Tuesday Afternoon, October 31, 2017

Actinides and Rare Earths Focus Topic
Room: 22 - Session AC+MI+SA+SU-TuA

Actinide and Rare Earth Theory
Moderator: Ladislav Havela, Charles University, Prague, Czech Republic

2:20pm **AC+MI+SA+SU-TuA1 Magnetic Susceptibility, Magnetic Resonance, and Bonding in Actinide Complexes: Ab-initio Calculations**, *Jochen Autschbach*, University of Buffalo, SUNY **INVITED**
Actinide complexes exhibit fascinating magnetic properties and interesting chemical bonding. An on-going research project in our group is devoted to first-principles calculations of magnetic resonance parameters (NMR, EPR), magnetic susceptibilities, and other spectroscopic parameters of actinide complexes in relation to their chemical bonding, in particular regarding the involvement of the 5f shell in metal-ligand bonding. We will present results from recent computational studies of magnetic resonance parameters and the magnetic susceptibility of f-element complexes utilizing relativistic quantum chemical methods.

References: Gendron, F. et al., 'Puzzling lack of temperature dependence of the PuO2 magnetic susceptibility explained according to ab-intio wavefunction calculations', J. Phys. Chem. Lett. 2017, 8, 673-678. 'Ligand NMR chemical shift calculations for paramagnetic metal complexes: 5f1 vs. 5f2 actinides', J. Chem. Theory Comput. 2016, 12, 5309-5321. 'Magnetic properties and electronic structure of neptunyl(VI) complexes: Wavefunctions, orbitals, and crystal-field models', Chem. Eur. J. 2014, 20, 7994-8011. Knecht, S. et al, 'A nonorthogonal state-interaction approach for matrix product state wave functions', J. Chem. Theory Comput. 2016, 12, 5881-5894. Silver, M. et al., 'Characterization of berkelium(III) dipicolinate and borate compounds in solution and the solid state', Science 2016, 353, aaf3762.

3:00pm **AC+MI+SA+SU-TuA3 Combining DMRG with Standard Relativistic Multireference Methods to Probe the Properties of Strongly Correlated Systems: Plutonium Oxides**, *Valérie Vallet, S. Kervazo,* CNRS / University of Lille, France, *F. Réal,* University of Lille, France, *A. Severo Pereira Gomes,* CNRS / University of Lille, France, *F. Virot,* IRSN, France **INVITED**
Actinide-containing complexes present formidable challenges for electronic structure methods due to the large number of degenerate or quasi-degenerate electronic states arising from partially occupied 5f and 6d shells. In particular, we focus our study here on volatile forms of plutonium such as PuO_2, PuO_3 or $PuO_2(OH)_2$, for which spectroscopic and thermodynamics properties are of interest.

To attain an accuracy comparable to that of experiments, highly accurate calculations including static and dynamic correlation effects as well as relativistic effects are required. Conventional multi-reference methods, however, can treat active spaces that are often at the upper limit of what is required for a proper treatment of species with complex electronic structures and large number of valence orbitals involved in chemical bonds, leaving no room for verifying their suitability.

In this work, we address first the issue of properly defining the active spaces in such calculations, and introduce a protocol to determine optimal active spaces based on the use of the Density Matrix Renormalization Group algorithm and concepts of quantum information theory.[1]

The guidance offered by this protocol allows us to define the suitable active space to compute the electronic structures

and the nature of the ground states with the desired accuracy, i.e. the clear multi-reference character of the wave-function of those compounds requires that the energies of formation to be computed with multi-configurational quantum chemical methods like CASSCF and CASPT2 and with spin-orbit interaction, treated here *a posteriori* with the state-interaction RASSI method. Specifically, our results illustrate the complex multi-configurational character of PuO_3. The computed thermodynamics quantities reach a high accuracy allowing us to predict the composition of the released volatile products.

5:00pm **AC+MI+SA+SU-TuA9 The Thermal Expansion of UC and UO_2 from First Principles Calculations - The Importance of Correlations Effects and Spin-orbit Coupling**, *Dominik Legut,* IT4Innovations Center, VSB - Technical University of Ostrava, Czech Republic, *U.D. Wdowik,* Pedagogical University, Poland, *P. Piekarz,* Polish Academy of Sciences, Poland, *G. Jaglo,* Pedagogical University, Poland, *L. Havela,* Charles University, Prague, Czech Republic
Uranium monocarbide, a potential fuel material for the generation IV reactors, is investigated within density functional theory. Its electronic, magnetic, elastic, and phonon properties are analyzed and discussed in terms of spin-orbit interaction and localized versus itinerant behavior of the 5f electrons. We demonstrate that the theoretical electronic structure, elastic constants, phonon dispersions, and their densities of states can reproduce accurately the results of x-ray photoemission and bremsstrahlung isochromat measurements as well as inelastic neutron scattering experiments only when the 5f states experience the spin-orbit interaction and simultaneously remain partially localized [1]. The partial localization of the 5f electrons could be represented by a moderate value of the on-site Coulomb interaction parameter of about 2 eV. The results of the present studies indicate that both strong electron correlations and spin-orbit effects are crucial for realistic theoretical description of the ground-state properties of uranium carbide. This is even more pronounced considering the thermal expansion and thermal conductivity of UC, where for the latter the optical phonon branches may cause a significant contributions [2]. We compare the novel material UC to the experimental data and to the presently used nuclear fuel material, UO_2 oxide. Here our calculations show that considering the exchange and electron correlations effects the generalized gradient approximation was successful in describing the phonon dispersion spectrum, thermal expansion, and heat capacity w.r.t to the recorded data [3]. For both materials the so-called direct method, based on the harmonic and quasi-harmonic approximation, was used [4]. To study the pressure dependence of the phonon frequencies of UO_2 we calculated phonon dispersions for several lattice constants. Our computed phonon spectra demonstrate the opening of a gap between the optical and acoustic modes induced by pressure. Taking into account the phonon contribution to the total free energy of UO_2 its thermal expansion coefficient and heat capacity have been computed from first-principles [3].

1. U. D. Wdowik, P. Piekarz, D. Legut, and G. Jaglo, Phys. Rev. B **94**, 054303 (2016).

2. P. Maldonado, L. Paolasini, P. M. Oppeneer, T. R. Forrest, A. Prodi, N. Magnani, A. Bosak, G. H. Lander, and R. Caciuffo,

Phys. Rev. B 93, 144301 (2016).

3. Y. Yun, D. Legut and P. M. Oppeneer, J. Nucl. Mat. **426**, 109 (2012).

4. K. Parlinski, Z.-Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997); K. Parlinski, Software PHONON, ver. 6.15, Krakow, Poland, (2015).

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