Modeling noncollinear magnetism in manganese oxides

Jin Soo Lim[1], Diomedes Saldana-Greco[1], Andrew M. Rappe[1]

[1]*Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104–6323*

Magnetism in oxides is presently the focus of intense research effort, both due to fundamental interest and due to potential applications. Magnetic oxides can enable ultrasensitive sensors, low-power computing, and metal-insulator transitions. In many cases, the magnetism is noncollinear, due either to magnetic frustration, relativistic spin-orbit coupling, or both. This opens up many complicated spin-spin interactions that lead to competing ground states and exotic interactions.

To enable accurate analysis of magnetic interactions in oxides, we revisit the pseudopotential approximation to enhance its ability to reproduce magnetic energetics. We find that DFT+U is not sufficient for differentiating subtle differences in magnetic properties, but that the fully anisotropic DFT+U+J Hamiltonian can be made to be quite accurate, in concert with a pseudopotential that has semicore states and nonlinear core correction. [1] With this improved pseudopotential, a wide range of spin patterns are successfully reproduced in a family of binary manganese oxides.

We use this new pseudopotential to investigate the nature of magnetism and its coupling to electric polarization in quadruple perovskite $CaMn_7O_{12}$. This material has helicoidal magnetic order, stemming from magnetic frustration in the (111) planes and ferromagnetic coupling between Mn^{3+} and Mn^{4+} ions. DFT+U+J calculations show that the experimentally-observed helicoidal order is energetically preferred, even in the absence of spin-orbit coupling and without symmetry-breaking ion displacements. This demonstrates that the main driver for the helicoidal order and the electronic ferroelectricity is nonrelativistic exchange striction. [2]

[1] J. S. Lim, D. Saldana-Greco, and A. M. Rappe, “Improved pseudopotential transferability for magnetic and electronic properties of binary manganese oxides from DFT+U+J calculations”, *Phys. Rev. B* **94**, 165151(1–10) (2016).

[2] J. S. Lim, D. Saldana-Greco, and A. M. Rappe, “Improper magnetic ferroelectricity of nearly pure electronic nature in helicoidal spiral $CaMn_7O_{12}$”, *Phys. Rev. B* **97**, 045115(1–7) (2018).