Relativistic effect determines the oxidation states: a study of Rh and Ir oxides by first principles methods

MAOSHENG MIAO, Materials Research Lab, University of California Santa Barbara, RAM SESHADRI, Materials Department & Department of Chemistry and Biochemistry, University of California Santa Barbara — The relativistic effect becomes significant on determining the structure and properties of 4d and 5d transition-metal compounds. It is found in some iridates that the relativistic effect, mainly contributed as spin-orbit interactions, can enhance the otherwise weak correlation of 5d electrons and cause an unusual Mott transition. Utilizing such effects in creating new phase such as topological insulator has grown into a hot spot in the frontier of functional oxide research. However, the relativistic effects on orbital energies, although important on determining the structure, has not been systematically studied. The general trend of the oxidation states of transition metals in the same group is to decrease with increasing atomic number. However, in contrast to this trend, Ir tends to form IrO$_2$ (4+) whereas Rh forms both Rh$_2$O$_3$ (3+) and RhO$_2$. Using relativistic and non-relativistic first principles calculations, we demonstrate that the unusually high oxidation state of Ir and the high stability of IrO$_2$ is caused by relativistic effect. Because relativity contracts the s and p orbitals, it repels Ir 5d electrons outwards and increases their energies. As a consequence, Ir tends to be oxidized to 4+ state and forms IrO$_2$.

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