Mechanism of Covalency Induced Polarization

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Covalency enhances the electric polarization produced by the ionic displacement for ferroelectric perovskite transition metal oxides (TMO). Furthermore, recent experimental and theoretical works on the organic ferroelectrics TTF-CA (tetrathiafulvalene-$p$-chloranil) have revealed that the covalency induced polarization is one to two orders of magnitude larger than that of the ionic polarization and that the two contributions are in the opposite direction [1-3]. Here we propose a formulation to analyze the detailed mechanism of the covalency induced polarization within the framework of maximally localized Wannier orbitals and apply it to an organic exotic ferroelectrics TTF-CA [4,6] and typical ferroelectric perovskite TMOs, BaTiO$_3$ and PbTiO$_3$ [5]. This formulation discriminates three components in the electronic contribution to the polarization. The first one corresponds to the point charge model, the second the intra-atomic or molecular polarization and the third comes from the electron transfer between unit cells. The framework of the present formulation is the same as the one proposed by Bhattacharjee and Waghmare [6]. We also propose a way of estimating the local charge projected on the atomic-like Wannier orbitals.