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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_2O_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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