Taming the d-shell: An Analysis of the Effect of GGA+U in Density Functional Theory Models of Lithium-ion Battery Positive Electrode Materials

Laurent Molino, Dalhousie University
Supervisor(s): Dahn, Jeff
Other authors: Cormier, Mark and Dahn, Jeff

Density functional theory (DFT) with the generalised gradient approximation (GGA) is an important method for modeling materials for energy storage. However in certain materials, including lithium-ion battery positive electrode materials, DFT GGA calculations model d-shell electrons as excessively delocalized. A computationally inexpensive solution to this problem is GGA+U. In GGA+U, a potential U is applied to d-shell electrons to improve electron localisation. However, a systematic analysis of the effect of the values of U on the properties of positive electrode materials has yet to be performed, and thus the choice of U values for these materials cannot be fully justified. The goal of this work is to perform such an analysis. GGA+U DFT calculations were performed on layered structures of Nickel, Cobalt, and Manganese using U values from zero to eight eV. Electronic and structural properties of each structure were calculated over the range of U studied, including unit-cell parameters, atom magnetizations, and lithium intercalation potentials. It was found that certain properties, importantly including lithium intercalation potential, change significantly over the range of U studied. This finding supports the conclusion that the value of U must be carefully chosen, and GGA+U may sometimes be inapplicable.