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# **Mixed-space approach for calculation of vibration-induced dipole-dipole interactions**

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By explicitly taking into account the effects of vibration-induced dipole-dipole interactions between periodic supercells, we derive an efficient formulation to calculate the phonon frequencies of an ionic crystal. We demonstrate that the vibration-induced dipole-dipole interactions lead to a constant contribution to the interatomic force constant in real space. It recovers the result by Cochran and Cowley at the long wavelength limit. Using MgO as the prototype, we demonstrate that a 16-atom  $2\times 2\times 2$  supercell of the primitive unit cell is sufficient to obtain the phonon dispersions when the dipole-dipole interactions are considered. We find that not properly taking into account the dipole-dipole interaction leads to oscillations along the  $(0,0,q)$  direction for the longitudinal optical phonon dispersion in a 128-atom elongated  $1\times 1\times 16$  supercell of the cubic structure .

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## I. INTRODUCTION

The phonon approach<sup>1-2</sup> is currently the most efficient method for predicting thermodynamic properties of a solid at finite temperatures. It has been implemented under the framework of first-principles theories: the linear-response<sup>3-4</sup> and supercell methods.<sup>5-6</sup> In the literature, the supercell method is also referred to as the direct approach, or the small displacement method, or the frozen phonon approach. In the linear-response method, the dynamical matrix is calculated in reciprocal space assuming that the electronic wave functions respond linearly to the change in atomic positions. In comparison, the supercell method calculates the interatomic force constants (IFC) in the real space using the Hellmann–Feynman theorem<sup>7</sup> for finding the force acting on an atom after perturbation from its equilibrium position.

The present work focuses on a long-standing problem within the supercell method, i.e. how to account for the effects of vibration-induced dipole-dipole interactions on the phonon frequencies of an ionic crystal or a polar material. For an ionic crystal, the longitudinal optical vibrations can induce the dynamical electric dipoles along the wave vector ( $\mathbf{q}$ ) direction. These dipoles, in turn, can act on the longitudinal optical vibrations, resulting in frequency splitting between the longitudinal optical (LO) and the transverse optical (TO) phonons.<sup>3</sup> Efforts to formulate or account for this effect dated back to the 1930s. Lyddane et al.<sup>8</sup> first accurately formulated the polar vibrations of cubic alkali halides at the long wavelength limit. Cochran and Cowley<sup>9</sup> demonstrated a systematic formulation suitable for a crystal with general symmetry. The computational formulations presented by Gonze and Lee<sup>4</sup> are suitable for an arbitrary  $\mathbf{q}$  point in the Brillouin zone by explicitly considering the dipole-dipole interactions although they are presently only implemented within the framework of the linear-response method. Other important works<sup>10-13</sup> involve calculations either using an elongated supercell specific for a

particular material or of the phonon frequencies at specific rather than arbitrary  $\mathbf{q}$  points in the Brillouin zone. To put it simply, calculating the phonon frequency of an ionic crystal at an arbitrary  $\mathbf{q}$  point in the Brillouin zone using a general supercell is still a challenge in the supercell method.

In a recent publication, we <sup>14</sup> proposed a mixed-space approach which could properly account for the contribution of the vibration-induced dipole-dipole interactions to the IFC in real space. In the present work we provide a systematic formulation by reconsidering the fundamental dipole-dipole interactions. Section II summarizes the general phonon theory of lattice vibrations in a crystal, emphasizing the concepts of Hamiltonian, the exact wave vector point, and the Fourier interpolation. In Sec. III, we demonstrate that the effect of vibration-induced dipole-dipole interactions on phonons is the addition of a constant to the IFC in real space. In Sec. IV, we discuss the formulation in terms of analytic and nonanalytic contributions and how to properly interpret the calculated phonon dispersions for MgO in the literature without considering the vibration-induced dipole-dipole interactions. As examples, Sec. V discusses two calculations for MgO, one with a 16-atom regular supercell and one with a 128-atom elongated supercell, demonstrating the accuracy of the mixed-space approach. Finally, Sec. VI is a summary.

## II. GENERAL PHONON THEORY

We start with a brief review of the phonon theory. For a system made up of infinitely repeating primitive unit cells with lattice vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , the Hamiltonian in a harmonic approximation can be expressed as: <sup>1,3</sup>

$$\text{Eq. 1, } H = -\frac{1}{2} \sum_P \sum_j^M \frac{\hbar^2}{\mu_j} \nabla^2 + \frac{1}{2} \sum_{P,Q} \sum_{j,k}^M \sum_{\alpha,\beta}^3 C_{\alpha\beta}^{jk}(P,Q) u_{\alpha}^j(P) u_{\beta}^k(Q),$$

where  $\hbar$  is the Planck constant,  $P$  and  $Q$  index the primitive unit cells within a crystal,  $j$  and  $k$  label the atoms within the primitive unit cell containing  $M$  atoms,  $\mu_j$  is the mass of atom  $j$ ,  $u_{\alpha}^j(P)$  ( $\alpha = 1, 2, 3$ ) is the Cartesian displacement from its static position of the  $j$ th atom in the  $P$ th primitive unit cell, and  $C_{\alpha\beta}^{jk}(P,Q)$  is the real-space IFC between the  $j$ th atom within the primitive unit cell  $P$  and  $k$ th atom within the primitive unit cell  $Q$ . Because of translational invariance  $C_{\alpha\beta}^{jk}(P,Q)$  depends on  $P$  and  $Q$  only through the difference <sup>3</sup>  $\mathbf{R} = \mathbf{R}_P - \mathbf{R}_Q$ , where  $\mathbf{R}_P$  represents position of the  $P$ th primitive unit cell in the crystal.

In principle, Eq. 1 cannot be solved directly since it has infinite dimensions. To reduce the dimension of the problem, the widely adopted solution <sup>1, 15</sup> is the ***periodic supercell approach*** by which the individual phonon vibration is described in the wave vector space. Considering the fact that phonon vibrations are periodic, we can choose to solve those vibrations at the exact wave vector ( $\mathbf{q}$ ) point,  $\mathbf{q}_S$ , defined for a specific system or a supercell,  $\mathbf{S}$ , built by enlarging the primitive unit cell by  $N_a$ ,  $N_b$ , and  $N_c$  times, along the direction of the primitive lattice vector  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , respectively, as

$$\text{Eq. 2, } \mathbf{q}_S^i \cdot \mathbf{S}_i = 2\pi * \text{Integer} \quad (\mathbf{i} = \mathbf{a}, \mathbf{b}, \mathbf{c})$$

To mimic a crystal, such a system is implicitly further enlarged by making infinitely-exact copies of the supercell  $\mathbf{S}$  over the whole space, including the atomic displacements. Within this periodic supercell system, we can separate the  $P$  dependent part of  $u_{\alpha}^j(P)$  in Eq. 1 by rewriting it as

$$\text{Eq. 3, } u_{\alpha}^j(P) = u_{\alpha}^j \exp(i\mathbf{q}_S \cdot \mathbf{R}_P)$$

noting that the term  $u_{\alpha}^j$  on the right hand side of Eq. 3 is now only dependent on the internal atomic position within the primitive unit cell. Substituting Eq. 3 into Eq. 1, the phonon problem is then reduced to the diagonalisation of the  $3M$ -dimensional dynamical matrix  $\mathbf{D}$  by finding roots of the secular determinant: <sup>1, 15</sup>

$$\text{Eq. 4, } \det|D_{\alpha\beta}^{jk}(\mathbf{q}_s) - \omega^2(\mathbf{q}_s)| = 0$$

where

$$\text{Eq. 5, } D_{\alpha\beta}^{jk}(\mathbf{q}_s) = \sum_P^N e^{i\mathbf{q}_s \cdot \mathbf{R}_P} \frac{1}{\sqrt{\mu_j \mu_k}} \Phi_{st}^{\alpha\beta}(P, 0)$$

in which  $N=N_a*N_b*N_c$  and we have utilized the results derived from the conditions of Eq. 2, i.e., at all  $\mathbf{q}_s$ 's,

$$\text{Eq. 6, } e^{i\mathbf{q}_s \cdot \mathbf{S}} = 1.$$

$\Phi_{st}^{\alpha\beta}(P, 0)$ , on the right hand side of Eq. 5, is called the accumulative IFC <sup>16</sup> since it represents the summation of  $C_{\alpha\beta}^{jk}(P, 0)$ , counting  $P$  and all its images resulted from repeating the supercell  $\mathbf{S}$  over the whole space as

$$\text{Eq. 7, } \Phi_{st}^{\alpha\beta}(P, 0) = \sum_S^{\infty} C_{\alpha\beta}^{jk}(P + \mathbf{S}, 0)$$

The solutions of Eq. 4,  $\omega_j(\mathbf{q}_s)$  ( $j=1, 2, \dots, 3M$ ), are the phonon frequencies.

The procedures described by Eq. 1-7 give the precise solutions for the phonon frequencies at those exact  $\mathbf{q}$  points, i.e., all  $\mathbf{q}_s$ 's. However, a realistic calculation of the thermodynamic properties of a material <sup>14, 17</sup> needs the accurate phonon density of states constructed by sampling the phonon frequencies at a very dense  $\mathbf{q}$  grid. This task cannot be precisely completed using just the exact  $\mathbf{q}$  points, implying the necessity of using a very large

supercell  $\mathbf{S}$  at prohibitively-expensive computational costs. The alternative practice <sup>3</sup> is to generalize the usage of Eq. 4 and Eq. 5 to the case where  $\mathbf{q}$  is away from the  $\mathbf{q}_\mathbf{S}$  for the already defined supercell  $\mathbf{S}$ , as

$$\text{Eq. 8, } D_{\alpha\beta}^{jk}(\mathbf{q}) = \sum_P^N e^{i\mathbf{q}\cdot\mathbf{R}_P} \frac{1}{\sqrt{\mu_j\mu_k}} \Phi_{st}^{\alpha\beta}(P,0)$$

and

$$\text{Eq. 9, } \det\left|D_{\alpha\beta}^{jk}(\mathbf{q}) - \omega^2(\mathbf{q})\right| = 0$$

The procedures by Eq. 8 and Eq. 9 are commonly viewed as Fourier interpolation. For this method, the input data are simply those calculated  $D_{\alpha\beta}^{jk}$  in a coarse grid or  $\Phi_{st}^{\alpha\beta}$  in a pre-defined supercell.

As a matter of fact, the Fourier interpolation <sup>3, 16</sup> with Eq. 8 is the standard procedure for the two major first-principles methods for phonons - the supercell method and the linear-response method. For metals, it is indeed found <sup>6, 18</sup> that the Fourier interpolation by Eq. 8 and Eq. 9 is a rather good approximation whereas for ionic crystals it is not straightforward due to the additional contribution from the vibration-induced dipole-dipole interactions.

### III. VIBRATION INDUCED DIPOLE-DIPOLE INTERACTION

#### A. Assumptions

For an ionic crystal, when the periodic supercell approach is employed, one has to distinguish two cases in calculating phonon frequencies:

- i) At the non-zero  $\mathbf{q}_\mathbf{S}$  – the lattice vibration does not result in macroscopic electric fields; and

- ii) Away from the  $\mathbf{q}_S$  - the lattice vibration result in macroscopic electric fields which could invalidate the accurate application of the Fourier interpolation by Eq. 8 and Eq. 9.

The effect of macroscopic electric fields on phonons is not yet well accounted for in previous implementations of the supercell method.<sup>16, 19</sup> This is due to the fact<sup>11</sup> that within the periodic supercell approach the first-principles calculation of  $\Phi_{st}^{\alpha\beta}(P,0)$  in Eq. 5 requires the macroscopic electric fields to vanish. We described a procedure below to handle the dipole-dipole interactions among the supercell  $S$ 's.

Let us consider a supercell  $S$  built up with  $N$  primitive unit cells and use  $\mathbf{M}$  to represent the instant dipole moment due to the lattice vibration. We know<sup>3, 9</sup> that for a lattice vibration, the direction of  $\mathbf{M}$  is always parallel to  $\hat{\mathbf{q}}$ , so we will use the scalar quantity  $\mathbf{M} \cdot \hat{\mathbf{q}}$  to represent the value of dipole moment. Thus, the potential energy due to the dipole-dipole interactions between the supercell  $S$ 's can be expressed as

$$\text{Eq. 10, } E(DI) = -\frac{1}{2}(\mathbf{M} \cdot \hat{\mathbf{q}})(\mathbf{E} \cdot \hat{\mathbf{q}})$$

where  $\mathbf{E}$  represents the effective macroscopic electric field, which itself represents the averaged result from the dipole-dipole interactions between the supercell  $S$ 's. Here we have also utilized the fact<sup>3, 9</sup> that  $\mathbf{E}$  is parallel to  $\hat{\mathbf{q}}$ .

## B. SIFC - contribution to the IFC by the dipole-dipole interaction among the supercells

As the electric polarization  $\mathbf{P}$  is also parallel to  $\hat{\mathbf{q}}$ , it is known<sup>1, 3, 9</sup> that

$$\text{Eq. 11, } \mathbf{E} \cdot \hat{\mathbf{q}} = -4\pi(\mathbf{P} \cdot \hat{\mathbf{q}})$$

and<sup>3</sup>



$$\text{Eq. 12, } \mathbf{P} \cdot \hat{\mathbf{q}} = \frac{\mathbf{M} \cdot \hat{\mathbf{q}}}{\Omega} + (\hat{\mathbf{q}} \cdot \boldsymbol{\chi} \cdot \hat{\mathbf{q}})(\mathbf{E} \cdot \hat{\mathbf{q}})$$

where  $\Omega = NV$  is the volume of the supercell  $\mathbf{S}$  with  $V$  being the volume of the primitive unit cell.  $\boldsymbol{\chi}$  in Eq. 12 is the dielectric susceptibility. We then get

$$\text{Eq. 13, } \mathbf{E} \cdot \hat{\mathbf{q}} = -\frac{4\pi}{\Omega} \frac{(\mathbf{M} \cdot \hat{\mathbf{q}})}{1 + 4\pi(\hat{\mathbf{q}} \cdot \boldsymbol{\chi} \cdot \hat{\mathbf{q}})} = -\frac{4\pi}{\Omega} \frac{(\mathbf{M} \cdot \hat{\mathbf{q}})}{(\hat{\mathbf{q}} \cdot \boldsymbol{\epsilon}^{(\infty)} \cdot \hat{\mathbf{q}})}$$

where  $\boldsymbol{\epsilon}^{(\infty)}$  is the macroscopic dielectric constant which is related with the dielectric susceptibility by

$$\text{Eq. 14, } \hat{\mathbf{q}} \cdot \boldsymbol{\epsilon}^{(\infty)} \cdot \hat{\mathbf{q}} = 1 + 4\pi(\hat{\mathbf{q}} \cdot \boldsymbol{\chi} \cdot \hat{\mathbf{q}})$$

Inserting Eq. 13 into Eq. 10, we obtain the contribution to the potential energy due to the dipole-dipole interaction between the repeated supercell  $\mathbf{S}$ 's as

$$\text{Eq. 15, } E(DI) = \frac{1}{2} \frac{4\pi}{\Omega} \frac{(\mathbf{M} \cdot \hat{\mathbf{q}})(\mathbf{M} \cdot \hat{\mathbf{q}})}{(\hat{\mathbf{q}} \cdot \boldsymbol{\epsilon}^{(\infty)} \cdot \hat{\mathbf{q}})}$$

As a result, we get SIFC - the contribution to the IFC by the dipole-dipole interaction between the supercells by finding the second derivative of the above potential energy with respect to the atomic displacement as

$$\text{Eq. 16, } \phi_{\alpha\beta}^{jk}(DI) = \frac{\partial^2 E(DI)}{\partial u_{\alpha}^j \partial u_{\beta}^k} = \frac{4\pi e^2}{NV} \frac{(\mathbf{Z}^j \cdot \hat{\mathbf{q}})_{\alpha} (\mathbf{Z}^k \cdot \hat{\mathbf{q}})_{\beta}}{(\hat{\mathbf{q}} \cdot \boldsymbol{\epsilon}^{(\infty)} \cdot \hat{\mathbf{q}})}$$

where  $e$  is the charge of an electron and  $\mathbf{Z}$  is Born effective charge tensor of an atom defined as <sup>4</sup>

$$\text{Eq. 17, } eZ_{\alpha\beta}^j = \frac{\partial M_{\beta}}{\partial u_{\alpha}^j}$$

Finally, to calculate the phonon frequencies of an ionic crystal at an arbitrary  $\mathbf{q}$  point in the Brillouin zone, we just need to re-cast the accumulative IFC in Eq. 8 as

$$\text{Eq. 18, } \Phi_{\alpha\beta}^{jk}(P,0) = \phi_{\alpha\beta}^{jk}(P,0) + \phi_{\alpha\beta}^{jk}(DI)$$

where  $\phi_{\alpha\beta}^{jk}(P,0)$  is the accumulative IFC calculated by the first-principles supercell method.<sup>19</sup>

#### IV. DISCUSSIONS

Eq. 16 plays a central role in the mixed-space approach.<sup>14</sup> It is interesting to note that the SIFC represents a constant contribution to the IFC and its value is mathematically of the order of  $\sim O(1/N)$ , which was observed in a previous elongated supercell calculation.<sup>10</sup> From a mathematical point of view, SIFC can be understood as a contribution to the zeroeth order term in the Fourier transformation.

Combining Eq. 8 and Eq. 18, we will show in the next subsection how the effect of SIFC on phonon frequency is dictated by the types of  $\mathbf{q}$  points. At the exact  $\mathbf{q}$  points (except at  $\mathbf{q} \rightarrow 0$ ), vibration-induced dipoles for the supercell vanish, such that the effect of SIFC on phonon frequency is zero. Note that if a  $\mathbf{q}$  point is exact or not is decided by the shape and size of the predefined supercell, as determined by Eq. 2. At the non-exact  $\mathbf{q}$  points, the effect of SIFC on phonon frequency is non-zero as discussed below.

##### A. Analytic and nonanalytic terms

Analytic and nonanalytic terms are terminologies used to distinguish the contributions to the dynamical matrix.<sup>1</sup> We can substitute Eq. 18 into Eq. 5 and see that

$$\text{Eq. 19, } D_{\alpha\beta}^{jk}(\mathbf{q}) = D_{\alpha\beta}^{jk}(\mathbf{q}; an) + D_{\alpha\beta}^{jk}(\mathbf{q}; na)$$

where the analytic and nonanalytic contributions to the dynamic matrix are as follows

$$\text{Eq. 20, } D_{\alpha\beta}^{jk}(\mathbf{q}; an) = \frac{1}{\sqrt{\mu_j \mu_k}} \sum_P^N \phi_{\alpha\beta}^{jk}(P,0) \exp\{i\mathbf{q} \cdot [\mathbf{R}(P) - \mathbf{R}(0)]\}$$

$$\text{Eq. 21, } D_{\alpha\beta}^{jk}(\mathbf{q}; na) = \frac{1}{\sqrt{\mu_j \mu_k}} \frac{4\pi e^2}{V} \frac{(\mathbf{Z}^j \cdot \hat{\mathbf{q}})_\alpha (\mathbf{Z}^k \cdot \hat{\mathbf{q}})_\beta}{(\hat{\mathbf{q}} \cdot \boldsymbol{\varepsilon}^{(\infty)} \cdot \hat{\mathbf{q}})} f(\mathbf{q})$$

with

$$\text{Eq. 22, } f(\mathbf{q}) = \frac{1}{N} \sum_P^N \exp\{i\mathbf{q} \cdot [\mathbf{R}(P) - \mathbf{R}(0)]\}$$

It can be seen that  $f(\mathbf{q})$  in Eq. 22 is an improvement over the damping formulation with the adjustable parameter developed by Parliński et al.<sup>20</sup>

## B. The effect of SIFC on the Fourier interpolation

We would like to correct one important viewpoint represented in the literature,<sup>10</sup> which states that the phonon frequencies calculated by the supercell method are only inaccurate at the vicinity of  $\mathbf{q} \rightarrow 0$  if the nonanalytic term is not considered. When  $\mathbf{q}$  is not at the exact  $\mathbf{q}$  point, we know that the phonon frequency calculated by Eq. 9 is an interpolation.<sup>3, 19</sup> From a mathematical point of view, it is required that all values of the IFC's at the known referencing data points be correct. If one or more of the reference IFC values are incorrect, the resulting errors will prorogate into the interpolated point. That is to say, for the Fourier interpolation to be sufficiently accurate, we must consider the effect of the phonon-induced dipole-dipole interaction on the potential energy in Eq. 1. In this context, Eq. 21 is an accurate interpolation for an ionic crystal.

We now associate Eq. 22 with Eq. 8 and Eq. 2. The purpose of Eq. 8 is to interpolate the dynamical matrix for an arbitrary  $\mathbf{q}$  point, utilizing the IFC's from one single predefined supercell calculation. The physical significance of the exact  $\mathbf{q}$  point defined in Eq. 2 is that at all  $\mathbf{q}_s$ 's the effect of SIFC on the phonon frequency is zero (except at  $\mathbf{q} = 0$ ). However, for an

arbitrary non-exact  $\mathbf{q}$  point, the effect of SIFC on the phonon frequency is not zero anymore and has to be considered. Specifically,  $f(\mathbf{q})$  in Eq. 22 has the properties of:

i)  $f(0)=1$ . This implies that in the long wave limit of  $\mathbf{q} \rightarrow 0$ , we get the result by Cochran and Cowley.<sup>9</sup>

ii)  $f(\mathbf{q})=0$  if  $\mathbf{q}$  is a nonzero exact  $\mathbf{q}$  point. This implies that the nonanalytic contribution to the phonon frequency is zero at all the nonzero exact  $\mathbf{q}$  points. We reiterate here that definition of the exact  $\mathbf{q}$  point is dependent on the supercell shape and size defined by Eq. 2. Physically, this can be understood by the fact that at a nonzero exact  $\mathbf{q}$  point, the vibration induced dipole moment for the supercell vanishes.

iii)  $f(\mathbf{q}) \neq 0$  if  $\mathbf{q}$  is not the exact  $\mathbf{q}$  point. When  $\mathbf{q}$  is not the exact  $\mathbf{q}$  point, Eq. 18 is a rather accurate input for interpolating the phonon frequency through Eq. 9 together with Eq. 8.

### C. Understanding the published results for MgO

Figure 1 shows the previously-calculated phonon dispersions of MgO by Alfè<sup>19</sup> using the supercell method (without considering the effect of SIFC) and linear-response method (including the vibration induced dipole-dipole interaction), which we take as an independent support of our point of view on the role of the vibration-induced dipole-dipole interaction on phonon frequency. For the supercell method, Alfè<sup>19</sup> reported two supercell calculations, one using the  $4 \times 4 \times 4$  128-atom supercell and another using the  $8 \times 8 \times 8$  1024-atom supercell, and the results were compared with the linear-response calculations using the  $4 \times 4 \times 4$   $\mathbf{q}$  grid and  $8 \times 8 \times 8$   $\mathbf{q}$  grid, respectively. It can be seen that the crossing points between the calculated results with the supercell method and the linear-response method are located at the exact  $\mathbf{q}$  points. Being away from the exact  $\mathbf{q}$  points, it is clearly seen that the errors of the calculated results by the supercell method are not limited to

the vicinity of  $\mathbf{q} \rightarrow 0$ , as shown by the oscillating-like line pattern for the high frequency longitudinal optical branch.

## V. COMPUTATIONAL DETAILS, RESULTS AND DISCUSSIONS

We have chosen MgO as the prototype in the present work. The computational procedure is:

- i) Calculate the Hessian matrix<sup>1, 15</sup> based on the supercell method using the projector-augmented wave (PAW) method<sup>22-23</sup> implemented in the Vienna *ab initio* simulation package (VASP, version 5.2). The exchange-correlation functional according to Ceperley and Alder as parameterized by Perdew and Zunger<sup>24</sup> was employed.
- ii) Calculate the Born effective charge tensor and the high frequency static dielectric tensor based on the primitive unit cell employing the linear-response theory implemented in VASP 5.2 by Gajdos et al.<sup>25</sup>
- iii) Modify the Hessian matrix outputted from VASP 5.2 by adding the term defined in Eq. 16 in order to account for the effect of SIFC.
- iv) Construct the dynamical matrix using Eq. 8 based on the modified Hessian matrix.
- v) Solve Eq. 9 for the phonon frequency for any chosen  $\mathbf{q}$  point in the Brillouin zone.

Two supercell calculations were performed in the present work. The first is with a predefined 16-atom  $2 \times 2 \times 2$  supercell of the primitive unit cell. Figure 2 shows that once the

effect of SIFC on phonons is properly considered using Eq. 16, the 16-atom supercell is enough for predicting the phonon dispersions of MgO. The minor differences between the phonon dispersions calculated with and without SIFC effects for the non-longitudinal optical phonons are caused by the small supercell size. Such differences are barely visible for the previously-published calculation<sup>14</sup> using the  $4\times4\times4$  supercell of the primitive unit cell and the one using 128-atom supercell showed below.

The second calculation uses a 128-atom  $1\times1\times16$  elongated supercell of the cubic unit cell. With this supercell, one can get 16 nonzero  $\mathbf{q}$  points along the  $(0,0,q)$  direction. In the past, elongated supercells<sup>10, 26-27</sup> were alternative ways to calculate the phonon dispersions for ionic crystals if one only needs accurate predictions for phonon frequencies at a few specific  $\mathbf{q}$  points. As shown in Figure 3, if the effect of SIFC on phonons is not properly considered, the supercell method can only predict the corrected phonon frequencies for the longitudinal optical phonons at the nonzero exact  $\mathbf{q}$  points. Being away from exact  $\mathbf{q}$  points, the longitudinal optical phonon dispersions with and without the effect of SIFC considered are different from each other.

Figure 2 and Figure 3 also show the  $(0,0,q)$  phonon dispersions for the case without SIFC (the dashed line) for the longitudinal optical phonon dispersion. The comparison between the results derived from the  $1\times1\times16$  elongated supercell and the  $2\times2\times2$  supercell demonstrates that our mixed-space approach properly takes into account the dipole-dipole interactions between the supercells.

## VI. Conclusion

In summary, our previously proposed mixed-space approach accounting for the effect of the vibration-induced dipole-dipole interaction on phonon frequencies is derived from the fundamental concept of electric dipole-dipole interactions among the supercells. We demonstrate that the contribution of the dipole-dipole interactions between the supercells to the interatomic force constant can be accounted for by adding a constant term into the real-space force constant. We use MgO as an example to compare the calculated phonon frequencies with and without the contribution with the former showing excellent agreement with experimental data.

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Figure captions.

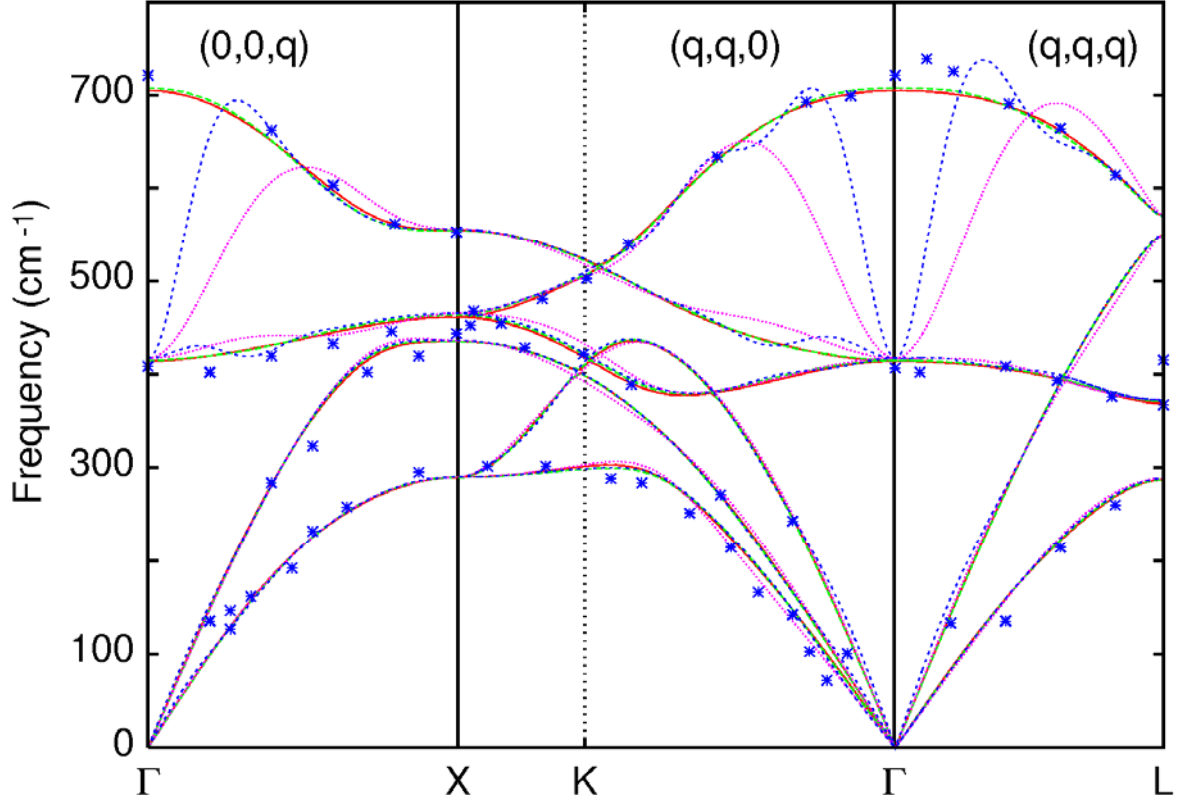


Figure 1. Phonon dispersions of MgO calculated with the supercell method and with linear response (Courtesy from Comput. Phys. Commun. and Alfè). Pink dotted and green dashed lines correspond to calculations with a  $4 \times 4 \times 4$  supercell (128 atoms) and a  $4 \times 4 \times 4$  equispaced grid of  $\mathbf{q}$ -points (linear response). Blue dashed and red solid lines correspond to calculations with an  $8 \times 8 \times 8$  supercell (1024 atoms) and an  $8 \times 8 \times 8$  grid of  $\mathbf{q}$ -points with the two methods, respectively. Experimental data are displayed with blue stars. For interpretation of the references and other legends in the figure, the reader is referred to Fig. 3 in the paper by Alfè.<sup>19</sup>

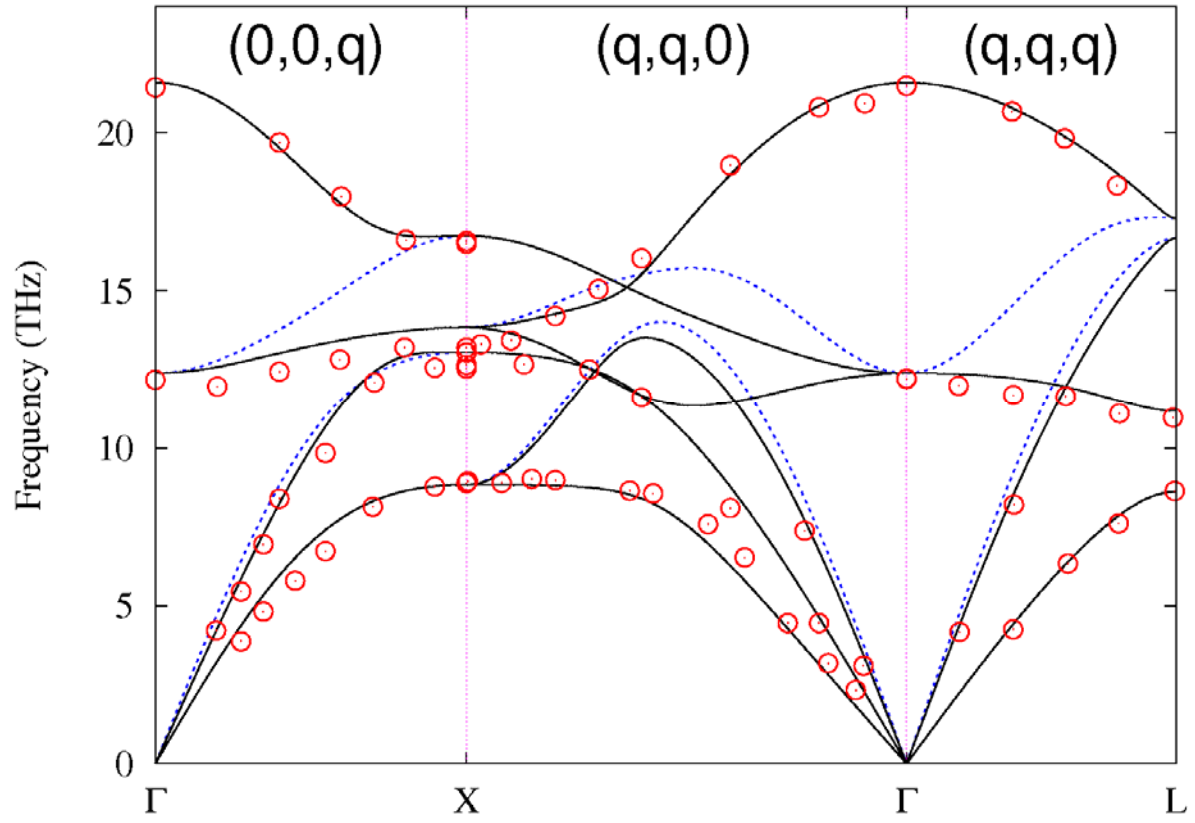


Figure 2. Phonon dispersions of MgO calculated with a 16-atom  $2 \times 2 \times 2$  supercell of the primitive unit cell. The solid (dashed) lines represent the present calculation with (without) considering the term represented by Eq. 16 which is the contribution to the IFC by the dipole-dipole interaction between the supercells. The open circles (red) are the inelastic neutron scattering data by Sangster et al.<sup>28</sup>

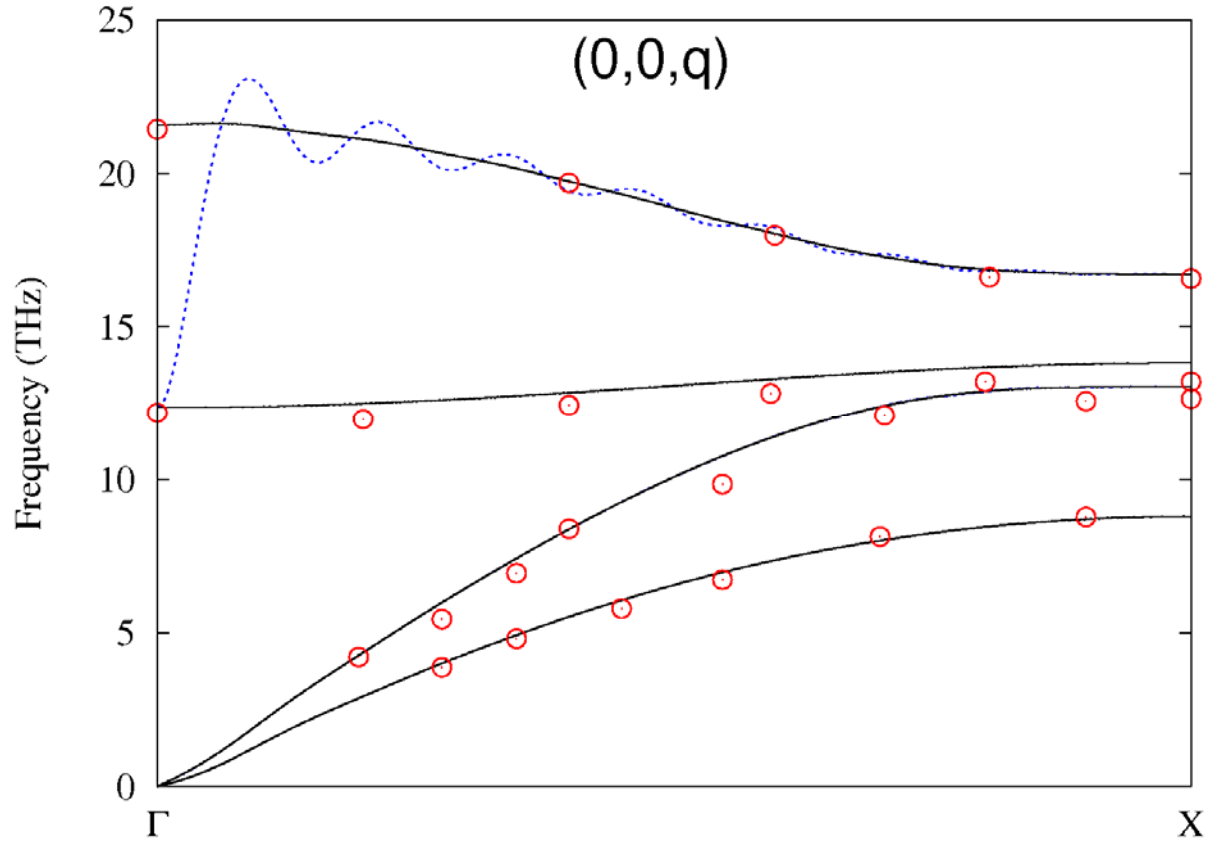


Figure 3. (0,0,q) Phonon dispersions of MgO calculated with a 128-atom  $1 \times 1 \times 16$  elongated supercell of the 8-atom cubic unit cell. The solid (dashed) lines represent the present calculation with (without) considering the term represented by Eq. 16 which is the contribution to the IFC by the dipole-dipole interaction between the supercells. The open circles (red) are the inelastic neutron scattering data by Sangster et al.<sup>28</sup>