Supplemental Material for Review Only for "Electron-Phonon Scattering in the Presence of Soft Modes and Electron Mobility in $SrTiO_3$ Perovskite from First Principles"

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Long-range dipole-dipole interactions in the TDEP / supercell method

In this short addendum, we sketch the derivation of Eq. 1 in the Supplemental Material, which writes the contribution to the IFCs from the long-range dipole-dipole interactions as

$$\Phi_{mn}^{L,\alpha\beta} = \frac{4\pi}{N\Omega} \sum_{K\neq\mathbf{0}} \frac{\left(K_\gamma Z_m^{*,\gamma\alpha}\right)\left(K_\eta Z_n^{*,\eta\beta}\right) e^{i\mathbf{K}\cdot(\tau^m-\tau^n)}}{\left(\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}\right) e^{\frac{(K\cdot\boldsymbol{\epsilon}\cdot K)}{4\Lambda^2}}} \quad . \tag{1}$$

To compute the IFC, we setup a $n_1 \times n_2 \times n_3$ supercell, defined here as the IFC cell. We label the lattice vectors of the unit cell as $\mathbf{R}_i$ and we limit $\mathbf{R}_i$ to be within the IFC cell. The lattice vectors of the IFC cell are denoted with $\mathbf{T}_i$ and the ion displacements as $\mathbf{u}^\mu\left(\mathbf{T}_i + \mathbf{R}_i\right)$, where μ labels the ions in the unit cell. For convenience, we use $m \equiv (\mathbf{R}, \mu)$ to label ions within the IFC cell, i.e., $\mathbf{u}^\mu\left(\mathbf{T} + \mathbf{R}\right) \equiv \mathbf{u}^m\left(\mathbf{T}\right)$. In DFT calculations of the IFC cell, we also need to adopt Born-von Karman (BvK) boundary conditions, which define a BvK supercell that represents the whole solid. We limit $\mathbf{T}$ to be within the Bvk supercell, and write as N_T the number of IFC cells in the BvK cell.

The IFCs can then be defined through the vibrational energy,

$$U = \frac{1}{2N_T} \sum_{ij,mn} \mathbf{u}^m\left(\mathbf{T}_i\right) \mathbf{\Phi}_{mn}\left(i,j\right) \mathbf{u}^n\left(\mathbf{T}_j\right).$$

Upon defining the cumulant IFCs as

$$\bar{\mathbf{\Phi}}_{mn} = \sum_{\mathbf{T}} \mathbf{\Phi}_{mn}\left(0, \mathbf{T}\right)$$

we can write

$$U = \frac{1}{2} \sum_{mn} \mathbf{u}^m \bar{\mathbf{\Phi}}_{mn} \mathbf{u}^n \tag{2}$$

The electrostatic potential generated by a dipole located at $\tau^m \equiv (\tau^\mu + \mathbf{R})$ and its images at $(\tau^m + T)$ is

$$\phi_m^d(r) = -\frac{4\pi i}{N\Omega} \frac{1}{4\pi\varepsilon_0} \sum_{\mathbf{K}\neq\mathbf{0}} \frac{\left(\mathbf{p}_m \cdot \mathbf{K}\right) e^{i\mathbf{K}\cdot(r-\tau^m)}}{\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}}, \tag{3}$$

where $\mathbf{K}\cdot T = 2\pi N$ are reciprocal lattice vectors of the IFC cell, and hereafter we set $\frac{1}{4\pi\varepsilon_0} = 1$. The potential generated by all dipoles within the IFC supercell and their images is $\phi^d\left(r\right) = \sum_m \phi_m^d\left(r\right)$, and its corresponding electric field $\mathbf{E}^d$ is

$$\mathbf{E}^d\left(r\right) = -\nabla\phi^d\left(r\right) = \sum_m \mathbf{E}_m^d\left(r\right) = -\sum_m \nabla\phi_m^d\left(r\right)$$

The potential energy of a dipole $\mathbf{p}$ in the electric field is $U = -\mathbf{p}\cdot\mathbf{E}$, so that the total potential energy due to the interactions between the dipoles reads

$$U^d = -\frac{1}{2}\sum_m \mathbf{p}_m \cdot \left[\mathbf{E}^d\left(\tau^m\right) - \mathbf{E}^d_m\left(\tau^m\right)\right],$$

where $\mathbf{p}_m \cdot \mathbf{E}^d_m\left(\tau^m\right)$ are self-interaction terms, which are included in $\mathbf{p}_m \cdot \mathbf{E}^d\left(\tau^m\right)$ and need to be subtracted to correctly compute U^d. We use $\bar{U}^d$ to denote sum of $-\mathbf{p}_m \cdot \mathbf{E}^d\left(\tau^m\right)$,

$$\begin{aligned}\bar{U}^d &= \frac{1}{2}\sum_m\sum_n \mathbf{p}_m \cdot \nabla\phi^d_n\left(r\right)|_{r=\tau^m} \\ &= \frac{2\pi}{N\Omega}\sum_{mn}\sum_{K\neq\mathbf{0}} \frac{\left(\mathbf{p}_m\cdot\mathbf{K}\right)\left(\mathbf{p}_n\cdot\mathbf{K}\right)e^{i\mathbf{K}\cdot\left(\tau^m-\tau^n\right)}}{\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}}\end{aligned}$$

It follows that the sum of the self interaction terms, $\bar{U}^d_s$, is

$$\begin{aligned}\bar{U}^d_s &= \frac{1}{2}\sum_m \mathbf{p}_m \cdot \nabla\phi^d_m\left(r\right)|_{r=\tau^m} \\ &= \frac{2\pi}{N\Omega}\sum_{m}\sum_{K\neq\mathbf{0}} \frac{\left(\mathbf{p}_m\cdot\mathbf{K}\right)\left(\mathbf{p}_m\cdot\mathbf{K}\right)}{\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}}.\end{aligned}$$

Therefore, the total potential energy due to the interactions between the dipoles, $U^d = \bar{U}^d - \bar{U}^d_s$, can be written as

$$U^d = \frac{2\pi}{N\Omega}\sum_{m\neq n}\sum_{K\neq\mathbf{0}} \frac{\left(\mathbf{p}_m\cdot\mathbf{K}\right)\left(\mathbf{p}_n\cdot\mathbf{K}\right)e^{i\mathbf{K}\cdot\left(\tau^m-\tau^n\right)}}{\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}}. \tag{4}$$

Since we are only interested in the long-range part of the dipole field, we use the Ewald summation approach to express the long-range part of the electrostatic potential generated by a dipole located at τ^m (see Eq. 3) as the reciprocal space sum

$$\phi^L_m\left(r\right) = -\frac{4\pi i}{N\Omega}\sum_{\mathbf{K}\neq\mathbf{0}} \frac{\left(\mathbf{p}_m\cdot\mathbf{K}\right)e^{i\mathbf{K}\cdot\left(r-\tau^m\right)}}{\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}} e^{-\frac{\left(K\cdot\boldsymbol{\epsilon}\cdot K\right)}{4\Lambda^2}},$$

where the parameter Λ defines the extent of the long-range part (the larger Λ, the more extensively dipole-dipole interactions are captured in the reciprocal space summation). The long-range part of U^d similarly reads

$$U^L = \frac{2\pi}{N\Omega}\sum_{m\neq n}\sum_{K\neq\mathbf{0}} \frac{\left(\mathbf{p}_m\cdot\mathbf{K}\right)\left(\mathbf{p}_n\cdot\mathbf{K}\right)e^{i\mathbf{K}\cdot\left(\tau^m-\tau^n\right)}}{\left(\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}\right)e^{\frac{\left(K\cdot\boldsymbol{\epsilon}\cdot K\right)}{4\Lambda^2}}}. \tag{5}$$

Using Eq. 2 to express the cumulative IFCs as second derivatives of the energy U^L, and writing the dipole moments $\mathbf{p}_m$ in terms of the Born effective charge tensor $Z^{*,\alpha\beta}_m$, the contribution to the IFCs from the long-range dipole-dipole interactions is

$$\Phi_{mn}^{L,\alpha\beta} = \frac{4\pi}{N\Omega} \sum_{K\neq\mathbf{0}} \frac{\left(K_\gamma Z_m^{*,\gamma\alpha}\right)\left(K_\eta Z_n^{*,\eta\beta}\right) e^{i\mathbf{K}\cdot(\tau^m-\tau^n)}}{\left(\mathbf{K}\cdot\boldsymbol{\epsilon}\cdot\mathbf{K}\right) e^{\frac{(K\cdot\boldsymbol{\epsilon}\cdot K)}{4\Lambda^2}}} \quad . \tag{6}$$

This is Eq. 1 in the Supplemental Material, which we wanted to briefly derive.

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