Theory for Surface Processes and Spectroscopies Focus Topic
Room Oregon Ballroom 203-204 - Session TH-TuP
Theory for Surface Processes and Spectroscopies Poster Session

TH-TuP-1 Evaluation of Covalent Bonding In Ionic Compounds*, Paul S. Bagus,* University of North Texas*; C. Nelin,* Consultant*; T. Vitova,* Karlsruhe Institute of Technology, Institue for Nuclear Waste Disposal, Germany*; B. Schacherl,* Karlsruhe Institute of Technology,KIT, INE, Germany

The extent of covalent bonding in ionic compounds like oxides and halides is of considerable importance for their chemical properties; see, for example Refs. [1-2]. It is often estimated from populations analyses either based on the original Mulliken formalism [3] or on more modern variants. [4-5] However, population analyses may have artifacts and be misleading. In contrast, we will be using a set of three criteria to estimate covalent character of orbitals in cluster models of compounds. [6] The methods are based on: (1) variation of orbital energies for different symmetry frontier orbitals; (2) estimates of the size of the orbitals as measured by an effective radius; and (3) projection of atomic orbitals. We examine the changes in covalency for two sets of compounds. The first set includes three nominally Ni(II) compounds: NiO, $Ni(OH)_2$, and $NiCO_3$. The second set are nominally oxidation state IV actinide dioxides UO_2, NpO_2, and PuO_2. As well as the covalency for ground state WFs, we also consider the different covalent character of cations where a core electron has been ionized or excited. The wavefunctions are obtained as fully relativistic *ab initio* solutions of Dirac Hartree-Fock and many body configuration interaction solutions. It is shown that there are surprising departures from the nominal oxidation states and that the changes are not always consistent with intuitive views of the changes in the covalent character of the different compounds.

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