THE ADIABATIC BOND CHARGE MODEL OF PHONONS

by

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Abstract

The dispersion relation between frequency and wavevector of atomic vibrations, or phonons, can be succinctly described by the adiabatic bond charge model, first developed by Weber. The model employs as few as four parameters to fit experiment. We investigated this model in order to better unify the description of the technologically relevant group IV elemental semiconductors (e.g. diamond, silicon, germanium, and gray tin) by replacing an ad hoc parameter introduced by Weber with one arising from quadrupolar interactions between the bond charges, and by fitting the parameters to density functional theory calculations. We also illustrate constant frequency surfaces embedded in wave vector space for the various modes of vibration for the first time. The bond charge model allows for rapid calculation of various quantities related to the interaction of phonons with electrons and photons as compared to density functional theory, especially in structures with little symmetry and for macroscopic structures, thus enabling the design of complicated electronic and photonic devices much more accurately.
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II. INTRODUCTION

This paper develops the adiabatic bond charge model of phonons in crystals, first proposed by Weber [1], by combining the formalisms of Maradudin [2], Lax [3], and Dresselhaus [4], among others [5, 6]. Maradudin’s text serves as the bedrock of much of phonon physics. Lax’s work functions as a one-stop shop for applying representation theory to the physics of phonons in crystals. Dresselhaus’ book explains the application of group representation theory to physics in many contexts, and serves to make any reader intimately familiar with such methods.

Weber’s adiabatic bond charge model accurately captures phonon dispersion throughout the Brillouin zone with a relatively small number of parameters fit to experimental data and principally involves nearest neighbor forces. The existence of bond charges is supported by X-ray diffraction experiments [7] and ab initio calculations, as shown in Figure 1. Weber’s theory is just one manifestation of the bond charge model, which has gone through various refinements even before there was experimental evidence for the existence of localized bond charges in crystals. Born’s [8] text was one of the most significant early investigations of phonons through rigid-ion models. Keating [9] introduced forces that resisted the bending of bond pairs about atoms. Phillips [10] first proposed the existence of localized bond charges based on theoretical considerations. Martin [11] was the first to construct a model that incorporated Phillips’ hypothetical bond charges, assuming that the bond charges always remained at their equilibrium position. Weber refined Martin’s model by allowing the bond charges to move, but with negligible inertia. Weber’s model has since been adapted to various material systems such as the III–V’s [12, 13], II–VI’s, III–nitrides [14], the various forms of carbon crystals such as nanotubes and graphene [15], as well as alloys thereof [16].

This paper synthesizes the work done on the bond charge model mentioned above and explores some of the fundamentals of phonons in crystals that have been passed over by previous authors. The paper is structured as follows: first, the forms of nearest neighbor force constants are determined in the full three dimensional problem; which are combined with long-range Coulombic interactions derived by Ewald’s method [17]; to form the full dynamical matrix which can be analyzed using group representation theory to fit the model to experiment; so the dispersion relation can be calculated throughout the entire Brillouin zone.
III. LATTICE DYNAMICAL EQUATIONS OF MOTION

This section explains the lattice dynamical equations of motion and their symmetries. These symmetries hold no matter the explicit functional form of the potentials between the atoms and bond charges, which will be discussed in later sections.

A. First Quantization

Consider the kinetic and harmonic potential energies

\[ T = \frac{1}{2} \sum_{\alpha i} M_\alpha (\dot{u}^{\alpha i})^2, \]  
\[ V = \frac{1}{2} \sum_{\alpha i, \beta j} u^{\alpha i} \cdot K^{\alpha i, \beta j} \cdot u^{\beta j}, \]

which lead to \(3sN\) equations of motion

\[ M_\alpha \ddot{u}^{\alpha i} + \sum_{\beta j} K^{\alpha i, \beta j} \cdot u^{\beta j} = 0, \]

where \(N\) is the number of cells, \(s\) is the number of particles in a cell, \(\alpha \in \{1, 2, \ldots, s\}\) labels the type of particle in cell \(i\), and \(\beta, j\) are alternative indices for \(\alpha, i\) respectively.

The normal motions of the system are those in which all particles have a common exponential time dependence \(e^{-i\omega t}\). The symmetry of the problem with respect to lattice translations,

\[ K^{\alpha i, \beta j} = K^{\alpha \beta}(j - i) \]
permits solutions of the planewave form

\[ u^{\alpha i} = b^\alpha(q) \exp(iq \cdot X^{\alpha i}) \exp(-i\omega t), \]  

(3.5)

where

\[ X^{\alpha i} = X^\alpha + X^i, \quad X^i \equiv i_1 a_1 + i_2 a_2 + i_3 a_3, \]  

(3.6)

is the position, relative to the origin, of the particle of type \( \alpha \) in cell \( i \), \( a_j \) are lattice translation vectors, \( X^i \) is the location of cell \( i \), \( X^\alpha \) is the coordinate of atom \( \alpha \) within cell \( i \), \( q \) is a wavevector, and \( b^\alpha(q) \) is a vector that depends upon \( q \).

With solutions of the planewave form, the \( 3sN \) equations of motion reduce to a mere \( 3s \) equations

\[ \sum_\beta R^{\alpha \beta}(q) \cdot b^\beta(q) = M_\alpha \omega^2(q) b^\alpha(q) \]  

(3.7)

for the dependence on \( \alpha \) and the suppressed cartesian indices of \( b^\alpha \). Here \( R \) is called the \textit{dynamical matrix}. That the correct dependence of \( u^{\alpha i} \) on \( i \) has been obtained follows from the fact that

\[ R^{\alpha \beta}(q) = \sum_j K^{\alpha \beta}(j - i) \exp[iq \cdot (X^{\beta j} - X^{\alpha i})] \]  

(3.8)

is independent of \( i \) in view of the translational invariance of \( K \) and the cyclic boundary conditions. The Hermiticity of \( K \) implies the Hermiticity of \( R \),

\[ R^{\alpha \beta}(q)^* = \tilde{R}^{\beta \alpha}(q). \]  

(3.9)

Here the transposition denoted by a tilde (\( \sim \)) is performed on the suppressed cartesian indices.

The planewave equations of motion have a set of solutions \( b^\alpha_t(q) \) for \( t \in \{1, 2, \ldots, 3s\} \) with frequency \( \omega_t(q) \) where \( t \) labels the irreducible representation of the solution. The usual orthogonality of eigenvectors of a hermitian matrix is modified slightly by the presence of \( M_\alpha \) on the right–side of the equations of motion resulting in the condition

\[ \sum_\alpha M_\alpha b^\alpha_t(q)^* \cdot b^\alpha_{t'}(q) = M \delta(t, t'), \]  

(3.10)

where \( M \) can be taken to be unity or the total mass of a unit cell.

The kinetic and potential energies are diagonalized by the transformation to normal coordinates

\[ u^{\alpha i} = N^{-1/2} \sum_{t,q} Q(t)(q)b^\alpha_t(q) \exp(iq \cdot X^{\alpha i}), \]  

(3.11)
where the $Q_t(q)$ are numbers which serve to create appropriate combinations of symmetry vectors $b^\alpha_t(q)$.

As an example of symmetry vectors, consider the vibrational modes of CO$_2$. The mirror symmetry through the C atom when the molecule is in equilibrium allows its vibrations to be decomposed into a mode that is symmetric with respect to mirroring through the C atom, and a mode that is antisymmetric (along with a bending mode). The displacement vectors for these modes of distinct symmetries are the so called symmetry vectors.

FIG. 2. Two of the three vibrational symmetry modes of CO$_2$.

In order to develop further theory without specifying particular symmetries, it is convenient to introduce planewave coordinates,

$$b^\alpha(q) = N^{-1/2} \sum_i u^{\alpha i} \exp(-i q \cdot X^{\alpha i})$$

as an intermediate step that takes account of the translational symmetry of the lattice. The remaining decomposition

$$b^\alpha(q) = \sum_t Q_t(q)b^\alpha_t(q)$$

can be performed using the behavior of the planewave coordinates under the rotational transformations ($S|v(S)$) of the space group of the crystal. Here $S$ is a point operation of the group and $v(S)$ is a translation composed with $S$, which depends upon $S$. As an example, consider a helix, which is symmetric with respect to a rotation combined with a translation.

The following symmetry considerations will require use of the following theorem, which clarifies the effect that such combined operations (rotations composed with translations) have on the planewave coordinates.
Theorem 1.

\[ O(S)b^\alpha(q) = Sb^{S^{-1}(\alpha)}(S^{-1}q), \quad (3.14) \]

where \( O(S) \equiv \exp[iq \cdot v(S)][S|v(S)] \), and \( S^{-1}(\alpha) \) is the name of the point that will be carried into \( \alpha \) by \((S|v(S))\). The \( S \) on the right hand side stands for the usual representation in 3–space of the rotation \( S \).

**Proof.** The point \( S^{-1}(\alpha) \) is carried into \((\alpha)\) by \( S \); hence the new displacement at \( \alpha \) is

\[ (u^{\alpha})' = Su^{S^{-1}(\alpha)}. \quad (3.15) \]

The planewave coordinate expansion implies that

\[ b^\alpha(q)' = N^{-1/2} \sum_i \exp(-iq \cdot X^{\alpha}) Su^{S^{-1}(\alpha)}. \quad (3.16) \]

We would like to be able to rewrite the sum in terms of the transformed index \( S^{-1}(i) \). Recall that the action of \( S^{-1} \) on \( X^{\alpha} \) induces the inverse action \( S \) on \( q \). Therefore, if \( S^{-1} \) is applied to \( X^{\alpha} \), then the inverse action \( S \) induced on \( q \) can be cancelled out by additionally performing \( S^{-1} \) on \( q \). Thus the expression \( S^{-1}q \cdot S^{-1}X^{\alpha} \) is equivalent to \( q \cdot X^{\alpha} \). This allows us to write the new planewave coordinate as

\[ b^\alpha(q)' = N^{-1/2} \sum_i \exp(-iS^{-1}q \cdot S^{-1}X^{\alpha}) Su^{S^{-1}(\alpha)}. \quad (3.17) \]

Note that the composite point operation / translation operation acts on \( X^{\alpha} \) according to

\[ X^{S^{-1}(\alpha)} \equiv (S|v(S))^{-1} X^{\alpha} = S^{-1}X^{\alpha} - S^{-1}v(S), \quad (3.18) \]

so we can express \( S^{-1}X^{\alpha} \) as

\[ S^{-1}X^{\alpha} = X^{S^{-1}(\alpha)} + S^{-1}v(S), \quad (3.19) \]

to rewrite the new planewave coordinate as

\[ b^\alpha(q)' = \frac{1}{\sqrt{N}} \sum_i \exp[-iS^{-1}q \cdot S^{-1}v(S)] \exp[-iS^{-1}q \cdot X^{S^{-1}(\alpha)}] Su^{S^{-1}(\alpha)}. \quad (3.20) \]

In the first exponential term we again see that the induced inverse action on \( q \) by performing \( S^{-1} \) on \( v(S) \) is canceled by performing \( S^{-1} \) on \( q \) as well, so

\[ \exp[-iS^{-1}q \cdot S^{-1}v(S)] = \exp[-iq \cdot v(S)]. \quad (3.21) \]
The new planewave coordinate now becomes

\[ b^\alpha(q)' = \frac{1}{\sqrt{N}} \exp[-i q \cdot v(S)] \sum_i \exp[-i S^{-1} q \cdot X^{s^{-1}(S)}] S u^{s^{-1}(S)}, \tag{3.22} \]

which is finally in a form where the summation index can be easily rewritten according to \( i \to S^{-1}(i) \) with the result that

\[ b^\alpha(q)' \equiv (S|v(S))b^\alpha(q) = \exp[-i q \cdot v(S)] S b^{s^{-1}(S)}(S^{-1}q), \tag{3.23} \]

as asserted by the theorem.

This theorem is often used in regard to the interior of the Brillouin zone with \( S^{-1}q = q \). The significance of the theorem is that the operators \( O(S) \) behave as if no translations were involved, that is, as if \( v(S) = 0 \), or \( q = 0 \). In other words, provided that symmetry operations are performed on the \( b^\alpha(q) \), these operations \( O(S) \) act as if \( q = 0 \), treating \( S \) as a point operation. The results are then valid for \( q \neq 0 \) as long as \( S^{-1}q = q \).

When \( q \) is at the zone boundary, there are additional operations such that

\[ S^{-1}q = q - K_S, \tag{3.24} \]

where \( K_S \) is a reciprocal lattice translation, which provide additional symmetry information if \( b^\alpha(q - K) \) can be related to \( b^\alpha(q) \). This relation is provided by the plane wave coordinate transformation and is

\[ b^\alpha(q - K) = \exp(iK \cdot X^\alpha)b^\alpha(q). \tag{3.25} \]

Figure 3 shows how the case of a wavevector within the zone differs from the case of one on the zone edge for a two dimensional crystal with the point group symmetry of the square. On the zone edge (d–f), wavevectors that are connected by a reciprocal lattice translation vector are considered equivalent. This is not the case for wavevectors away from the zone edge as in (a–c).

B. Consequences of Time Reversal

Translational invariance has reduced the problem involving a real matrix \( K \) of \( 3sN \) dimensions in configuration space to a complex \( 3s \times 3s \) matrix \( R(q) \) (equivalent to a real \( 6s \times 6s \) matrix) in reciprocal space. Since the diagonalization of a matrix requires a number
FIG. 3. Cases when the wavevector is within the Brillouin zone and has (a) only the trivial symmetry of the crystal, (b,c) the symmetry of a subgroup of the crystal, as compared to when the wavevector is on the zone edge (d–f) where some wavevectors are equivalent modulo a reciprocal lattice translation vector, shown as a dashed arrow in (d). The crystal is assumed to have the point group symmetry of the square.

of operations proportional to the cube of its dimension, a factor of $2^3$ in computing time will be saved if the matrix $R(q)$ (and the corresponding eigenvectors) can be transformed to real form. This reduction to real form can be accomplished by using the time–reversal invariance of the problem. In the domain of real displacements $u^m(t)$ obeying

$$\sum K^{\alpha\beta} u^\beta(t) = -M_\alpha \frac{\partial^2 u^\alpha}{\partial t^2},$$  \hspace{1cm} (3.26)

the fact that the time–reversed motion is also a solution is guaranteed because only even time derivatives occur. Even for a complex solution $u^\alpha(t) = u^\alpha \exp(-i\omega t)$, the resulting equations

$$\sum K^{\alpha\beta} u^\beta = M_\alpha \omega^2 u^\alpha,$$ \hspace{1cm} (3.27)

for the amplitudes have only real coefficients. Thus if $u^\alpha$ is a solution of the above equation, so is $(u^\alpha)^*$. Hence $(u^\alpha) \exp(-i\omega t)$ and $(u^\alpha)^* \exp(-i\omega t)$ are both solutions of Eq. (3.26) with the same sign of the frequency. Thus the time–reversed solution in the complex case can be defined as

$$[u^\alpha(t)]^T = [u^\alpha(-t)]^*,$$ \hspace{1cm} (3.28)

or

$$[u^\alpha]^T = (u^\alpha)^*.$$ \hspace{1cm} (3.29)
It follows from this equation and the linearity of Eq.(3.27) that, if \( u^\alpha \) is a solution of Eq.(3.27), then so is \( u^\alpha + (u^\alpha)^* \). In other words, the reality of \( K^{\alpha\beta} \) guarantees the possibility of real eigenvectors.

If there is an element \( Q \) that reverses \( q \), it can be combined with \( K_0 = \text{complex conjugation} \) to produce an element \( QK_0 \) that leaves \( q \) invariant. In group–theoretical language, the group of the wave vector \( G_q \) must be augmented by \( QK_0 \) to form the reversal group of the wave vector:

\[
G_{q,q} = G_q + QK_0 G_q
\]  

(3.30)

just as in the case of the group of the bond and the reversal group of the bond, which will be discussed in Section [IV.C]

The procedure by which \( R(q) \) can be made real will now be discussed. Consider the transformation property of \( R(q) \)

\[
R^{\alpha\beta} = \tilde{Q} R^{Q(\alpha),Q(\beta)}(Qq)Q.
\]  

(3.31)

For the special case in which \( Qq = -q \),

\[
R^{\alpha\beta} = \tilde{Q} R^{Q(\alpha),Q(\beta)}(q)Q.
\]  

(3.32)

or

\[
R^* = \Omega^{-1} R \Omega,
\]  

(3.33)

where

\[
\Omega^{\beta\gamma}_{\nu\nu} = \delta[\beta, Q(\beta)] Q_{\nu\nu},
\]  

(3.34)

and \( Q_{\nu\nu} \) is the real \( 3 \times 3 \) matrix representing the rotation \( Q \).

To make \( R \) real, let \( R = UR'U^{-1} \). Then \( R' \) will be real if \( U\tilde{U} = \Omega \), as is possible if \( \Omega \) is symmetric. Then let \( U = \Omega^{1/2} \) be the symmetric square root of \( \Omega \). Since \( \Omega \) is real and unitary, \( \tilde{\Omega} = \Omega^{-1} \) and the condition of symmetry \( \Omega^2 = 1 \) is then equivalent to the requirement that \( \Omega^2 = 1 \). But Eq.(3.31) implies that \( \Omega^2 = 1 \) if \( Q^2 = 1 \). Thus the dynamical matrix \( R^{\alpha\beta}(q) \) can be made real if there exists a reversal operator \( (Q|v(Q)) \) such that \( Q^2 = \text{the identity} \).

The taking of square roots of matrices can be avoided by imposing the condition

\[
\Omega b^*(q) = b(q),
\]  

(3.35)
where all indices have been suppressed. This is the case because if \( b \) is an eigenvector of \( R(q) \), Eq. (3.31) implies that \( \Omega b^* \) is also an eigenvector. Then \( b + \Omega b \) is also an eigenvector that obeys Eq. (3.35).

As an alternative viewpoint, note that constraint (3.35) is equivalent to requiring that the eigenvectors of the real matrix \( R' = \Omega^{-1/2} R \Omega^{1/2} \), namely, \( \Omega^{-1/2} b \), be real. Using \( Q^{-1} = Q \), requirement (3.35) can be rearranged in the form

\[
b^{\beta}(q)^* = Q \cdot b^{\beta(q)}(q),
\]

(3.36)

where \( Q \) is a \( 3 \times 3 \) matrix, and not the operator \( (Q|v(Q)) \).

Since the only reversal element possible for a general \( q \) is \( Q = I = \) the inversion, this case deserves attention. Equation (3.31) becomes

\[
R^{\alpha\beta}(q)^* = R^{\bar{\alpha}\bar{\beta}}(q),
\]

(3.37)

where \( \bar{\alpha} \) is an abbreviation for \( I(\alpha) \), the particle inverse to \( \alpha \). If each particle is at a center of symmetry, as in sodium chloride, \( R \) is already real. Constraint (3.36) would make all \( b^{\beta} \) purely imaginary. To remedy this for the inversion case, it is appropriate to remove a single phase factor and replace (3.36) by

\[
b^{\beta}(q)^* = b^{\bar{\beta}}(q).
\]

(3.38)

C. Making \( R(q) \) Real in Diamond–Structured Crystals

In the adiabatic approximation, only the atomic degrees of freedom enter into the dynamical matrix. In the elemental diamond structure, \( \alpha = 1, \bar{\alpha} = 2 \) are a pair of inverse atoms. Condition (3.37) together with the hermiticity of \( R \) guarantees that the matrix \( R \) has the form

\[
R \equiv \begin{bmatrix} R^{11} & R^{12} \\ R^{21} & R^{22} \end{bmatrix} = \begin{bmatrix} H & S \\ S^* & H^* \end{bmatrix},
\]

(3.39)

where \( H \) is hermitian and \( S \) is symmetric. The constraint (3.38) then takes the form

\[
(b^1)^* = b^2.
\]

(3.40)
Thus $b^2$ can be eliminated entirely by using $\text{Re} b^1$ and $\text{Im} b^1$ as independent variables. In particular, the unitary transformation $b' = V b$

$$
\begin{bmatrix}
\sqrt{2} \text{Re} b^1 \\
\sqrt{2} \text{Im} b^1
\end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -i & i \end{bmatrix} \begin{bmatrix} b^1 \\ b^2 \end{bmatrix}
$$

leads to the new dynamical matrix

$$
R' = V R V^{-1} = \begin{bmatrix}
\text{Re} (H + S) & \text{Im} (S - H) \\
\text{Im} (S + H) & \text{Re} (H - S)
\end{bmatrix},
$$

which is both real and symmetric.

**D. Calculating $R(q)$ in Diamond–Structured Crystals**

Once the force constant matrices have been determined, the elements of the dynamical matrix may be evaluated by performing the sum over lattice translation vectors $l$ in Eq.(3.8), rewritten here as

$$
R^{\alpha\beta}(q) = \sum_l K^{\alpha\beta}(l) \exp \left[ i q \cdot (X^{\beta l} - X^{\alpha 0}) \right].
$$

In Diamond, for the two atom types, $\alpha = 1, \beta = 2$, the element between them $R^{12}(q)$ involves the four nearest neighboring atoms at $(a/4)(111)$, $(a/4)(1\overline{1}1)$, $(a/4)(\overline{1}1\overline{1})$, and $(a/4)(\overline{1}\overline{1}1)$, since these points in the primitive cell can be brought into each other via lattice translation vectors.

For the origin atom $\alpha = 1$, and any of the bond charges, say $\beta = 3$, the element between them $R^{13}(q)$ involves only that single bond charge, since none of the bond charges in the primitive cell can be brought into each other via lattice translation vectors. In other words, there is only one force constant matrix in the sum.

However, the element between any two bond charges involves two force constant matrices in the sum because for every bond charge pair within the unit cell, there exists a pair that is formed by inversion through either bond charge.

In order to perform the adiabatic approximation, it is convenient to write the dynamical matrix in block form to show elements between two atoms, an atom and a bond charge, and between two bond charges as

$$
R = \begin{bmatrix}
R_{aa} & R_{ab} \\
R_{ba} & R_{bb}
\end{bmatrix}.
$$
Approximating the mass of the bond charges to be zero, the equations of motion are

\[ M_a \omega^2 \begin{bmatrix} b_a \\ 0 \end{bmatrix} = \begin{bmatrix} R_{aa} & R_{ab} \\ R_{ab}^+ & R_{bb} \end{bmatrix} \begin{bmatrix} b_a \\ b_b \end{bmatrix}, \]  

(3.45)

so the bond charge displacements may be written in terms of the atom displacements as

\[ b_b = -R^{-1}_{bb} R_{ab}^+ b_a \]

and the equations of motion become

\[ M_a \omega^2 b_a = (R_{aa} - R_{ab} R^{-1}_{bb} R_{ab}^+) b_a. \]  

(3.46)

The adiabatic approximation thus produces a new dynamical matrix

\[ D = R_{aa} - R_{ab} R^{-1}_{bb} R_{ab}^+ \]  

(3.47)

in the atom displacement basis \( b^1, b^2 \). As discussed in the previous section, the dynamical matrix can be made real by taking advantage of time–reversal symmetry and inversion symmetry between the two atoms. The real dynamical matrix is thus

\[ D' = V D V^{-1}, \]  

(3.48)

where

\[ V = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -i & i \end{bmatrix}. \]  

(3.49)

We have now exhausted all of the general symmetries of the equations of motion that exist for all possible potentials between the electrons and nuclei of a crystal. The next two sections will investigate the symmetries of the specific potentials used in the adiabatic bond charge model.
IV. QUANTUM MECHANICAL POTENTIALS

This section investigates the properties of the short range, spring–like forces which summarize quantum mechanical effects arising from orthogonality of the wavefunctions that describe the set of all electrons and nuclei in the crystal.

With the potential energy of the crystal of the form

\[ V = \frac{1}{2} \sum_{\alpha,i} \sum_{\beta,j} \mathbf{u}_{\alpha i} \cdot K_{\alpha i,\beta j} \mathbf{u}_{\beta j} \] (4.1)

invariance under lattice translations requires that

\[ K_{\alpha i,\beta j} = K_{\alpha,i+t,\beta,j+t} = K_{\alpha\beta} (j - i), \]

(4.2)

that is, any bond is identical to any other obtainable by a lattice translation. Thus a bond \( K^{ab} \) can be labeled by the stating atom \( \alpha \) and the bond vector

\[ b = X^{\beta j} - X^{\alpha i}. \]

(4.3)

In the space of the \( K^{ab} \) two space group operations, \( (S|v) \) and \( (S|v + t) \), that differ by a lattice translation are indistinguishable. In other words, \( K^{ab} \) generates a representation (appropriate to \( q = 0 \)) of the factor group \( G\setminus T \). Furthermore, only bond vectors \( b \) of a given length \( |b| \) are mixed by the group elements, so that one can calculate independently the number of first–neighbor constants, second–neighbor constants, and so on.

The simplest procedure for determining the form and number of independent force constants is to use the group of elements that leave the bond invariant plus the elements that reverse the bond. An operation that transforms a bond to a translationally equivalent position is regarded as an element of the group of the bond. A similar extension applies to reversal elements.

In the harmonic approximation, the potential energy is symmetric with respect to an interchange of all indices, which implies that \( K \) also has this symmetry:

\[ K_{\mu\nu}^{\alpha\beta} = K_{\nu\mu}^{\beta\alpha}, \]

(4.4)

or

\[ K^{\alpha\beta} = \bar{K}^{\beta\alpha}, \]

(4.5)
where $\tilde{K}$ indicates the transpose of $K$ with respect to its suppressed Cartesian indices.

If the displacements $u^{\alpha i}$ are altered by the amount $\Delta u^{\alpha i}$, the change in potential energy is

$$\Delta V = \frac{1}{2} \sum_{\alpha, i} \sum_{\beta, j} \left( u^{\alpha i} \cdot K^{\alpha i, \beta j} \cdot \Delta u^{\beta j} + \Delta u^{\alpha i} \cdot K^{\alpha i, \beta j} \cdot u^{\beta j} + \Delta u^{\alpha i} \cdot K^{\alpha i, \beta j} \cdot \Delta u^{\beta j} \right). \quad (4.6)$$

By reversing the order of the factors and then interchanging the names of the dummy indices, the middle term can be made to take two new forms:

$$\sum_{\alpha, i} \sum_{\beta, j} u^{\beta j} \cdot \tilde{K}^{\alpha i, \beta j} \cdot \Delta u^{\alpha i} = \sum_{\alpha, i} \sum_{\beta, j} u^{\alpha i} \cdot \tilde{K}^{\beta j, \alpha i} \cdot \Delta u^{\beta j}. \quad (4.7)$$

The symmetry of $K$ with respect to interchanging all indices then shows that the second term is identical to the first; thus

$$\Delta V = \sum_{\alpha, i} \sum_{\beta, j} \left( u^{\alpha i} \cdot K^{\alpha i, \beta j} \cdot \Delta u^{\beta j} + \frac{1}{2} \Delta u^{\alpha i} \cdot K^{\alpha i, \beta j} \cdot \Delta u^{\beta j} \right). \quad (4.8)$$

If the changes $\Delta u^{\alpha i}$ are such as to leave the potential energy invariant for arbitrary initial configurations, the coefficient of each $u^{\alpha i}$ and the term independent of all $u$ in $\Delta V$ must vanish:

$$\sum_{\beta j} K^{\alpha i, \beta j} \cdot \Delta u^{\beta j} = 0, \quad (4.9)$$

$$\sum_{\beta j} K^{\alpha i, \beta j} = 0, \quad (4.10)$$

since $\Delta u^{\beta j}$ is arbitrary. This constraint will be referred to as the condition of infinitesimal translational invariance.

Now consider a member $(S|v)$ of the crystal group that restores the crystal to itself:

$$(X^{\alpha i})' = X^{\alpha' i'} = S \cdot X^{\alpha i} + v. \quad (4.11)$$

The total vector $X^{\alpha i} + u^{\alpha i}$ is transformed into

$$(X^{\alpha i} + u^{\alpha i})' = S \cdot (X^{\alpha i} + u^{\alpha i}) + v. \quad (4.12)$$

Consider the difference

$$(X^{\alpha i} + u^{\alpha i})' - X^{\alpha' i'} \equiv (u^{\alpha i})' = S \cdot u^{\alpha i}, \quad (4.13)$$
which is a small displacement from the position \( X^{\alpha',i'} \) of the renamed particle,

\[
(\alpha',i') = S(\alpha,i).
\]  

(4.14)

In this case, the potential energy can be computed by giving each particle \((\alpha',i')\) the displacement \( S \cdot u^{\alpha i} \):

\[
V' = \frac{1}{2} \sum (S \cdot u^{\alpha i}) \cdot K^{\alpha',\beta j'} \cdot (S \cdot u^{\beta j}).
\]  

(4.15)

Since, aside from renaming the particles, the crystal has been merely rotated, it is the case that \( V' = V \). This is equivalent to introducing a new force constant matrix

\[
V' = \frac{1}{2} \sum u^{\alpha i} \cdot K^{\alpha i,\beta j} \cdot u^{\beta j},
\]  

(4.16)

where

\[
K^{\alpha i,\beta j} = S^{-1} \cdot K^{\alpha',\beta j'} \cdot S.
\]  

(4.17)

The invariance of the potential energy under the group operations, \( V' = V \) or \( K' = K \), leads to a series of conditions that limit the number of independent constants among the \( K \)s. In this way, all the force constants between the set of equivalent bonds can be expressed in terms of those of a prototype bond.

**A. The Number of Force Constants**

Representation theory can be used to determine the number of independent parameters needed to characterize each bond.

The force constant matrices transform according to

\[
SK_{\mu \nu}^{\alpha i,\beta j} = \sum K_{\mu' \nu'}^{S(\alpha i),S(\beta j)} S_{\mu' \mu} S_{\nu' \nu}.
\]  

(4.18)

Interchanging all of the indices leads to

\[
SK_{\nu \mu}^{\beta j,\alpha i} = \sum K_{\mu' \nu'}^{S(\beta j),S(\alpha i)} S_{\mu' \nu} S_{\nu' \mu},
\]  

(4.19)

but in view of the symmetry of \( K \) in the harmonic approximation, the left hand sides are identical. The symmetric and antisymmetric parts of \( K \) generate separate representations:

\[
S_{\mu \nu}(K^{\alpha i,\beta j})^\pm = \sum (K_{\mu' \nu'}^{\alpha',\beta' j'})^\pm \Delta_{\alpha' \beta' \mu' \nu',\alpha i,\beta j,\mu \nu}(S),
\]  

(4.20)
where

\[
\Delta^{\pm}_{\alpha'i',\beta'j',\mu'\nu',\alpha\beta,\mu\nu}(S) = \frac{1}{2} \delta[\alpha'i', S(\alpha i)] \delta[\beta'j', S(\beta j)] S_{\mu\nu} S_{\nu'\mu} \\
\pm \frac{1}{2} \delta[\alpha'i', S(\beta j)] \delta[\beta'j', S(\alpha i)] S_{\mu'\nu} S_{\nu'\mu}.
\] (4.21)

In the harmonic approximation, only the symmetric part (+) affects the potential energy.

The trace of this representation provides a character for the system, namely

\[
\chi_{\text{sys}}(S) = \frac{1}{2} \sum_{\alpha i, \beta j} \delta[\alpha i, S(\alpha i)] \delta[\beta j, S(\beta j)] [\chi(S)]^2 \\
+ \frac{1}{2} \sum_{\alpha i, \beta j} \delta[\alpha i, S(\beta j)] \delta[\beta j, S(\alpha i)] \chi(S^2).
\] (4.22)

This equation can be split into terms \((\alpha i < \beta j)\) that correspond to bonds, and terms \((\alpha i = \beta j)\) that correspond to particles:

\[
\chi_{\text{sys}}(S) = \sum_{\alpha i < \beta j} \chi_{\alpha i,\beta j}(S) + \sum_{\beta j} \chi_{\beta j}(S),
\] (4.23)

where

\[
\chi_{\alpha i,\beta j} = [\chi(S)]^2 J_{\alpha i,\beta j}(S) + \chi(S^2) J'_{\alpha i,\beta j}(S),
\]

\[
\chi_{\beta j}(S) = \frac{1}{2} \{[\chi(S)]^2 + \chi(S^2)\} J_{\beta j,\beta j}(S),
\]

\[
J_{\alpha i,\beta j}(S) = \delta[\alpha i, S(\alpha i)] \delta[\beta j, S(\beta j)],
\]

\[
J'_{\alpha i,\beta j}(S) = \delta[\alpha i, S(\beta j)] \delta[\beta j, S(\alpha i)],
\]

that is, \(J_{\alpha i,\beta j}(S) = 1\) if \(S\) belongs to the group of the bond, and \(J'_{\alpha i,\beta j}(S) = 1\) if \(S\) is a reversal element for the bond.

B. Group of the Particle

Equation (4.23) suggests that the total number of force constants in a crystal can be decomposed into the number of constants in \(K^{\alpha i,\beta j}\) associated with each bond and the number of constants in \(K^{\beta j,\beta j}\) associated with each particle. A particular particle \(p\) can be focused on by using only the elements of the group \(G_p\) of the particle, that is, the elements in \(G\) that restore \(p\) to itself. Since \(K^{pp}\) is a symmetric tensor in its cartesian indices, the
number of independent parameters in $K^{pp}$ is equal to the number of times the identity representation appears in the symmetric product space of the polar vector, $(\Gamma_p \times \Gamma_p)_{\text{sym}}$.

$$N_p = \frac{1}{g_p} \sum_{S \in G_p} \frac{1}{2} \left\{ [\chi(S)]^2 + \chi(S^2) \right\}$$

$$= \frac{1}{g_p} \sum_{S \in G} \frac{1}{2} \left\{ [\chi(S)]^2 + \chi(S^2) \right\} J_{pp}(S).$$

(4.24)

The space $(\Gamma_p \times \Gamma_p)_{\text{sym}}$ is of interest here because the displacement vectors $u^{\alpha i}$ transform as polar vectors, $K$ is a tensor relating two such polar vectors, and only terms of second order have been retained in the potential energy.

**C. Group of the Bond**

Similarly, let $G_{pq}$ be the group of all elements that leave the bond invariant or reverse it. Then the number of force constants associated with this bond is

$$N_{pq} = \frac{1}{g_{pq}} \sum_{S \in G} \left\{ [\chi(S)]^2 J_{pq}(S) + \chi(S^2) J'_{pq}(S) \right\}.$$  

(4.25)

If $[pq]$ denotes the set of bonds equivalent to $(pq)$, then $g/g_{pq}$ must be the number of bonds in this set. Writing

$$\frac{1}{g_{pq}} \sum_S = \frac{1}{g} \frac{g}{g_{pq}} \sum_S = \frac{1}{g} \sum_{(pq) \in [pq]} \sum_S$$

(4.26)

and summing over all prototype bonds $(pq)$, the total number of force constants associated with all bonds is

$$N_{\text{bonds}} = \frac{1}{g} \sum_{\alpha i < \beta j} \sum_S \chi_{\alpha i, \beta j}(S).$$

(4.27)

**D. Force Constants in Diamond–Structured Crystals**

To account for the contribution of the bond charges to the potential energy, the unit cell of a diamond structured crystal is chosen according to Fig. IV D. With this unit cell, the primitive translation vectors belong to the face-centered cubic (FCC) lattice. The group of the atomic lattice is $O^7_h$, the “diamond” group. The atomic lattice consists of two interpenetrating FCC lattices of cube edge $a$. The origin is at an atom in one sublattice and $\tau = (a/4)(1,1,1)$ connects this atom to its nearest neighbor, which is the origin of of
the second FCC lattice. With a choice of origin between the two atoms, the 48 operations can be divided into 24 simple operations constituting the tetrahedral point group $T_d$ and 24 compound operations that can be obtained by multiplying the first 24 by $(i|\tau)$, where $i$ is the inversion. See Table I. The simple operations transform each sublattice into itself, whereas the compound operations, in addition, interchange the two sublattices. For example, $J = (i|\tau)$ is an inversion about the point halfway between two sublattices.

![Image](111)[111][111][111][111][111]  

**FIG. 4.** The unit cell of elemental diamond–structured crystals have two distinct atoms and four distinct bond charges positioned at the midpoint of the atomic bonds at equilibrium.

The group of the bond between atoms along (111) $K^{12}$ is $C_{3v}$ of point operations $\epsilon$, $\delta_{3xyz}$, $\delta_{3xyz}^{-1}$, $\rho_{xyz}$, $\rho_{\bar{yz}}$, $\rho_{\bar{zx}}$, $\rho_{\bar{xy}}$. The reversal elements are these elements multiplied by the inversion: $(i|\tau)$, $(\sigma_{6xyz}|\tau)$, $(\sigma_{6xyz}|\tau)^{-1}$, $(\delta_{2yz}|\tau)$, $(\delta_{2zx}|\tau)$, $(\delta_{2xy}|\tau)$. The number of independent constants can be calculated according to

$$N_b = \frac{1}{6} \left\{ \chi^2(E) + 2\chi^2(8C_3) + 3\chi^2(6JC_2) \right\}$$

$$= \frac{1}{6} \left\{ (3)^2 + 2(0)^2 + 3(1)^2 \right\} = 2,$$

(4.28)
\[ N'_b = \frac{1}{6} \left\{ \chi(J^2) + 2\chi(8JC^2) + 3\chi(6C^2) \right\} \]
\[ = \frac{1}{6} \left\{ \chi(E) + 2\chi(8C_3) + 3\chi(E) \right\} = 2, \]  
(4.29)

\[ N_{bb} = \frac{1}{2} (N_b + N'_b) = 2, \]  
(4.30)

where \( \chi(S) \) is the character of \( S \) in the polar vector representation, which is the representation \( \Gamma^{-15} \) in the diamond group. Thus there are \( N_{bb} = 2 \) independent constants and the reversal elements do not reduce this number.

Now the form of \( K^{12} \) can be determined. The cyclic permutation of indices produced by \( \delta_{3xyz} \) causes \( K^{12} \) to have the form

\[
K^{12} = \begin{bmatrix}
\alpha' & \beta & \beta' \\
\beta' & \alpha & \beta \\
\beta & \beta' & \alpha'
\end{bmatrix}.
\]  
(4.31)

The reflection plane \( \rho_{xy} \) interchanges \( x \) and \( y \) causing \( K_{12}^{12} = K_{21}^{12} \), that is, \( \beta = \beta' \), so that

\[
K^{12} = \begin{bmatrix}
\alpha' & \beta' & \beta' \\
\beta' & \alpha & \beta \\
\beta' & \beta' & \alpha'
\end{bmatrix}.
\]  
(4.32)

Since this form has 2 independent constants, all of the symmetries have been taken into account. The bond between the origin atom and the bond charge along \((111)\) will clearly have this same form,

\[
K^{13} = \begin{bmatrix}
\alpha & \beta & \beta \\
\beta & \alpha & \beta \\
\beta & \beta & \alpha
\end{bmatrix}.
\]  
(4.33)

Since the bond charges are at points of inversion, \( K^{23} = K^{13} \).

These bonds serve as prototypes, being able to be brought into the bonds along \((1\overline{1}1)\), \((\overline{1}1\overline{1})\), and \((\overline{1}\overline{1}1)\) by appropriate similarity transformations, as shown in Eq.(4.17). The prototype is brought into the bond along \((\overline{1}1\overline{1})\) by a twofold rotation about \( z, \delta_{2z} \), which reverses the signs of \( x \) and \( y \), which changes the signs of the \( xz \) and \( xy \) components of the tensor, but not the \( xy \) component. A complete set of matrices for the bond between atoms
and bond charges is

\[ K^{14}_{(111)} = \begin{bmatrix} \alpha & \bar{\beta} & \beta \\ \bar{\beta} & \alpha & \beta \\ \beta & \beta & \alpha \end{bmatrix}, \quad K^{15}_{(111)} = \begin{bmatrix} \alpha & \bar{\beta} & \beta \\ \bar{\beta} & \alpha & \bar{\beta} \\ \beta & \beta & \alpha \end{bmatrix}, \quad K^{16}_{(111)} = \begin{bmatrix} \alpha & \beta & \bar{\beta} \\ \beta & \alpha & \bar{\beta} \\ \bar{\beta} & \bar{\beta} & \alpha \end{bmatrix}. \]  

(4.34)

The full set of matrices for the bonds between atoms has the same form. By the condition of infinitesimal translational invariance expressed by Eq. (4.10), self-terms are evaluated according to

\[ K^{11} = -\sum_{\beta} K^{1\beta} = -4(\alpha + \alpha') \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \]  

(4.35)

and not

\[ \frac{\partial^2 V}{\partial u^\alpha_{\mu} \partial u^\alpha_{\nu}} \text{ evaluated at } u^\alpha = 0. \]  

(4.36)

There are still the forces between the bond charges, which were shown by Keating to ensure that the crystal can resist shear waves. However, Keating attributed this bond-bending force to the interaction between the atoms, while the bond charge model attributes these forces solely to the interaction between the bond charges.

Consider the bond between the bond charges along (111) and (111), \( K^{36} \). The bond elements are \( \epsilon, \rho_{xy} \), and their inversions \((i|\tau), (\delta_{2xy}|\tau)\). The reversal elements are \( \delta_{2z}, \rho_{xy}, \) and their inversions \((\rho_z|\tau), (\delta_{2xy}|\tau)\). Here

\[ N_b = \frac{1}{4} \left\{ [\chi(\epsilon)]^2 + [\chi(\rho_{xy})]^2 + [\chi(i|\tau)]^2 + [\chi(\delta_{2xy}|\tau)]^2 \right\} \]

\[ = \frac{1}{4} (3^2 + 1^2 + (-3)^2 + (-1)^2) = 5, \]  

(4.37)

\[ N'_b = \frac{1}{4} \left\{ [\chi(\delta_{z}^3)] + [\chi(\rho_{xy}^2)] + [\chi((\rho_{z}|\tau)^2)] + [\chi((\delta_{2xy}|\tau)^2)] \right\} \]

\[ = \frac{1}{4} \left\{ 4\chi(\epsilon) \right\} = 3, \]

(4.38)

\[ N_{bb} = \frac{1}{2} (5 + 3) = 4. \]  

(4.39)

Symmetry under \( \rho_{xy} \) interchanges \( x \) and \( y \), and requires

\[ K_{22} = K_{11}, \quad K_{12} = K_{21}, \]

\[ K_{13} = K_{23}, \quad K_{31} = K_{32}. \]  

(4.40)
or

\[ K^{36} = \begin{bmatrix} \mu & \nu & \tau \\ \nu & \mu & \tau \\ \delta & \delta & \lambda \end{bmatrix} \] (4.41)

having five constants, or one more than necessary. Application of \( \delta_{2z} \), which reverses the signs of \( x \) and \( y \) and sends \( u^3 \) into \( u^6 \), yields \( K^{63} \) in terms of \( K^{36} \) with the result

\[ K^{63} = \begin{bmatrix} \mu & \nu & -\tau \\ \nu & \mu & -\tau \\ -\delta & -\delta & \lambda \end{bmatrix} \] (4.42)

but in the harmonic approximation \( K^{63} = K^{36} \), or

\[
\begin{bmatrix} \mu & \nu & -\delta \\ \nu & \mu & -\delta \\ -\tau & -\tau & \lambda \end{bmatrix} = \begin{bmatrix} \mu & \nu & \tau \\ \nu & \mu & \tau \\ \delta & \delta & \lambda \end{bmatrix}
\] (4.43)

so that \( \tau = -\delta \) and

\[ K^{36} = \begin{bmatrix} \mu & \nu & \delta \\ \nu & \mu & \delta \\ \delta & \delta & \lambda \end{bmatrix} \] (4.44)

having four constants. All symmetries have been taken into account. The force constant matrices between the various pairs of bond charges can be calculated by performing similarity transforms on this prototype.

E. Force constants related to potentials

The adiabatic bond charge model incorporates two fundamental types of interparticle potentials: central potentials and bending potentials. In the case of central potentials, the particles are assumed to interact pairwise through a potential which is a function only of the magnitude of their separation. Denote the potential of the interaction of a particle of type \( \alpha \) with a particle of type \( \beta \) which is a distance \( r \) from it by \( \phi_{\alpha \beta}(r) \), then the potential energy of the crystal can be written as

\[ V = \frac{1}{2} \sum_{i,j}^{\prime} \phi_{\alpha \beta}(r(i\alpha,j\beta)). \] (4.45)
In this expression \( r(\alpha; \beta) \) is the instantaneous distance between the atoms \((\alpha)\) and \((\beta)\), the prime on the sum indicates that the terms in it with \((\alpha) = (\beta)\) are to be omitted, while the factor \( \frac{1}{2} \) corrects for the fact that all interactions are counted twice in the sum. When each particle in the crystal undergoes a vector displacement \( u(\alpha) \) from its rest position, we can express \( r(\alpha; \beta) \) as

\[
r(\alpha; \beta) = \left[ x^2(\alpha; \beta) + 2x(\alpha; \beta) \cdot u(\alpha; \beta) + u^2(\alpha; \beta) \right]^{1/2},
\]

where the following abbreviations have been used:

\[
x(\alpha; \beta) = x(\alpha) - x(\beta),
\]

\[
u(\alpha; \beta) = u(\alpha) - u(\beta).
\]

The potential energy can now be expanded in powers of the components \( \{u_\mu(\alpha; \beta)\} \) as

\[
V = \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} \phi(x(\alpha; \beta)) + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} \phi_\mu(\alpha; \beta) u_\mu(\alpha; \beta) + \frac{1}{4} \sum_{ij} \sum_{\alpha\beta} \phi_{\mu\nu}(\alpha; \beta) u_\mu(\alpha; \beta) u_\nu(\alpha; \beta) + \cdots
\]

The expansion coefficients are given by

\[
\phi_\mu(\alpha; \beta) = \frac{\partial}{\partial r_\mu} \phi(r) \bigg|_{r=x(\alpha; \beta)} = \frac{x_\mu}{x} \phi'(x),
\]

\[
\phi_{\mu\nu}(\alpha; \beta) = \frac{\partial^2}{\partial r_\mu \partial r_\nu} \phi(r) \bigg|_{r=x(\alpha; \beta)} = \frac{x_\mu x_\nu}{x^2} \left[ \phi''(x) - \frac{1}{x} \phi'(x) \right] + \delta_{\mu\nu} \frac{\phi'(x)}{x},
\]

where the prime denotes differentiation with respect to the argument. The potential derivatives are related to the force constants \( K_{\mu\nu}^{\alpha\beta} \).
The second order contribution to the potential energy can be written as
\[
V_2 = \frac{1}{4} \sum_{i\alpha\mu} \sum_{j\beta\nu} \phi_{\mu\nu}(i\alpha; j\beta)[u_{\mu}(i\alpha)u_{\nu}(i\alpha) - u_{\mu}(j\beta)u_{\nu}(j\beta)]
- u_{\mu}(j\beta)u_{\nu}(i\alpha) + u_{\mu}(j\beta)u_{\nu}(j\beta)] \tag{4.52}
\]
\[
= \frac{1}{2} \sum_{i\alpha\mu} \sum_{j\beta\nu} \phi_{\mu\nu}(i\alpha; j\beta)[u_{\mu}(i\alpha)u_{\nu}(i\alpha) - u_{\mu}(i\alpha)u_{\nu}(j\beta)].
\]
Thus for central potentials,
\[
K^i\alpha_j\beta_{\mu\nu} = -\phi_{\mu\nu}(i\alpha; j\beta), \quad (i\alpha) \neq (j\beta)
\]
\[
K^{i\alpha,i\alpha}_{\mu\nu} = \sum_{j\beta} \phi_{\mu\nu}(i\alpha; j\beta). \tag{4.53}
\]
In the diamond structure the force constant between the origin atom and the atom located at \(r_0(111)/\sqrt{3}\) is therefore
\[
K^{12} = -\frac{1}{3} \begin{bmatrix}
A + 2B & A - B & A - B \\
A - B & A + 2B & A - B \\
A - B & A - B & A + 2B
\end{bmatrix}, \tag{4.54}
\]
where \(A \equiv \phi_{aa}''\) and \(B \equiv \phi_{aa}'/r_0\), derivatives of the central potential between atoms. Thus the parameters deduced by symmetry arguments are related to the potential derivatives according to
\[
\frac{1}{3} \begin{bmatrix}
\bar{1} & \bar{2} \\
\bar{1} & 1
\end{bmatrix}
\begin{bmatrix}
\phi_{aa}'' \\
\phi_{aa}'/r_0
\end{bmatrix} = \begin{bmatrix}
\alpha' \\
\beta'
\end{bmatrix}, \tag{4.55}
\]
or inversely,
\[
\begin{bmatrix}
\phi_{aa}'' \\
\phi_{aa}'/r_0
\end{bmatrix} = \begin{bmatrix}
\bar{1} & \bar{2} \\
\bar{1} & 1
\end{bmatrix}
\begin{bmatrix}
\alpha' \\
\beta'
\end{bmatrix}. \tag{4.56}
\]
Similarly, the atom–bond charge central potential derivatives are related to the parameters deduced by symmetry according to
\[
\begin{bmatrix}
\phi_{ab}'' \\
\phi_{ab}'/r_0
\end{bmatrix} = \begin{bmatrix}
\bar{1} & \bar{2} \\
\bar{1} & 1
\end{bmatrix}
\begin{bmatrix}
\alpha \\
\beta
\end{bmatrix}. \tag{4.57}
\]
Now consider the three–body bending potential between bond charges relative to an atom,
\[
\phi_{bb} = \frac{1}{4} \frac{A}{\mathbf{x}_\alpha \cdot \mathbf{x}_\beta} \left( \mathbf{r}_\alpha \cdot \mathbf{r}_\beta - \mathbf{x}_\alpha \cdot \mathbf{x}_\beta \right)^2, \tag{4.58}
\]
where $x^\alpha$ is the position of bond–charge $\alpha$ measured from one of the atoms in the unit cell. The first derivative of this potential is

$$\frac{\partial \phi_{bb}}{\partial r^b_\nu} = \frac{A}{4x^\alpha \cdot x^\beta} (r^\alpha \cdot r^\beta - x^\alpha \cdot x^\beta) r^\alpha_\nu.$$  (4.59)

The second derivative is

$$\frac{\partial^2 \phi_{bb}}{\partial r^\alpha_\mu \partial r^\beta_\nu} = \frac{A}{4x^\alpha \cdot x^\beta} \left[ r^\alpha_\nu r^\beta_\mu + (1 - \delta_{\alpha\beta}) \delta_{\mu\nu} (r^\alpha \cdot r^\beta - x^\alpha \cdot x^\beta) \right].$$  (4.60)

Thus the expansion coefficient is

$$\left. \frac{\partial^2 \phi_{bb}}{\partial r^\alpha_\mu \partial r^\beta_\nu} \right|_{r=x} = \frac{Ax^\alpha x^\beta}{4x^\alpha \cdot x^\beta}. $$  (4.61)

In the diamond structure, considering the bond charges located at $\frac{1}{2} \tau (111)/\sqrt{3}$ and $\frac{1}{2} \tau (\bar{1}1\bar{1})/\sqrt{3}$, it is the case that $\cos \theta = -1/3$, so

$$K_{36} = -\left. \frac{\partial^2 \phi_{bb}}{\partial r^3 \partial r^6} \right|_{r=x} = \frac{A}{4} \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} = \begin{bmatrix} \mu & \nu & \delta \\ \nu & \mu & \delta \\ \delta & \delta & \lambda \end{bmatrix}.$$  (4.62)

Thus the symmetry parameters are related to each other and the bond bending parameter according to

$$\mu = \nu = \delta = -\lambda = A/4.$$  (4.63)

If the bending potential between bond charges was instead written as

$$\phi_{bb} = \frac{\frac{1}{2} A}{4x^\alpha \cdot x^\beta} (r^\alpha \cdot r^\beta - \bar{a}^2)^2,$$  (4.64)

where an additional bond bending parameter is introduced such that $\bar{a}^2 \neq x^\alpha \cdot x^\beta$, then the symmetry parameters would be related to the two bond bending parameters by

$$\mu = \frac{3}{4} A(2 - \bar{a}^2), \quad \nu = \delta = \frac{3}{4} A, \quad \lambda = -\frac{9}{4} A\bar{a}^2,$$  (4.65)

or

$$\nu = \delta, \quad \lambda = 3(\mu - 2\delta).$$  (4.66)

Weber found it necessary to use this augmented form of the bond bending potential for the case of diamond.
Weber himself thought this alternative form of the bond bending potential was physically unmotivated and ad hoc. Density functional theory calculations show that the bond charge cloud in the group IV elemental diamond structured crystals has a quadrupolar moment. It should be expected that this quadrupolarity give rise to an asymmetry in the resistance to bending in the equilibrium plane of two bond charge clouds as compared to bending out of that plane. The original Keating bending potential does not afford a distinction between these two types of bending. To make this distinction, let there be another spring constant associated with the change in the cross product between the position vectors of the bond charges,

\[ \lambda_{\alpha\beta} = \frac{1}{2} \left[ (u_{\alpha} + r_{\alpha}) \times (u_{\beta} + r_{\beta}) - (r_{\alpha} \times r_{\beta}) \right] \cdot (r_{\alpha} \times r_{\beta})/2r^{3}, \]  

which in the limit of small displacements \( u \) becomes

\[ \lambda_{\alpha\beta} = \left[ (r_{\alpha} \times u_{\beta}) + (u_{\alpha} \times r_{\beta}) \right] \cdot (r_{\alpha} \times r_{\beta})/2r^{3}, \]  

or

\[ \lambda_{\alpha\beta} = \frac{1}{2} r^{-1} u_{\alpha} \cdot (r_{\alpha} - \cos \theta r_{\beta}) + \frac{1}{2} r^{-1} u_{\beta} \cdot (r_{\beta} - \cos \theta r_{\alpha}). \]  

The additional bond bending potential with spring constant \( \bar{A} \)

\[ \bar{\phi}_{bb} = \frac{1}{2} \bar{A} \lambda_{\alpha\beta}^{2} \]  

gives rise to the expansion coefficient

\[ \frac{\partial^{2} \bar{\phi}_{bb}}{\partial u^{i}_{\alpha} \partial u^{j}_{\beta}} = \bar{A} \frac{1}{4r^{2}} (r^{i}_{\alpha} - \cos \theta r^{i}_{\beta})(r^{j}_{\beta} - \cos \theta r^{j}_{\alpha}) \]  

and the force constant matrix

\[ \bar{K}_{36} = \frac{\bar{A}}{27} \begin{bmatrix} 1 & 1 & 2 \\ 1 & 1 & 2 \\ 2 & 2 & 4 \end{bmatrix}. \]  

Now the sum of the original Keating bending force constant matrix and this new one can be compared to the group theoretical force constant matrix to arrive at the relations

\[ \mu = \nu = \frac{1}{4} A + \frac{1}{27} \bar{A}, \]  

\[ \delta = \frac{1}{4} A - \frac{2}{27} \bar{A}, \]  

\[ \lambda = -\frac{1}{4} A - \frac{4}{27} \bar{A} = \delta - 2\mu, \]
or more compactly
\begin{equation}
\nu = \mu, \quad \lambda = \delta - 2\mu.
\end{equation}
(4.76)

If \( \delta = \mu \), then \( \lambda = -\mu \), just as is the case with no quadrupolar term in the bending potential. Unlike this new total bending potential, Weber’s ad hoc adaptation cannot degenerate to the case without quadrupolarity if \( \delta = \mu \).
V. COULOMB FORCES AND EWALD’S METHOD

So far only short–range forces have been investigated. However, in ionic crystals the dominant role is played by the long–range Coulomb forces. This section investigates the equations of motion of a crystal lattice in the case that the elements of the dynamical matrix $C_{\mu\nu}(\kappa\kappa'|q)$ contain a contribution from Coulomb forces. The force constants $K_{\mu\nu}(\kappa\kappa';l'\kappa')$ can therefore be written as the sum of two terms, one representing the contribution from the Coulomb forces, $K_{\mu\nu}^{C}(\kappa\kappa';l'\kappa')$, and the second representing the contribution from the non–Coulomb forces, $K_{\mu\nu}^{N}(\kappa\kappa';l'\kappa')$. The elements of the dynamical matrix $C_{\mu\nu}(\kappa\kappa'|q)$ correspondingly separate into a Coulomb and a non–Coulomb part

$$C_{\mu\nu}(\kappa\kappa'|q) = T_{\mu\nu}(\kappa\kappa'|q) + R_{\mu\nu}(\kappa\kappa'|q),$$

where

$$T_{\mu\nu}(\kappa\kappa'|q) = (M_{\kappa}M_{\kappa'})^{-1/2} \sum_{l'} K_{\mu\nu}^{C}(l\kappa';l'\kappa') e^{-i\mathbf{q}\cdot\mathbf{x}(l\kappa;l'\kappa')}$$

$$R_{\mu\nu}(\kappa\kappa'|q) = (M_{\kappa}M_{\kappa'})^{-1/2} \sum_{l'} K_{\mu\nu}^{N}(l\kappa';l'\kappa') e^{-i\mathbf{q}\cdot\mathbf{x}(l\kappa;l'\kappa')}.$$  

The atomic force constants obtained from the Coulomb potential energy between two ions of charges $e_{\kappa}$ and $e_{\kappa'}$ separated by a distance $r$,

$$\phi_{\kappa\kappa'}^{C}(r) = e_{\kappa}e_{\kappa'}/r,$$

have the form

$$K_{\mu\nu}^{C}(l\kappa;l'\kappa') = -\frac{\partial^2}{\partial r_{\mu} \partial r_{\nu}} \left\{ \frac{e_{\kappa} e_{\kappa'}}{r} \right\}_{r=\mathbf{x}(l\kappa;l'\kappa')} (l\kappa) \neq (l'\kappa')$$

$$K_{\mu\nu}^{C}(l\kappa;l\kappa') = \sum_{l'\kappa'} \frac{\partial^2}{\partial r_{\mu} \partial r_{\nu}} \left\{ \frac{e_{\kappa} e_{\kappa'}}{r} \right\}_{r=\mathbf{x}(l\kappa;l'\kappa')}.$$  

Consequently, the elements of $T_{\mu\nu}(\kappa\kappa'|q)$ can be written out for $\kappa \neq \kappa'$ explicitly as

$$T_{\mu\nu}(\kappa\kappa'|q) = -\frac{e_{\kappa} e_{\kappa'}}{(M_{\kappa}M_{\kappa'})^{1/2}} \sum_{l'} \left( \frac{\partial^2}{\partial r_{\mu} \partial r_{\nu}} \frac{1}{r} \right) e^{-i\mathbf{q}\cdot\mathbf{x}(l\kappa;l'\kappa')}.$$  

The diagonal elements, on the other hand, have a more complicated form. From Eqs.
and (5.5) it is the case that

\[ T_{\mu\nu}(\kappa\kappa|q) = \frac{1}{M_\kappa} K^C_{\mu\nu}(l\kappa;l\kappa) + \frac{1}{M_\kappa} \sum'_{l'\kappa'} K^C_{\mu\nu}(l\kappa;l'\kappa') e^{-iq\cdot x(l\kappa;l'\kappa')} \]

(5.8)

\[ = \frac{1}{M_\kappa} \sum'_{l'\kappa'} \frac{\partial^2}{\partial r_\mu \partial r_\nu} \frac{e_\kappa e_{\kappa'}}{r} \bigg|_{r = x(l\kappa;l'\kappa')} \]

\[ - \frac{1}{M_\kappa} \sum'_{l'\kappa'} \left( \frac{\partial^2}{\partial r_\mu \partial r_\nu} \frac{e_\kappa e_{\kappa'}}{r} \right) e^{-iq\cdot r} \bigg|_{r = x(l\kappa;l'\kappa')} , \]

(5.9)

It is now formally convenient to add in the term with \((l'\kappa') = (l\kappa)\) in the first sum on the right hand side of this equation, and to add in the term with \(l' = l\) in the second sum. The two terms are singular, but they are equal and cancel between the two terms on the right hand side of this equation. In this way,

\[ T_{\mu\nu}(\kappa\kappa|q) = \frac{1}{M_\kappa} \sum'_{l'\kappa'} \frac{\partial^2}{\partial r_\mu \partial r_\nu} \frac{e_\kappa e_{\kappa'}}{r} \bigg|_{r = x(l\kappa;l'\kappa')} \]

\[ - \frac{1}{M_\kappa} \sum'_{l'\kappa'} \left( \frac{\partial^2}{\partial r_\mu \partial r_\nu} \frac{e_\kappa e_{\kappa'}}{r} \right) e^{-iq\cdot r} \bigg|_{r = x(l\kappa;l'\kappa')} , \]

(5.10)

where there are now no restrictions on the summations. This is convenient because we can now combine the results given by Eqs. (5.7) and (5.9) to write

\[ T_{\mu\nu}(\kappa\kappa'|q) = -\left( \frac{1}{M_\kappa M_{\kappa'}} \right)^{1/2} \sum'_{l'\kappa'} \left( \frac{\partial^2}{\partial r_\mu \partial r_\nu} \frac{e_\kappa e_{\kappa'}}{r} \right) e^{-iq\cdot r} \bigg|_{r = x(l\kappa;l'\kappa')} \]

\[ + \delta_{\kappa\kappa'} \frac{1}{M_\kappa} \sum'_{\kappa''l'\kappa'} \left( \frac{\partial^2}{\partial r_\mu \partial r_\nu} \frac{e_\kappa e_{\kappa''}}{r} \right) \bigg|_{r = x(l\kappa;l'\kappa'')} . \]

The matrix elements (5.3) and (5.10) are expressed in the form of direct lattice sums. In the case of short range interactions between atoms such a representation is the most convenient one, since in summing over the lattice sites it suffices to include the contributions from only a few shells of neighbors surrounding the site \((l\kappa)\). However, Coulomb forces are long–range forces, and the series (5.10) converge slowly for them. This can be overcome, since it is to be expected from the properties of Fourier transforms that the series representing long–range forces will converge rapidly in reciprocal space.

Before developing Ewald’s method to overcome the slow convergence of the Coulomb force constants in three dimensions, let us consider the one dimensional case, consisting of an infinite linear chain of atoms of the same elemental species interspersed with bond charges that evenly divide the atomic bonds, as shown in Fig. 5. The unit cell consists of one atom.
FIG. 5. An infinite linear chain of atoms of the same elemental species (white circles) interspersed with bond charges (black circles) that evenly divide the atomic bonds. The dashed vertical line marks a mirror symmetry that simplifies the calculation of the Coulombic force constants.

(labeled by $\kappa = 1$) and one bond charge ($\kappa = 2$). For the cell to be electrically neutral, it must be the case that $e_1 = -e_2 = Ze$. Consider the Coulombic force constant between the atom and bond charge,

$$T(12|q) = \frac{2Z^2e^2}{\sqrt{M_1M_2}} \sum_{l=-\infty}^{\infty} \frac{e^{-iqr}}{r^3} \bigg|_{r=x(la/2)},$$

(5.11)

where $r = la + \frac{1}{2}a$ for bond charges to the right of the mirror line going through the atom in Fig.5 and $r = -(la + \frac{1}{2}a)$ for bond charges to the left. For each $e^{-iqr}$ term in the sum coming from the right of the atom, there is a corresponding $e^{+iqr}$ term coming from the left of the atom. The $r^{-3}$ term is invariant in the mirrored pairs. Therefore the two complex exponentials of each mirrored pair can be combined to form a purely real cosine term, so the sum can be written as

$$\sum_{l=-\infty}^{\infty} \frac{e^{-iqr}}{r^3} = 2 \sum_{l=0}^{\infty} \frac{\cos[q(la + \frac{1}{2}a)]}{|la + \frac{1}{2}a|^3} = \frac{2^4}{a^3} \sum_{l=0}^{\infty} \frac{\cos[\frac{1}{2}qa(2l + 1)]}{(2l + 1)^3}. \tag{5.12}$$

If we rewrite the wavevector as $q = 2\alpha/a$, then we can study the series

$$C_3(\alpha) = \sum_{k=0}^{\infty} \frac{\cos(2k + 1)\alpha}{(2k + 1)^3}, \quad \alpha \in (0, \pi),$$

(5.13)

where we’ve switched index labels to avoid confusion between $l$s and $1$s. For the case of a wavevector in the opposite orientation, we note that since $\cos$ is an even function, so is the series.

This series as written converges slowly. J. Boersma and J. P. Dempsey studied this series
in connection to Legendre’s chi–function,
\[ \chi_n(z) = \sum_{k=0}^{\infty} \frac{z^{2k+1}}{(2k+1)^n}, \quad |z| \leq 1, \quad n = 2, 3, 4, \ldots, \] (5.14)
and found a rapidly converging form in terms of the Riemann zeta–function, \( \zeta(z) \). Their expression for the series is
\[ C_3(\alpha) = \frac{7}{8} \zeta(3) + \sum_{k=0}^{\infty} \frac{1 - 2^{-(2k+1)}}{(2k+2)(2k+3)(2k+4)} \zeta(2k+2) \frac{\alpha^{2k+4}}{\pi^{2k+2}} \]
\[ - \frac{1}{4} \alpha^2 \left( \frac{3}{2} + \log 2 - \log |\alpha| \right), \quad |\alpha| \leq \pi. \] (5.15)
Figure 6 compares the convergence of the two forms of the series. Except for values of \( \alpha \) near \( \pi \), the Riemann zeta–function form of the series has a dramatically greater rate of convergence. Collecting terms, the Coulombic force constant between atoms and bond charges is
\[ T(12|q) = \frac{2^5 Z^2 e^2}{a^3 \sqrt{M_1 M_2}} C_3(\alpha), \] (5.16)
where \( q = 2\alpha/a \) so that \( |\alpha| \leq \pi \).

Now consider the Coulombic force constant between the atoms
\[ T(11|q) = \frac{2Z^2 e^2}{M_1} \sum_{l=-\infty}^{\infty} \left[ \frac{1}{|l|a^3} - \frac{1}{|l|a + \frac{3}{2} a^3} - \frac{e^{-i q \cdot r}}{r^3} \right]_{r=x(01;l1)}. \] (5.17)
The first and second terms in the sum can be written as
\[ \frac{2^3}{a^3} \sum_{l=-\infty}^{\infty} \left[ \frac{1}{|2l|^3} - \frac{1}{|2l + 1|^3} \right] = -\frac{2^4}{a^3} \frac{3}{4} \left[ \frac{4}{3} \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k^3} \right] = -\frac{2^2}{a^3} 3 \zeta(3), \] (5.18)
where \( \zeta \) is the Riemann zeta function. The third term in the sum can be written as
\[ \sum_{l=-\infty}^{\infty} \frac{e^{-i q \cdot r}}{r^3} = 2 \sum_{l=1}^{\infty} \frac{\cos(qa 2l)}{|al|^3} = \frac{2^5}{a^3} \sum_{l=1}^{\infty} \frac{\cos(\frac{1}{2} qa 2l)}{(2l)^3}. \] (5.19)
If we rewrite the wavevector as \( q = 2\alpha/a \), then the series can be written as
\[ \sum_{k=1}^{\infty} \frac{\cos(2k\alpha)}{(2k)^3}, \quad \alpha \in (0, \pi). \] (5.20)
Unfortunately, no accelerated form has been found for this series. Collecting these results, the Coulombic force constant between atoms is
\[ T(11|q) = -\frac{2^3 Z^2 e^2}{a^3 M_1} \left[ 3 \zeta(3) + 2^3 \sum_{k=1}^{\infty} \frac{\cos(2k\alpha)}{(2k)^3} \right], \] (5.21)
FIG. 6. The convergence rates of the two forms of the series involved in the one–dimensional Coulombic force constants are shown in terms of the distance between successive terms in the series. The convergence of the two series depends upon the value of the parameter $|\alpha| \leq \pi$.

where $q = 2\alpha/a$ so that $|\alpha| \leq \pi$.

In three dimensions, no rapidly converging closed form version of the series involved in the Coulombic force constants has been found to exist. Instead, Ewald provided a general numerical scheme that breaks the series up into a part that converges rapidly in configuration space and one that converges rapidly in wavevector space. To go over to an expansion in reciprocal space it is necessary to rewrite $T_{\mu\nu}(\kappa \kappa' | \mathbf{q})$ in terms of the Fourier component of
the force constants $K^C_{\mu\nu}(\kappa\kappa'|q) = -e_\kappa e_{\kappa'} \sum_\nu \left( \frac{\partial^2}{\partial r_\mu \partial r_\nu} \right) \frac{1}{r} e^{-iq\cdot r} \bigg|_{r=x(\kappa\kappa')}. \quad (5.22)$

Comparing this expression with Eq.(5.10),

$$ T_{\mu\nu}(\kappa\kappa'|q) = (M_\kappa M_{\kappa'})^{-1/2} K^C_{\mu\nu}(\kappa\kappa'|q) - \delta_{\kappa\kappa'} \frac{1}{M_\kappa} \sum_{\kappa''} K^C_{\mu\nu}(\kappa\kappa''|0). \quad (5.23) $$

Note that the divergent term arising in Eq.(5.22) when $(\ell'\kappa'') = (\ell\kappa)$ is compensated by exactly the same term from $K^C_{\mu\nu}(\kappa\kappa''|0)$ in Eq.(5.23).

Define the Fourier transform of the pair potential $\phi^C_{\kappa\kappa'}(r)$ by

$$ \phi^C_{\kappa\kappa'}(r) = (2\pi)^{-3} \int d^3 k \ e^{i\mathbf{q}\cdot \mathbf{r}} \hat{\phi}^C_{\kappa\kappa'}(\mathbf{q}). \quad (5.24) $$

Substituting this expression into Eq.(5.22), and making use of the result that

$$ \sum_l e^{iq\cdot x(l)} = N \Delta(q) = \left(\frac{2\pi}{{\nu}_a}\right)^3 \sum_\tau \delta(q - \tau), \quad (5.25) $$

where the second equation holds when we regard $q$ as a continuous, rather than a discrete, variable, it is the case that

$$ K^C_{\mu\nu}(\kappa\kappa'|q) = \frac{1}{{\nu}_a} \sum_\tau (\tau + q)_\mu (\tau + q)_\nu \hat{\phi}^C_{\kappa\kappa'}(|\tau + q|) \times e^{i\tau\cdot (x(\kappa) - x(\kappa')). \quad (5.26) $$

A momentum representation of the kind given by Eq.(5.26) for the case of Coulomb interaction forces was first used in crystal physics by Ewald.\[17\] Ewald’s method will be described here in a form which is applicable to an arbitrary system of periodically arrayed charges. This derivation is attributed to Shockley by Kittel.\[24\]

The essential point of this method is that the energy of interaction of two point charges $e_\kappa$ and $e_{\kappa'}$, separated by a distance $r$

$$ \phi^C_{\kappa\kappa'}(r) = e_{\kappa\kappa'}/r, \quad (5.27) $$

can be rewritten in the form

$$ \phi^C_{\kappa\kappa'}(r) = \phi^1_{\kappa\kappa'}(r) + [\phi^C_{\kappa\kappa'}(r) - \phi^1_{\kappa\kappa'}(r)] = \phi^1_{\kappa\kappa'}(r) + \phi^2_{\kappa\kappa'}(r). \quad (5.28) $$
In this expression $\phi_{kk'}^1(r)$ is the potential energy of a point charge $e_\kappa$ at a distance $r$ from a three–dimensional Gaussian charge distribution

$$\rho(r) = e_{\kappa'}(P/\pi)^{3/2} \exp(-P r^2),$$  \hspace{1cm} (5.29)

the total charge in which is $e_{\kappa'}$. Knowing $\rho(r)$ we can obtain $\phi_{kk'}^1(r)$ and $\phi_{kk'}^2(r)$ from electrostatics. As we will see, $\phi_{kk'}^1(r)$ is finite at $r = 0$, and approaches a Coulomb interaction for large values of $r$. It is therefore convenient to express the contribution from $\phi_{kk'}^1(r)$ to the force constants $K_{\mu\nu}(kk'|q)$ as a lattice sum over the translation vectors of the reciprocal lattice, as in Eq.(5.26).

The function $\phi_{kk'}^2(r)$, on the other hand, diverges for $r = 0$, and decreases rapidly with increasing $r$. In this sense it behaves as an ordinary, short range interaction potential. It is therefore convenient to express the contribution of $\phi_{kk'}^2(r)$ to the force constants $K_{\mu\nu}(kk'|q)$ in the form of a direct lattice sum, as in Eq.(5.3). The value of the parameter $P$, which determines the width of the Gaussian charge distribution, can be chosen so as to make both lattice sums rapidly convergent. Values of $P$ of the magnitude of $P \approx r_0^{-2}$, where $r_0$ is the nearest neighbor separation between ions, in general seem to produce rapid convergence of both sums. Inasmuch as the total expression for $\phi_{kk'}^C(r)$, Eq.(5.28), is independent of $P$, the fact that the charge distribution $\rho(r)$ determining $\phi_{kk'}^1(r)$, has been chosen to be Gaussian is of no significance. The particular choice of a Gaussian is made because it leads to simple, rapidly convergent expressions for the direct and reciprocal lattice contributions to the force constants.

For the determination of $\phi_{kk'}^1(r)$ we require the Fourier transform of the charge distribution $\rho(r)$,

$$\hat{\rho}(q) = e_{\kappa'}(P/\pi)^{3/2} \int d^3r \exp(-P r^2)e^{-iq\cdot r} = e_{\kappa'} \exp(-q^2/4P).$$  \hspace{1cm} (5.30)

If we now make use of Eq.(5.23), we obtain from Poisson’s equation the result that

$$\hat{\phi}_{kk'}^1(q) = (4\pi e_\kappa e_{\kappa'}/q^2) \exp(-q^2/4P).$$  \hspace{1cm} (5.31)

Substituting this expression into Eq.(5.26), we obtain for the contribution of $\phi_{kk'}^1(r)$ to $K_{\mu\nu}^C(kk'|q)$,

$$[K_{\mu\nu}^C(kk'|q)]_1 = \frac{1}{v_{a}} \sum_\tau (\tau + q)_{\mu}(\tau + q)_{\nu} \frac{4\pi e_\kappa e_{\kappa'}}{|\tau + q|^2} \times \exp \left(-\frac{|\tau + q|^2}{4P}\right) e^{i\tau \cdot [x(\kappa)-x(\kappa')]}.$$  \hspace{1cm} (5.32)
The function $\phi_{\kappa\kappa'}^2(r)$ can also be obtained by arguments familiar from electrostatics. Recalling its definition, Eq.(5.28), we have that it is given by

$$\phi_{\kappa\kappa'}^2(r) = e_\kappa \left\{ \frac{e_{\kappa'}}{r} - \frac{1}{r} \int_0^r d^3r' \rho(r') - \int_r^\infty d^3r' \frac{\rho(r')}{r'} \right\}. \quad (5.33)$$

The first term is the potential due to a point charge $e_{\kappa'}$ at the origin, the second is the contribution from the Gaussian charge distribution Eq.(5.29) lying inside a sphere of radius $r$ about the origin, and the third is from that part lying outside the sphere. Since $\rho(r)$ is normalized to $e_{\kappa'}$, we can rewrite Eq.(5.33) as

$$\phi_{\kappa\kappa'}^2(r) = e_\kappa e_{\kappa'} \frac{2}{\sqrt{\pi} r} \int_r^\infty ds \exp(-s^2). \quad (5.34)$$

The contribution to the force constants from this function is conveniently expressed by means of the representation

$$[K_{\mu\nu}^C(\kappa\kappa'|\mathbf{q})]_2 = -\sum_{\nu'} \left( \frac{\partial^2}{\partial x_\mu \partial y_{\nu'}} \phi_{\kappa\kappa'}^2(r) \right) e^{-iq \cdot r} \bigg|_{r = x(l\kappa;l'\kappa')}$$

$$= -e_{\kappa\kappa'} P^{3/2} \sum_{\nu'} H_{\mu\nu}(\sqrt{P}|x(l\kappa;l'\kappa')|) e^{-iq \cdot x(l\kappa;l'\kappa')}, \quad (5.35)$$

where

$$H_{\mu\nu}(x) = \frac{\partial^2}{\partial x_\mu \partial x_{\nu'}} \frac{2}{\sqrt{\pi} x} \int_x^\infty ds \exp(-s^2)$$

$$= \left\{ \frac{x_\mu x_{\nu'}}{x^2} \left[ \frac{3}{x^3} \operatorname{erfc} x + \frac{2}{\sqrt{\pi}} \left( \frac{3}{x^2} + 2 \right) \exp(-x^2) \right] - \delta_{\mu\nu} \left[ \frac{1}{x^3} \operatorname{erfc} x + \frac{2}{\sqrt{\pi}} \frac{1}{x^2} \exp(-x^2) \right] \right\}, \quad (5.36)$$

and $\operatorname{erfc} x$ is the complementary error function,

$$\operatorname{erfc} x = \frac{2}{\sqrt{\pi}} \int_x^\infty ds \exp(-s^2) \equiv x H(x). \quad (5.37)$$

Bearing in mind the difference between the definitions of the coefficients $T_{\mu\nu}(\kappa\kappa'|\mathbf{q})$ for $\kappa \neq \kappa'$ and for $\kappa = \kappa'$, we can write the equations of motion of the lattice in terms of the sum $[K_{\mu\nu}^C(\kappa\kappa'|\mathbf{q})]_1 + [K_{\mu\nu}^C(\kappa\kappa'|\mathbf{q})]_2$ as

$$\omega_j^2(\mathbf{q}) \omega_{\mu}(\kappa|\mathbf{q}) = \sum_{\kappa'\nu'} R_{\mu\nu}(\kappa\kappa'|\mathbf{q}) \omega_{\nu}(\kappa'|\mathbf{q})$$

$$- \sum_{\nu} \frac{1}{M_{\kappa}} \left\{ \sum_{\kappa''} [K_{\mu\nu}^C(\kappa\kappa''|\mathbf{0})]_1 + \sum_{\kappa''} [K_{\mu\nu}^C(\kappa\kappa''|\mathbf{0})]_2 \right\} \omega_{\nu}(\kappa|\mathbf{q})$$

$$- \sum_{\kappa'\nu'} (M_{\kappa'} M_{\kappa})^{-1/2} \left\{ \sum_{\kappa'} [K_{\mu\nu}^C(\kappa\kappa'|\mathbf{q})]_1 + \sum_{\kappa'} [K_{\mu\nu}^C(\kappa\kappa'|\mathbf{q})]_2 \right\} \omega_{\nu}(\kappa'|\mathbf{q}). \quad (5.38)$$
Let us now look more closely at the result given by Eq. (5.32), and in particular let us separate out explicitly the term with $\tau = 0$. As $q \to 0$ this term is not a regular function of $q$ because it contains $q^2$ in the denominator. Its limiting value as $q \to 0$ depends on the direction along which the point $q = 0$ is approached. It will be convenient to separate out explicitly the part of the term $\tau = 0$ which is not regular and to rewrite Eq. (5.32) in the form

\[
[K^C_{\mu\nu}(\kappa\kappa'|q)]_1 = \frac{4\pi}{v_a} \left\{ \frac{q_\mu q_\nu}{q^2} e_\kappa e_{\kappa'} + \frac{q_\mu q_\nu}{q^2} \left[ \exp \left( -\frac{q^2}{4P} \right) - 1 \right] e_\kappa e_{\kappa'} \right. \\
+ \sum_{\tau \neq 0} \frac{(\tau + q)_\mu (\tau + q)_\nu}{|\tau + q|^2} e_\kappa e_{\kappa'} \exp \left( -\frac{|\tau + q|^2}{4P} \right) e^{i\tau \cdot (x(\kappa) - x(\kappa'))} \right\}. 
\tag{5.39}
\]

The second and third terms on the right hand side of Eq. (5.34) are now regular functions of $q$ in the limit as $q \to 0$. In the second term the factor $[\exp(-q^2/4P) - 1]$ is proportional to $q^2$ for small $q$, and therefore cancels the factor of $q^2$ in the denominator of this term. Substituting Eq. (5.39) into Eq. (5.38) we see that the nonanalytic term on the right hand side of Eq. (5.39) does not contribute to the first term in the braces on the right hand side of Eq. (5.38) because the electrical neutrality of each unit cell requires that

\[
\sum_\kappa e_\kappa = 0. \tag{5.40}
\]

However, this nonanalytic term remains in the next to last term of this equation, where it takes the form

\[
\sum_{\kappa'\nu} \frac{e_\kappa}{(M_\kappa)^{1/2}} \frac{4\pi q_\mu q_\nu}{q^2} \frac{e_{\kappa'}}{(M_{\kappa'})^{1/2}} w_{\nu}(\kappa'|q_j) = -\frac{e_\kappa}{(M_\kappa)^{1/2}} E_\mu. \tag{5.41}
\]

The vector $E$ defined implicitly in this fashion has the physical interpretation that it is the amplitude of a macroscopic electric field, which has its origin in the presence of dipoles at the sites of our lattice, whose moments are

\[
p_\nu(\kappa') = \frac{e_{\kappa'}}{(M_{\kappa'})^{1/2}} w_{\nu}(\kappa'|q_j) e^{i q \cdot x(\kappa')} \tag{5.42}
\]

Separating the contribution from the macroscopic field explicitly in Eq. (5.38), we can rewrite it in the form

\[
\omega^2 w_\mu(\kappa|q_j) = \sum_{\kappa'\nu} R_{\mu\kappa'}(\kappa\kappa'|q) w_{\nu}(\kappa'|q_j) + \sum_{\kappa'\nu} \frac{e_\kappa e_{\kappa'\nu}}{M_\kappa} Q_{\mu\nu}(\kappa\kappa'|0) w_{\nu}(\kappa|q_j) \\
- \sum_{\kappa'\nu} \frac{e_\kappa e_{\kappa'}}{(M_\kappa M_{\kappa'})^{1/2}} Q_{\mu\kappa'}(\kappa\kappa'|q) w_{\nu}(\kappa'|q_j) - \frac{e_\kappa}{(M_\kappa)^{1/2}} E_\mu, \tag{5.43}
\]

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where $E_\mu$ is defined by Eq. (5.41) and $Q_{\mu\nu}(\kappa\kappa'|q)$ is equal to

$$Q_{\mu\nu}(\kappa\kappa'|q) = -\frac{4\pi q_\mu q_\nu}{v_a} \left[ \exp \left( -\frac{q^2}{4P} \right) - 1 \right] - \frac{4\pi}{v_a} \sum_{\tau \neq 0} \frac{(\tau + q)_{\mu}(\tau + q)_{\nu}}{|\tau + q|^2} \exp \left( -\frac{|\tau + q|^2}{4P} \right) e^{i\tau \cdot [x(\kappa) - x(\kappa')]} + P^{3/2} \sum_{l'\neq 0} H_{\mu\nu}(\sqrt{P} l\kappa; l'\kappa') e^{-iql\kappa} e^{i\tau \cdot x(l\kappa; l'\kappa')}.$$  

(5.44)

In this fashion Ewald’s method, in addition to providing a method for transforming slowly convergent lattice sums into rapidly convergent sums, enables us to separate off the terms in the equations of motion of an ionic crystal which are not regular in the limit as $q \to 0$, and which in this long wavelength limit have a simple physical interpretation as the macroscopic electric field.

Because the function $H_{\mu\nu}(x)$ is singular at $|x| = 0$, $Q_{\mu\nu}(\kappa\kappa'|q)$ is singular when $\kappa = \kappa'$, the divergence coming from the term $l' = l$ in the last term. This is due to the inclusion of the energy of interaction of an ion with itself in obtaining the expression for $T_{\mu\nu}(\kappa\kappa'|q)$. Although this singularity is canceled between the second and third terms of Eq. (5.43), and consequently does not enter the equations of motion of the crystal, it is nevertheless convenient to redefine $Q_{\mu\nu}(\kappa\kappa'|q)$ in such a way that the divergence is removed and the resulting expression has a ready physical interpretation. This can be done in the following way.

A periodic array of dipoles whose moments are given by

$$p(l\kappa) = p(\kappa) e^{iq \cdot x(l\kappa)}$$  

(5.45)

gives rise to a macroscopic electric field given by

$$E(x) = E e^{iq \cdot x}$$  

(5.46)

and

$$E_\mu = -\frac{4\pi}{v_a} \hat{q}_\mu \sum_{\kappa} \hat{q}_\nu p_\nu(\kappa).$$  

(5.47)

The total Coulomb field at the point $x$ in the crystal, however, differs from the macroscopic field and is given by

$$E_\mu = \sum_{l\kappa\nu} \left( \frac{\partial^2}{\partial x_\mu \partial x_\nu} \frac{1}{|x(l\kappa) - x|} \right) p_\nu(\kappa) e^{iq \cdot x(l\kappa)}.$$  

(5.48)
The total Coulomb field at a lattice point, such as at \( \mathbf{x} = \mathbf{x}(0) \), due to dipoles at all the other lattice sites (called the exciting, local, or effective field) is given by

\[
E_{\mu}^{\text{eff}}(0) = \lim_{x \to x(0)} \left\{ \sum_{\kappa \nu} \left( \frac{1}{|x(l) - x|} \left( \frac{\partial^2}{\partial x_\mu \partial x_\nu} - 1 \right) \right) p_\nu(\kappa) e^{i\mathbf{q} \cdot \mathbf{x}(\kappa)} - \sum_{\nu} \left( \frac{\partial^2}{\partial x_\mu \partial x_\nu} \right) p_\nu(\kappa) e^{i\mathbf{q} \cdot \mathbf{x}(\kappa)} \right\},
\]

(5.49)

Just as before, replace \( |\mathbf{x}(l) - \mathbf{x}|^{-1} \) in the first term on the right hand side of this equation by

\[
\frac{1}{|\mathbf{x}(l) - \mathbf{x}|} = \frac{1}{(2\pi)^3} \int d^3q e^{i\mathbf{q} \cdot (\mathbf{x}(l) - \mathbf{x})} \frac{4\pi}{q^2} \exp \left( - \frac{q^2}{4P} \right) + \frac{\text{erfc}(\sqrt{P}|\mathbf{x}(l) - \mathbf{x}|)}{|\mathbf{x}(l) - \mathbf{x}|}.
\]

(5.50)

When this is done and the sum over \( l \) is carried out, the passage to the limit in Eq. (5.49) can be carried out with the result that

\[
E_{\mu}^{\text{eff}}(0) = \left[ E_{\mu} + \sum_{\kappa \nu} Q_{\mu\nu}(\kappa\kappa')|\mathbf{q}| p_\nu(\kappa') \right] e^{i\mathbf{q} \cdot \mathbf{x}(\kappa)},
\]

(5.51)

where the matrix \( Q_{\mu\nu}(\kappa\kappa'|\mathbf{q}) \) is that defined by Eq. (5.44), but with one difference: for the case \( \kappa = \kappa' \) the function \( H_{\mu\nu}(\mathbf{x}) \) is replaced by the function \( H_{\mu\nu}^0(\mathbf{x}) \) in the term \( l' = l \), where

\[
H_{\mu\nu}^0(\mathbf{x}) = \frac{\partial^2}{\partial x_\mu \partial x_\nu} \left( - \frac{2}{\sqrt{\pi}} \frac{1}{x} \int_0^x ds \exp(-s^2) \right).
\]

(5.52)

This function has the following value at zero argument:

\[
H_{\mu\nu}^0(0) = \frac{4}{3\sqrt{\pi}} \delta_{\mu\nu}.
\]

(5.53)

This replacement in the singular terms clearly does not affect the equations of motion and \( Q_{\mu\nu}(\kappa\kappa'|\mathbf{q}) \) now possesses a unique limit as \( \mathbf{q} \) tends to zero.
VI. FITTING TO EXPERIMENT

This section shows how to project into one dimensional symmetry modes of the dynamical matrix to find algebraic relations between eigenvalues and the model parameters. This method also connects the microscopic force constants in the bond charge model to the macroscopic elastic constants in diamond–structured crystals. By performing these calculations for all of the one dimensional modes at various points in the Brillouin zone, one can greatly accelerate the process of finding a least squares fit to experiment. Alternatively, one could perform a brute force method, solving the full dynamical matrix eigenvalue problem for particular numerical choices of the parameters. The projection method is superior because the process of finding a fit is already computational expensive, relying on simulated annealing or genetic algorithms, so any time saved in calculating the eigenvalues of the dynamical matrix is precious.

A. Energy equilibrium condition

The number of independent model parameters to fit experiment can be reduced by one by deriving an energy equilibrium condition. Picture the crystal being formed by bringing together the constituent particles from infinity, arranged in the specified structure with atomic nearest neighbors with a separation \( r \), and decreasing \( r \) until the value \( r_0 \) corresponding to the minimum value of the potential energy is reached. This minimum represents the balance between the attractive Coulomb interaction, which tends to draw the ions closer together, and the short range repulsive interaction, which tends to separate them. The repulsive energy per primitive cell is given by

\[
E(r)_{\text{repulsive}} = 4\phi_{aa}(r) + 8\phi_{ab}(r) + 12\phi_{bb}(r),
\]

since there are four bonds in a cell. The factor of twelve is derived by noting that there are six pairs of bond charges, but the bending potential is a three body potential between a pair of bond charges relative to an atom. Since there are two atoms referred to by this three body potential, there are \( 6 \times 2 = 12 \) such potentials per primitive cell. The electrostatic energy of interaction per unit cell is given by

\[
E(r)_{\text{electrostatic}} = \frac{1}{2} \sum_{\alpha} \sum_{j\beta \neq 0\alpha} \frac{e_\alpha e_\beta}{|\vec{x}(j\beta) - \vec{x}(0\alpha)|}.
\]
This expression can be written in a simpler form if the charge $e_\alpha$ at the site $\alpha$ is measured in units of the smallest charge in the crystal, $ze$, where $e$ is the magnitude of the fundamental charge. Thus,

$$e_\alpha = ze\xi_\alpha,$$  \hspace{1cm} (6.3)

where $\xi = 2$ for atoms and $\xi = -1$ for bond charges, ensuring that the primitive cell is charge neutral. Since the electrostatic energy is inversely proportional to some unit of length, choose this length to be the nearest neighbor atomic separation $r$, so that

$$E_{\text{electrostatic}} = -\frac{\alpha_M(ze)^2}{r},$$  \hspace{1cm} (6.4)

indicating explicitly that the electrostatic energy is attractive. The coefficient $\alpha_M$ is a dimensionless number, called the *Madelung constant* which is given by

$$\alpha_M = -\frac{1}{2} \sum_\alpha \sum_{j \beta \neq 0 \alpha} \frac{r \xi_\alpha \xi_\beta}{|\mathbf{x}(j \beta) - \mathbf{x}(0 \alpha)|}. \hspace{1cm} (6.5)$$

The total energy per unit cell is therefore given by

$$E(r) = -\frac{\alpha_M(ze)^2}{r} + 4\phi'_{aa}(r) + 8\phi'_{ab}(r) + 12\phi'_{bb}(r).$$  \hspace{1cm} (6.6)

The minimum value of this expression occurs at $r = r_0$ the equilibrium nearest neighbor separation between atoms, which is determined by

$$dE(r_0) = 0 = \frac{\alpha_M(ze)^2}{r_0^2} + 4\phi'_{aa}(r_0) + 8\phi'_{ab}(r_0) + 12\phi'_{bb}(r_0).$$  \hspace{1cm} (6.7)

The particle positions are to be varied while the angles between the bonds are held constant, so that the particles always form a regular tetrahedron. By varying the particle positions in this way, the derivative of the bond bending potential is

$$\phi'_{bb}(r) = \frac{1}{2} A r_0^{-2}(r^2 - r_0^2)r \cos \theta,$$  \hspace{1cm} (6.8)

and thus vanishes at equilibrium. The energy equilibrium condition can thus be written as

$$dE(r_0) = 0 = \frac{\alpha_M(ze)^2}{r_0^2} + 4\phi'_{aa}(r_0) + 8\phi'_{ab}(r_0).$$  \hspace{1cm} (6.9)

Weber reported the equilibrium condition to be

$$dE(r_0) = 0 = \frac{\alpha_M(ze)^2}{r_0^2} + 2\phi'_{aa}(r_0) + 2\phi'_{ab}(\frac{1}{2}r_0) + r_0^2 \phi'_{bb}(\frac{1}{12}r_0^2).$$  \hspace{1cm} (6.10)

The differences in our expressions arises from several differences of convention. First, we have absorbed a factor of $\frac{1}{2}$ into our definition of the Madelung constant, in keeping with Maradudin. Second, he has absorbed a factor of 2 into his definition of $\phi'_{ab}$ and a factor of 12 into $\phi'_{bb}$. Also, he does not explicitly note that at equilibrium $\phi'_{bb} = 0$. 

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B. Acoustic and Optic Phonons at $\Gamma$

Certain points in the Brillouin zone are labeled by symbols indicating that they are points of special symmetry (e.g. $\Gamma, X, L$) or are typical points on lines of special symmetry (e.g. $\Lambda, \Delta, \Sigma$) or on planes of special symmetry (e.g. $A, B$). A representation of the group of the wave vector $G_q$ is labeled by the symbol that denotes the point plus a subscript or superscript specifying a particular irreducible representation of $G_q$. The point $q = 0$ is conventionally denoted as $\Gamma$.

In the adiabatic approximation, the symmetry of phonon modes are dictated by the structure of the atomic lattice, that is, the symmetries due to bond charges are irrelevant. The modes are characterized by the displacements $(b^1, b^2)$ of the two atoms in the primitive cell. The actions of operators such as $(\alpha|0)$ and $(\alpha|\tau)$ in this six–dimensional space are represented by

$$D(\alpha|0) = \begin{bmatrix} D^p(\alpha) & 0 \\ 0 & D^p(\alpha) \end{bmatrix}, \quad D(\alpha|\tau) = \begin{bmatrix} 0 & D^p(\alpha) \\ D^p(\alpha) & 0 \end{bmatrix},$$

where $D^p(\alpha)$ is the ordinary $3 \times 3$ polar vector representation of $\alpha$. This form for $D(\alpha|\tau)$ follows from the fact that $(\alpha|\tau)$ interchanges the two sublattices. The characters are of the form

$$\chi^{\text{atom}}(\alpha|0) = 2\chi^p(\alpha), \quad \chi^{\text{atom}}(\alpha|\tau) = 0.$$

The polar vector representation for the diamond group is $\Gamma_{15}^-$. Table I presents the character table for the factor group $G \backslash T$ of the diamond group $O^7_h$ at $q = 0$. This is simply the table for the point group $O_h$ except for the fact that the group elements are cosets. The last column $\Gamma_{\text{atom}}$ lists the characters obtained from Eq.(6.12) and clearly satisfies

$$\Gamma_{\text{atom}} = \Gamma_{15}^- + \Gamma_{25}^+, \quad (6.13)$$

since the characters of the direct sum of representations are the arithmetic sum of the characters of the representations. Thus the vibrations at $q = 0$ consist of two triply degenerate modes. Since

$$(i|\tau) \begin{bmatrix} b^1 \\ b^2 \end{bmatrix} = \begin{bmatrix} 0 & \bar{1} \\ \bar{1} & 0 \end{bmatrix} \begin{bmatrix} b^1 \\ b^2 \end{bmatrix} = - \begin{bmatrix} b^2 \\ b^1 \end{bmatrix}, \quad (6.14)$$
TABLE I. Character table at \( \Gamma \) for factor group \( O_{h}^{2} \).

<table>
<thead>
<tr>
<th>Class</th>
<th>Element</th>
<th>( \Gamma^{\pm}_{1} )</th>
<th>( \Gamma^{\pm}_{2} )</th>
<th>( \Gamma^{\pm}_{12} )</th>
<th>( \Gamma^{\pm}_{15} )</th>
<th>( \Gamma^{\pm}_{25} )</th>
<th>( \Gamma_{\text{atom}} )</th>
<th>( \Gamma_{\text{full}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E )</td>
<td>( \epsilon )</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>( 3C_{4}^{2} )</td>
<td>( \delta_{2x} )</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>( 6JC_{4} )</td>
<td>( \sigma_{4x} )</td>
<td>( \pm 1 )</td>
<td>( \mp 1 )</td>
<td>0</td>
<td>( \pm 1 )</td>
<td>( \mp 1 )</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>( 6JC_{2} )</td>
<td>( \rho_{yz} )</td>
<td>( \pm 1 )</td>
<td>( \mp 1 )</td>
<td>0</td>
<td>( \mp 1 )</td>
<td>( \pm 1 )</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>( 8C_{3} )</td>
<td>( \delta_{3xyz} )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( J )</td>
<td>( (i</td>
<td>\tau) )</td>
<td>( \pm 1 )</td>
<td>( \pm 1 )</td>
<td>( \pm 2 )</td>
<td>( \pm 3 )</td>
<td>( \pm 3 )</td>
<td>0</td>
</tr>
<tr>
<td>( 3JC_{4}^{2} )</td>
<td>( (\rho_{x}</td>
<td>\tau) )</td>
<td>( \pm 1 )</td>
<td>( \pm 1 )</td>
<td>( \pm 2 )</td>
<td>( \mp 1 )</td>
<td>( \pm 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( 6C_{4} )</td>
<td>( (\delta_{4x}</td>
<td>\tau) )</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>( 6C_{2} )</td>
<td>( (\delta_{2xy}</td>
<td>\tau) )</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>( 8JC_{3} )</td>
<td>( (\sigma_{6xyz}</td>
<td>\tau) )</td>
<td>( \pm 1 )</td>
<td>( \pm 1 )</td>
<td>( \mp 1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

the fact that \( \Gamma^{-}_{15} \) is odd and \( \Gamma^{+}_{25} \) is even under \( (i|\tau) \) implies that the form of these solutions is

\[
\Gamma^{-}_{15} \sim (b, b), \quad \Gamma^{+}_{25} \sim (b, -b). \tag{6.15}
\]

The triple degeneracy consists in the fact that the displacement may have arbitrary orientation. The mode \( \Gamma^{+}_{25} \) is referred to as “optic”, since it involves a relative motion of atoms in the unit cell that, in other materials, might possibly generate an electric moment and produce optical absorption. However, the symmetry of elemental diamond crystals prohibits odd electric moments, as is shown in the section on electric moments. The mode \( \Gamma^{-}_{15} \) is referred to as “acoustic”, since all atoms in the cell have the same motion.

Before taking the adiabatic approximation, the bond charge degrees of freedom must be taken into account. The symmetry of the problem changes in this case. Now the actions of operators such as \( (\alpha|0) \) and \( (\alpha|\tau) \) in this eighteen–dimensional space are represented by forms such as

\[
D(\epsilon|0) = D^{p}(\epsilon)I_{6}, \quad D(i|\tau) = \begin{bmatrix}
D^{p}(i) & 0 \\
0 & D^{p}(i)
\end{bmatrix}, \tag{6.16}
\]

with particles whose positions are left invariant contributing to the main diagonal. These
characters thus take the form
\[ \chi^{\text{full}}(\epsilon|0) = 6\chi^p(\epsilon), \quad \chi^{\text{full}}(i|\tau) = 4\chi^p(i|\tau). \tag{6.17} \]

This calculation is specific to each class of operators. Once the characters are found, the great orthogonality theorem provides a method to decompose the representation into its irreducible parts
\[ k^j = (1/g) \sum_c n_c \chi_c \chi_c^*, \tag{6.18} \]
where \( k^j \) is the component of irreducible representation \( j \), \( g \) is the total number of operators in the group, \( c \) labels the class, and \( n_c \) is the number of operators in a class. The result of this calculation is
\[ \Gamma_{\text{full}} = \Gamma_{2}^- + \Gamma_{12}^- + 3\Gamma_{15}^- + \Gamma_{25}^+ + \Gamma_{25}^- . \tag{6.19} \]
Notice that \( \Gamma_{\text{atom}} \in \Gamma_{\text{full}} \).

C. Vibrations at \( \Delta = (q,0,0) \)

An examination of the complete table of representative elements for the diamond space group (Table 6.12) enables the selection of those that are within \( G_q \). The point group of the wave vector is simply the group \( C_{4v} \), with the axis along the (100) direction.

Since \( \Delta \) is an interior point of the Brillouin zone, use can be made of the ordinary character table of \( C_{4v} \), provided that \( O(S) \) is regarded as the group elements. It is conventional, however, to list the elements as \( (S|\psi(S)) \) and to state the characters of these elements. This leads to Table II with the extra phase factors \( \lambda \). The representations of this point group are labeled \( \Delta_i \) as a reminder that they are associated with the point \( \Delta \) in the Brillouin zone. Also included in the table are some representations of \( \Gamma \) and \( X \) that are not necessarily irreducible with respect to the group at \( \Delta \).

The representations in this group can be made compatible with the representations at the \( \Gamma \) point by using the character table and recalling that the character of the direct sum of representations is the arithmetic sum of the characters of each representation. Thus the compatibility relations are
\[ \text{acoustic:} \quad \Gamma_{15}^- \equiv \Gamma_{15} = \Delta_1 + \Delta_5 , \]
\[ \text{optic:} \quad \Gamma_{25}^+ \equiv \Gamma'_{25} = \Delta'_2 + \Delta_5 , \tag{6.20} \]
TABLE II. Group characters at $\Delta = (q, 0, 0)$. $\lambda = \exp(-iqa/4)$, $t_{xy} = (a/2)(1,1,0)$; at $X, \lambda = -i$.

<table>
<thead>
<tr>
<th>Class</th>
<th>Element</th>
<th>$\Delta_1$</th>
<th>$\Delta_2$</th>
<th>$\Delta'_2$</th>
<th>$\Delta'_1$</th>
<th>$\Delta_5$</th>
<th>$\Gamma_{15}^-$</th>
<th>$\Gamma_{25}^+$</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$X_3$</th>
<th>$X_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$\epsilon$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$3C_4^2$</td>
<td>$\delta_{2x}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-2</td>
<td>-1</td>
<td>-1</td>
<td>2</td>
<td>2</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>$6C_4$</td>
<td>$(\delta_{4x}, \delta^{-1}_{4x}</td>
<td>^\tau)$</td>
<td>$\lambda$</td>
<td>$-\lambda$</td>
<td>$-\lambda$</td>
<td>$\lambda$</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$3JC_4^2$</td>
<td>$(\rho_y, \rho_x</td>
<td>\tau)$</td>
<td>$\lambda$</td>
<td>$\lambda$</td>
<td>$-\lambda$</td>
<td>$-\lambda$</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$6JC_2$</td>
<td>$(\rho_{yz}, \rho_{zy})$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

thus

$$\Delta_{atom} = \Delta_1 + \Delta'_2 + 2\Delta_5.$$

Since $\Delta_5$ is two dimensional, one can anticipate that it corresponds to the transverse vibrations. It appears twice, once for transverse optic (TO) and once for transverse acoustic (TA). Since these modes have the same symmetry, they will interact, and their forms will depend on the force constants. By contrast, $\Delta_1$ and $\Delta'_2$, which will be shown shortly to be longitudinal acoustic (LA) and longitudinal optic (LO), respectively, do not interact, and each appears once in the direction $(q,0,0)$. Thus the form of these modes is uniquely determined by symmetry alone.

D. The longitudinal modes: $\Delta_1 = \text{LA}$, $\Delta'_2 = \text{LO}$

The symmetry vectors can be found by projecting into each irreducible representation. First consider the mode $\Delta_1$. Since $\Delta_1$ is one dimensional, the elaborate machinery of projection operations is not required. This projection can be done simply by requiring that the mode be an eigenvector of each operation $(S|v)$ with the eigenvalue $\chi^{\Delta_1}(S|v)$, or more simply, in accord with Theorem II an eigenvector of $O(S)$ regarded as a point operation $S$ with eigenvalue $\chi^{\Delta_1}[O(S)]$, namely, the value in Table III with $\lambda$ set to unity. Using the notation

$$\begin{bmatrix} b_x^1 & b_x^2 \\ b_y^1 & b_y^2 \\ b_z^1 & b_z^2 \end{bmatrix} = \begin{bmatrix} b_x^1 & b_x^2 \\ -b_y^1 & -b_y^2 \\ -b_z^1 & -b_z^2 \end{bmatrix} = \mathbf{b},$$

(6.22)
it is clear that the requirement that $\delta_{2x}$ have eigenvalue +1 forces $\Delta_1$ to have the longitudinal form

$$b(\Delta_1) = \begin{bmatrix} b^1_x & b^2_x \\ 0 & 0 \\ 0 & 0 \end{bmatrix}.$$  (6.23)

Mode $\Delta'_2$ has the same character for $\delta_{2x}$ and so has the same longitudinal form. Mode $\Delta_5$ has as this character $-1$, causing this mode to be purely transverse.

Since it is the case that

$$O(\rho_y) \begin{bmatrix} b^1_x & b^2_x \\ 0 & 0 \\ 0 & 0 \end{bmatrix} = \begin{bmatrix} b^2_x & b^1_x \\ 0 & 0 \\ 0 & 0 \end{bmatrix},$$  (6.24)

the eigenvalue +1 of associated with $\Delta_1$ makes $b^2_x = b^1_x$, whereas $-1$ of $\Delta'_2$ makes $b^2_x = -b^1_x$.

Thus $\Delta_1$ is called LA and $\Delta'_2$ is called LO, and

$$b(\Delta_1) = \begin{bmatrix} 1 & 1 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}, \quad b(\Delta'_2) = \begin{bmatrix} 1 & 1 \\ 0 & 0 \end{bmatrix},$$  (6.25)

As anticipated, these modes, which are not repeated in the space, have a form that is dictated by symmetry alone. Notice that the LA and LO modes are not coupled by the dynamics. For $\Delta_1$, the $b^1(q)$ and $b^2(q)$ are in phase for all $q$. In terms of the direct space displacements for both $\Delta_1$ and $\Delta'_2$,

$$\frac{u^2}{u^1} = \frac{\exp[iq \cdot (X^2 - X^1)]b^2}{b^1} = \frac{\exp(iq \cdot \tau)b^2}{b^1}. \quad (6.26)$$

At the zone boundary point $X$, $q = (2\pi/a)(1, 0, 0)$ and $\exp(iq \cdot \tau) = i$, so that

$$\frac{u^2}{u^1} = \frac{ib^2}{b^1}. \quad (6.27)$$

Thus the actual displacements of the atoms at $X$ in the two modes are

$$\mathbf{u}(\Delta_1, X) = \begin{bmatrix} 1 & i \\ 0 & 0 \end{bmatrix}, \quad \mathbf{u}(\Delta'_2, X) = \begin{bmatrix} 1 & i \\ 0 & 0 \end{bmatrix},$$  (6.28)

so that at the zone boundary it is difficult to tell which of these modes is optic and which is acoustic. Indeed the compatibility relation

$$X_1 = \Delta_1 + \Delta'_2 \quad (6.29)$$

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obtained from Table II with \( \lambda = -i \) shows that these modes become degenerate at this point.

Before making the adiabatic approximation, the full problem has the symmetry

\[
\Delta_{\text{full}} = \Delta'_1 + \Delta_2 + 3\Delta_1 + 3\Delta'_2 + 5\Delta_5. \tag{6.30}
\]

Notice that the LA and LO modes now each have the identity representation repeated 3 times, so they can each be described by 3 independent constants, according to the same reasoning that was applied to the force constants. The full eigenvector for \( \Delta_1 \) can be found as follows:

A two–fold rotation about the \( x \)–axis causes the interchanges

\[
y \leftarrow \bar{y}, \ z \leftarrow \bar{z}, \ 3 \leftarrow 5, \ 4 \leftarrow 6, \ 5 \leftarrow 3, \ 6 \leftarrow 4, \tag{6.31}
\]

\[
\delta_{2x} \mathbf{b} = \begin{bmatrix}
  b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 & b_x^6 & b_x^1
\end{bmatrix} = \mathbf{b}
\]

\[
\Rightarrow \mathbf{b} = \begin{bmatrix}
  0 & b_3^3 & b_4^4 & b_5^5 & b_6^6 & b_x^6 & b_x^1 & 0
\end{bmatrix}. \tag{6.33}
\]

Reflection through the plane orthogonal to the \( y \)–axis and an interchange of the sublattices causes

\[
y \leftarrow \bar{y}, \ 3 \leftarrow 4, \ 4 \leftarrow 3, \ 5 \leftarrow 6, \ 6 \leftarrow 5, \tag{6.34}
\]

\[
(\rho_y \tau) \mathbf{b} = \begin{bmatrix}
  b_1^2 & b_2^1 & b_3^4 & b_4^3 & b_5^4 & b_6^3 & b_x^4 & b_x^3
\end{bmatrix} = \mathbf{b}
\]

\[
\Rightarrow \mathbf{b} = \begin{bmatrix}
  0 & b_3^3 & b_4^4 & b_5^5 & b_6^6 & b_x^6 & b_x^1 & 0
\end{bmatrix}. \tag{6.36}
\]

A four–fold rotation about the \( x \)–axis and interchanging sublattices causes

\[
y \leftarrow \bar{z}, \ z \leftarrow y, \ 3 \leftarrow 6, \ 4 \leftarrow 3, \ 5 \leftarrow 4, \ 6 \leftarrow 5, \tag{6.37}
\]
\[(\delta_{4x}|\tau)b = \begin{bmatrix} b_x^1 & b_x^1 & b_x^3 & b_x^3 & b_x^3 & b_x^3 \\ 0 & 0 & b_z^3 & -b_z^3 & -b_z^3 & -b_z^3 \\ 0 & 0 & b_y^3 & b_y^3 & b_y^3 & b_y^3 \end{bmatrix} = b \] (6.38)

\[\Rightarrow b = \begin{bmatrix} b_x^1 & b_x^1 & b_x^3 & b_x^3 & b_x^3 & b_x^3 \\ 0 & 0 & b_y^3 & -b_y^3 & -b_y^3 & -b_y^3 \\ 0 & 0 & b_y^3 & b_y^3 & b_y^3 & b_y^3 \end{bmatrix}. \] (6.39)

Thus

\[b(\Delta_1) = \begin{bmatrix} a & a & b & b & b \\ 0 & 0 & c & \bar{c} & c \\ 0 & 0 & c & c & \bar{c} \end{bmatrix}, \] (6.40)

which has three independent parameters, as anticipated.

The symmetry vector for this mode can be used to connect the microscopic force constant parameters to one of the macroscopic elastic constants by making a direct comparison between the equation for sound waves and the long–wavelength limit of the dynamical equations. The sound wave equations take the form

\[M\omega^2 u = D \cdot u, \] (6.41)

where

\[D_{\mu\nu} = \left( \frac{\pi^2}{2} \right) a C_{\mu\nu b} q_a q_b. \] (6.42)

For cubic crystals, the $\Delta_1$, or LA mode along the (100) direction has the soundwave equation element

\[D(\Delta_1) = a C_{11} \frac{\pi^2 q^2}{2}. \] (6.43)

The corresponding expression from the bond charge model can be found by having the dynamical matrix act on the $b(\Delta_1)$ symmetry vector. The bond charge components $b$, and $c$ of the symmetry vector can be solved for by taking the adiabatic approximation so that the bond charge masses are set to zero. The atom component $a$ of the symmetry vector is set to unity. The bond charge model calculation is connected to the soundwave equation by taking the long wavelength limit, retaining only terms up to second order in the wavevector magnitude in the dynamical matrix. The resulting exact algebraic expression for the eigenvalue of the dynamical matrix can be quite monstrous. However, the Coulombic force constant ought to be considerably smaller than any of the other force constants, which
account for quantum mechanical orthogonality in the bound electron wavefunctions. Thus the algebraic expression for the eigenvalue can be simplified by retaining only terms up to first order in the ratio of the Coulombic force constant to any of the other force constants.

For the $\Delta_1$ mode, we find

$$D(\Delta_1) \frac{2}{\pi^2 q^2} = \frac{1}{2} \alpha + \alpha' + 2 \mu + 2.21 \frac{z^2}{\epsilon}, \quad (6.44)$$

which is described by the independent microscopic force constant parameters defined in Eqs. (4.31), (4.33), (4.44). Thus the microscopic force constant parameters are related to the macroscopic elastic constant by

$$a C_{11} = \frac{1}{2} \alpha + \alpha' + 2 \mu + 2.21 \frac{z^2}{\epsilon}. \quad (6.45)$$

Now consider the symmetry vectors in the $\Delta'_2$ (LO) mode. In the limit as $q \to 0$, this mode allows the microscopic force constants to be connected to the $\Gamma$ point longitudinal optic frequency $\omega_{\text{LO}}^2(\Gamma)$.

The character of $\delta_{2x}$ is the same in this mode as it is in $\Delta_1$, so

$$\rightarrow b = \begin{bmatrix} b_1^x & b_2^x & b_3^x & b_4^x & b_5^x & b_6^x \\ 0 & 0 & b_4^y & b_3^y & -b_5^y & -b_6^y \\ 0 & 0 & b_4^z & b_3^z & -b_5^z & -b_6^z \end{bmatrix}. \quad (6.46)$$

Reflection through the plane orthogonal to the $y$–axis and an interchange of the sublattices causes

$$y \leftarrow \bar{y}, 3 \leftarrow 4, 4 \leftarrow 3, 5 \leftarrow 6, 6 \leftarrow 5, \quad (6.47)$$

$$\begin{bmatrix} b_2^x & b_1^x & b_4^x & b_3^x & b_5^x & b_6^x \\ 0 & 0 & -b_4^y & -b_3^y & b_5^y & b_6^y \\ 0 & 0 & b_4^z & b_3^z & -b_5^z & -b_6^z \end{bmatrix} = -b $$

$$\rightarrow b = \begin{bmatrix} b_1^x & -b_2^x & b_3^x & -b_4^x & b_5^x & b_6^x \\ 0 & 0 & b_4^y & b_3^y & -b_5^y & -b_6^y \\ 0 & 0 & b_4^z & b_3^z & -b_5^z & b_6^z \end{bmatrix}. \quad (6.48)$$

A four–fold rotation about the $x$–axis and interchanging sublattices causes

$$y \leftarrow \bar{z}, z \leftarrow y, 3 \leftarrow 6, 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5, \quad (6.49)$$
\[
(\delta_{4x}|\tau)b = \begin{bmatrix}
b_1^x & -b_1^x & b_3^x & -b_3^x & b_2^x \\
0 & 0 & -b_3^z & b_3^z & b_2^z \\
0 & 0 & -b_3^y & b_3^y & b_2^y \\
\end{bmatrix} = -b 
\]  
\[= \Rightarrow b = \begin{bmatrix}
b_1^x & -b_1^x & b_3^x & -b_3^x & b_2^x \\
0 & 0 & -b_3^z & b_3^z & b_2^z \\
0 & 0 & -b_3^y & b_3^y & b_2^y \\
\end{bmatrix} = -b \]  
\[= \Rightarrow b = \begin{bmatrix}
b_1^x & -b_1^x & b_3^x & -b_3^x & b_2^x \\
0 & 0 & -b_3^z & b_3^z & b_2^z \\
0 & 0 & -b_3^y & b_3^y & b_2^y \\
\end{bmatrix} \]  

Thus
\[
b(\Delta_2') = \begin{bmatrix}a & \bar{a} & b & \bar{b} & b \\
0 & 0 & c & \bar{c} & \bar{c} \\
0 & 0 & c & \bar{c} & c \\
\end{bmatrix}, \]  
\[= \Rightarrow b(\Delta_2') = \begin{bmatrix}a & \bar{a} & b & \bar{b} & b \\
0 & 0 & c & \bar{c} & \bar{c} \\
0 & 0 & c & \bar{c} & c \\
\end{bmatrix} \]

which has three independent parameters, again, as anticipated. Following the same procedure as for the previous mode, but this time focusing on the zeroth order terms the depend upon the wavevector magnitude, we find that
\[
D(\Delta_2') = M\omega_{LO}^2(\Gamma) = 4\alpha + 8\alpha'. \]  
\[= \Rightarrow b(\Delta_2') = \begin{bmatrix}a & \bar{a} & b & \bar{b} & b \\
0 & 0 & c & \bar{c} & \bar{c} \\
0 & 0 & c & \bar{c} & c \\
\end{bmatrix} \]

E. \(\Sigma\) modes \((q,q,0)\)

The characters in Table III yields the compatibility relations:
\[
\Gamma_2^- = \Sigma_3, \]
\[
\Gamma_{12}^- = \Sigma_2 + \Sigma_3, \]
\[
\Gamma_{15}^- = \Sigma_1 + \Sigma_3 + \Sigma_4, \]
\[
\Gamma_{25}^- = \Sigma_1 + \Sigma_2 + \Sigma_4, \]
\[
\Gamma_{25}^+ = \Sigma_1 + \Sigma_2 + \Sigma_3. \]

Thus
\[
\Sigma_{\text{atom}} = 2\Sigma_1 + \Sigma_2 + 2\Sigma_3 + \Sigma_4, \]
\[
\Sigma_{\text{full}} = 5\Sigma_1 + 3\Sigma_2 + 6\Sigma_3 + 4\Sigma_4. \]

Once again, \(\Sigma_{\text{atom}}\) indicates which modes will exist in the adiabatic approximation while \(\Sigma_{\text{full}}\) indicates the degeneracy added by the bond charges. As \(\Sigma_4\) is contained in \(\Gamma_{15}^-\) but not \(\Gamma_{25}^+\), this representation must be acoustic, and since it is one dimensional, it will provide a
simple connection between the microscopic force constants and a macroscopic elastic constant. Since $\Sigma_4$ appears four times in $\Sigma_{\text{full}}$, this space will be spanned by four symmetry vectors each described by one parameter. The symmetry vectors are determined as follows:

A reflection about the plane orthogonal to the unit vector in the (110) direction causes

$$x \leftrightarrow y, \ 4 \leftrightarrow 5,$$

$$\rho_{xy} b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \\ b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \\ b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} = -b$$

$$\Rightarrow b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & -b_5^5 & b_6^6 \\ -b_1^1 & -b_2^2 & -b_3^3 & -b_4^4 & b_5^5 & -b_6^6 \\ 0 & 0 & 0 & b_4^4 & -b_4^4 & 0 \end{bmatrix}.\quad (6.59)$$

A reflection about the plane orthogonal to the unit vector in the (001) direction and an interchange of the sublattices causes

$$z \leftarrow \bar{z}, \ 1 \leftrightarrow 2, \ 3 \leftrightarrow 6, \ 4 \leftrightarrow 5,$$

$$\rho_z b = \begin{bmatrix} b_2^2 & b_1^1 & b_6^6 & -b_4^4 & b_5^5 & b_3^3 \\ -b_2^2 & -b_1^1 & -b_6^6 & -b_4^4 & b_5^5 & -b_3^3 \\ 0 & 0 & 0 & b_4^4 & -b_4^4 & 0 \end{bmatrix} = b$$

$$\Rightarrow b = \begin{bmatrix} b_1^1 & b_1^1 & b_3^3 & b_4^4 & b_4^4 & b_3^3 \\ -b_1^1 & -b_1^1 & -b_3^3 & -b_4^4 & b_4^4 & -b_3^3 \\ 0 & 0 & 0 & b_4^4 & -b_4^4 & 0 \end{bmatrix}.\quad (6.62)$$
As this form has four independent constants, all symmetries have been taken into account and so the symmetry vector is

\[ b(\Sigma_4) = \begin{bmatrix} a & a & b & c & c & b \\ \bar{a} & \bar{a} & \bar{b} & \bar{c} & \bar{c} & \bar{b} \\ 0 & 0 & 0 & d & \bar{d} & 0 \end{bmatrix} . \] (6.63)

Following the same procedure as for the other modes, we find that

\[ D(\Sigma_4) \frac{2}{\pi^2 q^2} = \alpha - \beta + 2\alpha' - 2\beta' - 3\mu - 2\nu + \lambda + 30.75 \frac{z^2}{\epsilon} . \] (6.64)

Notice that the atomic displacements are orthogonal to both the direction of propagation (110) and the z–axis (001), so this mode is transverse acoustic. For this mode, the soundwave equation is

\[ D(\Sigma_4) = a(C_{11} - C_{12}) \frac{\pi^2 q^2}{2} , \] (6.65)

but \( a C_{11} \) is related to the microscopic force constants via Eq.(6.45), so it must be the case that

\[ a C_{12} = -\frac{1}{2} \alpha + \beta - \alpha' + 2\beta' + 2\nu - \mu - \lambda - 28.54 \frac{z^2}{\epsilon} . \] (6.66)

F. The modes \( \Lambda = (q,q,q) \) and \( L = (\pi/a)(1,1,1) \)

The compatibility relations are of the form (see Table IV)

\[
\begin{align*}
\Gamma^-_2 &= \Lambda_1, \\
\Gamma^-_{12} &= \Lambda_3, \\
\Gamma^-_{15} &= \Lambda_1 + \Lambda_3, \\
\Gamma^-_{25} &= \Lambda_2 + \Lambda_3, \\
\Gamma^+_2 &= \Lambda_1 + \Lambda_3.
\end{align*}
\] (6.67)

Thus

\[
\begin{align*}
\Lambda_{\text{atom}} &= 2\Lambda_1 + 2\Lambda_3, \\
\Lambda_{\text{full}} &= 5\Lambda_1 + \Lambda_2 + 6\Lambda_3.
\end{align*}
\] (6.68)

The invariance of \( \Lambda_1 \) under the threefold rotation \( \delta_{3xyz} \) guarantees that \( \Lambda_1 \) is longitudinal, with an atomic displacement symmetry vector of the form \((a, a, a; b, b, b)\). The solution of a
TABLE IV. Character table at $\Lambda = (q, q, q)$

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Lambda_1$</th>
<th>$\Lambda_2$</th>
<th>$\Lambda_3$</th>
<th>$\Gamma_{12}^-$</th>
<th>$\Gamma_{15}^-$</th>
<th>$\Gamma_{27}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$\delta_{3yz}$, $\delta_{3xy}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$\rho_{yz}$, $\rho_{xz}$, $\rho_{xy}$</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

A pair of simultaneous equations for $b/a$ determines the LO and LA modes and frequencies, since this mode appears twice in $\Lambda_{atom}$. As $q \to 0$, the LA mode must have $b/a \to +1$, while the LO mode must have $b/a \to -1$. Since $\Lambda_{full}$ contains $\Lambda_1$ five times, but this symmetry admits both acoustic and optic modes, there are at most five independent parameters needed to describe the LA symmetry vector. A threefold rotation about (111) causes

$$x \leftarrow z, \ y \leftarrow x, \ z \leftarrow y, \ 4 \leftarrow 5, \ 5 \leftarrow 6, \ 6 \leftarrow 4,$$

$$\delta_{3yz} b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} = b \quad (6.69)$$

$$\delta_{3xy} b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} = b \quad (6.70)$$

$$\rho_{yz} b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} \quad (6.71)$$

A reflection about the plane orthogonal to (011) causes

$$y \leftrightarrow z, \ 4 \leftrightarrow 6,$$

$$\rho_{yz} b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} = b \quad (6.72)$$

$$\rho_{yz} b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} = b \quad (6.73)$$

$$\rho_{yz} b = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} = \begin{bmatrix} b_1^1 & b_2^2 & b_3^3 & b_4^4 & b_5^5 & b_6^6 \end{bmatrix} \quad (6.74)$$

which has five independent constants before considering the behavior of $b_x^2/b_x^1$ as $q \to 0$. Since $\Lambda_1$ occurs five times in $\Lambda_{full}$, all symmetries have been taken into account.
At the zone boundary, the compatibility relations obtained by comparing Table IV with Table V are

\[ L_1^+ = \Lambda_1, \quad L_2^- = \Lambda_1, \quad L_1^- = \Lambda_2, \quad L_2^+ = \Lambda_2, \quad L_3^+ = \Lambda_3, \quad L_3^- = \Lambda_3, \]

so that one longitudinal mode approaches \( L_1^+ \) and the other \( L_2^- \). Whichever has the lower frequency will be called LA. Although LA is odd at \( q = 0 \), it is not necessarily odd at the zone boundary. The representations at the zone boundary are distinguished from those in the interior by being even or odd under inversion.

**TABLE V. Character table at \( L = (\pi/a)(1, 1, 1) \)**

<table>
<thead>
<tr>
<th>Element</th>
<th>( L_1^\pm )</th>
<th>( L_2^\pm )</th>
<th>( L_3^\pm )</th>
<th>( \Gamma_2^- )</th>
<th>( \Gamma_{12}^- )</th>
<th>( \Gamma_{15}^- )</th>
<th>( \Gamma_{25}^\pm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon )</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>( \delta_{3xyz}, \delta_{3xyz}^{-1} )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( (\delta_{3y}, \delta_{2x}, \delta_{2y}</td>
<td>\tau) )</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>( (i</td>
<td>\tau)(\alpha</td>
<td>\tau) )</td>
<td>( \pm \chi(\alpha</td>
<td>\tau) )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Consider the symmetry vector in \( L_2^- \). After taking account of \( \delta_{3xyz} \), which has the same character in \( \Lambda_1, L_1^\pm, L_2^\pm \), a twofold rotation about the vector \((0 \bar{1} 1)\) and interchanging the sublattices causes

\[ x \leftarrow \bar{x}, \quad y \leftarrow \bar{z}, \quad z \leftarrow \bar{y}, \quad 1 \Rightarrow 2, \quad 4 \Rightarrow 6, \]

\[ (\delta_{2y}|\tau)b = \begin{bmatrix} -b_x^2 & -b_x^1 & -b_x^2 & -b_x^4 & -b_x^1 & -b_x^4 \\ -b_x^2 & -b_x^1 & -b_x^2 & -b_y^4 & -b_x^4 & -b_x^1 \\ -b_x^2 & -b_x^1 & -b_x^2 & -b_y^4 & -b_x^4 & -b_x^1 \end{bmatrix} = -b \]

\[ \Rightarrow b = \begin{bmatrix} b_x^1 & b_x^1 & b_x^3 & b_x^4 & b_x^1 & b_x^4 \\ b_x^1 & b_x^1 & b_x^3 & b_y^4 & b_x^4 & b_x^1 \\ b_x^1 & b_x^1 & b_x^3 & b_y^4 & b_x^4 & b_x^1 \end{bmatrix}. \]

So far, this symmetry vector is in \( L_2^- + L_2^+ \), which has four independent parameters. The other symmetry operators provide no additional information that would separate out \( L_2^- \) and \( L_2^+ \). To accomplish this, consider the mode \( L_1^\pm \).
Since \( \chi(\delta_{2y_2}|\tau) = +1 \) in \( L_1^\pm \),

\[
\mathbf{b}(L_1^- + L_1^+) = \begin{bmatrix}
a & \bar{a} & 0 & b & 0 & \bar{b} \\
\bar{a} & a & 0 & 0 & \bar{b} & b \\
a & \bar{a} & 0 & \bar{b} & b & 0
\end{bmatrix}.
\] (6.79)

\( L_1^- \) and \( L_1^+ \) are distinguished by the characters of the inversion,

\[
(i|\tau)\mathbf{b}(L_1^\pm) = \begin{bmatrix}
a & \bar{a} & 0 & \bar{b} & 0 & b \\
a & \bar{a} & 0 & 0 & b & \bar{b} \\
a & \bar{a} & 0 & b & \bar{b} & 0
\end{bmatrix} = \pm \mathbf{b}(L_1^\pm).
\] (6.80)

Thus

\[
\mathbf{b}(L_1^+ = \Lambda_1) = \begin{bmatrix}
a & \bar{a} & 0 & 0 & 0 & 0 \\
\bar{a} & a & 0 & 0 & 0 & 0 \\
a & \bar{a} & 0 & 0 & 0 & 0
\end{bmatrix},
\] (6.81)

and

\[
\mathbf{b}(L_1^- = \Lambda_2) = \begin{bmatrix}
0 & 0 & 0 & \bar{b} & 0 & b \\
0 & 0 & 0 & b & \bar{b} & 0 \\
0 & 0 & 0 & b & \bar{b} & 0
\end{bmatrix}.
\] (6.82)

Now that the single \( \Lambda_2 \) in \( \Lambda_{\text{full}} \) has been identified as being compatible with \( L_1^- \), it must be the case that the four symmetry vectors found in the space \( L_2^- + L_2^+ \) are in fact wholly in the space \( L_2^- \), which is compatible with \( \Lambda_1 \). Thus the LA symmetry vector is

\[
\mathbf{b}(\Lambda_1 = L_2^-) = \begin{bmatrix}
a & a & b & c & d & c \\
a & a & b & d & c & c \\
a & a & b & c & c & d
\end{bmatrix},
\] (6.83)

with four independent parameters.

For this mode the soundwave equation has

\[
\mathbf{D}(\Lambda_1 = L_2^-) = a(C_{11} + 2C_{12} + 4C_{44}) \frac{\pi^2 q^2}{2},
\] (6.84)

but \( aC_{11} \) and \( aC_{12} \) are related to the microscopic force constants via Eq.(6.45) and (6.66), respectively, so

\[
aC_{44} = \frac{1}{2}\alpha + \alpha' + \mu + \lambda - 1.11z^2/\epsilon - (\frac{1}{2}\beta + \beta' - 17.65z^2/\epsilon)^2 / (\frac{1}{2}\alpha + \alpha') \cdot
\] (6.85)
Collecting all of the relations between the model parameters and the experimentally observable quantities, along with the statement of energy equilibrium, we can fit the bond charge model to experiment using the relations

\[
dE(r_0) = 0 = \frac{\alpha M (ze)^2}{r_0^2} + 2\phi'_{aa}(r_0) + 2\phi'_{ab}(\frac{1}{2}r_0) + r_0\phi'_{bb}(-\frac{1}{12}r_0^2),
\]

\[
M\omega^2_{LO}(\Gamma) = 4\alpha + 8\alpha',
\]

\[
a C_{11} = \frac{1}{2}\alpha + \alpha' + 2\mu + 2.21z^2/\epsilon, \quad \text{(6.86)}
\]

\[
a C_{12} = -\frac{1}{2}\alpha + \beta - \alpha' + 2\beta' + 2\nu - \mu - \lambda - 28.54\frac{z^2}{\epsilon},
\]

\[
a C_{44} = \frac{1}{2}\alpha + \alpha' + \mu + \lambda - 1.11z^2/\epsilon - \left(\frac{1}{2}\beta + \beta' - 17.65z^2/\epsilon\right)^2 / \left(\frac{1}{2}\alpha + \alpha'\right).
\]

**VII. PHONON DISPERSION IN DIAMOND**

Once the model has been fit using the relations in (6.86), the dispersion relation can now be calculated at points in the irreducible prism of the Brillouin zone, as shown in Fig. 7, which shows the dispersion in diamond along lines of high symmetry. The points of high symmetry are labeled in the context of the entire first Brillouin zone of Fig. 8. For each branch, a series of constant frequency surfaces is drawn in the full first Brillouin zone in Figs. 9 through 14. At any point on each of these surfaces, the position vector is parallel to the phase velocity, while the vector normal to the surface is parallel to the group velocity, which points in the direction of energy propagation.

Notice in Figs. 13 and 14 that the phase and group velocity vectors are rarely parallel for the transverse acoustic branches. These constant frequency surfaces can be used to understand and predict the phenomenon of phonon–focusing \[18-20\].
FIG. 7. Phonon dispersion in diamond along lines of symmetry is shown. The points of high symmetry are marked by letters and correspond to the points labeled in Fig. 8. Data are from Ref. [21], dashed curves are drawn from density functional calculations, and solid curves are drawn from the bond charge model.

FIG. 8. First Brillouin zone of a face-centered cubic lattice is shown.
FIG. 9. Constant frequency surface in the first Brillouin zone of the longitudinal optic branch in diamond.

FIG. 10. Constant frequency surface in the first Brillouin zone of the highest transverse optic branch in diamond.

FIG. 11. Constant frequency surface in the first Brillouin zone of the lowest transverse optic branch in diamond.
FIG. 12. Constant frequency surface in the first Brillouin zone of the longitudinal acoustic branch in diamond.

FIG. 13. Constant frequency surfaces in the first Brillouin zone of the highest transverse acoustic branch in diamond.

FIG. 14. Constant frequency surface in the first Brillouin zone of the lowest transverse acoustic branch in diamond.
FIG. 15. The surfaces of constant frequency lend insight into phonon focusing are shown. Panel (a) shows the coordinate basis for the surfaces of constant frequency of (b) the slow and (d) fast transverse acoustic modes of diamond. Panel (c) shows the measured focusing pattern along the (100) direction in diamond as reported in [19]. The brightest shape in (c) is due to the slow transverse modes of panel (b) and the fainter shape at an angle of $\pi/4$ to the bright shape is due to the fast transverse modes of panel (d).


