Many body effects on the formal charge of 3*d* - Transition Metal Doped $BaTiO_3$

Subhasish Mandal[1, 2], R. E. Cohen[2, 3], K. Haule[4]

[1]Department of Applied Physics, Yale University, New Haven, Connecticut, USA
[2] Geophysical Laboratory, Carnegie Institution of Washington, Washington D.C, USA
[3] Department of Earth Sciences, University College London, London, UK,
[4] Department of Physics, Rutgers University, Piscataway, New Jersey, USA

One route to magnetoelectric materials, which couple magnetism and ferroelectricity, is to dope ferroelectrics with magnetic ions. Such materials are of interest for electronics that can integrate data processing and memory operation in a single device [1-4]. In addition, most commercial transducer materials have added Mn impurity to improve piezoelectric properties, mechanical quality factor, and coercive field, and to decrease electrical conductivity. To find the role of the impurity atom in these materials, one important task is to understand the charge transfer process. The first order problem is to finding an accurate charge state and 3*d* occupation of the magnetic impurity, and therefore it needs a detail understanding of atomic nature of the impurity in a crystal.

Using density functional theory (DFT) in combination with dynamical mean field theory (DMFT) in Mn doped $BaTiO_3$, we find a different charge state and 3*d*- orbital occupations than obtained from either DFT or DFT+U. We find that the explicit treatment of many-body effects induced by the Hund's rule coupling in Mn shows a donor charge state of Mn^{2+}, instead of usual acceptor charge state of Mn^{4+} as is found in both DFT and DFT+U. The differences in electron density reveal that charge transfer due to strong Hubbard interactions is not sufficient to describe the electron correlations in transition metal doped ferroelectrics.

In the DFT-DMFT method, the self-energy, sampling all Feynman diagrams local to the impurity Mn ion, is added to the DFT Kohn-Sham Hamiltonian [5, 6]. This implementation is fully self-consistent and all-electron [5, 6]. The computations are converged with respect to charge density, impurity level, chemical potential, self-energy, lattice, and impurity Green's functions. The lattice is represented using the full potential linear augmented plane wave method, implemented in the WIEN2K [7] package in its generalized gradient approximation [Wu-Cohen GGA]. The continuous time quantum Monte Carlo method is used to solve the quantum impurity problem and to obtain the local self-energy due to the correlated Mn 3d orbitals. A unit cell containing 40 atoms including one Mn ion (at Ti site) is used for our simulations. 40,000000 Monte Carlo steps are used for each iteration.

We show the density of states obtained from DFT, DFT+U, and DFT+DMFT methods and charge density difference plot between each method. To quantify the probability of finding an Mn atom in the solid in one of the atomic states, we will present atomic histogram and its dependence on U and J. We will show how Hund's rule coupling affects the 3*d*-orbital occupancy in this material.

Acknowledgements:
This work is supported by ONR grants N00014-12-1-1038 and N00014-14-1-0561, by the ERC Advanced grant ToMCaT, and by the Carnegie Institution.

References

[1] D. V. Efremov, J. V. D. Brink, and D. I. Khomskii, Nature Mat. **3**, 853 (2004).

[2] C. Ederer and N. A. Spaldin, Nature Mat. **3**, 849 (2004).
[3] Y. Shauai *et al.* J. Appl. Phys. **109**, 084105 (2011)
[4] X. Tong, Y-H Lin, S. Zhang, Y. Wang, and C. -W. Nan, J. Appl. Phys. **104**, 066108 (2008).
[5] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A.Marianetti, Rev. Mod. Phys. **78**, 865 (2006).
[6] K. Haule, C.-H. Yee, and K. Kim, Phys. Rev. B 81, 195107 (2010).
[7] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, in An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, edited by K. Schwarz (Vienna University of Technology, Austria, 2001).