Ab initio Theoretical Studies on Multiferroicity in Transition Metal Oxides

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"Multiferroics" are attractive multifunctional materials where magnetism and ferroelectricity are strongly coupled [1,2]. They are also playgrounds for magnetoelectric effect, which enables control of magnetization via external electric field. Multiferroics can be classified according to different driving forces, which primarily break the spatial inversion symmetry paving the way to ferroelectricity: (i) spin order, (ii) charge order and (iii) orbital order. In this talk, theoretical studies on the various multiferroics based on density functional theory (DFT) will be summarized.

In the first group, plenty of studies have been focused on spin-driven ferroelectricity in perovskite rare-earth manganites, RMnO$_3$. It has been known that antisymmetric Dzyaloshinskii–Moriya interaction causes weak electric polarization in spin-spiral TbMnO$_3$, while exchange striction mechanism causes stronger polarization in E-type antiferromagnetic HoMnO$_3$. Recently, a high-pressure experiment reported that TbMnO$_3$ shows the magnetoelectric phase transition to have large polarization, which is caused by the magnetic transition as confirmed by a DFT calculation [3].

In the second group, LuFe$_2$O$_4$ has emerged as a prototype of charge-order induced multiferroics for a long time, however, recently magnetite (Fe$_3$O$_4$) has been also suggested as a new candidate, which would depict it as the first multiferroic known to mankind. Magnetite shows the first-order metal-insulator Verwey transition at T_V = 120 K, below which the crystal structure has a polar Cc space group. By comparing the polar crystal structure with the centrosymmetric structure via DFT calculation, we got the sizable ferroelectric polarization, which value is consistent with the experimental measurement [4]. It is revealed that the ferroelectricity is induced by a polar charge-ordering and the polarization is primarily caused by local electric dipoles between divalent and trivalent Fe ions in magnetite.

If time permits, I would like to introduce an alternative mechanism of magnetoelectric effect, called "spin-dependent *pd* hybridization". It has been reported that the mechanism can be responsible for the magnetoelectric effect observed in Ba$_2$CoGe$_2$O$_7$, where two neighboring Co spins are aligned in a C-type antiferromagnetic configuration. According to a theoretical analysis, the microscopic origin of the magnetoelectricity is based on two relevant ingredients, i.e., the anisotropic *p-d* hybridization between Co and O states and the on-site spin-orbit coupling at Co sites [5]. This mechanism may be applied to magnetoelectric effect measured in magnetite [6].

References

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