Studies of Phase Stability and Properties of TiO_2 Polymorphs and Ti_4O_7 Magnéli Phases with Diffusion Monte Carlo

Ye Luo[1], Anouar Benali[1], Luke Shulenburger[2], Jaron Krogel[3], Olle Heinonen[1], Paul Kent[3]

[1] Argonne National Laboratory
[2] Sandia National Laboratories
[3] Oak Ridge National Laboratory

In the past decades, many studies have focused on the fundamental properties of TiO_2 due to its important role in effectively converting solar energy such as in photovoltaic batteries and photocatalic water splitting. TiO_2 presents many stable and metastable phases of which, Rutile Anatase and Brookite are the most studied. Using density functional theory (DFT), the energy ordering of these phases depends strongly on the scheme describing the electronic correlation, for instance GGA+U and Hybrid functionals, often tied to an empirical parameter for reproducibility with no guarantee of predictability. We present the first analysis of the polymorphic energy ordering and properties of three naturally existing polymorphs Rutile, Anatase and Brookite, by performing the highly accurate ab initio calculation with fixed node diffusion Monte Carlo (DMC) implemented in QMCPACK. Recently, Magnéli phases such as Ti_4O_7 with ordered reduced structures from TiO_2 have been experimentally identified forming conducting pathways in resistive switching devices. We also present the study of Ti_4O_7 in three electronic spin configurations by DMC calculations.