Phonons

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1 Introduction

blah blah blah

2 Examples

2.1 Linear chain

A linear (one-dimension) harmonic chain is shown in top row of fig. 1. The lattice sites are labeled by numbers i, $i+1$, etc. The mass of each atom is m. Call the positions $x_i = a \times i + u_i$ with a the lattice constant. Each atom is connected to its nearest neighbor by a harmonic spring with spring constant K. The potential energy of the system is

$$\begin{aligned} U(\{x\}) = U &= \frac{K}{2}\sum_i \left[x_i - x_{i+1} - a\right]^2 \\ &= \frac{K}{2}\sum_i \left[(ai + u_i) - (ai + a + u_{i+1}) - a\right]^2 \\ &= \frac{K}{2}\sum_i \left[u_i - u_{i+1}\right]^2. \end{aligned} \tag{1}$$

Call the force on any atom $F_j = -\partial U/\partial u_j$. It is

$$\begin{aligned} F_j = -\frac{K}{2}\frac{\partial}{\partial u_j}\left[(u_j - u_{j+1})^2 + (u_{j-1} - u_j)^2\right] &= -K\left[(u_j - u_{j+1}) - (u_{j-1} - u_j)\right] \\ &= -K[2u_j - u_{j+1} - u_{j-1}]. \end{aligned} \tag{2}$$

Newtons equations are $ma_i = F_i$ with a_i the acceleration of the atom at site i.

$$ma_i = m\ddot{u}_i = -K[2u_i - u_{i+1} - u_{i-1}]. \tag{3}$$

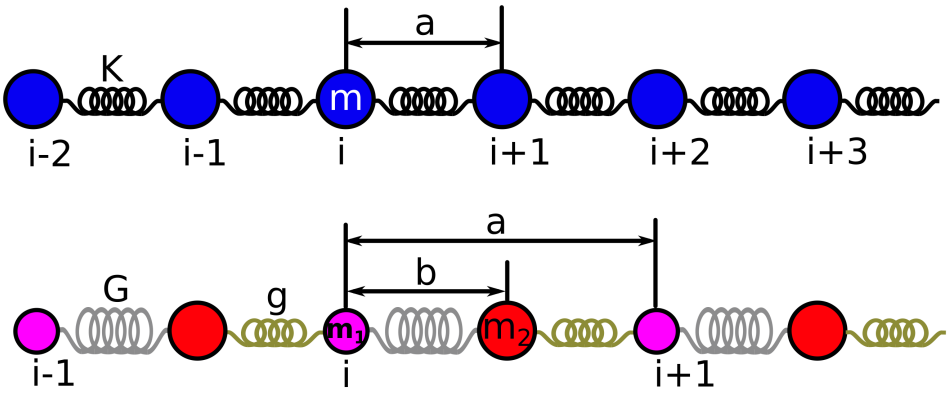

Fig. 1:

The goal is to solve this equation for for all $u_i(t)$. If we can do this, we know the trajectories of the atoms in the system and can, in principle, calculate their velocities, energies, etc. and all other physical observables of the system. So the goal is to solve these equations. However, the derivatives on the lhs make this hard to work with. Moreover, atoms at different sites are coupled which makes the problem harder. We can overcome both issues by Fourier transforming in both space and time. We assume that the linear chain forms a Born-Von Kármán (BvK) ring with N sites in it. The Fourier transform and its inverse are

$$\begin{aligned} u_k(\omega) &= \frac{1}{\sqrt{2\pi N}} \sum_n \int dt u_n(t) \exp(-iqna + i\omega t) \\ u_n(t) &= \frac{1}{\sqrt{2\pi N}} \sum_q \int d\omega u_q(\omega) \exp(iqna - i\omega t). \end{aligned} \tag{4}$$

We want to transform Newton's equations to Fourier space where it will be easier to solve for $u_q(\omega)$. We can then invert the Fourier transform and determine $u_n(t)$ again. Newton's equations 3 become

$$\begin{aligned} m\omega^2 u_q(\omega) = K[2 - \exp(iq) - \exp(-iq)]u_q(\omega) = 2K(1 - \cos(q))u_q(\omega) \\ = 4K \sin^2(qa/2) \end{aligned} \tag{5}$$

Different wave-vectors q are decoupled and their equations of motion are identical so we have made a lot of progress. Note that for every q, there is a different $\omega \equiv \omega(q)$ that solves it. What remains is to determine the wave-vector dependence of $\omega(q)$: we call this the *dispersion*.

$$\omega(q) = 2\sqrt{\frac{K}{m}} \left|\sin\left(\frac{qa}{2}\right)\right| \tag{6}$$

Note that in the limit $qa \to 0$, $\omega(q) = a\sqrt{K/m}|q|$, i.e. the dispersion is linear with speed $\partial\omega/\partial q \equiv c = a\sqrt{K/m}$. In the opposite limit $qa \to \pm\pi$, $\omega(q) \to 2\sqrt{K/M}$ with speed $\partial\omega/\partial q = 0$.

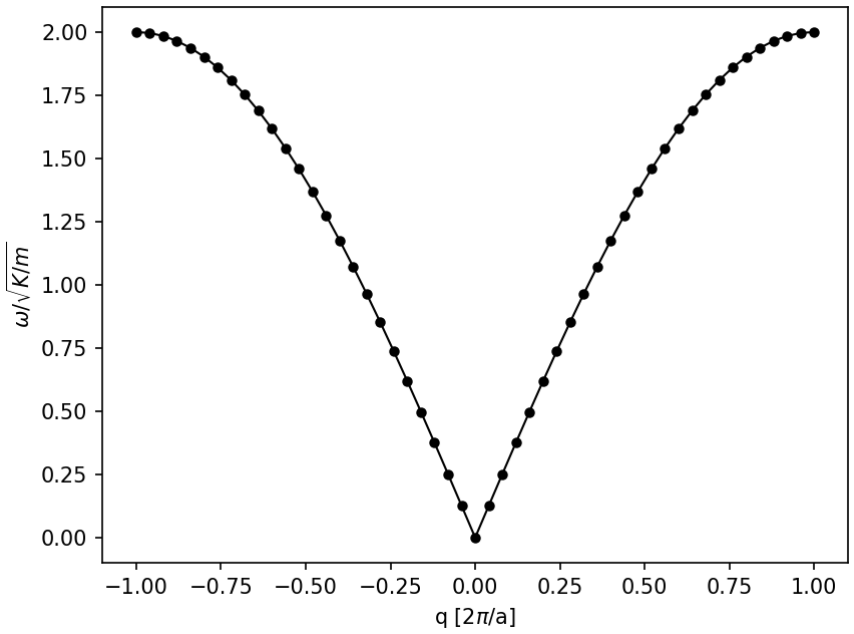

Fig. 2: Caption

Explicitly work out the real space displacements and plot them near the zone center and at the zone boundary.

2.2 Diatomic chain

If there are multiple atoms with different masses and multiple bonds with different lengths and stiffness, the equations become more complicated. The bottom row in fig. 1 shows a diatomic chain of different masses m_1 and m_2 coupled by different springs with spring constants G and g. The potential energy is

$$U = \frac{1}{2}\sum_i \left[G(u_{i,1} - u_{i,2})^2 + g(u_{i,2} - u_{i+1,1})^2\right]. \tag{7}$$

We also allow for different bond lengths though it won't matter in what follows. The force on atom 1 in unitcell j is

$$\begin{aligned} F_{j,1} = -\frac{1}{2}\frac{\partial}{\partial u_{j,1}}\left[G(u_{j,1} - u_{j,2})^2 + g(u_{j-1,2} - u_{j,1})^2\right] &= -\left[G(u_{j,1} - u_{j,2}) - g(u_{j-1,2} - u_{j,1})\right] \\ &= -[(G+g)u_{j,1} - Gu_{j,2} - gu_{j-1,2}] \end{aligned} \tag{8}$$

and for atom 2 in cell j

$$F_{j,2} = -\frac{1}{2}\frac{\partial}{\partial u_{j,2}}\left[G(u_{j,1}-u_{j,2})^2 + g(u_{j,2}-u_{j+1,1})^2\right] = -\left[-G(u_{j,1}-u_{j,2}) + g(u_{j,2}-u_{j+1,1})\right]$$
$$= -[(G+g)u_{j,2} - Gu_{j,1} - gu_{j+1,1}]. \tag{9}$$

The equations of motion are

$$\begin{aligned} m_1\ddot{u}_{i,1} &= -[(G+g)u_{j,1} - Gu_{j,2} - gu_{j-1,2}] \\ m_2\ddot{u}_{i,2} &= -[(G+g)u_{j,2} - Gu_{j,1} - gu_{j+1,1}] \end{aligned} \tag{10}$$

which in Fourier space become

$$\begin{aligned} m_1\omega^2 u_{q,1} &= [(G+g)u_{q,1} - Gu_{q,2} - gu_{q,2}\exp(-iqa)] \\ m_2\omega^2 u_{q,2} &= [(G+g)u_{q,2} - Gu_{q,1} - gu_{q,1}\exp(iqa)] \end{aligned} \tag{11}$$

We've decoupled the equations for neighboring unitcells into independent equations, one for each q. Still, atoms within the unitcell are coupled. The solutions of eqs. 11 are not independent and will involve relative displacements of each atom in the unitcell. There are two equations above, so there will be two different sets of $u_{q,1}$ and $u_{q,2}$, one set that that solves each equation. The goal now is to find the sets of relative displacements that satisfy these equations. To start, we write the coupled set of equations in matrix form:

$$\omega_q^2 \begin{pmatrix} m_1 & 0 \\ 0 & m_2 \end{pmatrix} \begin{pmatrix} u_{q,1} \\ u_{q,2} \end{pmatrix} = \begin{pmatrix} (G+g) & -(G+g\exp(-iqa)) \\ -(G+g\exp(iqa)) & (G+g) \end{pmatrix} \begin{pmatrix} u_{q,1} \\ u_{q,2} \end{pmatrix} \tag{12}$$

We call the matrix of force constants on the right hand side the "force constant matrix" $\hat{G}_q$. Now introduce the notation $u_{q,i}(\omega) = \epsilon_{q,i}(\omega)/\sqrt{m_i}$ with $\epsilon_{q,i}(\omega)$ the (generally complex) frequency dependent amplitude of displacement of the i^{th} atom in the unitcell. The appearance of $\sqrt{m_i}$ in the denominator will become clear soon. Plug this new equations into eq. 12 above:

$$\omega_q^2 \begin{pmatrix} m_1^{1/2} & 0 \\ 0 & m_2^{1/2} \end{pmatrix} \begin{pmatrix} \epsilon_{q,1} \\ \epsilon_{q,2} \end{pmatrix} = \hat{G}_q \begin{pmatrix} m_1^{-1/2} & 0 \\ 0 & m_2^{-1/2} \end{pmatrix} \begin{pmatrix} \epsilon_{q,1} \\ \epsilon_{q,2} \end{pmatrix} \tag{13}$$

This is like an "eigenvalue problem" that we solve by diagonalization but differs by the matrix on the lhs: we call that matrix $\hat{M}$. Also define the vector $\boldsymbol{\epsilon}_q = (\epsilon_{q,1}, \epsilon_{q,2})^T$. We call the equation above a "generalized eigenvalue problem." We solve by first inverting $\hat{M}$, multiplying the equation by $\hat{M}^{-1}$, and then diagonalizing the resulting eigenvalue problem. Since $\hat{M}$ is diagonal already, it's inverse is simply given by

$$\hat{M}^{-1} = \begin{pmatrix} m_1^{-1/2} & 0 \\ 0 & m_2^{-1/2} \end{pmatrix} \tag{14}$$

which we note is already present on the rhs. Then

$$\begin{gathered}\hat{M}^{-1}\hat{G}_q\hat{M}^{-1} = \\ \begin{pmatrix} m_1^{-1/2} & 0 \\ 0 & m_2^{-1/2} \end{pmatrix} \begin{pmatrix} (G+g) & -(G+g\exp(-iqa)) \\ -(G+g\exp(iqa)) & (G+g) \end{pmatrix} \begin{pmatrix} m_1^{-1/2} & 0 \\ 0 & m_2^{-1/2} \end{pmatrix} = \\ \begin{pmatrix} \dfrac{G+g}{m_1} & -\dfrac{G+g\exp(-iqa)}{\sqrt{m_1 m_2}} \\ -\dfrac{G+g\exp(iqa)}{\sqrt{m_1 m_2}} & \dfrac{G+g}{m_2} \end{pmatrix} \equiv \hat{D}_q\end{gathered} \tag{15}$$

The matrix $\hat{D}_q$ is called the "dynamical matrix". It has elements $D_q^{ij} = \Phi_q^{ij}/\sqrt{m_i m_j}$ where Φ_q^{ij} is defined by the matrix elements above. Note that $D_q^{21} = \bar{D}_q^{12}$ where $\bar{\cdot}$ represents complex conjugation. It's clear that $\hat{D}_q^{ij}$ is Hermitian. It can be shown that the eigenvalues of a Hermitian matrix are real and that the eigenvectors are orthonormal[1]. Then

$$\omega_q^2 \boldsymbol{\epsilon}_q = \hat{D}_q \boldsymbol{\epsilon}_q \tag{16}$$

is clearly an eigenvalue problem. There are two distinct vectors $\boldsymbol{\epsilon}_{q\nu}$ and eigenvalues $\omega_{q\nu}^2$ that solve eq. 16. More generally, if the dynamical matrix is d dimensional, there are d solutions. For $d > 2$, solving the equation is hard by hand and instead it is usually done numerically on a computer. For $d = 2$, we can diagonalize by hand and get an analytical solution. For now, we drop the q and ν dependence for convenience. The eigenvalues $\epsilon \equiv \omega^2$ are given as the roots of the equation

$$\det \begin{pmatrix} D_{11} - \epsilon & D_{12} \\ \bar{D}_{12} & D_{22} - \epsilon \end{pmatrix} = (D_{11} - \epsilon)(D_{22} - \epsilon) - |D_{12}|^2 = 0. \tag{17}$$

We find

$$\begin{aligned} \omega_{q\pm}^2 &= \frac{1}{2}(D_{11} + D_{22}) \pm \frac{1}{2}\sqrt{(D_{11} + D_{22})^2 - 4(D_{11}D_{22} - |D_{12}|^2)} \\ &= \frac{1}{2}(D_{11} + D_{22}) \pm \frac{1}{2}\sqrt{(D_{11} - D_{22})^2 + 4|D_{12}|^2)} \\ &= \frac{G+g}{2}\left[\frac{1}{m_1} + \frac{1}{m_2}\right] \pm \sqrt{\left(\frac{G+g}{2}\right)^2 \left[\frac{1}{m_1} - \frac{1}{m_2}\right]^2 + \frac{G^2 + g^2 + 2Gg\cos(qa)}{m_1 m_2}} \\ &= \frac{(G+g)(m_1+m_2)}{2m_1 m_2} \pm \frac{\sqrt{(G+g)^2(m_1+m_2)^2 - 16Ggm_1m_2\sin^2(qa/2)}}{2m_1 m_2} \end{aligned} \tag{18}$$

[1] We are free to pick an arbitrary scale factor for each row in eq. 11. I.e. we are free to arbitrarily normalize the eigenvectors of $\hat{D}_q$. Doing so is convenient later.

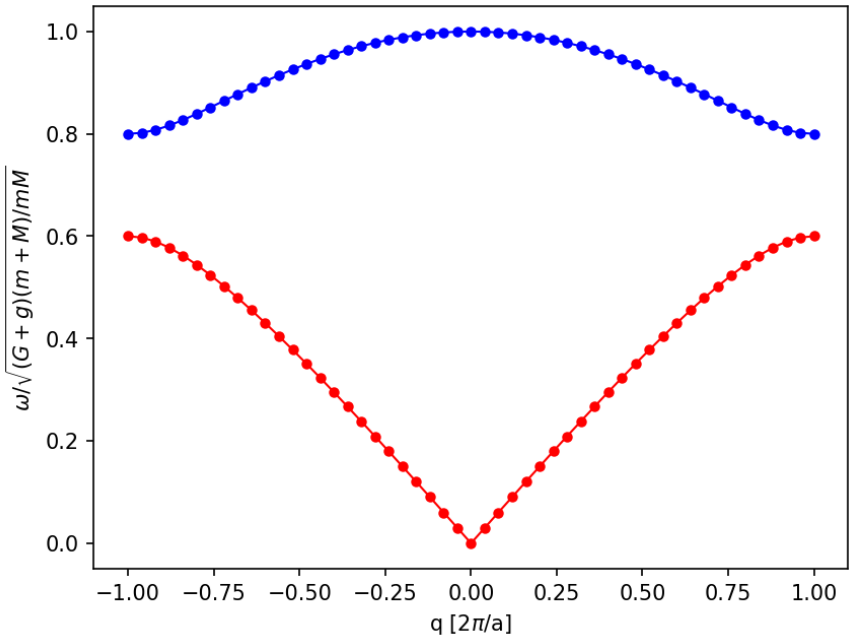

Fig. 3: Caption

where the two eigenvalues are labeled by the $\pm$. In the limit $qa \to 0$, $\sin^2(qa/2) \approx (qa/2)^2$ and

$$\begin{aligned}\omega_\pm^2 &= \frac{(G+g)(m_1+m_2)}{2m_1m_2} \pm \frac{\sqrt{(G+g)^2(m_1+m_2)^2 - 4Ggm_1m_2(qa)^2}}{2m_1m_2} \\ &\approx \frac{(G+g)(m_1+m_2)}{2m_1m_2} \pm \frac{(G+g)(m_1+m_2)}{2m_1m_2}\left(1 - \frac{2Ggm_1m_2(qa)^2}{(G+g)^2(m_1+m_2)^2}\right)\end{aligned} \tag{19}$$

which has two solutions,

$$\begin{aligned}\omega_+^2 &= \frac{(G+g)(m_1+m_2)}{m_1m_2} - O[(qa)^2] \\ \omega_-^2 &= \frac{Ggm_1m_2(qa)^2}{(G+g)(m_1+m_2)} \\ \omega_+ &= \sqrt{\frac{(G+g)(m_1+m_2)}{m_1m_2}} \\ \omega_- &= a\sqrt{\frac{Gg}{(G+g)(m_1+m_2)}}|q|\end{aligned} \tag{20}$$

We can calculate the eigenvectors $\boldsymbol{\epsilon}_{q\pm}$ by substituting eq. 18 into eq. 16.

$$\begin{aligned}\omega_{q\nu}^2 \epsilon_{q\nu,1} &= D_{11}\epsilon_{q\nu,1} + D_{12}\epsilon_{q\nu,2} \\ \omega_{q\nu}^2 \epsilon_{q\nu,2} &= \bar{D}_{12}\epsilon_{q\nu,1} + D_{22}\epsilon_{q\nu,2}\end{aligned} \tag{21}$$

to find

$$\frac{\epsilon_{q\nu,1}}{\epsilon_{q\nu,2}} = \frac{D_{12}}{\omega_{q\nu}^2 - D_{11}} \tag{22}$$

Hermiticity of the dynamical matrix means we only need to solve one of these equations. It's clear that we can't fix an overall scale in $\boldsymbol{\epsilon}'_{q\nu} = c(\epsilon_{q\nu,1}, \epsilon_{q\nu,2})^T = (\epsilon'_{q\nu,1}, \epsilon'_{q\nu,2})^T$ since $\epsilon'_{q\nu,1}/\epsilon'_{q\nu,2} = \epsilon_{q\nu,1}/\epsilon_{q\nu,2}$ where the overall scale has disappeared. To fix this ambiguity, we pick a such that each eigenvector is normalized: $\boldsymbol{\epsilon}^\dagger_{q\nu} \cdot \boldsymbol{\epsilon}_{q\nu} = 1$.

$$\begin{aligned} \boldsymbol{\epsilon}^\dagger_{q\nu} \cdot \boldsymbol{\epsilon}_{q\nu} = 1 &= |c|^2(|\epsilon_{q\nu,1}|^2 + |\epsilon_{q\nu,2}|^2) \\ c &= \frac{1}{\sqrt{|\epsilon_{q\nu,1}|^2 + |\epsilon_{q\nu,2}|^2}} \end{aligned} \tag{23}$$

Moreover, the eigenvectors of are orthogonal:

$$\begin{aligned} \boldsymbol{\epsilon}^\dagger_{q+} \cdot \boldsymbol{\epsilon}_{q-} &= \bar{\epsilon}_{q+,1}\epsilon_{q-,1} + \bar{\epsilon}_{q+,2}\epsilon_{q-,2} \\ = \bar{\epsilon}_{q+,2}\epsilon_{q-,2}&\left(\frac{|D_{12}|^2}{\omega_{q-}^2\omega_{q+}^2 - D_{11}(\omega_{q+}^2 + \omega_{q-}^2) + D_{11}^2} + 1\right) \\ = \bar{\epsilon}_{q+,2}\epsilon_{q-,2}&\left(\frac{|D_{12}|^2}{-|D_{12}|^2} + 1\right) = 0 \end{aligned} \tag{24}$$

Now that we have the eigenvectors of the dynamical matrix, we can recover the atomic displacements: $\epsilon_{q,\alpha} = \sum_\nu \boldsymbol{\epsilon}_{q\nu,\alpha} \cdot \hat{e}_\alpha = \sum_\nu \epsilon_{q\nu,\alpha}$. Then

$$\begin{aligned} u_{n,\alpha}(t) &= \frac{1}{\sqrt{m_\alpha N}} \sum_{q\nu} A_{q\nu,\alpha}\epsilon_{q\nu,\alpha} \exp(iqna - i\omega_{q\nu}t) \\ &= \frac{1}{\sqrt{m_\alpha N}} \sum_{q\nu} Q_{q\nu,\alpha}(t) \exp(iqna) \end{aligned} \tag{25}$$

with

$$Q_{q\nu,\alpha}(t) = A_{q\nu}\epsilon_{q\nu,\alpha} \exp(-i\omega_{q\nu}t) \tag{26}$$

This quantity $Q_{q\nu,\alpha}(t)$ is called the "normal mode coordinate". Each atom participates in a wave-like displacement of the crystal; the wave-like displacements are the "phonons" or normal modes (normal meaning orthogonal). They are linearly independent and complete so we can express any arbitrary displacement (around equilibrium) of all of the atoms as a superposition over the phonon modes. There are md branches or "modes" (m is the number of atoms in the primitive unitcell, d the spatial dimension) at every q point; each branch is linearly independent of all others at every q point.

Basically we are saying that the atomic displacement can be expressed as Fourier series over the different modes. $\epsilon_{q\nu,\alpha}$ is the α^{th} component of a periodic wave-like displacement of the atoms; i.e. it is the *relative* amplitude of displacement of the α^{th} atom relative to all of the others. The coefficient $A_{q\nu}$ is the amplitude of the ν^{th} mode with wavevector q. The frequency of the oscillation is given by $\omega_{q\nu}$. Note that since $u_{n,\alpha}(t)$ is generally real, it is required that $\bar{Q}_{q\nu,\alpha}(t) = Q_{-q\nu,\alpha}(t)$.

Explicitly work out the real space displacements and plot them near the zone center and at the zone boundary. Important to plot both branches to distinguish between acoustic and optical modes.

2.3 General formulation of lattice dynamics

Just like above, we are going to specialize to crystals. In a crystal, the atoms form an ordered lattice of cells that are "periodic" in space. At low enough temperature but finite, the atoms only move a little bit and oscillate around their average positions. Then it is reasonable to describe the coordinates of the atoms as small displacements around the equilibrium geometry. We start by defining our lattice vectors $\boldsymbol{R}_i$ where i is an integer labeling each unitcell. Inside each unitcell sits m atoms that we label by indices α. We call the equilibrium position of the α^{th} atom in the i^{th} unitcell $\boldsymbol{r}_{i\alpha}^{(0)} = \boldsymbol{R}_i + \boldsymbol{\tau}_\alpha$. The time dependence is given by the instantaneous displacement $\boldsymbol{u}_{i\alpha}(t)$. Then $\boldsymbol{r}_{i\alpha}(t) = \boldsymbol{R}_i + \boldsymbol{\tau}_\alpha + \boldsymbol{u}_{i\alpha}(t)$. We assume there are N unitcells in the crystal and that there are periodic boundary conditions in all directions.

The potential energy of the system of atoms is $U(\boldsymbol{r})$. The special cases of the harmonic chains above was that they were second order in position; in general, the potential energy $U(\boldsymbol{r})$ is not a quadratic function of the positions. A fairly reasonable general expression is a potential energy that only depends on *pair* interactions between the atoms. This could be e.g. the Coulomb interaction. Let the pair potential be $\phi_{\alpha\beta}(\boldsymbol{r}_{i\alpha} - \boldsymbol{r}_{j\beta})$. The potential energy is then

$$U(\boldsymbol{r}(t)) = \frac{1}{2}\sum_{ij\alpha\beta} \phi_{\alpha\beta}(\boldsymbol{r}_{i\alpha}(t) - \boldsymbol{r}_{j\beta}(t)) = \frac{1}{2}\sum_{ij\alpha\beta} \phi_{\alpha\beta}\left([\boldsymbol{r}_{i\alpha}^{(0)} - \boldsymbol{r}_{j\beta}^{(0)}] + [\boldsymbol{u}_{i\alpha}(t) - \boldsymbol{u}_{j\beta}(t)]\right). \quad (27)$$

The factor of $1/2$ is to account for "double counting" the pair interactions: once for $(i\alpha, j\beta)$ and once for $(j\beta, i\alpha)$. This is a reasonable model that accounts for most interactions in nature, e.g. the Coulomb interaction. We are still stuck because, for most U, the equations of motion are intractable. We make progress by noting that at low enough temperature where the displacements are small, we can Taylor expand the potential energy in the displacements and drop high order terms. We have

$$U(\boldsymbol{r}) = U_0 + \sum_{i\alpha} \boldsymbol{u}_{i\alpha}^T \cdot \left(\frac{\partial U(\boldsymbol{r})}{\partial \boldsymbol{u}_{i\alpha}}\right)\Bigg|_{\boldsymbol{u}=0} + \frac{1}{2}\sum_{ij\alpha\beta} \boldsymbol{u}_{i\alpha}^T \cdot \left(\frac{\partial^2 U(\boldsymbol{r})}{\partial \boldsymbol{u}_{i\alpha}\partial \boldsymbol{u}_{j\beta}}\right)\Bigg|_{\boldsymbol{u}=0} \cdot \boldsymbol{u}_{j\beta} + \cdots \quad (28)$$

The 0^{th} order term $U_0 = 1/2\sum_{ij\alpha\beta}\phi_{\alpha\beta}(\boldsymbol{r}_{i\alpha}^{(0)} - \boldsymbol{r}_{j\beta}^{(0)})$ is just the electrostatic potential energy in the crystal's equilibrium geometry. It is a constant independent of the displacements so it won't affect the dynamics at all. We can ignore it in what follows. The next term contains $-\boldsymbol{F}_{i\alpha}^{(0)} = \partial U/\partial \boldsymbol{u}_{i\alpha}|_{\boldsymbol{u}=0}$ which is just the force on the α^{th} atom in the i^{th} unitcell in equilibrium... note however that forces are vanishing in equilibrium by definition! In the same sense, we know the energy is minimized in equilibrium: the condition for this to be true is that all first derivatives vanish. I.e. the 1^{st} order term vanishes, so we drop it. The

next interesting term is the 2^{nd} order one and we stop expanding there. Then

$$\begin{aligned} U_{harm}(\boldsymbol{r}) \equiv U(\boldsymbol{r}) &= \frac{1}{2}\sum_{ij\alpha\beta} \boldsymbol{u}_{i\alpha}^T \hat{\Phi}_{ij,\alpha\beta} \boldsymbol{u}_{j\beta} \\ \hat{\Phi}_{ij,\alpha\beta} &= \left(\frac{\partial^2 U(\boldsymbol{r})}{\partial \boldsymbol{u}_{i\alpha} \partial \boldsymbol{u}_{j\beta}} \right)\Big|_{\boldsymbol{u}=0} \end{aligned} \tag{29}$$

where $\hat{\Phi}_{ij,\alpha\beta}$ is called the "force constant matrix". For any general term in the series we have (in 3D)

$$\boldsymbol{u}_{i\alpha}^T \hat{\Phi}_{ij,\alpha\beta} \boldsymbol{u}_{j\beta} \equiv \boldsymbol{u}_{i\alpha}^T \cdot \hat{\Phi}_{ij,\alpha\beta} \cdot \boldsymbol{u}_{j\beta} = \sum_{\mu\nu} u_{i\alpha}^{\mu} \Phi_{ij,\alpha\beta}^{\mu\nu} u_{j\beta}^{\nu} =$$

$$\begin{pmatrix} u_{i\alpha}^x & u_{i\alpha}^y & u_{i\alpha}^z \end{pmatrix} \begin{pmatrix} \frac{\partial^2 U}{\partial u_{i\alpha}^x \partial u_{j\beta}^x} & \frac{\partial^2 U}{\partial u_{i\alpha}^x \partial u_{j\beta}^y} & \frac{\partial^2 U}{\partial u_{i\alpha}^x \partial u_{j\beta}^z} \\ \frac{\partial^2 U}{\partial u_{i\alpha}^y \partial u_{j\beta}^x} & \frac{\partial^2 U}{\partial u_{i\alpha}^y \partial u_{j\beta}^y} & \frac{\partial^2 U}{\partial u_{i\alpha}^y \partial u_{j\beta}^z} \\ \frac{\partial^2 U}{\partial u_{i\alpha}^z \partial u_{j\beta}^x} & \frac{\partial^2 U}{\partial u_{i\alpha}^z \partial u_{j\beta}^y} & \frac{\partial^2 U}{\partial u_{i\alpha}^z \partial u_{j\beta}^z} \end{pmatrix} \begin{pmatrix} u_{j\beta}^x \\ u_{j\beta}^y \\ u_{j\beta}^z \end{pmatrix} \tag{30}$$

which hopefully makes clear the meaning of calling the force constant matrix a matrix. The elements are $\Phi_{ij,\alpha\beta}^{\mu\nu} = \partial^2 U / \partial u_{i\alpha}^{\mu} \partial u_{j\beta}^{\nu}$. There are some interesting symmetries of the force constants that will be useful later. (i) Obviously the order of differentiation doesn't matter, so $\hat{\Phi}_{ij,\alpha\beta} \equiv \hat{\Phi}_{ji,\beta\alpha}$. (ii) Since translating the entire crystal by a vector $\boldsymbol{d}$ doesn't change the energy (i.e. it doesn't stretch any bonds), then $U(\boldsymbol{r}^{(0)}) = U(\boldsymbol{r}^{(0)} + \boldsymbol{d})$ and

$$U(\boldsymbol{r}^{(0)}) - U(\boldsymbol{r}^{(0)} + \boldsymbol{d}) = \frac{1}{2}\sum_{ij\alpha\beta} \boldsymbol{d}^T \hat{\Phi}_{ij,\alpha\beta} \boldsymbol{d} = \frac{N}{2} \boldsymbol{d}^T \left(\sum_{\boldsymbol{R}\alpha\beta} \hat{\Phi}_{\boldsymbol{R},\alpha\beta} \right) \boldsymbol{d} = 0 \tag{31}$$

where we used translational invariance to reduce to a single sum over lattice vectors $\boldsymbol{R}$. Since the displacement $\boldsymbol{d}$ can be arbitrary, it must be true that

$$\sum_{\boldsymbol{R}\alpha\beta} \hat{\Phi}_{\boldsymbol{R},\alpha\beta} = 0. \tag{32}$$

So now for the equations of motion. The (harmonic) force on the α^{th} atom in the i^{th} cell is $\boldsymbol{F}_{i\alpha} = -\partial U / \partial \boldsymbol{u}_{i\alpha} = m_\alpha \ddot{\boldsymbol{u}}_{i\alpha}$. Explicitly

$$m_\alpha \ddot{\boldsymbol{u}}_{i\alpha} = -\sum_{j\beta} \hat{\Phi}_{ij,\alpha\beta} \boldsymbol{u}_{j\beta} \tag{33}$$

Similar reasoning as for the force constants above shows that the force on any atom should vanish if the whole crystal is displaced by a vector $\boldsymbol{d}$.

$$\boldsymbol{F}_{i\alpha} = 0 = \hat{\Phi}_{\boldsymbol{R},\alpha\beta} = -\left(\sum_{j\beta} \hat{\Phi}_{ij,\alpha\beta} \right) \boldsymbol{d} \tag{34}$$

Since $\boldsymbol{d}$ is arbitrary, we find

$$\sum_{j\beta} \hat{\Phi}_{ij,\alpha\beta} = 0. \tag{35}$$

Some re-arranging (and shifting $\boldsymbol{R}_i$ to the origin) results in

$$\hat{\Phi}_{\boldsymbol{0},\alpha\alpha} = -\sum_{\boldsymbol{R}\beta}{}' \hat{\Phi}_{\boldsymbol{R},\alpha\beta}. \tag{36}$$

where the $'$ on the sum means to sum over all terms but $\hat{\Phi}_{\boldsymbol{0},\alpha\alpha}$. Basically we are saying that, in equilibrium, the forces between atom α in the unitcell at the origin and all other atoms in the crystal must vanish.

Just like above for the harmonic chains, we make progress solving the equations of motion by Fourier transforming. Let[2]

$$\begin{aligned} \boldsymbol{u}_{i\alpha}(t) &= \frac{1}{\sqrt{m_\alpha N}} \sum_{\boldsymbol{q}} \int \frac{d\omega}{\sqrt{2\pi}} \boldsymbol{\epsilon}_{\boldsymbol{q}\alpha}(\omega) \exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i - i\omega t) \\ \boldsymbol{\epsilon}_{\boldsymbol{q}\alpha}(\omega) &= \sqrt{\frac{m_\alpha}{N}} \sum_{i} \int \frac{dt}{\sqrt{2\pi}} \boldsymbol{u}_{i\alpha}(t) \exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_i + i\omega t) \end{aligned} \tag{37}$$

and plug in to eq. 33

$$N\omega^2 \boldsymbol{\epsilon}_{\boldsymbol{q}\alpha} = \sum_{\boldsymbol{q}'\beta} \left[\sum_{ij} \frac{\hat{\Phi}_{ij,\alpha\beta}}{\sqrt{m_\alpha m_\beta}} \exp(i\boldsymbol{q}'\cdot\boldsymbol{R}_j) \exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_i) \right] \boldsymbol{\epsilon}_{\boldsymbol{q}'\beta}. \tag{38}$$

We define $\hat{\Phi}_{ij,\alpha\beta}/\sqrt{m_\alpha m_\beta} = \hat{C}_{\alpha\beta}(\boldsymbol{R}_j - \boldsymbol{R}_i)$ and introduce the coordinate transformation $\boldsymbol{R}_j = \boldsymbol{R} + \boldsymbol{R}_i$, i.e. we shift $\boldsymbol{R}_j$ by a constant $\boldsymbol{R}_i$. Then instead of summing over $\boldsymbol{R}_i$, we sum over $\boldsymbol{R} = \boldsymbol{R}_j - \boldsymbol{R}_i$. Then

$$\begin{aligned} &\sum_{ij} \hat{C}_{\alpha\beta}(\boldsymbol{R}) \exp(i\boldsymbol{q}'\cdot\boldsymbol{R}_j) \exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_i) \\ &= \sum_{\boldsymbol{R}} \hat{C}_{\alpha\beta}(\boldsymbol{R}) \exp(i\boldsymbol{q}'\cdot\boldsymbol{R}) \sum_{i} \exp(-i(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{R}_i) = N\delta_{\boldsymbol{q}\boldsymbol{q}'} \hat{D}_{\alpha\beta}(\boldsymbol{q}') \end{aligned} \tag{39}$$

and

$$\omega^2 \boldsymbol{\epsilon}_{\boldsymbol{q}\alpha} = \sum_{\beta} \hat{D}_{\alpha\beta}(\boldsymbol{q}) \boldsymbol{\epsilon}_{\boldsymbol{q}\beta} \tag{40}$$

[2] There is an ambiguity in the phase here. We could expand using either $\exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_i)$ or $\exp(-i\boldsymbol{q}\cdot\boldsymbol{r}^{(0)}_{i\alpha}) = \exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_i)\exp(-i\boldsymbol{q}\cdot\boldsymbol{\tau}_\alpha)$. Since we sum over $\boldsymbol{R}_i$, we can pull the $\boldsymbol{\tau}_\alpha$ phase out. It is clear that the only difference is the phase of $\boldsymbol{\epsilon}_{\boldsymbol{q}\alpha}$, which we can remove by a unitary transformation anyway. However, in some cases (e.g. studying polarization), it is useful to choose the second convention. For type-setting convenience, I chose the first convention in these notes. In my other notes (and in particular, in my mean-field theory Hubbard model notes) I pick the latter. I did this because, in my codes, I choose that later since it easier just to use the relative position vectors and not have to separately track $\boldsymbol{R}_i$ and $\boldsymbol{\tau}_\alpha$.

with

$$\hat{D}_{\alpha\beta}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} \frac{\hat{\Phi}_{\boldsymbol{R},\alpha\beta}}{\sqrt{m_\alpha m_\beta}} \exp(i\boldsymbol{q}\cdot\boldsymbol{R}). \tag{41}$$

Compactly,

$$\omega^2 \begin{pmatrix} \boldsymbol{\epsilon}_{\boldsymbol{q}1} \\ \boldsymbol{\epsilon}_{\boldsymbol{q}2} \\ \vdots \\ \boldsymbol{\epsilon}_{\boldsymbol{q}N} \end{pmatrix} = \begin{pmatrix} \hat{D}_{11}(\boldsymbol{q}) & \hat{D}_{12}(\boldsymbol{q}) & \cdots & \hat{D}_{1N}(\boldsymbol{q}) \\ \hat{D}_{21}(\boldsymbol{q}) & \hat{D}_{22}(\boldsymbol{q}) & \cdots & \hat{D}_{2N}(\boldsymbol{q}) \\ \vdots & \vdots & \ddots & \vdots \\ \hat{D}_{N1}(\boldsymbol{q}) & \hat{D}_{N2}(\boldsymbol{q}) & \cdots & \hat{D}_{NN}(\boldsymbol{q}) \end{pmatrix} \begin{pmatrix} \boldsymbol{\epsilon}_{\boldsymbol{q}1} \\ \boldsymbol{\epsilon}_{\boldsymbol{q}2} \\ \vdots \\ \boldsymbol{\epsilon}_{\boldsymbol{q}N} \end{pmatrix} \tag{42}$$

represents the set of coupled equations for all atoms in the unitcell. The fact that we only have to look in a single unitcell is due to the lattice periodicity; the displacements in other unitcells is fixed by the phase $\exp(i\boldsymbol{q}\cdot\boldsymbol{R})$ in the Fourier transform of the displacements. Just like with the diatomic chain, we solve this by calculating the eigenvalues and eigenvectors. We assume we can easily diagonalize this equation on a computer (though we have to do it once for every $\boldsymbol{q}$). We call the eigenvectors that solve the equation $\boldsymbol{\epsilon}_{\boldsymbol{q}\nu}$ and label the different eigenvectors by ν. Compactly, we write the secular equation as

$$\omega^2_{\boldsymbol{q}\nu}\boldsymbol{\epsilon}_{\boldsymbol{q}\nu} = \hat{D}(\boldsymbol{q})\boldsymbol{\epsilon}_{\boldsymbol{q}\nu}. \tag{43}$$

The eigenvectors are

$$\begin{aligned} \boldsymbol{\epsilon}_{\boldsymbol{q}\nu} &= (\epsilon^x_{\boldsymbol{q}\nu,1}, \epsilon^y_{\boldsymbol{q}\nu,1}, \epsilon^z_{\boldsymbol{q}\nu,1}, \epsilon^x_{\boldsymbol{q}\nu,2}, \epsilon^y_{\boldsymbol{q}\nu,2}, \epsilon^z_{\boldsymbol{q}\nu,2}, \cdots, \epsilon^x_{\boldsymbol{q}\nu,N}, \epsilon^y_{\boldsymbol{q}\nu,N}, \epsilon^z_{\boldsymbol{q}\nu,N})^T \\ &= (\boldsymbol{\epsilon}_{\boldsymbol{q}\nu,1}, \boldsymbol{\epsilon}_{\boldsymbol{q}\nu,2}, \cdots, \boldsymbol{\epsilon}_{\boldsymbol{q}\nu,N})^T. \end{aligned} \tag{44}$$

They are assumed orthonormalized such that $\boldsymbol{\epsilon}^\dagger_{\boldsymbol{q}\mu}\cdot\boldsymbol{\epsilon}_{\boldsymbol{q}\nu} = \delta_{\mu\nu}$; orthogonality is due to $\hat{D}(q)$ being Hermitian and normalization can be enforced by applying an arbitrary scale factor. The atom displacements can be calculated from

$$\epsilon^\mu_{\boldsymbol{q},\alpha} = \sum_\eta \boldsymbol{\epsilon}_{\boldsymbol{q}\eta}\cdot\hat{\boldsymbol{e}}^\mu_\alpha = \sum_\eta \epsilon^\mu_{\boldsymbol{q}\eta,\alpha}. \tag{45}$$

With this

$$\begin{aligned} \boldsymbol{u}_{i\alpha}(t) &= \frac{1}{\sqrt{m_\alpha N}} \sum_{\boldsymbol{q}\eta} A_{\boldsymbol{q}\eta}\boldsymbol{\epsilon}_{\boldsymbol{q}\eta,\alpha} \exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i - i\omega_{\boldsymbol{q}\eta}t) \\ &\frac{1}{\sqrt{m_\alpha N}} \sum_{\boldsymbol{q}\eta} \boldsymbol{Q}_{\boldsymbol{q}\eta,\alpha}(t) \exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i) \\ \boldsymbol{Q}_{\boldsymbol{q}\eta,\alpha}(t) &= A_{\boldsymbol{q}\eta}\boldsymbol{\epsilon}_{\boldsymbol{q}\eta,\alpha}\exp(-i\omega_{\boldsymbol{q}\eta}t) \\ \boldsymbol{\epsilon}_{\boldsymbol{q}\eta,\alpha} &= \epsilon^x_{\boldsymbol{q}\eta,\alpha}\hat{\boldsymbol{e}}^x_\alpha + \epsilon^y_{\boldsymbol{q}\eta,\alpha}\hat{\boldsymbol{e}}^y_\alpha + \epsilon^z_{\boldsymbol{q}\eta,\alpha}\hat{\boldsymbol{e}}^z_\alpha \end{aligned} \tag{46}$$

where $A_{\boldsymbol{q}\nu}$ is a (complex) scalar amplitude for each mode and $\boldsymbol{q}$ point. Note that since the $3d$ displacements are real, $\bar{\boldsymbol{Q}}_{\boldsymbol{q}\eta,\alpha}(t) = \boldsymbol{Q}_{-\boldsymbol{q}\eta,\alpha}(t)$.

Just like in the $1d$ case, we are saying that the atomic displacement can be expressed as Fourier series over the different modes. The difference is that $\boldsymbol{\epsilon}_{\boldsymbol{q}\nu,\alpha}$ is now a $3d$ vector that gives the displacement of the α^{th} atom in $3d$ space relative to the other atoms. The

coefficient $A_{\boldsymbol{q}\eta}$ has the same meaning as before: it is the Fourier coefficient of the η^{th} mode with wavevector $\boldsymbol{q}$.

The combination $\boldsymbol{\epsilon}_{\boldsymbol{q}\eta,\alpha} \exp(i\boldsymbol{q}\cdot\boldsymbol{R})$ is a wave-like modulation of the crystal lattice involving relative displacements of each atom in each unitcell. This is what can be called a "phonon". Note that the underlying modulation of the lattice is periodic: i.e. $\boldsymbol{\epsilon}_{\boldsymbol{q}\eta,\alpha}$ is the same in every unitcell. The variation from unitcell-to-unitcell is from the complex exponential which gives a wave-like modulation of the underlying periodic displacements: this is why the phonons are called "lattice waves". (Note also that they are Bloch functions, just like electron wave functions in crystals.) The dynamics of the atoms is given by the equations of motion eq. 43. Each phonon solves eq. 43 and since they are linearly independent, each evolves in time independently of the others. The time evolution is a periodic oscillation of the displacement given by the phase $\exp(-i\omega_{\boldsymbol{q}\eta}t)$. The field of study of the dynamics of lattice waves is called "lattice dynamics".

Explicitly work out the real space displacements. Can't really plot them for the general problem, but whatevs.

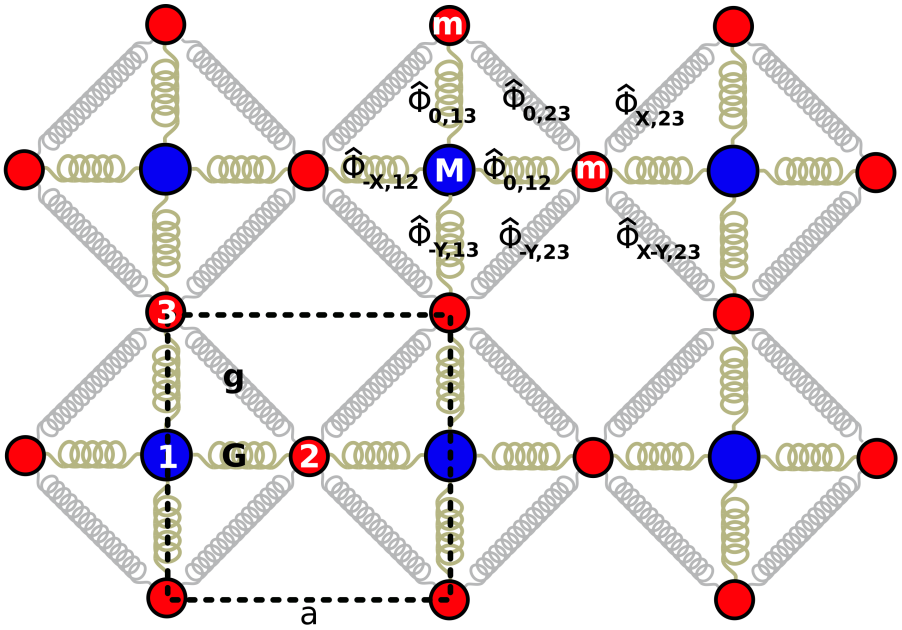

Fig. 4:

3 Two dimensional perovskite

As an example, let us work out the phonons for the model in fig. 4. It is supposed to model a Cu-O plane in a cuprate: atom type 1 with mass M is supposed to be Cu and atoms 2 and 3 with mass m are supposed to be oxygen. Each Cu atom is coupled to 4 neighboring O atoms by massless springs with spring constant G. For now, let us ignore the bonds between the O atoms 1 and 3 and assume the only bonds are those between Cu and O. The energy of each bond is

$$U_{bond} = \frac{G}{2}(|\boldsymbol{r}_1(t) - \boldsymbol{r}_2(t)| - r_0)^2. \tag{47}$$

This is the energy of a harmonic spring; displacing $\boldsymbol{r}_1$ or $\boldsymbol{r}_2$ from equilibrium stretches or compresses the spring, costing energy. r_0 is the equilibrium bond length; obviously it is just half of a lattice constant $a/2$. The total potential energy of the crystal is

$$\begin{aligned} U(\boldsymbol{r}) = \frac{G}{2}\sum_{\boldsymbol{R}} \big[&(|\boldsymbol{r}_{\boldsymbol{R},1}(t) - \boldsymbol{r}_{\boldsymbol{R},2}(t)| - r_0)^2 + (|\boldsymbol{r}_{\boldsymbol{R},1}(t) - \boldsymbol{r}_{\boldsymbol{R},3}(t)| - r_0)^2 \\ &(|\boldsymbol{r}_{\boldsymbol{R},1}(t) - \boldsymbol{r}_{\boldsymbol{R}-\hat{\boldsymbol{x}},2}(t)| - r_0)^2 + (|\boldsymbol{r}_{\boldsymbol{R},1}(t) - \boldsymbol{r}_{\boldsymbol{R}-\hat{\boldsymbol{y}},3}(t)| - r_0)^2\big]. \end{aligned} \tag{48}$$

Due to the periodic boundary conditions, atoms on the right edge are coupled to atoms on the left edge and vice versa. Note, this sum only goes from 1→2, not from 2→1 etc. remove factor of 2?

We need to calculate the force constants $\Phi^{\mu\nu}_{i\alpha,j\beta} = (\partial^2 U/\partial u^\mu_{i\alpha}\partial u^\nu_{j\beta})_0$. Note that $\partial/\partial u = (\partial r/\partial u)\partial/\partial r = \partial/\partial r$ It will be convenient to generalize a little and study a model that

includes harmonic bonds to all neighbors. We define the pair potential as

$$\phi_{ij}^{\alpha\beta}(\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta})=\frac{1}{2}K_{ij}^{\alpha\beta}(|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|-l_{ij}^{\alpha\beta})^2 \tag{49}$$

and the crystal potential energy as

$$U=\frac{1}{2}\sum_{ij,\alpha\beta}\phi_{ij}^{\alpha\beta}(\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta})=\frac{1}{4}\sum_{ij,\alpha\beta}K_{ij}^{\alpha\beta}(|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|-l_{ij}^{\alpha\beta})^2. \tag{50}$$

$K_{ij}^{\alpha\beta}$ is the spring constant between atoms $(i\alpha)$ and $(j\beta)$ (α^{th} atom in the i^{th} cell etc.). $l_{ij}^{\alpha\beta}$ is the equilibrium bond length. We have

$$\begin{aligned}\frac{\partial U}{\partial u_{i\alpha}^{\mu}}&=\frac{1}{4}\sum_{j\beta,k\gamma}K_{jk}^{\beta\gamma}\left[\delta_{ij}\delta_{\alpha\beta}\frac{\partial}{\partial u_{j\beta}^{\mu}}(|\boldsymbol{r}_{j\beta}-\boldsymbol{r}_{k\gamma}|-l_{jk}^{\beta\gamma})^2+\delta_{ik}\delta_{\alpha\gamma}\frac{\partial}{\partial u_{k\gamma}^{\mu}}(|\boldsymbol{r}_{j\beta}-\boldsymbol{r}_{k\gamma}|-l_{jk}^{\beta\gamma})^2\right]\\&=\frac{1}{2}\sum_{k\gamma}K_{ik}^{\alpha\gamma}\frac{\partial}{\partial u_{i\alpha}^{\mu}}(|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{k\gamma}|-l_{ik}^{\alpha\gamma})^2\end{aligned} \tag{51}$$

The derivative is tricky:

$$\frac{1}{2}\frac{\partial}{\partial u_{i\alpha}^{\mu}}(|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{k\gamma}|-l_{jk}^{\beta\gamma})^2=(|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{k\gamma}|-l_{jk}^{\beta\gamma})\frac{\partial}{\partial u_{i\alpha}^{\mu}}|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{k\gamma}| \tag{52}$$

with

$$\frac{\partial}{\partial u_{i\alpha}^{\mu}}|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{k\gamma}|=\frac{1}{2}\frac{\partial r_{i\alpha}^{\mu}}{\partial u_{i\alpha}^{\mu}}\frac{\partial}{\partial r_{i\alpha}^{\mu}}\sqrt{\sum_{\nu}(r_{i\alpha}^{\nu}-r_{k\gamma}^{\nu})^2}=\frac{r_{i\alpha}^{\mu}-r_{k\gamma}^{\mu}}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{k\gamma}|}. \tag{53}$$

Then

$$\frac{\partial U}{\partial u_{i\alpha}^{\mu}}=\sum_{j\beta}K_{ij}^{\alpha\beta}\frac{(r_{i\alpha}^{\mu}-r_{j\beta}^{\mu})}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|}\left((r_{i\alpha}^{\mu}-r_{j\beta}^{\mu})-l_{ij}^{\alpha\beta}\right)=\sum_{j\beta}K_{ij}^{\alpha\beta}(r_{i\alpha}^{\mu}-r_{j\beta}^{\mu})\left[1-\frac{l_{ij}^{\alpha\beta}}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|}\right]. \tag{54}$$

Next, we need to calculate

$$\begin{aligned}\frac{\partial^2 U}{\partial u_{i\alpha}^{\mu}\partial u_{j\beta}^{\nu}}&=K_{ij}^{\alpha\beta}\frac{\partial}{\partial u_{j\beta}^{\nu}}\left((r_{i\alpha}^{\mu}-r_{j\beta}^{\mu})\left[1-\frac{l_{ij}^{\alpha\beta}}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|}\right]\right)\\&=-K_{ij}^{\alpha\beta}\left[1-\frac{l_{ij}^{\alpha\beta}}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|}\right]\delta_{\mu\nu}-K_{ij}^{\alpha\beta}l_{ij}^{\alpha\beta}(r_{i\alpha}^{\mu}-r_{j\beta}^{\mu})\frac{\partial}{\partial u_{j\beta}^{\nu}}\frac{1}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|}\\&=-K_{ij}^{\alpha\beta}\left[1-\frac{l_{ij}^{\alpha\beta}}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|}\right]\delta_{\mu\nu}-K_{ij}^{\alpha\beta}l_{ij}^{\alpha\beta}\frac{(r_{i\alpha}^{\mu}-r_{j\beta}^{\mu})(r_{i\alpha}^{\nu}-r_{j\beta}^{\nu})}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|^3}\end{aligned} \tag{55}$$

i.e. we find

$$\frac{\partial^2 U}{\partial u^\mu_{i\alpha}\partial u^\nu_{j\beta}} = -K^{\alpha\beta}_{ij}\left(\delta_{\mu\nu}\left[1-\frac{l^{\alpha\beta}_{ij}}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|}\right]+l^{\alpha\beta}_{ij}\frac{(r^\mu_{i\alpha}-r^\mu_{j\beta})(r^\nu_{i\alpha}-r^\nu_{j\beta})}{|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}|^3}\right). \tag{56}$$

which for equilibrium positions ($|\boldsymbol{r}_{i\alpha}-\boldsymbol{r}_{j\beta}| = l^{\alpha\beta}_{ij}$) is[3]

$$\Phi^{\mu\nu}_{i\alpha,j\beta} = \left(\frac{\partial^2 U}{\partial u^\mu_{i\alpha}\partial u^\nu_{j\beta}}\right)_0 = -K^{\alpha\beta}_{ij}\frac{(r^\mu_{i\alpha}-r^\mu_{j\beta})(r^\nu_{i\alpha}-r^\nu_{j\beta})}{[l^{\alpha\beta}_{ij}]^2}. \tag{57}$$

Note that the phenomenological model introduced above doesn't provide a method to calculate $\hat{\Phi}_{ii,\alpha,\alpha}$ which is a valid force constant: it is called the *self-term*. It arises from the interaction of the α^{th} atom in the i^{th} unitcell and the rest of the crystal and we need it to satisfy the acoustic sum rule. The usual "trick" to calculate it is to use eq. 36. Once we have calculated the force constants between all pairs, we can calculate the self-terms by calculating the sum in eq. 36.

3.1 Cu-O coupling

Now back to solving the Cu-O model we came up with. Let us work out the dynamical matrices $\hat{D}_{\alpha\beta}(\boldsymbol{q})$. We only need to calculate $\hat{D}_{11},(\boldsymbol{q})$, $\hat{D}_{12}(\boldsymbol{q})$, $\hat{D}_{13}(\boldsymbol{q})$, $\hat{D}_{22}(\boldsymbol{q})$, $\hat{D}_{23}(\boldsymbol{q})$, and $\hat{D}_{33}(\boldsymbol{q})$ since the rest can be determined by Hermiticity of the dynamical matrix. Also note that, since the atoms 2 and 3 aren't bonded, the dynamical matrices between them are necessarily 0. The force constant matrices we can calculate from eq. 57 are

$$\begin{aligned}\hat{\Phi}_{\mathbf{0},12} = \hat{\Phi}_{-\boldsymbol{x},12} &= \begin{pmatrix}-G & 0\\ 0 & 0\end{pmatrix}\\ \hat{\Phi}_{\mathbf{0},13} = \hat{\Phi}_{-\boldsymbol{y},13} &= \begin{pmatrix}0 & 0\\ 0 & -G\end{pmatrix}\end{aligned} \tag{58}$$

and from eq. 36

$$\begin{aligned}\hat{\Phi}_{\mathbf{0},11} &= -(\hat{\Phi}_{\mathbf{0},12}+\hat{\Phi}_{-\boldsymbol{x},12}+\hat{\Phi}_{\mathbf{0},13}+\hat{\Phi}_{-\boldsymbol{y},13})\\ &= \begin{pmatrix}2G & 0\\ 0 & 2G\end{pmatrix}\\ \hat{\Phi}_{\mathbf{0},22} &= -(\hat{\Phi}_{\mathbf{0},21}+\hat{\Phi}_{\boldsymbol{x},21})\\ &= \begin{pmatrix}2G & 0\\ 0 & 0\end{pmatrix}\\ \hat{\Phi}_{\mathbf{0},33} &= -(\hat{\Phi}_{\mathbf{0},31}+\hat{\Phi}_{\boldsymbol{y},31})\\ &= \begin{pmatrix}0 & 0\\ 0 & 2G\end{pmatrix}\end{aligned} \tag{59}$$

[3] This is now verified by a finite difference calculation with LAMMPS.

So then

$$\begin{aligned}
\hat{D}_{11}(\boldsymbol{q}) &= \frac{\hat{\Phi}_{\mathbf{0},11}}{M} \\
\hat{D}_{12}(\boldsymbol{q}) &= \frac{1}{\sqrt{Mm}}\left[\hat{\Phi}_{\mathbf{0},12} + \hat{\Phi}_{-\boldsymbol{x},12}\exp(-iq_x)\right] = \frac{\hat{\Phi}_{\mathbf{0},12}}{\sqrt{Mm}}\left[1+\exp(-iq_x)\right] \\
\hat{D}_{13}(\boldsymbol{q}) &= \frac{1}{\sqrt{Mm}}\left[\hat{\Phi}_{\mathbf{0},13} + \hat{\Phi}_{-\boldsymbol{y},13}\exp(-iq_y)\right] = \frac{\hat{\Phi}_{\mathbf{0},13}}{\sqrt{Mm}}\left[1+\exp(-iq_y)\right] \\
\hat{D}_{22}(\boldsymbol{q}) &= \frac{\hat{\Phi}_{\mathbf{0},22}}{m} \\
\hat{D}_{33}(\boldsymbol{q}) &= \frac{\hat{\Phi}_{\mathbf{0},33}}{m}
\end{aligned} \tag{60}$$

and

$$\hat{D}(\boldsymbol{q}) = \begin{pmatrix} \hat{D}_{11}(\boldsymbol{q}) & \hat{D}_{12}(\boldsymbol{q}) & \hat{D}_{13}(\boldsymbol{q}) \\ \hat{D}_{12}^{\dagger}(\boldsymbol{q}) & \hat{D}_{22}(\boldsymbol{q}) & 0 \\ \hat{D}_{13}^{\dagger}(\boldsymbol{q}) & 0 & \hat{D}_{33}(\boldsymbol{q}) \end{pmatrix} \tag{61}$$

Let's solve the dynamical matrix "by hand" for a few special cases: we will do $\boldsymbol{q} = \Gamma = (0,0)$, $\boldsymbol{q} = X = (1/2, 0)$, and $\boldsymbol{q} = M = (1/2, 1/2)$. Let's do Γ first. Define $a = 2G/M$, $b = -2G/\sqrt{Mm}$, and $c = 2G/m$. The dynamical matrix at Γ is

$$\hat{D}(\Gamma) = \begin{pmatrix} a & 0 & b & 0 & 0 & 0 \\ 0 & a & 0 & 0 & 0 & b \\ b & 0 & c & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & b & 0 & 0 & 0 & c \end{pmatrix} \tag{62}$$

which has eigenvalues $(0, 0, \omega_-^2, \omega_-^2, \omega_+^2, \omega_+^2)$. Explicitly,

$$\begin{aligned}
\omega_{\pm}^2 &= \frac{1}{2}\left[(a+c) \pm \sqrt{a^2 - 2ac + 4b^2 + c^2}\right] = \frac{2G}{Mm}\left[(M+m) \pm (M+m)\right] \\
\omega_+ &= \sqrt{\frac{2G(M+m)}{Mm}} \\
\omega_- &= 0
\end{aligned} \tag{63}$$

At the X point, the dynamical matrix is

$$\hat{D}(X) = \begin{pmatrix} a & 0 & 0 & 0 & 0 & 0 \\ 0 & a & 0 & 0 & 0 & b \\ 0 & 0 & c & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & b & 0 & 0 & 0 & c \end{pmatrix} \tag{64}$$

which has eigenvalues $(0, 0, a, c, \omega_-^2, \omega_+^2)$. The eigenvalues $\omega_\pm^2$ are the same as in eq. 63. Finally, the dynamical matrix at M is

$$\hat{D}(M) = \begin{pmatrix} a & 0 & 0 & 0 & 0 & 0 \\ 0 & a & 0 & 0 & 0 & 0 \\ 0 & 0 & c & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & c \end{pmatrix} \tag{65}$$

which is already diagonal. The eigenvalues are $(0, 0, a, a, c, c)$ Note that, as long as $M \neq m$, then there is a phonon "band gap" in the dispersions. Let m_+ bet the mass of the lighter atom and m_- the mass of the heavier one. The gap is

$$\Delta = \sqrt{\frac{2G}{m_+}} - \sqrt{\frac{2G}{m_-}} = \sqrt{\frac{2G}{m_+ m_-}} \left(\sqrt{m_+} - \sqrt{m_-}\right) \tag{66}$$

solve all across the BZ, note what the eigenvectors look like. In particular, note that there is NO full breathing mode. I think the reason there are no full breathing modes is that this is basically two linear-chain models oriented perpendicular to each other. The only possible longitudinal displacements in this model coupling neighboring nor perpendicular Cu-O chains. Also note that there are vanishing-energy modes all across the BZ; these are modes that don't stretch the Cu-O bonds. In particular, any displacement of the O perpendicular to the bond only stretches the bond to 2nd order in displacement, so is vanishing energy cost. Plot displacements. Explain that coupling the O atoms in the same octahedra changes this. Note that, even with O-O coupling, rotating the octahedra still only stretches bonds to 2nd order in displacements, i.e. vanishing energy cost...

3.2 O-O coupling

For the model to host full-breathing phonons, we have to couple neighboring O-O atoms in the same octahedra. These bonds are represented by the g-springs in fig. 4. Need to plot dispersions for this model and note the eigenvectors at particular places. Also mention that there is still a 0-energy mode at the BZ boundary: this is the octahedral rotation mode, i.e. the tetragonal instability. There are no bonds that cost energy to rotate the octahedra.

3.3 The tetragonal instability

In the model with both Cu-O and O-O bonds, there is still and instability. There is a tetragonal instability since it costs no energy to rotate the octahedra; rotating the octahedra doesn't stretch any bonds. We can remove the instability in a few ways.

(i) We could add next-nearest neighbor coupling between the Cu and O atoms. See fig. **??**. These bonds may be physically relevant and they do indeed stabilize the rotational modes. But this isn't the most sensible way to do it.

(ii) The most reasonable way to remove the tetragonal instability is to put cations back

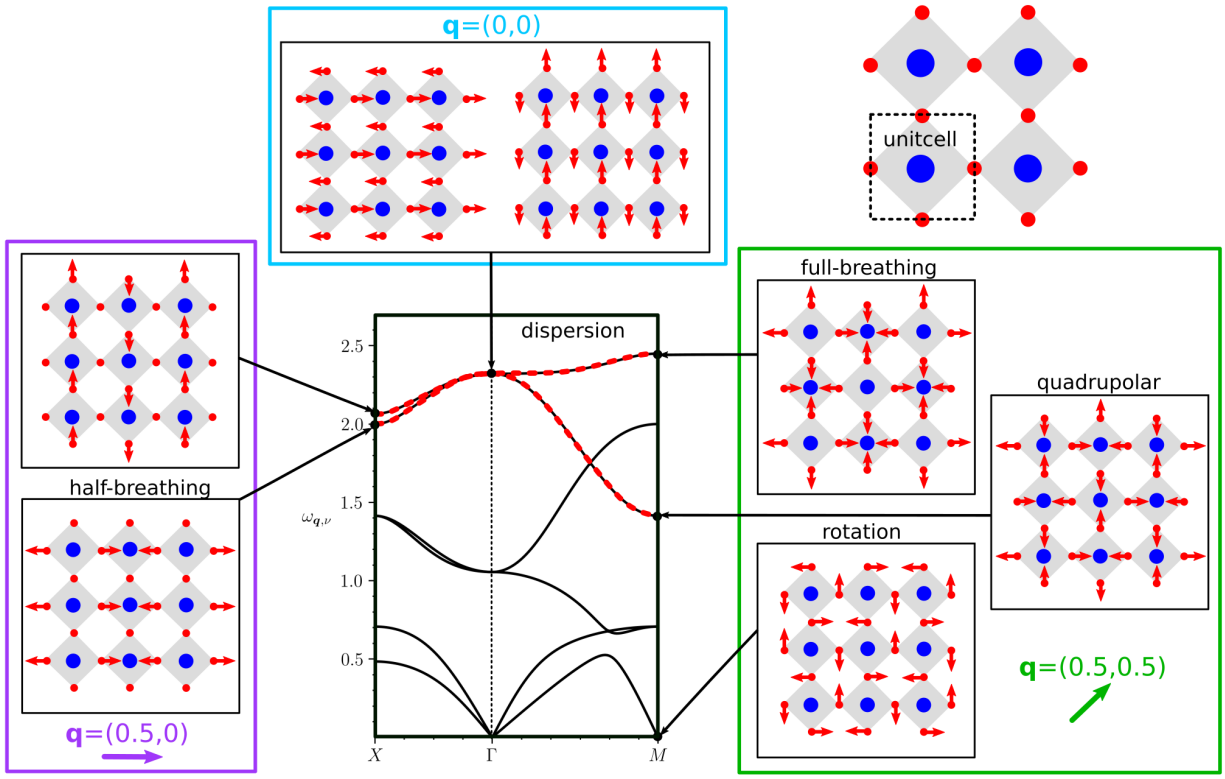

Fig. 5: Bond-stretching optical phonon displacements in the 2d perovskite model with nearest-neighbor Cu-O and O-O coupling.

into the model. E.g. in $PbTiO_3$, the O atoms are coupled to the Pb sublattice and rotating the TiO_6 octahedra stretches the bonds between the Pb and O atoms, costing energy. This will stabilize the rotational modes. This is a more sensible way to stabilize the rotations than adding next-nearest neighbor Cu-O bonds: note that so far, we have ignored the cations in our model, which is unphysical. We included only the anions (TM metal site/octahedra) because we only cared the phonons that couple to the electrons on the TM site. These phonons are the octahedral optical modes. However, if we care about stabilizing the rotational modes, the most reasonable thing to do is put the cations back into the model.

4 Area modulation

Since we are postulating that the volume modulation of the octahedra by the phonons changes the on-site Hubbard energy, we need a way to calculate the volume modulation in terms of the phonon coordinates. We could do this using the theory of elasticity (see below, §C). However, this method involves some simplifying assumptions that we would like to avoid. So we derive a more general method here.

Instead of specializing the the breathing phonons (e.g. fig. 7), let us work out the more general case of an arbitrary distortion (see fig. 6). Note that in the case of a 2d model, we are calculating areas instead of volumes; however, the method here is conceptually equivalent to volume changes in 3d and I will use the words “volume” and “area” interchangeably in

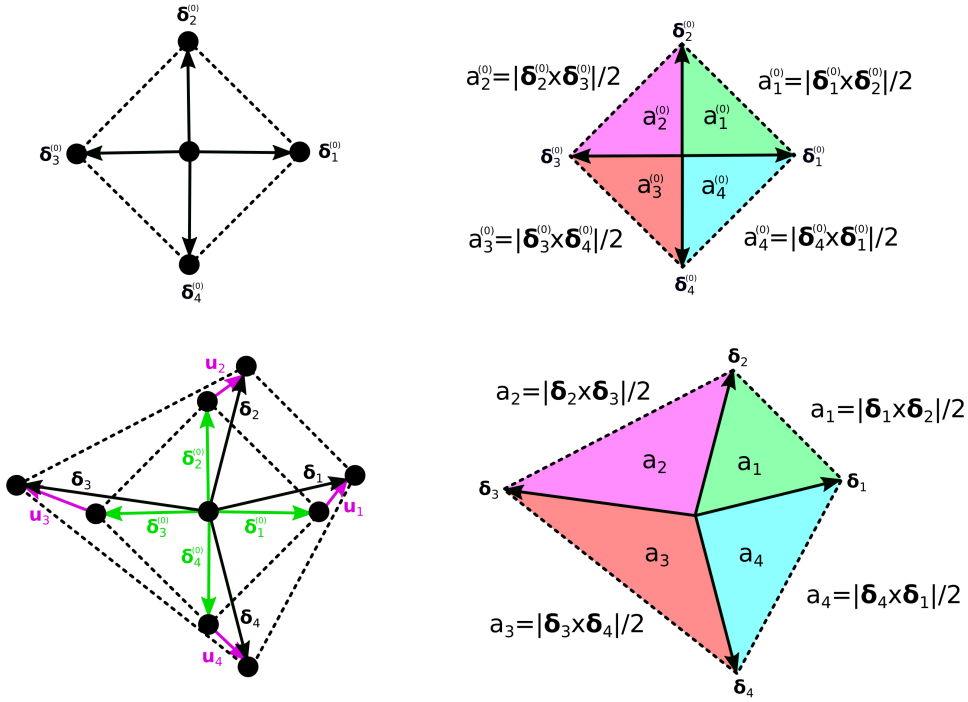

Fig. 6: Caption

what follows.

Assume the center of the octahedra contains a transition metal (TM) atom: e.g. Cu or Ni. We will place the center of the octahedra at the origin. There are 4 neighbors that make up the vertices; we label them $1-4$. The vectors from the TM atom to the vertices are labeled $\boldsymbol{\delta}_i$. The vectors in equilibrium (i.e. no distortion) are $\boldsymbol{\delta}_i^{(0)}$ and the displacements are $\boldsymbol{u}_i$. Then $\boldsymbol{\delta}_i = \boldsymbol{\delta}_i^{(0)} + \boldsymbol{u}_i$.

The area of the octahedra is $A = \sum_{i=1}^{4} a_i = a_1 + a_2 + a_3 + a_4$ and similarly for $A^{(0)} = a_1^{(0)} + a_2^{(0)} + a_3^{(0)} + a_4^{(0)} = 4a^{(0)}$. The *relative* area modulation is $\xi \equiv \Delta A/A^{(0)} = (A - A^{(0)})/A^{(0)}$. Note that $\Delta A = A - 4a^{(0)} = \sum_i (a_i - a^{(0)}) = \sum_i \Delta a_i$. We can calculate the area of any triangle by taking half of the magnitude of the cross product of the bond-vectors spanning it. This will give us half the area of the parallelogram spanned by the bond-vectors; i.e. the area the triangle. For example (careful to pick the + sign)

$$\begin{aligned} a_1 &= \frac{1}{2}(\boldsymbol{\delta}_1 \times \boldsymbol{\delta}_2)\cdot\hat{\boldsymbol{z}} = \frac{1}{2}(\delta_1^x\delta_2^y - \delta_1^y\delta_2^x) \\ a_1^{(0)} = a^{(0)} &= \frac{1}{2}(\boldsymbol{\delta}_1^{(0)} \times \boldsymbol{\delta}_2^{(0)})\cdot\hat{\boldsymbol{z}} = \frac{1}{2}(\delta_1^{(0)x}\delta_2^{(0)y} - \delta_1^{(0)y}\delta_2^{(0)x}) \end{aligned} \tag{67}$$

In terms of the displacements, we write $\boldsymbol{\delta}_i = \boldsymbol{\delta}_i^{(0)} + \boldsymbol{u}_i$. The area of triangle $a_1 \equiv a_{12}$ is

$$\begin{gathered}\Delta a_{12} = \frac{1}{2}[(\boldsymbol{\delta}_1^{(0)} + \boldsymbol{u}_1) \times (\boldsymbol{\delta}_2^{(0)} + \boldsymbol{u}_2)] \cdot \hat{\boldsymbol{z}} = \\ \frac{1}{2}(\delta_1^{(0)x} + u_1^x)(\delta_2^{(0)y} + u_2^y) - (\delta_1^{(0)y} + u_1^y)(\delta_2^{(0)x} + u_2^x) = \\ \frac{1}{2}(2a^{(0)} + u_1^x\delta_2^{(0)y} + \delta_1^{(0)x}u_2^y - u_1^y\delta_2^{(0)x} - \delta_1^{(0)y}u_2^x) + O(u^2).\end{gathered} \tag{68}$$

Dropping $O(u^2)$ terms, we find

$$\Delta a_{12} = \frac{1}{2}(\delta_1^{(0)x}u_2^y - \delta_1^{(0)y}u_2^x + u_1^x\delta_2^{(0)y} - u_1^y\delta_2^{(0)x}) = \frac{1}{2}[\boldsymbol{\delta}_1^{(0)} \times \boldsymbol{u}_2 - \boldsymbol{\delta}_2^{(0)} \times \boldsymbol{u}_1] \cdot \hat{\boldsymbol{z}}. \tag{69}$$

For the change in area of any arbitrary 2d polygon polygon with n sides (the 2d octahedra is the special case $n = 4$):

$$\begin{gathered}\Delta A = \sum_{i=1}^{n} \Delta a_i \equiv [\Delta a_{12} + \Delta a_{23} + \cdots \Delta a_{n-1n} + \Delta a_{n1}] = \\ \frac{1}{2}[\boldsymbol{\delta}_1^{(0)} \times \boldsymbol{u}_2 - \boldsymbol{\delta}_2^{(0)} \times \boldsymbol{u}_1 + \boldsymbol{\delta}_2^{(0)} \times \boldsymbol{u}_3 - \boldsymbol{\delta}_3^{(0)} \times \boldsymbol{u}_2 + \cdots \\ \boldsymbol{\delta}_{n-1}^{(0)} \times \boldsymbol{u}_n - \boldsymbol{\delta}_n^{(0)} \times \boldsymbol{u}_{n-1} + \boldsymbol{\delta}_n^{(0)} \times \boldsymbol{u}_1 - \boldsymbol{\delta}_1^{(0)} \times \boldsymbol{u}_n] \cdot \hat{\boldsymbol{z}} = \\ \frac{1}{2}[\boldsymbol{\delta}_1^{(0)} \times (\boldsymbol{u}_2 - \boldsymbol{u}_n) + \boldsymbol{\delta}_2^{(0)} \times (\boldsymbol{u}_3 - \boldsymbol{u}_1) + \cdots \\ \boldsymbol{\delta}_{n-1}^{(0)} \times (\boldsymbol{u}_n - \boldsymbol{u}_{n-2}) + \boldsymbol{\delta}_n^{(0)} \times (\boldsymbol{u}_1 - \boldsymbol{u}_{n-1})] \cdot \hat{\boldsymbol{z}} \\ \Delta A = \frac{1}{2}\left(\sum_{i=1}^{n} \boldsymbol{\delta}_i^{(0)} \times (\boldsymbol{u}_{i+1} - \boldsymbol{u}_{i-1})\right) \cdot \hat{\boldsymbol{z}}.\end{gathered} \tag{70}$$

The index i is cyclic; for n neighbors, $i = n + 1 = 1$.

4.1 2d perovskite optical phonons

For the specific case of the 2d octahedra,

$$\begin{gathered}\Delta A = \frac{1}{2}[\boldsymbol{\delta}_1^{(0)} \times (\boldsymbol{u}_2 - \boldsymbol{u}_4) + \boldsymbol{\delta}_2^{(0)} \times (\boldsymbol{u}_3 - \boldsymbol{u}_1) + \\ \boldsymbol{\delta}_3^{(0)} \times (\boldsymbol{u}_4 - \boldsymbol{u}_2) + \boldsymbol{\delta}_4^{(0)} \times (\boldsymbol{u}_1 - \boldsymbol{u}_3)] \cdot \hat{\boldsymbol{z}}.\end{gathered} \tag{71}$$

There are 2 commonly studied optical modes that strongly modulate the volume; the half- and full-breathing modes. Another phonon close in energy and degenerate at the zone center is the quadrupolar mode; however, the quadrupolar phonon doesn't modulate the volume so doesn't couple to the electrons. Still, it is a good juxtapose to the breathing phonons. The breathing phonons and the quadrupolar mode are shown in fig. 7. Let us work out ΔA for each of these. First, note that displacement can be decomposed into modes as. Each arrow (i.e. component of the displacements $A_{\boldsymbol{q}\nu}\boldsymbol{\epsilon}_{\boldsymbol{q}\nu,\alpha}/\sqrt{m_\alpha}$) has the same amplitude: call it d. The

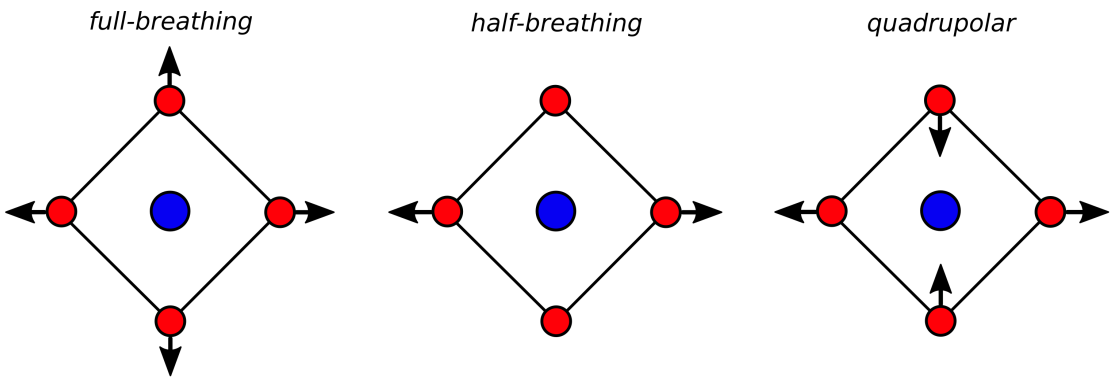

Fig. 7: Caption

rest of the displacements are 0. The bond-lengths are l. Then

$$\begin{aligned}\Delta A_{FB} &= dl(\hat{\boldsymbol{x}} \times \hat{\boldsymbol{y}} - \hat{\boldsymbol{y}} \times \hat{\boldsymbol{x}} + \hat{\boldsymbol{x}} \times \hat{\boldsymbol{y}} - \hat{\boldsymbol{y}} \times \hat{\boldsymbol{x}}) \cdot \boldsymbol{z} = 4dl(\hat{\boldsymbol{x}} \times \hat{\boldsymbol{y}}) \cdot \boldsymbol{z} \\ &= 4dl \\ \Delta A_{HB} &= dl(-\hat{\boldsymbol{y}} \times \hat{\boldsymbol{x}} - \hat{\boldsymbol{y}} \times \hat{\boldsymbol{x}}) \cdot \boldsymbol{z} = 2dl(\hat{\boldsymbol{x}} \times \hat{\boldsymbol{y}}) \cdot \boldsymbol{z} \\ &= 2dl \\ \Delta A_{QP} &= dl(-\hat{\boldsymbol{x}} \times \hat{\boldsymbol{y}} - \hat{\boldsymbol{y}} \times \hat{\boldsymbol{x}} - \hat{\boldsymbol{x}} \times \hat{\boldsymbol{y}} - \hat{\boldsymbol{y}} \times \hat{\boldsymbol{x}}) \cdot \boldsymbol{z} \\ &= 0.\end{aligned} \tag{72}$$

The full-breathing phonon couples most strongly to the charge on the TM atom; the half-breathing mode couples less strongly; the quadrupolar mode doesn't couple to the charge. These results are consistent with what we know about electron-phonon coupling in 2d perovskite like Mott-Hubbard systems.

5 Volume modulation

Here, we calculate the volume modulation of the octahedra in 3d. An octahedra is made of 8 tetrahedra (see fig. 8): $V = \sum_{i=1}^{8} v_i$. The volume of a given tetrahedron, v_i, is 1/6 the volume the paralelliped spanned by the 3 edges connected to a single vertex. We pick the the tetrahedra in a given octahedra to have the edges shown in fig. 8. The central coordinate is assumed be at the origin so that the edge vectors are just the relative position vectors to the other vertices.

The equilibrium volume of an irregular tetrahedron is

$$v^{(0)} = \frac{1}{6}\boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{\delta}_c^{(0)}) \tag{73}$$

and the instantaneous volume is

$$v = \frac{1}{6}\boldsymbol{\delta}_a \cdot (\boldsymbol{\delta}_b \times \boldsymbol{\delta}_c). \tag{74}$$

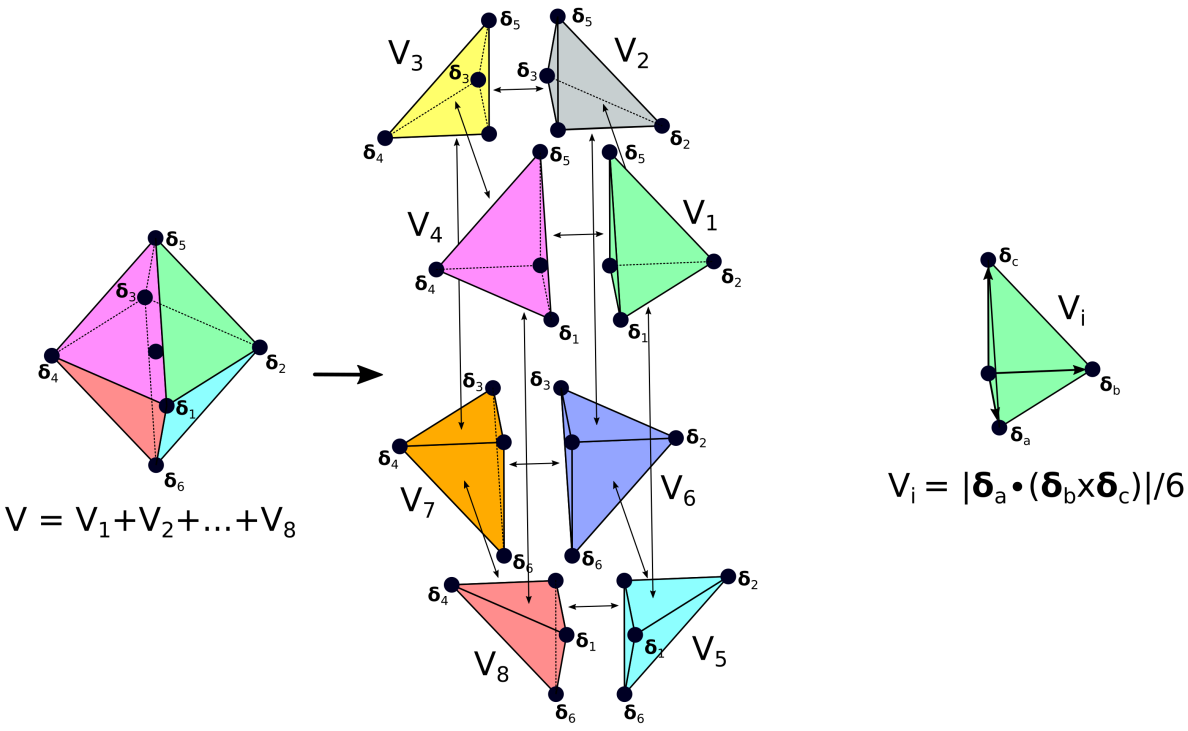

Fig. 8: Caption

Note that it is crucial to pick the vectors according to the right hand rule so that the sign of the volume is correct. The change in volume is

$$\Delta V = V - V^{(0)} = \sum_{i=1}^{8} (v_i - v_i^{(0)}) = \sum_{i=1}^{8} \Delta v_i. \tag{75}$$

With $\boldsymbol{\delta}_a = \boldsymbol{\delta}_a^{(0)} + \boldsymbol{u}_a$ (dropping the index i for now),

$$\begin{aligned} 6v = \boldsymbol{\delta}_a \cdot (\boldsymbol{\delta}_b \times \boldsymbol{\delta}_c) = (\boldsymbol{\delta}_a^{(0)} + \boldsymbol{u}_a) \cdot [(\boldsymbol{\delta}_b^{(0)} + \boldsymbol{u}_b) \times (\boldsymbol{\delta}_c^{(0)} + \boldsymbol{u}_c)] = \\ \boldsymbol{\delta}_a^{(0)} \cdot [(\boldsymbol{\delta}_b^{(0)} + \boldsymbol{u}_b) \times (\boldsymbol{\delta}_c^{(0)} + \boldsymbol{u}_c)] + \boldsymbol{u}_a \cdot [(\boldsymbol{\delta}_b^{(0)} + \boldsymbol{u}_b) \times (\boldsymbol{\delta}_c^{(0)} + \boldsymbol{u}_c)] = \\ \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{\delta}_c^{(0)}) + \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{u}_c) + \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{u}_b \times \boldsymbol{\delta}_c^{(0)}) + \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{u}_b \times \boldsymbol{u}_c) + \\ \boldsymbol{u}_a \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{\delta}_c^{(0)}) + \boldsymbol{u}_a \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{u}_c) + \boldsymbol{u}_a \cdot (\boldsymbol{u}_b \times \boldsymbol{\delta}_c^{(0)}) + \boldsymbol{u}_a \cdot (\boldsymbol{u}_b \times \boldsymbol{u}_c) \\ \approx \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{\delta}_c^{(0)}) + \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{u}_c) + \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{u}_b \times \boldsymbol{\delta}_c^{(0)}) + \boldsymbol{u}_a \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{\delta}_c^{(0)}). \end{aligned} \tag{76}$$

where, on the last line, we drop terms that are $O(\boldsymbol{u}^2)$ since we are assuming small displacements (harmonic approximation). For each tetrahedron, the change in volume is then

$$\begin{aligned} 6\Delta v = 6(v - v^{(0)}) = \boldsymbol{\delta}_a \cdot (\boldsymbol{\delta}_b \times \boldsymbol{\delta}_c) - \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{\delta}_c^{(0)}) = \\ \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{u}_c) + \boldsymbol{\delta}_a^{(0)} \cdot (\boldsymbol{u}_b \times \boldsymbol{\delta}_c^{(0)}) + \boldsymbol{u}_a \cdot (\boldsymbol{\delta}_b^{(0)} \times \boldsymbol{\delta}_c^{(0)}). \end{aligned} \tag{77}$$

Following the notation in fig. 8, and making sure to stick to the right-hand rule, we can use this formula to calculate $6\Delta V = 6\sum_{i=1}^{8} \Delta v_i$. After substantial re-arranging,

$$\begin{aligned} 6\Delta V = \boldsymbol{u}_1 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_4^{(0)} - \boldsymbol{\delta}_2^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_2^{(0)} - \boldsymbol{\delta}_4^{(0)})] + \\ \boldsymbol{u}_2 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)})] + \\ \boldsymbol{u}_3 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_2^{(0)} - \boldsymbol{\delta}_4^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_4^{(0)} - \boldsymbol{\delta}_2^{(0)})] + \\ \boldsymbol{u}_4 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)})] + \\ \boldsymbol{u}_5 \cdot [\boldsymbol{\delta}_2^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)}) + \boldsymbol{\delta}_4^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)})] + \\ \boldsymbol{u}_6 \cdot [\boldsymbol{\delta}_2^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)}) + \boldsymbol{\delta}_4^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)})] \end{aligned} \tag{78}$$

or more succinctly,

$$\Delta V = \frac{1}{6} \sum_{i=1}^{8} \boldsymbol{u}_i \cdot \boldsymbol{\beta}_i \tag{79}$$

where $\boldsymbol{\beta}_i$ is defined according to the equation above.

note: $\boldsymbol{a}\cdot(\boldsymbol{b}\times\boldsymbol{c})=\boldsymbol{b}\cdot(\boldsymbol{c}\times\boldsymbol{a})=\boldsymbol{c}\cdot(\boldsymbol{a}\times\boldsymbol{b})$ ... swap 5 and 6 to be 1st so that the remaining terms are 'in plane' and can be related by swapping order in cross products (gains a minus sign) ... drop $O(u^2)$ terms

$$\begin{aligned}
&\boldsymbol{\delta}_1^{(0)}\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{u}_5)+\boldsymbol{\delta}_1^{(0)}\cdot(\boldsymbol{u}_2\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_1\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\\
&\boldsymbol{\delta}_2^{(0)}\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{u}_5)+\boldsymbol{\delta}_2^{(0)}\cdot(\boldsymbol{u}_3\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_2\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\\
&\boldsymbol{\delta}_3^{(0)}\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{u}_5)+\boldsymbol{\delta}_3^{(0)}\cdot(\boldsymbol{u}_4\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_3\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\\
&\boldsymbol{\delta}_4^{(0)}\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{u}_5)+\boldsymbol{\delta}_4^{(0)}\cdot(\boldsymbol{u}_1\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_4\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\\
&\boldsymbol{\delta}_2^{(0)}\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{u}_6)+\boldsymbol{\delta}_2^{(0)}\cdot(\boldsymbol{u}_1\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_2\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_6^{(0)})+\\
&\boldsymbol{\delta}_3^{(0)}\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{u}_6)+\boldsymbol{\delta}_3^{(0)}\cdot(\boldsymbol{u}_2\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_3\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_6^{(0)})+\\
&\boldsymbol{\delta}_4^{(0)}\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{u}_6)+\boldsymbol{\delta}_4^{(0)}\cdot(\boldsymbol{u}_3\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_4\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_6^{(0)})+\\
&\boldsymbol{\delta}_1^{(0)}\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{u}_6)+\boldsymbol{\delta}_1^{(0)}\cdot(\boldsymbol{u}_4\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_1\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_6^{(0)})
\end{aligned}\tag{80}$$

...

$$\begin{aligned}
&\boldsymbol{u}_1\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_2\cdot(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_1^{(0)})+\boldsymbol{u}_5\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_2^{(0)})+\\
&\boldsymbol{u}_2\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_3\cdot(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_2^{(0)})+\boldsymbol{u}_5\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_3^{(0)})+\\
&\boldsymbol{u}_3\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_4\cdot(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_3^{(0)})+\boldsymbol{u}_5\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_4^{(0)})+\\
&\boldsymbol{u}_4\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_5^{(0)})+\boldsymbol{u}_1\cdot(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_4^{(0)})+\boldsymbol{u}_5\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_1^{(0)})+\\
&\boldsymbol{u}_2\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_1\cdot(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_2^{(0)})+\boldsymbol{u}_6\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_1^{(0)})+\\
&\boldsymbol{u}_3\cdot(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_2\cdot(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_3^{(0)})+\boldsymbol{u}_6\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_2^{(0)})+\\
&\boldsymbol{u}_4\cdot(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_3\cdot(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_4^{(0)})+\boldsymbol{u}_6\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_3^{(0)})+\\
&\boldsymbol{u}_1\cdot(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_6^{(0)})+\boldsymbol{u}_4\cdot(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_1^{(0)})+\boldsymbol{u}_6\cdot(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_4^{(0)})
\end{aligned}\tag{81}$$

...

$$\begin{aligned}
&\boldsymbol{u}_1\cdot[(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_5^{(0)})+(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_4^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_2^{(0)})+(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_6^{(0)})]+\\
&\boldsymbol{u}_2\cdot[(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_1^{(0)})+(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_5^{(0)})+(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_6^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_3^{(0)})]+\\
&\boldsymbol{u}_3\cdot[(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_2^{(0)})+(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_5^{(0)})+(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_6^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_4^{(0)})]+\\
&\boldsymbol{u}_4\cdot[(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_3^{(0)})+(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_5^{(0)})+(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_6^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_1^{(0)})]+\\
&\boldsymbol{u}_5\cdot[(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_2^{(0)})+(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_3^{(0)})+(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_4^{(0)})+(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_1^{(0)})]+\\
&\boldsymbol{u}_6\cdot[(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_1^{(0)})+(\boldsymbol{\delta}_3^{(0)}\times\boldsymbol{\delta}_2^{(0)})+(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_3^{(0)})+(\boldsymbol{\delta}_1^{(0)}\times\boldsymbol{\delta}_4^{(0)})]
\end{aligned}\tag{82}$$

...

$$\begin{aligned}
&\boldsymbol{u}_1\cdot[-(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_2^{(0)})+(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_4^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_2^{(0)})-(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_4^{(0)})]+\\
&\boldsymbol{u}_2\cdot[(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_1^{(0)})-(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_3^{(0)})-(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_1^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_3^{(0)})]+\\
&\boldsymbol{u}_3\cdot[(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_2^{(0)})-(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_4^{(0)})-(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_2^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_4^{(0)})]+\\
&\boldsymbol{u}_4\cdot[(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_3^{(0)})-(\boldsymbol{\delta}_5^{(0)}\times\boldsymbol{\delta}_1^{(0)})-(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_3^{(0)})+(\boldsymbol{\delta}_6^{(0)}\times\boldsymbol{\delta}_1^{(0)})]+\\
&\boldsymbol{u}_5\cdot[-(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_1^{(0)})+(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_3^{(0)})-(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_3^{(0)})+(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_1^{(0)})]+\\
&\boldsymbol{u}_6\cdot[(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_1^{(0)})-(\boldsymbol{\delta}_2^{(0)}\times\boldsymbol{\delta}_3^{(0)})+(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_3^{(0)})-(\boldsymbol{\delta}_4^{(0)}\times\boldsymbol{\delta}_1^{(0)})]
\end{aligned}\tag{83}$$

...

$$
\begin{aligned}
&\boldsymbol{u}_1 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_4^{(0)} - \boldsymbol{\delta}_2^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_2^{(0)} - \boldsymbol{\delta}_4^{(0)})] + \\
&\boldsymbol{u}_2 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)})] + \\
&\boldsymbol{u}_3 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_2^{(0)} - \boldsymbol{\delta}_4^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_4^{(0)} - \boldsymbol{\delta}_2^{(0)})] + \\
&\boldsymbol{u}_4 \cdot [\boldsymbol{\delta}_5^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)}) + \boldsymbol{\delta}_6^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)})] + \\
&\boldsymbol{u}_5 \cdot [\boldsymbol{\delta}_2^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)}) + \boldsymbol{\delta}_4^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)})] + \\
&\boldsymbol{u}_6 \cdot [\boldsymbol{\delta}_2^{(0)} \times (\boldsymbol{\delta}_1^{(0)} - \boldsymbol{\delta}_3^{(0)}) + \boldsymbol{\delta}_4^{(0)} \times (\boldsymbol{\delta}_3^{(0)} - \boldsymbol{\delta}_1^{(0)})]
\end{aligned}
\tag{84}
$$

6 Quantum Theory of Phonons

We now work out the quantum theory of the harmonic chain. For generality, let us work on a lattice with a basis. We write down the Hamiltonian using the usual methods of first quantization: i.e. we replace position and momentum by their respective operators; the position or the α^{th} atom in the i^{th} unitcell is $\hat{\boldsymbol{r}}_{i\alpha} = \boldsymbol{R}_i + \boldsymbol{\tau}_\alpha + \hat{\boldsymbol{u}}_{i\alpha}$. Since the unitcell and basis vectors are constant, they are not operators; rather, the displacement is the dynamical variable we care about and we promote it to an operator. The momentum conjugate to $\hat{u}^\mu_{i\alpha}$ is $\hat{p}^\mu_{i\alpha}$. The commutation relation is $[\hat{u}^\mu_{i\alpha}, \hat{p}^\nu_{j\beta}] = i\delta_{ij}\delta_{\alpha\beta}\delta_{\mu\nu}$ (in units with $\hbar \neq 1$, $[\hat{u}^\mu_{i\alpha}, \hat{p}^\nu_{j\beta}] = i\hbar\delta_{ij}\delta_{\alpha\beta}\delta_{\mu\nu}$). The Hamiltonian operator is[4]

$$\begin{aligned}\hat{H} = \sum_{i\alpha} \frac{\hat{\boldsymbol{p}}_{i\alpha}\cdot\hat{\boldsymbol{p}}_{i\alpha}}{2m_\alpha} + U(\hat{\boldsymbol{r}}) &= \sum_{i\alpha} \frac{\hat{\boldsymbol{p}}_{i\alpha}\cdot\hat{\boldsymbol{p}}_{i\alpha}}{2m_\alpha} + \frac{1}{2}\sum_{ij\alpha\beta} \hat{\boldsymbol{u}}^T_{i\alpha}\Phi_{ij,\alpha\beta}\hat{\boldsymbol{u}}_{j\beta} \\ &= \sum_{i\alpha,\mu} \frac{(\hat{p}^\mu_{i\alpha})^2}{2m_\alpha} + \frac{1}{2}\sum_{ij\alpha\beta,\mu\nu} \Phi^{\mu\nu}_{ij,\alpha\beta}\hat{u}^\mu_{i\alpha}\hat{u}^\nu_{j\beta}\end{aligned} \tag{85}$$

We make progress by Fourier transforming. For the displacements, we have

$$\begin{aligned}\hat{u}^\mu_{i\alpha} &= N^{-1/2}\sum_{\boldsymbol{q}} \hat{u}^\mu_{\boldsymbol{q}\alpha}\exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i) \\ \hat{u}^\mu_{\boldsymbol{q}\alpha} &= N^{-1/2}\sum_{i} \hat{u}^\mu_{i\alpha}\exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_i)\end{aligned} \tag{86}$$

For the momentum operators, there is a minor subtlety: we *define* the Fourier transform to have opposite the phase of the displacements so that the commutation relation of the Fourier transformed operators is preserved. Explicitly

$$\begin{aligned}\hat{p}^\mu_{i\alpha} &= N^{-1/2}\sum_{\boldsymbol{q}} \hat{p}^\mu_{\boldsymbol{q}\alpha}\exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_i) \\ \hat{p}^\mu_{\boldsymbol{q}\alpha} &= N^{-1/2}\sum_{i} \hat{p}^\mu_{i\alpha}\exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i)\end{aligned} \tag{87}$$

and

$$\begin{aligned}[\hat{u}^\mu_{\boldsymbol{k}\alpha}, \hat{p}^\nu_{\boldsymbol{q}\beta}] &= N^{-1}\sum_{ij}[\hat{u}^\mu_{i\alpha}, \hat{p}^\nu_{j\beta}]\exp(-i\boldsymbol{k}\cdot\boldsymbol{R}_i)\exp(i\boldsymbol{q}\cdot\boldsymbol{R}_j) \\ &= N^{-1}\sum_{ij} i\delta_{ij}\delta_{\alpha\beta}\delta_{\mu\nu}\exp(-i\boldsymbol{k}\cdot\boldsymbol{R}_i)\exp(i\boldsymbol{q}\cdot\boldsymbol{R}_j) \\ &= \frac{i\delta_{\alpha\beta}\delta_{\mu\nu}}{N}\sum_i \exp(i(\boldsymbol{q}-\boldsymbol{k})\cdot\boldsymbol{R}_i) = i\delta_{\boldsymbol{q}\boldsymbol{k}}\delta_{\alpha\beta}\delta_{\mu\nu}\end{aligned} \tag{88}$$

has the same structure as the real-space commutation relation. Alternatively, we could have picked that phase of the Fourier transform to be the same for momentum and displacement, in which case the commutator would have been $[\hat{u}^\mu_{\boldsymbol{k}\alpha}, \hat{p}^{\dagger\nu}_{\boldsymbol{q}\beta}] = i\delta_{\boldsymbol{q}\boldsymbol{k}}\delta_{\alpha\beta}\delta_{\mu\nu}$. Whatever.

[4] I am leaving the "hat" off of $\Phi_{ij\alpha\beta}$ to avoid confusing the matrix with an operator; hopefully the context makes it clear

Lets us work out the momentum space version of the kinetic and potential energy terms of the Hamiltonian separately.

$$\hat{T} = \sum_{i\alpha,\mu} \frac{(\hat{p}^{\mu}_{i\alpha})^2}{2m_\alpha} = N^{-1} \sum_{\boldsymbol{kq}} \sum_{\alpha\mu} \frac{\hat{p}^{\mu}_{\boldsymbol{k}\alpha} \hat{p}^{\mu}_{\boldsymbol{q}\alpha}}{2m_\alpha} \sum_i \exp(-i(\boldsymbol{k}+\boldsymbol{q})\cdot \boldsymbol{R}_i) = \sum_{\boldsymbol{q}\alpha,\mu} \frac{\hat{p}^{\mu}_{-\boldsymbol{q}\alpha} \hat{p}^{\mu}_{\boldsymbol{q}\alpha}}{2m_\alpha} \tag{89}$$

Since momentum is a Hermitian operator, note that we can also write $\hat{p}^{\mu}_{-\boldsymbol{q}\alpha} = (\hat{p}^{\mu}_{\boldsymbol{q}\alpha})^\dagger$ and similarly for the displacement operators. Now for the potential energy.

$$U = \frac{1}{2} \sum_{ij\alpha\beta,\mu\nu} \Phi^{\mu\nu}_{ij,\alpha\beta} \hat{u}^{\mu}_{i\alpha} \hat{u}^{\nu}_{j\beta} = \frac{1}{2N} \sum_{\boldsymbol{kq}} \sum_{\alpha\beta,\mu\nu} \hat{u}^{\mu}_{\boldsymbol{k}\alpha} \hat{u}^{\nu}_{\boldsymbol{q}\beta} \sum_{ij} \Phi^{\mu\nu}_{ij,\alpha\beta} \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_i) \exp(i\boldsymbol{q}\cdot\boldsymbol{R}_j) \tag{90}$$

Using translational invariance of the force constants and substituting $\boldsymbol{R}_i = \boldsymbol{R}_j - \boldsymbol{R}$

$$\begin{aligned} U &= \frac{1}{2N} \sum_{\boldsymbol{kq}} \sum_{\alpha\beta,\mu\nu} \hat{u}^{\mu}_{\boldsymbol{k}\alpha} \hat{u}^{\nu}_{\boldsymbol{q}\beta} \left(\sum_{\boldsymbol{R}} \Phi^{\mu\nu}_{\boldsymbol{R},\alpha\beta} \exp(-i\boldsymbol{k}\cdot\boldsymbol{R}) \right) \sum_j \exp(i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{R}_i) \\ &= \frac{1}{2} \sum_{\boldsymbol{kq}} \delta_{-\boldsymbol{kq}} \sum_{\alpha\beta,\mu\nu} \hat{u}^{\mu}_{\boldsymbol{k}\alpha} \hat{u}^{\nu}_{\boldsymbol{q}\beta} \left(\sum_{\boldsymbol{R}} \Phi^{\mu\nu}_{\boldsymbol{R},\alpha\beta} \exp(-i\boldsymbol{q}\cdot\boldsymbol{R}) \right) \\ &= \frac{1}{2} \sum_{\boldsymbol{q}} \sum_{\alpha\beta,\mu\nu} \hat{u}^{\mu}_{-\boldsymbol{q}\alpha} \hat{u}^{\nu}_{\boldsymbol{q}\beta} \left(\sum_{\boldsymbol{R}} \Phi^{\mu\nu}_{\boldsymbol{R},\alpha\beta} \exp(i\boldsymbol{q}\cdot\boldsymbol{R}) \right). \end{aligned} \tag{91}$$

So then finally

$$U = \frac{1}{2} \sum_{\boldsymbol{q}} \sum_{\alpha\beta,\mu\nu} \hat{u}^{\mu}_{-\boldsymbol{q}\alpha} \hat{u}^{\nu}_{\boldsymbol{q}\beta} D^{\mu\nu}_{\alpha\beta}(\boldsymbol{q}) \tag{92}$$

with $D^{\mu\nu}_{\alpha\beta}(\boldsymbol{q})$ the dynamic matrix elements defined earlier in eq. 41. The Hamiltonian in momentum space is

$$\hat{H} = \frac{1}{2} \sum_{\boldsymbol{q}} \sum_{\alpha\beta,\mu\nu} \left[\frac{\hat{p}^{\mu}_{-\boldsymbol{q}\alpha} \hat{p}^{\nu}_{\boldsymbol{q}\beta}}{\sqrt{m_\alpha m_\beta}} \delta_{\mu\nu}\delta_{\alpha\beta} + \sqrt{m_\alpha m_\beta} \hat{u}^{\mu}_{-\boldsymbol{q}\alpha} \hat{u}^{\nu}_{\boldsymbol{q}\beta} D^{\mu\nu}_{\alpha\beta}(\boldsymbol{q}) \right] \tag{93}$$

Let's define $\hat{P}^{\mu}_{\boldsymbol{q}\alpha} = \hat{p}^{\mu}_{\boldsymbol{q}\alpha}/\sqrt{m_\alpha}$ and $\hat{U}^{\mu}_{\boldsymbol{q}\alpha} = \sqrt{m_\alpha}\hat{u}^{\mu}_{\boldsymbol{q}\alpha}$. Then

$$\begin{aligned} \hat{H} &= \frac{1}{2} \sum_{\boldsymbol{q}} \sum_{\alpha\beta,\mu\nu} \left[\hat{P}^{\mu}_{-\boldsymbol{q}\alpha} \hat{P}^{\nu}_{\boldsymbol{q}\beta} \delta_{\mu\nu}\delta_{\alpha\beta} + \hat{U}^{\mu}_{-\boldsymbol{q}\alpha} \hat{U}^{\nu}_{\boldsymbol{q}\beta} D^{\mu\nu}_{\alpha\beta}(\boldsymbol{q}) \right] \\ &= \frac{1}{2} \sum_{\boldsymbol{q}} \sum_{\alpha\beta,\mu\nu} \left[\hat{P}^{\dagger\mu}_{\boldsymbol{q}\alpha} \hat{P}^{\nu}_{\boldsymbol{q}\beta} \delta_{\mu\nu}\delta_{\alpha\beta} + \hat{U}^{\dagger\mu}_{\boldsymbol{q}\alpha} \hat{U}^{\nu}_{\boldsymbol{q}\beta} D^{\mu\nu}_{\alpha\beta}(\boldsymbol{q}) \right]. \end{aligned} \tag{94}$$

The dynamical matrix couples position operators on different atoms in the unitcell. We will decouple them by changing basis; i.e. we will diagonalize in the dynamical matrix in (α, β) indices.

6.1 Diagonalizing the Dynamical Matrix

Define the "vectors"

$$\begin{aligned}\hat{\boldsymbol{U}}_{\boldsymbol{q}} &= (\hat{U}^x_{\boldsymbol{q}1}, \hat{U}^y_{\boldsymbol{q}1}\hat{U}^z_{\boldsymbol{q}1}, \cdots, \hat{U}^x_{\boldsymbol{q}n}, \hat{U}^y_{\boldsymbol{q}n}\hat{U}^z_{\boldsymbol{q}n})^T \\ \hat{\boldsymbol{U}}^\dagger_{\boldsymbol{q}} &= (\hat{U}^{\dagger x}_{\boldsymbol{q}1}, \hat{U}^{\dagger y}_{\boldsymbol{q}1}\hat{U}^{\dagger z}_{\boldsymbol{q}1}, \cdots, \hat{U}^{\dagger x}_{\boldsymbol{q}n}, \hat{U}^{\dagger y}_{\boldsymbol{q}n}\hat{U}^{\dagger z}_{\boldsymbol{q}n})\end{aligned} \tag{95}$$

with n the number of atoms in the unitcell. At each $\boldsymbol{q}$-point, we need to solve $\hat{\boldsymbol{U}}^\dagger_{\boldsymbol{q}} D_{\boldsymbol{q}} \hat{\boldsymbol{U}}_{\boldsymbol{q}}$. Define $V_{\boldsymbol{q}}$ as the unitary matrix that diagonalizes $D_{\boldsymbol{q}}$ and $\Omega_{\boldsymbol{q}}$ the diagonal representation of the dynamical matrix; i.e. $V^\dagger_{\boldsymbol{q}} D_{\boldsymbol{q}} V_{\boldsymbol{q}} = \Omega_{\boldsymbol{q}}$. Then

$$\hat{\boldsymbol{U}}^\dagger_{\boldsymbol{q}} D_{\boldsymbol{q}} \hat{\boldsymbol{U}}_{\boldsymbol{q}} = \hat{\boldsymbol{U}}^\dagger_{\boldsymbol{q}} V_{\boldsymbol{q}} V^\dagger_{\boldsymbol{q}} D_{\boldsymbol{q}} V_{\boldsymbol{q}} V^\dagger_{\boldsymbol{q}} \hat{\boldsymbol{U}}_{\boldsymbol{q}} = \hat{\boldsymbol{Q}}^\dagger_{\boldsymbol{q}} \Omega_{\boldsymbol{q}} \hat{\boldsymbol{Q}}_{\boldsymbol{q}} \tag{96}$$

with $\hat{\boldsymbol{Q}}^\dagger_{\boldsymbol{q}} = \hat{\boldsymbol{U}}^\dagger_{\boldsymbol{q}} V_{\boldsymbol{q}}$. Note that the diagonal elements of $\Omega_{\boldsymbol{q}}$ are exactly the same eigenvalues as in the classical lattice dynamical problem. I.e. we can call the eigenvalues $\Omega_{\boldsymbol{q}\lambda} \equiv \omega^2_{\boldsymbol{q}\lambda}$ with λ labelling the "branches" or "modes". There are $3n$ modes; one for each atom and direction. We also define $\hat{\boldsymbol{\pi}}^\dagger_{\boldsymbol{q}} = \hat{\boldsymbol{P}}^\dagger_{\boldsymbol{q}} V^\dagger_{\boldsymbol{q}}$ and $\hat{\boldsymbol{\pi}}_{\boldsymbol{q}} = V_{\boldsymbol{q}} \hat{\boldsymbol{P}}_{\boldsymbol{q}}$. In this basis, the Hamiltonian can be written

$$\hat{H} = \frac{1}{2}\sum_{\boldsymbol{q}} \left[\hat{\boldsymbol{P}}^\dagger_{\boldsymbol{q}} \cdot \hat{\boldsymbol{P}}_{\boldsymbol{q}} + \hat{\boldsymbol{U}}^\dagger_{\boldsymbol{q}} D_{\boldsymbol{q}} \hat{\boldsymbol{U}}_{\boldsymbol{q}}\right] = \frac{1}{2}\sum_{\boldsymbol{q}\lambda} \left[\hat{\pi}^\dagger_{\boldsymbol{q}\lambda}\hat{\pi}_{\boldsymbol{q}\lambda} + \omega^2_{\boldsymbol{q}\lambda}\hat{Q}^\dagger_{\boldsymbol{q}\lambda}\hat{Q}_{\boldsymbol{q}\lambda}\right]. \tag{97}$$

Note that these new operators still satisfy the commutation relation

$$[\hat{Q}_{\boldsymbol{k}\lambda}, \hat{\pi}_{\boldsymbol{q}\gamma}] = [(V^\dagger_{\boldsymbol{k}}\hat{\boldsymbol{U}}_{\boldsymbol{k}})^\lambda, (V_{\boldsymbol{q}}\hat{\boldsymbol{P}}_{\boldsymbol{q}})^\gamma]. \tag{98}$$

In index notation, (σ, δ are composite indices for basis atom index and direction)

$$\begin{aligned}\hat{Q}_{\boldsymbol{k}\lambda} &= (V^\dagger_{\boldsymbol{k}}\hat{\boldsymbol{U}}_{\boldsymbol{k}})^\lambda = \sum_\sigma [V^\dagger_{\boldsymbol{k}}]^{\lambda\sigma}\hat{U}_{\boldsymbol{k}\sigma} \\ \hat{\pi}_{\boldsymbol{q}\gamma} &= (V_{\boldsymbol{q}}\hat{\boldsymbol{P}}_{\boldsymbol{q}})^\gamma = \sum_\delta V^{\gamma\delta}_{\boldsymbol{q}}\hat{P}_{\boldsymbol{q}\delta}.\end{aligned} \tag{99}$$

Then

$$\begin{aligned}[\hat{Q}_{\boldsymbol{k}\lambda}, \hat{\pi}_{\boldsymbol{q}\gamma}] = [(V^\dagger_{\boldsymbol{k}}\hat{\boldsymbol{U}}_{\boldsymbol{k}})^\lambda, (V_{\boldsymbol{q}}\hat{\boldsymbol{P}}_{\boldsymbol{q}})^\gamma] = \sum_{\sigma\delta}[V^\dagger_{\boldsymbol{k}}]^{\lambda\sigma}V^{\gamma\delta}_{\boldsymbol{q}}[\hat{U}_{\boldsymbol{k}\sigma}, \hat{P}_{\boldsymbol{q}\delta}] = \\ \sum_{\sigma\delta}[V^\dagger_{\boldsymbol{k}}]^{\lambda\sigma}V^{\gamma\delta}_{\boldsymbol{q}}\sqrt{\frac{m_\sigma}{m_\delta}}[\hat{u}_{\boldsymbol{k}\sigma}, \hat{p}_{\boldsymbol{q}\delta}] = i\delta_{\boldsymbol{k}\boldsymbol{q}}\sum_{\sigma\delta}[V^\dagger_{\boldsymbol{k}}]^{\lambda\sigma}V^{\gamma\delta}_{\boldsymbol{q}}\sqrt{\frac{m_\sigma}{m_\delta}}\delta_{\sigma\delta} = i\delta_{\boldsymbol{k}\boldsymbol{q}}\sum_\sigma [V^\dagger_{\boldsymbol{k}}]^{\lambda\sigma}V^{\gamma\sigma}_{\boldsymbol{q}}.\end{aligned} \tag{100}$$

For $\boldsymbol{k} \neq \boldsymbol{q}$ the commutator vanishes as required. For $\boldsymbol{k} = \boldsymbol{q}$[5]

$$\sum_\sigma [V^\dagger_{\boldsymbol{k}}]^{\lambda\sigma}V^{\gamma\sigma}_{\boldsymbol{k}} = \sum_\sigma \bar{V}^{\sigma\lambda}_{\boldsymbol{k}}V^{\gamma\sigma}_{\boldsymbol{k}} = \delta_{\lambda\gamma} \tag{101}$$

[5] Double check this... I think the conjugate matrix should be transposed relative to what it is now... I may have made an error earlier.

which follows from orthonormality of the unitary matrices (i.e. of the eigenvectors of the dynamical matrix). So then finally

$$[\hat{Q}_{\boldsymbol{k}\lambda}, \hat{\pi}_{\boldsymbol{q}\gamma}] = i\delta_{\boldsymbol{k}\boldsymbol{q}}\delta_{\lambda\gamma} \tag{102}$$

which has the same structure as the usual displacement and momentum $\hat{u}$ and $\hat{p}$.

6.2 Second quantization

In our new basis, the Hamiltonian is

$$\hat{H} = \frac{1}{2}\sum_{\boldsymbol{q}\lambda}\left[\hat{\pi}^\dagger_{\boldsymbol{q}\lambda}\hat{\pi}_{\boldsymbol{q}\lambda} + \omega^2_{\boldsymbol{q}\lambda}\hat{Q}^\dagger_{\boldsymbol{q}\lambda}\hat{Q}_{\boldsymbol{q}\lambda}\right]. \tag{103}$$

We want to change basis one last time to "second quantized" creation and annihilation operators:

$$\begin{aligned}\hat{a}^\dagger_{\boldsymbol{q}\lambda} &= \sqrt{\frac{\omega_{\boldsymbol{q}\lambda}}{2}}\left(\hat{Q}^\dagger_{\boldsymbol{q}\lambda} - \frac{i}{\omega_{\boldsymbol{q}\lambda}}\hat{\pi}_{\boldsymbol{q}\lambda}\right)\\ \hat{a}_{\boldsymbol{q}\lambda} &= \sqrt{\frac{\omega_{\boldsymbol{q}\lambda}}{2}}\left(\hat{Q}_{\boldsymbol{q}\lambda} + \frac{i}{\omega_{\boldsymbol{q}\lambda}}\hat{\pi}^\dagger_{\boldsymbol{q}\lambda}\right).\end{aligned} \tag{104}$$

The commutation relation for these things is

$$\begin{aligned}[\hat{a}_{\boldsymbol{k}\gamma}, \hat{a}^\dagger_{\boldsymbol{q}\lambda}] &= \sqrt{\frac{\omega_{\boldsymbol{k}\gamma}\omega_{\boldsymbol{q}\lambda}}{4}}\left(\hat{Q}_{\boldsymbol{k}\gamma} + \frac{i}{\omega_{\boldsymbol{k}\gamma}}\hat{\pi}^\dagger_{\boldsymbol{k}\gamma}\right)\left(\hat{Q}^\dagger_{\boldsymbol{q}\lambda} - \frac{i}{\omega_{\boldsymbol{q}\lambda}}\hat{\pi}_{\boldsymbol{q}\lambda}\right) -\\ &\sqrt{\frac{\omega_{\boldsymbol{k}\gamma}\omega_{\boldsymbol{q}\lambda}}{4}}\left(\hat{Q}^\dagger_{\boldsymbol{q}\lambda} - \frac{i}{\omega_{\boldsymbol{q}\lambda}}\hat{\pi}_{\boldsymbol{q}\lambda}\right)\left(\hat{Q}_{\boldsymbol{k}\gamma} + \frac{i}{\omega_{\boldsymbol{k}\gamma}}\hat{\pi}^\dagger_{\boldsymbol{k}\gamma}\right) =\\ &-i\sqrt{\frac{\omega_{\boldsymbol{k}\gamma}\omega_{\boldsymbol{q}\lambda}}{4}}\left(\frac{\hat{Q}_{\boldsymbol{k}\gamma}\hat{\pi}_{\boldsymbol{q}\lambda}}{\omega_{\boldsymbol{q}\lambda}} - \frac{\hat{\pi}_{\boldsymbol{q}\lambda}\hat{Q}_{\boldsymbol{k}\gamma}}{\omega_{\boldsymbol{q}\lambda}} + \frac{\hat{Q}^\dagger_{\boldsymbol{q}\lambda}\hat{\pi}^\dagger_{\boldsymbol{k}\gamma}}{\omega_{\boldsymbol{k}\gamma}} - \frac{\hat{\pi}^\dagger_{\boldsymbol{k}\gamma}\hat{Q}^\dagger_{\boldsymbol{q}\lambda}}{\omega_{\boldsymbol{k}\gamma}}\right) =\\ -i\sqrt{\frac{\omega_{\boldsymbol{k}\gamma}\omega_{\boldsymbol{q}\lambda}}{4}}&\left(\frac{1}{\omega_{\boldsymbol{q}\lambda}}[\hat{Q}_{\boldsymbol{k}\gamma}, \hat{\pi}_{\boldsymbol{q}\lambda}] + \frac{1}{\omega_{\boldsymbol{k}\gamma}}[\hat{Q}^\dagger_{\boldsymbol{q}\lambda}, \hat{\pi}^\dagger_{\boldsymbol{k}\gamma}]\right) = -i\sqrt{\frac{\omega_{\boldsymbol{k}\gamma}\omega_{\boldsymbol{q}\lambda}}{4}}\left(\frac{i\delta_{\boldsymbol{k}\boldsymbol{q}}\delta_{\lambda\gamma}}{\omega_{\boldsymbol{q}\lambda}} + \frac{i\delta_{-\boldsymbol{k},-\boldsymbol{q}}\delta_{\lambda\gamma}}{\omega_{\boldsymbol{k}\gamma}}\right)\end{aligned} \tag{105}$$

i.e.

$$[\hat{a}_{\boldsymbol{k}\gamma}, \hat{a}^\dagger_{\boldsymbol{q}\lambda}] = \delta_{\boldsymbol{k}\boldsymbol{q}}\delta_{\lambda\gamma} \tag{106}$$

which is indeed the commutation relation for second quantized Fock space operators. Inverting the transformation (and recalling that $\hat{\pi}^\dagger_{\boldsymbol{q}\lambda} = \hat{\pi}_{-\boldsymbol{q}\lambda}$ and $\hat{Q}^\dagger_{\boldsymbol{q}\lambda} = \hat{Q}_{-\boldsymbol{q}\lambda}$):

$$\begin{aligned}
\hat{Q}_{\boldsymbol{q}\lambda} &= \frac{1}{\sqrt{2\omega_{\boldsymbol{q}\lambda}}}(\hat{a}^\dagger_{-\boldsymbol{q}\lambda} + \hat{a}_{\boldsymbol{q}\lambda}) \\
\hat{Q}^\dagger_{\boldsymbol{q}\lambda} &= \frac{1}{\sqrt{2\omega_{\boldsymbol{q}\lambda}}}(\hat{a}^\dagger_{\boldsymbol{q}\lambda} + \hat{a}_{-\boldsymbol{q}\lambda}) \\
\hat{\pi}_{\boldsymbol{q}\lambda} &= i\sqrt{\frac{\omega_{\boldsymbol{q}\lambda}}{2}}(\hat{a}^\dagger_{\boldsymbol{q}\lambda} - \hat{a}_{-\boldsymbol{q}\lambda}) \\
\hat{\pi}^\dagger_{\boldsymbol{q}\lambda} &= i\sqrt{\frac{\omega_{\boldsymbol{q}\lambda}}{2}}(\hat{a}^\dagger_{-\boldsymbol{q}\lambda} - \hat{a}_{\boldsymbol{q}\lambda}).
\end{aligned} \tag{107}$$

Let's insert these into the Hamiltonian:

$$\begin{aligned}
\hat{H} = \frac{1}{2}\sum_{\boldsymbol{q}\lambda}\left[\hat{\pi}^\dagger_{\boldsymbol{q}\lambda}\hat{\pi}_{\boldsymbol{q}\lambda} + \omega^2_{\boldsymbol{q}\lambda}\hat{Q}^\dagger_{\boldsymbol{q}\lambda}\hat{Q}_{\boldsymbol{q}\lambda}\right] = \\
\frac{1}{2}\sum_{\boldsymbol{q}\lambda}\frac{\omega_{\boldsymbol{q}\lambda}}{2}\left[-(\hat{a}^\dagger_{-\boldsymbol{q}\lambda} - \hat{a}_{\boldsymbol{q}\lambda})(\hat{a}^\dagger_{\boldsymbol{q}\lambda} - \hat{a}_{-\boldsymbol{q}\lambda}) + (\hat{a}^\dagger_{\boldsymbol{q}\lambda} + \hat{a}_{-\boldsymbol{q}\lambda})(\hat{a}^\dagger_{-\boldsymbol{q}\lambda} + \hat{a}_{\boldsymbol{q}\lambda})\right] = \\
\frac{1}{2}\sum_{\boldsymbol{q}\lambda}\frac{\omega_{\boldsymbol{q}\lambda}}{2}\left(2\hat{a}^\dagger_{\boldsymbol{q}\lambda}\hat{a}_{\boldsymbol{q}\lambda} + 2\hat{a}^\dagger_{-\boldsymbol{q}\lambda}\hat{a}_{-\boldsymbol{q}\lambda} + 2\right) = \frac{1}{2}\sum_{\boldsymbol{q}\lambda}\omega_{\boldsymbol{q}\lambda}\left(2\hat{a}^\dagger_{\boldsymbol{q}\lambda}\hat{a}_{\boldsymbol{q}\lambda} + 2\right).
\end{aligned} \tag{108}$$

To summarize, the second quantized phonon Hamiltonian is

$$\hat{H} = \sum_{\boldsymbol{q}\lambda}\omega_{\boldsymbol{q}\lambda}\left(\hat{a}^\dagger_{\boldsymbol{q}\lambda}\hat{a}_{\boldsymbol{q}\lambda} + \frac{1}{2}\right). \tag{109}$$

For many purposes, e.g. working with the Hamiltonian in eq. 85 or with electron-phonon coupling which is $\sim \hat{u}$, we need to write the displacements in terms of second quantized operators. Using eqs. 46 and 107, the displacements can be written (ignoring the time dependence)[6]

$$\hat{\boldsymbol{u}}_{i\alpha} = \sum_{\boldsymbol{q}\eta}\frac{\hat{\boldsymbol{Q}}_{\boldsymbol{q}\eta,\alpha}}{\sqrt{m_\alpha N}}\exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i) = \sum_{\boldsymbol{q}\eta}\frac{\boldsymbol{\epsilon}_{\boldsymbol{q}\eta,\alpha}}{\sqrt{2m_\alpha\omega_{\boldsymbol{q}\eta}N}}(\hat{a}^\dagger_{-\boldsymbol{q}\eta} + \hat{a}_{\boldsymbol{q}\eta})\exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i). \tag{110}$$

We will use this result extensively later when studying electron-phonon coupling.

[6] I think I used the wrong symbols above... or something. The problem is that $\hat{\boldsymbol{Q}}$ is supposed to include the eigenvector $\boldsymbol{\epsilon}$ and amplitude $\hat{A}$, but what I wrote in eq. 107 only includes the amplitdue. Oh well.

7 Free phonon propagator

Assuming that we already know how to write down the free Fermion action, we want to calculate the propagator:

$$G(\alpha, \tau - \tau') = -\langle T_\tau \{\hat{\psi}_\alpha(\tau)\hat{\psi}^\dagger_\alpha(\tau')\}\rangle = -Z^{-1}\int \mathcal{D}(\bar{\psi},\psi)\psi_\alpha(\tau)\bar{\psi}_\alpha(\tau')\exp(-S[\bar{\psi},\psi])$$

with action

$$S[\bar{\psi},\psi] = \sum_\alpha \int_0^\beta d\tau \bar{\psi}_\alpha(\tau)\left[\partial_\tau + \xi_\alpha\right]\psi_\alpha(\tau).$$

We assume we already diagonalized the Hamiltonian; α is the "band" index and $\xi_\alpha = \epsilon_\alpha - \mu$ is the eigenvalue ϵ_α minus the chemical potential μ. The fields in Matsubara frequency space are

$$\psi_\alpha(\tau) = \beta^{-1/2}\sum_n \exp(-i\omega_n\tau)\psi_\alpha(i\omega_n)$$

$$\psi_\alpha(i\omega_n) = \beta^{-1/2}\int_0^\beta d\tau \exp(i\omega_n\tau)\psi_\alpha(\tau)$$

$$\omega_n = \frac{\pi(2n+1)}{\beta}$$

Then

$$S[\bar{\psi},\psi] = \sum_{\alpha n} \bar{\psi}_\alpha(i\omega_n)\left[-i\omega_n + \xi_\alpha\right]\psi_\alpha(i\omega_n)$$

can be integrated. Using Grassman Gaussian integration rules, we find

$$G(\alpha, i\omega_n) = -\langle\hat{\psi}_\alpha(i\omega_n)\hat{\psi}^\dagger_\alpha(i\omega_n)\rangle = \frac{1}{i\omega_n - \xi_\alpha}. \tag{111}$$

If we are considering spinful particles, we simply have to put $\alpha \to \alpha\sigma$. The imaginary time version is recovered by inverse Matsubara transforming

$$G(\alpha,\tau) = \beta^{-1}\sum_n G(\alpha, i\omega_n)\exp(-i\omega_n\tau)$$

$$G(\alpha, i\omega_n) = \int_0^\beta d\tau G(\alpha,\tau)\exp(i\omega_n\tau)$$

Sometimes we need to calculate the particle number; we could naively guess that $n_\alpha = \langle\psi^\dagger_\alpha\psi_\alpha\rangle$ is the number of particles in the α^{th} singe particle level. However, this is implicitly evaluated at equal-time and the functional integral is ill defined. What we really need to calculate is

$$n_\alpha = \lim_{\tau\to 0^+}\langle T_\tau\{\hat{\psi}^\dagger_\alpha(\tau)\hat{\psi}_\alpha(0)\}\rangle = -\lim_{\tau\to 0^+} G(\alpha,\tau) =$$
$$= \beta^{-1}\sum_n G(\alpha, i\omega_n)\exp(i\omega_n 0^+).$$

A Mean-squared displacements

The mean-squared thermal displacement (MSD) for the quantum harmonic oscillator is

$$\langle x^2 \rangle$$

where $\langle \cdot \rangle \equiv \langle \Omega | \cdot | \Omega \rangle$ means thermal expectation value with $|\Omega\rangle$ the thermal ground state. The Hamiltonian is the usual

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

with $\hat{p} = -i\hbar\partial_x$. We use the creation/annihilation operator basis:

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i}{m\omega} \hat{p} \right)$$
$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega} \hat{p} \right)$$

in which the position and momentum operators are

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} \left(\hat{a}^\dagger + \hat{a} \right)$$
$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}} \left(\hat{a}^\dagger - \hat{a} \right).$$

The commutation relation for the creation/annihilation operators is $[\hat{a}, \hat{a}^\dagger] = 1$. The Hamiltonian is

$$\hat{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right).$$

The quantum number n labels the eigenstates of $\hat{a}^\dagger \hat{a} \equiv \hat{n}$; the eigenvalues are given by $\hat{n}|n\rangle = n|n\rangle$. Then $\hat{H}|n\rangle = E_n|n\rangle$ with

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right).$$

The constant energy shift $\hbar\omega/2$ is applied to all states and can be safely subtracted away. We call it $E_0 \equiv \hbar\omega/2$ and define $E_n = n\hbar\omega$. In thermal equilibrium, the ground state $|\Omega\rangle = \sum_n \exp(-E_n/kT)|n\rangle$ is a thermal state. The expectation value is

$$\langle n \rangle \equiv n_{BE} = \frac{1}{\exp(\hbar\omega/k_B T) - 1}.$$

Then

$$\langle H \rangle \equiv E = \hbar\omega \langle n \rangle + \frac{\hbar\omega}{2}$$

and the MSD is

$$\langle x^2 \rangle = \frac{\hbar}{2m\omega} \langle (\hat{a}^\dagger + \hat{a})^2 \rangle = \frac{\hbar}{2m\omega} (2\langle n \rangle + 1).$$

At high temperature ($k_BT/\hbar\omega \gg 1$), we can approximate

$$\langle x^2 \rangle \approx \frac{k_BT}{m\omega^2}$$

which agrees with the analogous MSD for a classical oscillator:

$$\langle x^2 \rangle = Z(T)^{-1} \int dx x^2 \exp\left(-\frac{1}{2}\beta m\omega^2 x^2\right) = \frac{k_BT}{m\omega^2}.$$

For a D-dimensional isotropic harmonic oscillator,

$$\hat{H} = \sum_i^D \left(\frac{\hat{p}_i^2}{2m} + \frac{1}{2}m\omega^2\hat{x}_i^2\right) = \hbar\omega \sum_i^D \left(\hat{a}_i^\dagger \hat{a}_i + \frac{1}{2}\right).$$

The thermal expectation value is

$$\langle H \rangle = D\hbar\omega \left(\langle n \rangle + \frac{1}{2}\right).$$

For N independent, identical oscillators in D dimensions,

$$\hat{H} = \sum_i^{DN} \left(\frac{\hat{p}_i^2}{2m} + \frac{1}{2}m\omega^2\hat{x}_i^2\right) = \hbar\omega \sum_i^{DN} \left(\hat{a}_i^\dagger \hat{a}_i + \frac{1}{2}\right)$$
$$\langle H \rangle = DN\hbar\omega \left(\langle n \rangle + \frac{1}{2}\right).$$

and the mean-squared displacements are ...

B Fourier transform of harmonic potential

Let $\phi(r) = K(r-l)^2/2$ where $r \equiv |\boldsymbol{r}|$ and $k > 0$ and $l \geq 0$.

$$\phi(\boldsymbol{q}) = \frac{K}{2}\int \frac{d\boldsymbol{r}}{(2\pi)^{3/2}}(r-l)^2 \exp(-i\boldsymbol{q}\cdot\boldsymbol{r}) = \frac{K}{2}\int \frac{d\boldsymbol{r}}{(2\pi)^{3/2}}(r^2 - 2rl - l^2)\exp(-i\boldsymbol{q}\cdot\boldsymbol{r}).$$

Evidently we need to do integrals of the form

$$I_n(\boldsymbol{q}) = C\int \frac{d\boldsymbol{r}}{(2\pi)^{3/2}} r^n \exp(-i\boldsymbol{q}\cdot\boldsymbol{r})$$

with $n \in \{0,1,2\}$ and C a constant. Use the Rayleigh plane wave expansion formula:

$$\exp(i\boldsymbol{q}\cdot\boldsymbol{r}) = 4\pi \sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l j_l(kr) Y_l^m(\hat{\boldsymbol{q}}) Y_l^{m*}(\hat{\boldsymbol{r}}), \tag{112}$$

and the fact that $r^n = \sqrt{4\pi}Y_0^0(\hat{\boldsymbol{r}})r^n$ with $Y_0^0(\hat{\boldsymbol{r}}) = 1/\sqrt{4\pi}$. We can write

$$I_n(q) = C\sqrt{8}\sum_{lm}(-i)^l Y_l^m(\hat{\boldsymbol{q}})\int drr^{n+2}j_l(qr)\int d\hat{\boldsymbol{r}}Y_0^0(\hat{\boldsymbol{r}})Y_l^{m*}(\hat{\boldsymbol{r}}) = C\sqrt{\frac{2}{\pi}}\int drr^{n+2}j_0(qr).$$

The spherical Bessel function is related to the ordinary ones by

$$j_n(x) = \sqrt{\frac{\pi}{2x}}J_{n+1/2}(x).$$

Then

$$I_n(q) = C\sqrt{\frac{2}{\pi}}\int drr^{2+n}j_0(qr) = C\int drr\frac{r^{n+1}}{\sqrt{qr}}J_{1/2}(qr).$$

c this obviously wont converge, duh. the integral of r^2 over all space is infinite.

C Elasticity

This section was originally included because I wanted to write the electron-phonon coupling, which is proportional to the volume modulation by the phonons, as a form of deformation potential. I.e. as the divergence of the displacements. However, I found a better way to do it and am keeping these notes for whatever use they may have later.

Assume we are dealing with a continuously deformable elastic medium. A deformable medium is one that changes shape under applied force; "continous" means that no tears or holes form. A "deformation" is a transformation that takes coordinates of the parcels of material at time $t = 0$, $\boldsymbol{r}(0)$, and smoothly displaces them to a new coordinates at time t, $\boldsymbol{r}(t)$; in other words, it introduces a relative displacement between parts of the body (e.g. stretching, squishes, twisting). Let the transformation describing the deformation be called $\boldsymbol{u}(\boldsymbol{r}(0), t)$, i.e. the function $\boldsymbol{u}(\boldsymbol{r}(0), t)$ returns the time-dependent displacement of the piece of material originally at $\boldsymbol{r}(0)$. In math,

$$\boldsymbol{r}(t) = \boldsymbol{r}(0) + \boldsymbol{u}(\boldsymbol{r}(0), t). \tag{113}$$

In what follows, we will usually omit the t-dependence for notational convenience. It is to be understood that $\boldsymbol{u}(\boldsymbol{r})$ depends on t and the *initial* coordinates $\boldsymbol{r}(0)$. Assume that the we will look at deformations over short times; i.e. that time t is very close to $t_0 = 0$. Since the deformation must be continuous, $\boldsymbol{u}$ has to be small (in the sense that $\boldsymbol{u}(t \to 0) \to 0$. Now suppose that we know $\boldsymbol{u}$ with respect to a particular coordinate; say $\boldsymbol{r}_0$. We want to describe the evolution of a nearby piece of material: $\boldsymbol{r}_1$. Let the vector $\delta\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_0$ be the vector pointing from $\boldsymbol{r}_0$ to $\boldsymbol{r}_1$ (see fig. 9). Then $\boldsymbol{u}(\boldsymbol{r}_1) = \boldsymbol{u}(\boldsymbol{r}_0 + \delta\boldsymbol{r})$. If we pick $\boldsymbol{r}_1$ to be close to $\boldsymbol{r}_0$, then $\delta\boldsymbol{r}$ is small and we can expand $\boldsymbol{u}(\boldsymbol{r}_1)$ to 1^{st} order in $\delta\boldsymbol{r}$.

$$\boldsymbol{u}(\boldsymbol{r}_1) \approx \boldsymbol{u}(\boldsymbol{r}_0) + \left.\frac{\partial\boldsymbol{u}(\boldsymbol{r})}{\partial\boldsymbol{r}}\right|_{\boldsymbol{r}=\boldsymbol{r}_0}\cdot\delta\boldsymbol{r} + O[(\delta\boldsymbol{r})^2]. \tag{114}$$

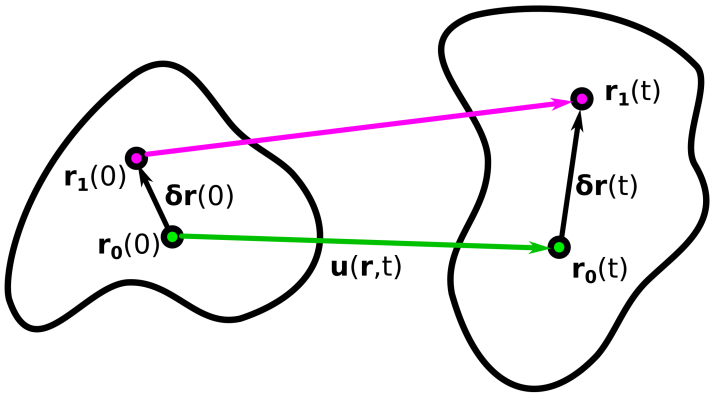

Fig. 9: Caption

For notational convenience, we define

$$\partial_\mu \boldsymbol{u} = \partial_\mu u^\nu \hat{\boldsymbol{e}}^\nu \equiv \sum_{\nu\in\{xyz\}} \left.\frac{\partial \boldsymbol{u}(\boldsymbol{r})}{\partial \boldsymbol{r}}\right|_{\boldsymbol{r}=\boldsymbol{r}_0} \hat{\boldsymbol{e}}^\nu \tag{115}$$

which introduces the Einstein summation convention and a shorthand for the partial derivative in one line! The requirement to evaluate the derivative at $\boldsymbol{r} = \boldsymbol{r}_0$ will (hopefully) be clear from context. Putting ν up top doesn't have any special meaning; it is simply to avoid it colliding with the subscripts 0, 1, ...

For simplicity, shift $\boldsymbol{r}_0 \to 0$ and assume $\boldsymbol{u}(\boldsymbol{r}_0) = 0$, i.e. the origin is stationary under the deformation. Then $\delta\boldsymbol{r} \to \boldsymbol{r}$ and

$$\begin{aligned} \boldsymbol{u} &= (\boldsymbol{\nabla}\boldsymbol{u})\cdot\boldsymbol{r} = (\partial_\mu \boldsymbol{u}) r^\mu \\ u^\nu &= (\partial_\mu u^\nu) r^\mu \end{aligned} \tag{116}$$

The quantities $\partial_\mu u^\nu$ are components of the "elasticity tensor"

$$\begin{aligned} \boldsymbol{\nabla}\boldsymbol{u} &= \begin{pmatrix} \partial_x u^x & \partial_y u^x & \partial_z u^x \\ \partial_x u^y & \partial_y u^y & \partial_z u^y \\ \partial_x u^z & \partial_y u^z & \partial_z u^z \end{pmatrix} \\ &= \begin{pmatrix} \partial_x u^x & (\partial_y u^x + \partial_x u^y)/2 & (\partial_z u^x + \partial_x u^z) \\ (\partial_y u^x + \partial_x u^y)/2 & \partial_y u^y & (\partial_z u^y + \partial_y u^z)/2 \\ (\partial_z u^x + \partial_x u^z)/2 & (\partial_z u^y + \partial_y u^z)/2 & \partial_z u^z \end{pmatrix} \\ &+ \begin{pmatrix} 0 & (\partial_y u^x - \partial_x u^y)/2 & (\partial_z u^x - \partial_x u^z)/2 \\ -(\partial_y u^x - \partial_x u^y)/2 & 0 & (\partial_z u^y - \partial_y u^z)/2 \\ -(\partial_z u^x - \partial_x u^z)/2 & -(\partial_z u^y - \partial_y u^z)/2 & 0 \end{pmatrix} \end{aligned} \tag{117}$$

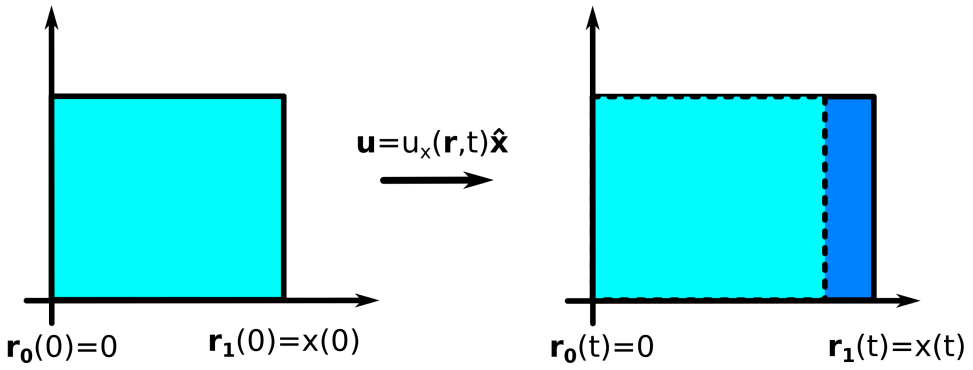

Fig. 10: Caption

where we decompose the tensor into a symmetric and anti-symmetric part:

$$\begin{aligned}\partial_\mu u^\nu &= \frac{1}{2}(\partial_\mu u^\nu + \partial_\nu u^\mu) + \frac{1}{2}(\partial_\mu u^\nu - \partial_\nu u^\mu) \\ &\equiv \eta_{\mu\nu} + \tau_{\mu\nu}\end{aligned} \tag{118}$$

The tensors $\boldsymbol{\eta}$ with components $\eta_{\mu\nu}$ and $\boldsymbol{\tau}$ with components $\tau_{\mu\nu}$ are the *strain* and *rotation* tensors respectively. Let's ignore rotations for now and focus on the strain tensor. The off-diagonal components correspond to shearing. Let us also ignore these and focus on the diagonal components.

C.1 Dilation

We want to know what the diagonal components tell us about the deformation. Look at fig. 10: this shows a deformation $\boldsymbol{u} = u_x\hat{\boldsymbol{e}}^x$ corresponding to homogeneous elongation of a box along the x-axis. The other dimensions are left unchanged. The right coordinate of the edge of the box is originally at $\boldsymbol{r}_1(0) = x(0)\hat{\boldsymbol{e}}^x$. After deformation, it is at $\boldsymbol{r}_1(t) = x(t)\hat{\boldsymbol{e}}^x$. We want to use the theory developed above to relate this transformation to the strain tensor, $\eta_{\mu\nu}$. Recall from eq. 114 that we can write (no summation convention)

$$\boldsymbol{r}_1(t) = \boldsymbol{r}_1(0) + [\boldsymbol{\nabla u}]\cdot\boldsymbol{r}_1(0) = x(0) + \eta_{xx}x(0) \tag{119}$$

where we used the fact that the only non-vanishing component of $\boldsymbol{\nabla u}$ is $\partial_x u_x \equiv \eta_{xx}$. Rearranging, we find

$$\eta_{xx} = \frac{x(t) - x(0)}{x(0)}. \tag{120}$$

It turns out the diagonal components of the strain tensor are the relative elongation of the medium by the deformation $\boldsymbol{u}$!

To belabor this, let's consider another deformation; this time, the box is elongated along both the x- and y-axes (fig. 11). Note that the original area of the box is $A(0) = x(0)y(0)$. After the deformation, we have $x(t) = x(0)[1 + \eta_{xx}]$ and $y(t) = y(0)[1 + \eta_{yy}]$ since the

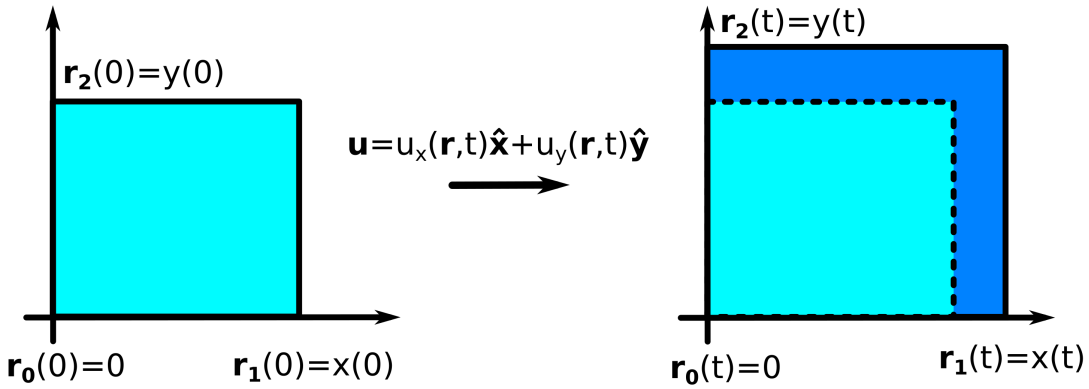

Fig. 11: Caption

deformation does not shear or rotate the box. We have

$$A(t) = x(t)y(t) \approx x(0)y(0)[1 + \eta_{xx} + \eta_{yy}] \tag{121}$$

where we drop the $\eta_{xx}\eta_{yy}$ term (recall that the deformation is small, so $O(\eta^2) \ll O(\eta)$). I.e.

$$\eta_{xx} + \eta_{yy} = \frac{A(t) - A(0)}{A(0)}. \tag{122}$$

Extending this reasoning to a $3D$ deformation with non-vanishing η_{zz}, it is clear that $\eta_{xx} + \eta_{yy} + \eta_{zz} \equiv \mathrm{tr}(\boldsymbol{\eta}) = \boldsymbol{\nabla} \cdot \boldsymbol{u}$ represents the relative change in the volume of the medium around $\boldsymbol{r}$ under deformation $\boldsymbol{u}$. This is what we call "dilation": it is expanding/shrinking of the medium.