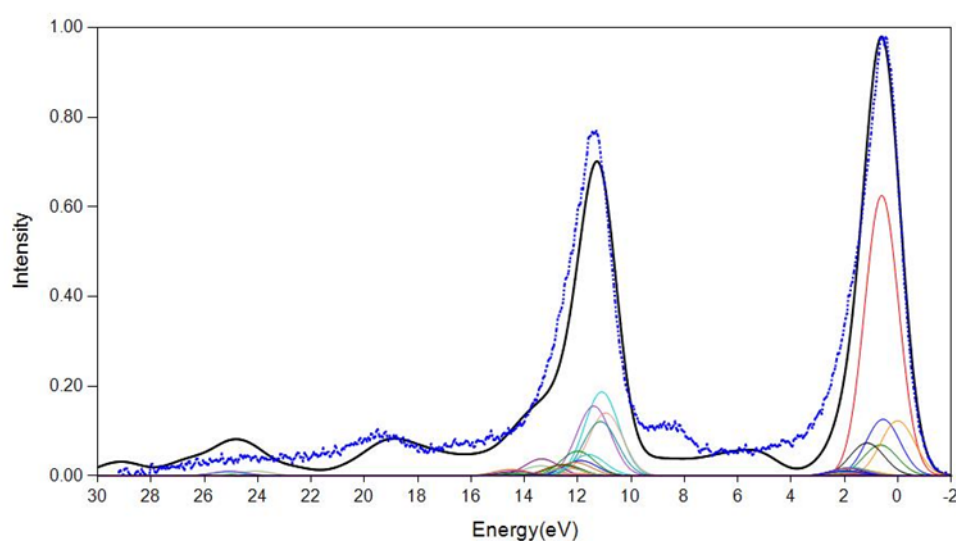

II. Program enhancements.

A. Diagonalization of the Hamiltonian Representing Many-Body Effects. A major bottleneck with our calculation of many body effects has been the complete diagonalization of large ~50,000 and larger, dimension matrices which represent atomic angular momentum coupling and recoupling and which also represent shake effects from metal ligand binding orbitals into metal-ligand anti-bonding orbitals. A new LAPACK diagonalization routine has been added for these diagonalizations and it can also be used with multi-threading. The improved performance with this new diagonalization is shown in the figure below where three curves are shown. The first curve represents the time taken with the original EISPACK diagonalization routine, the second curve shows the improvement, by approximately a factor of 4-5, of the timing for the new LAPACK program; both of these curves are for serial performance. The third curve shows the additional improvement, of ~25%, from using multi-treading to improve performance. This improvement is clearly allows the extension of our treatment of many-body effects through the inclusion of configurations that represent additional excitations. The possibility that this opens for more accurate predictions of fine structure in XPS spectra is also discussed below. We have also carried out discussions with colleagues in the PNNL NWChem project for the use of parallel diagonalization features available within NWChem that will allow further major improvements in the time of diagonalization of the Hamiltonian matrices.

Clearly, we are now in a position to investigate a range of many body effects with diagonalization of the H matrix that take of order a few hours where with the earlier diagonalization package had taken a couple of days. This new capability allows us to make more complete and through investigations of the active orbital and configuration spaces. For example with the use of larger active spaces and improved treatment of the spin-orbit splitting, we have been able to significantly improve our agreement with the XPS spectra for U(V) Oxide as shown in the figure below.

B. Calculation of XPS and XAS Intensities. In order to predict the XPS and XAS spectra, it is not sufficient to only calculate the energies of the core-excited final states. It is also

necessary to calculate the intensities, or transition moments, between the initial states and the excited states. For XPS, the transition moment is given, within the Sudden Approximation, SA, by the square of overlap integrals between the wavefunctions for the initial state where an appropriate core electron has been annihilated and the final core-hole states. For the XAS spectra, the transition moment involves, to a good approximation, the square of dipole matrix elements between the wavefunctions for the initial and final states. If the same set of orbitals is used for the initial and final, core excited, wavefunctions, the calculation of these matrix elements is trivial. However, the use of a single set of orbitals neglects the relaxation, in the final configuration which allows the electrons to respond to the presence of the core hole in the excited configuration. This neglect leads to XPS BE's that are seriously in error and to XAS energetics that will require large configuration mixing to correct the neglect of the orbital relaxation. On the other hand, different sets of orbitals for the initial and final configurations is possible provided one uses the calculation of determinants and minors required in the formalism established by Lowdin; see Phys. Rev. **97**, 1474 (1955). Our programs for the calculations of these matrix elements are based on a cofactor analysis that implements the Lowdin formulation. Hey presented a bottleneck in our work because the cofactors were calculated repeatedly for each pair of initial and final states and because they were limited to wavefunctions for high symmetries, D2h. This required that we make artificial changes in the geometries of systems to force them to have high symmetry and it prevented us from treating many systems of interest. The removal of these bottlenecks has been an ongoing effort. While the mathematical requirements are straightforward, the coding of the set of programs that compute one-electron and many-electron matrix elements has been time consuming. A first important step was to completely reorganize the calculation of matrix elements so that the matrix elements between determinants were computed only once and not repeatedly. Since the transitions must be computed to a very large number of final states, this lead to an immense improvement in time required for the calculation of matrix elements for high symmetry clusters.

The next major steps were to extend our calculation to systems with lower symmetry. The calculation of dipole matrix elements was extended from high symmetry to lower symmetry cases where the symmetry is only C_{2v}. This has allowed us to study O ligand edges and "squashed" geometry models of the complex geometry of U oxides as discussed in Sec. II, above. The next step is to treat cases where the abelian point group symmetry is Cs or C1, where C! is the case where there are no abelian symmetry operations at all. This symmetry is of particular importance since it is necessary for us to use C1 symmetry to treat cluster models of the rhombohedral symmetry of many X_2O_3 crystals The difficulty here is that it is necessary to extend the calculation from dealing with real one and many electron matrix elements to using complex arithmetic to calculate these terms. Most of the extensions to convert our codes were completed in the Award period and efforts to finish the calculation will be continued through the PNNL subcontract that the PI presently holds. Of course, enhancements will be ongoing in the quest of the treatment of ever more complex materials with ever higher accuracy.

IV. Publications Acknowledging DOE Support for the period January 2013 to December, 2015.

1. Paul S. Bagus, Eugene S. Ilton, and Connie J. Nelin, "The interpretation of XPS spectra: Insights into materials properties", Surf. Sci. Reports, **68**, 273 (2013).
2. Paul S. Bagus and Eugene S. Ilton, "Theory for the XPS of Actinides", Topics in Catalysis, **56**, 1121 (2013).

3. Paul S. Bagus, Connie J. Nelin, and Eugene S. Ilton, "Theoretical modeling of the U4f XPS for U(VI) and U(IV) oxides", *J. Chem. Phys.*, **139**,244704 (2013)

4. Paul S. Bagus, Connie J. Nelin, and Eugene S. Ilton, "Theoretical modeling of the U4f XPS for U(VI) and U(IV) oxides", *J. Chem. Phys.*, **139**,244704 (2013)

5. William E. Kaden, Christin Büchner, Leonid Lichtenstein, Stefanie Stuckenholz, Franziska Ringleb, Markus Heyde, Martin Sterrer, Hans-Joachim Freund, Livia Giordano, Gianfranco Pacchioni, Connie J. Nelin, and Paul S. Bagus, "Understanding Surface Core-Level Shifts using the Auger Parameter; a study of Pd atoms adsorbed on SiO_2 ultra-thin films", Phys. Rev. B, **89**, 115436 (2014).

6. Connie J. Nelin, Paul S. Bagus, and Eugene S. Ilton, "Theoretical Analysis of the U L_3-Edge NEXAFS in U Oxides", *RSC Advances*, **4**, 7148 (2014).

7. Paul S. Bagus and Connie J. Nelin, "Covalent Interactions In Oxides", *J. Elec. Spectros. And Related Phenom.*, **194**, 37 (2014).

8. Connie J. Nelin, Felix Uhl, Volker Staemmler, Paul S. Bagus, Yuichi Fujimori, Martin Sterrer, Helmut Kuhlenbeck, and Hans-Joachim Freund, "Surface Core Level Binding Energy Shifts for MgO(100)", Phys. Chem. Chem. Phys. **16**, 21953 (2014).

9. N. Pueyo Bellafont, F. Illas, and Paul S. Bagus, "Validation of Koopmans' Theorem For Density Functional Theory Binding Energies", *Phys. Chem. Chem. Phys*. **17**, 4015 (2015).

10. Paul S. Bagus, Michel J. Sassi, and Kevin M. Rosso, "Intermediate Coupling For Core-Level Excited States: Consequences For X-Ray Absorption Spectroscopy", *J. Elec. Spectros. and Related Phenom.*, **200**, 174 (2015).

11. N. Pueyo Bellafont, Paul S. Bagus, and F. Illas, "Prediction of core level binding energies in density functional theory: rigorous definition of initial and final state contributions and implications on the physical meaning of Kohn-Sham energies", *J. Chem. Phys.* **142**, 214102 (2015).

12. J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tyliszczak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordland, T. C. Wang, and P. S. Bagus, "Oxidation and Crystal Field Effects in Uranium", *Phys. Rev. B* **92**, 035111 (2015).