Finite-size correction for first-principles point defect calculations using a supercell approach

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Point defects in semiconductors and insulators play a decisive role in determining materials properties. However, it is not straightforward to fully investigate their concentrations and atomic and electronic structures in experiments, and first-principles calculations have emerged as a valuable tool for the study of defects in recent years.

First-principles calculations for solids usually adopt three-dimensional periodic boundary conditions. Then, charged defect calculations can include huge errors up to several eV due to the limitation of supercell sizes [1-3]. Recently, Freysoldt, Neugebauer, and Van de Walle (FNV) proposed a remarkable scheme to correct the finite size errors [3]. This allows us to estimate the correction energy up to the $L^{-3}$ order, where $L$ is the dimension of the supercell, without additional first-principles calculations. The great advantage is that it can be applied to computationally very demanding calculations using, for instance, hybrid functionals and quantum Monte Carlo, which can treat only very limited sizes of supercells. The original FNV correction scheme is, however, applicable only to cubic systems because it is assumed that the long-range Coulomb interaction is screened by a dielectric constant. Very recently, we extended the FNV correction scheme by rewriting the formalism using an anisotropic form with a dielectric matrix [4]. With systematic assessment of the corrective capability, the extended FNV scheme has been found to excellently correct the formation energies of a wide variety of charged defects in diverse materials.

In this study, we apply the extended FNV scheme to the formation energy of the oxygen vacancy with $q$=+2 charge ($V_{O}^{+2}$), $E\{V_{O}^{+2}\}$, in lithium titanate β-Li$_{2}$TiO$_{3}$, which has been studied for the use in lithium ion batteries. The crystal structure and removed oxygen ion are shown in Fig.1. As inferred from the layered structure, the diagonal components of the dielectric matrix are very different [4]. First-principles calculations were performed with the PAW method [5] as implemented in the VASP code [6], and calculation conditions were kept consistent with those in Ref. [4].

The correction energy of the FNV scheme is the sum of a point-charge (PC) correction energy and an alignment-like term [4]. The latter is estimated from potential offset between the defect-induced potential ($V_{q/b}$) and PC potential ($V_{PC,q/b}$), and can be written as $-q\Delta V_{PC,q/b|\text{far}}$, where $q$ is a defect charge, $\Delta V_{PC,q/b} = V_{q/b} - V_{PC,q/b}$, and $\Delta V_{PC,q/b|\text{far}}$ is $\Delta V_{PC,q/b}$ far from a defect and its images [3, 4]. Figure 2(a) shows $V_{q/b}$, $V_{PC,q}$, and $\Delta V_{PC,q/b}$ of $V_{O}^{+2}$ in a $2 \times 2 \times 2$ supercell. $V_{q/b}$ and $V_{PC,q}$ widely scatter even at the same distance from the defect, reflecting the anisotropic screening feature, and $\Delta V_{PC,q/b}$ converges in a region far from the defect. $\Delta V_{PC,q/b|\text{far}}$ was determined by averaging $\Delta V_{PC,q/b}$ at the atomic positions outside of the sphere in contact with the Wigner-Seitz cell. Figure 2(b) shows $E\{V_{O}^{+2}\}$ without and with corrections at different levels as a function of cell size and shape. Without corrections, $E\{V_{O}^{+2}\}$ widely scatters depending on the supercell size and
shape. The isotropic FNV correction with a dielectric constant, which is typically adopted by many authors, does not avail to correct \( E_f[V_{O^{2+}}] \). On the other hand, the anisotropic PC drastically reduces the cell size/shape dependence. The potential alignmentlike term in the anisotropic FNV scheme successfully corrects the remaining cell size/shape dependence, and it almost vanishes in large supercells.

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References

FIG. 1. Crystal structure of \( \beta \)-Li\(_2\)TiO\(_3\). The position of the oxygen vacancy introduced in this study is shown in circles.

FIG. 2. (a) Defect-induced potential \((V_{gb})\), point-charge potential \((V_{PC,q})\), and their differences \((\Delta V_{PC,q,qgb})\) at the atomic sites in a \( \beta \)-Li\(_2\)TiO\(_3\), \(2 \times 2 \times 2\) supercell with \(V_{O^{2+}}\). The region for averaging \(\Delta V_{PC,q,qgb}\) and its averaged value are expressed in the width and height of the arrow, respectively. (b) Uncorrected and corrected formation energies of \(V_{O^{2+}}\) as a function of the supercell size and shape. Zero is set to the anisotropic FNV corrected formation energy calculated with the \(2 \times 3 \times 1\) supercell.