Metamaterial superconductors: proof of principle simulation

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Abstract

A concept and theory for producing higher temperature BCS superconductors is explained. The idea is to engineer phonons by introducing large periodicities (we call this supermodulation) in sheets of material with nanofabrication techniques, and thereby influence the T_c of the material. This report presents the theory we base the idea upon and shows preliminary results of that theory implemented in a computer simulation. The theory replaces the usually used BCS electron phonon coupling parameter $N(0)V$, which assumes the electron scattering potential is the same for all wavelengths, with $\lambda = \sum_{\mathbf{q}} \frac{2}{\omega_{\mathbf{q}} N(0)} \sum_{\mathbf{k}} |M_{\mathbf{k},\mathbf{k}+\mathbf{q}}|^2 \delta(\varepsilon_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}})$, which takes the details of electron phonon scattering into account through the matrix element $M_{\mathbf{k},\mathbf{k}+\mathbf{q}}$. This element is calculated based on a tight binding Hamiltonian where the electron hopping parameter is modulated by atomic displacements. The parameter λ can be related to the T_c of a material thgrough $k_B T_c = 1.13\hbar\omega_D e^{\frac{-1}{\lambda}}$. The algorithm used by a computer simulation of this theory written in the programming language MATLAB is described.

Contents

Chapter 1

Introduction

Since the discovery of high T_c superconductivity, the focus has shifted away from the conventional superconductors despite the fact that they remain better understood from a theoretical point of view. Conventional superconductors fall into the framework of the BCS theory, in which the cause of superconductivity has been shown to be electron phonon coupling and our idea to produce higher temperature conventional superconductors begins with this.

The idea here is to alter the phonon dispersion of conventional superconductors so that the electron phonon interaction becomes stronger and BCS theory predicts that the T_c of a given material should increase as a result.

Rather than influencing the phonon dispersion by chemical means and altering the material on the atomic level, the idea is to use nanofabrication techniques to embed much larger periodicities in thin films of superconductors. The first and easiest concept is to produce films of material with periodically recurring holes with a diameter of perhaps hundreds of unit cells (limited by the nanofabrication techniques at our disposal). Before producing samples to test this concept in reality, it was opted to attempt to provide a proof of principle by way of a computer simulation.

The simulation is based on a tight binding Hamiltonian, a variant of the Barišić-Labbé-Friedel (BLF) Hamiltonian in which the electron hopping parameter is modulated by atomic displacements. The electron and phonon terms of this Hamiltonian can be diagonalized by the usual Fourier transforms and second quatized phonon oscillator operators. When these variables are found and substituted in the electron-phonon coupling term of the Hamiltonian, a matrix element $M_{\mathbf{k},\mathbf{k}+\mathbf{q}}$ emerges, which is a matrix element for electron-phonon scattering processes from $\mathbf{k}$ to $\mathbf{k}+\mathbf{q}$ in the Brillouin zone.

This matrix element can be linked to the T_c of a material through a parameter which is given by

$$\lambda = \sum_{\mathbf{q}} \frac{2}{\omega_{\mathbf{q}} N(0)} \sum_{\mathbf{k}} |M_{\mathbf{k},\mathbf{k}+\mathbf{q}}|^2 \delta(\varepsilon_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}}). \tag{1.1}$$

This parameter can be related to the T_c of a material through, for example[*],

$$k_B T_c = 1.13\hbar\omega_D e^{\frac{-1}{\lambda}}. \tag{1.2}$$

In principle, this makes it possible to calculate the strength of the electron phonon interaction from this BLF Hamiltonian, and link it to the T_c of a material, but the calculation can only be done analytically for the simple cases of the one dimensional monoatomic and diatomc chains.

Since we will eventually produce samples with periodicities much larger than a single unit cell, we need a way to carry out the calculation leading up to the λ parameter for arbitrary "unit cell" size and composition. We refer to our somewhat artificial unit cells as *supermodulations* to avoid confusing our nanofabricated large periodicites with the much smaller unit cells. We use the term *supermodulation length* (symbol: L) to denote the number of atoms in one such "unit cell" or supermodulation.

The calculation mentioned above becomes impossible to carry out analytically for large supermodulation lengths, but it turns out that a formula can be derived which relates the general scattering matrix element, for arbitrary supermodulation, to the monoatomic matrix element which can be obtained analytically.

Thus we have all steps required to get from our model Hamiltonian to the T_c of a material. These steps are worked out in detail and presented in the form of a procedure in the next two chapters of this thesis, as well as the example calculations of the monoatomic and diatomic chains.

That procedure has been implemented in a computer simulation using the programming language MATLAB, and the last chapter of this thesis presents preliminary results obtained using that simulation.

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[*] Other relations between T_c and such scattering potentials exist, depending on the strenght of the electron-phonon coupling.

Chapter 2

Motivation

The general idea of the project this thesis is part of is to manufacture higher T_c BCS superconductors with nanofabrication techniques. This chapter contains an overview of the full picture, touching briefly on all its aspects. Specifically it deals with the link between BCS superconductivity and the theory the rest of the thesis uses, a brief overview of the most important points of that theory and the preliminary idea for fabricating the devices to test the concept in practice.
A note on notation: in the remainder of this document vectors are denoted with an arrow, so $\vec{v}$, while boldcase is used for matrices and for subscrips that contain vector and band index information, for example $\omega_{\mathbf{k}}$ denotes a phonon dispersion relation where $\mathbf{k}$ contains wavevectors $\vec{k}$ in the Brillouin zone and band index.

2.1 Beyond BCS electron phonon coupling

In BCS theory, the cause of superconductivity is taken to be electron phonon interaction and the most important parameter for characterizing electron phonon coupling is $N(0)V$, the electron density of states at Fermi level multiplied by the potential energy associated with changing the momentum of an electron. BCS theory assumes this potential energy to be constant for all wavevectors up to some cutoff vector, and predicts that the critical temperature of a superconductor and this parameter are related through the exponential [3] [2]

$$k_B T_c = 1.13\hbar\omega_D e^{\frac{-1}{N(0)V}}. \tag{2.1}$$

Here, ω_D is the Debye cutoff frequency.
The idea is to replace the parameter $N(0)V$ with a parameter which takes the phonons into account in greater detail. This parameter is called λ (*not* the penetration depth) and is given by [4]

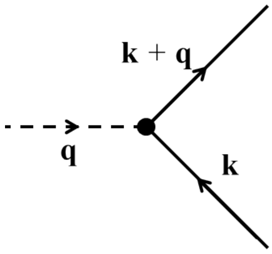

Figure 2.1: *Feynmann diagram of the electron phonon scattering process with amplitude* $M_{\mathbf{k},\mathbf{k}+\mathbf{q}}$

$$\lambda = \sum_{\mathbf{q}} \frac{2}{\omega_{\mathbf{q}} N(0)} \sum_{\mathbf{k}} |M_{\mathbf{k},\mathbf{k}+\mathbf{q}}|^2 \delta(\varepsilon_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}}), \tag{2.2}$$

where $M_{\mathbf{k},\mathbf{k}+\mathbf{q}}$ is the matrix element for scattering an electron from a state $\mathbf{k}$ to a state $\mathbf{k}+\mathbf{q}$, as depicted in diagram form in figure 2.1. The $\omega_{\mathbf{q}}$ is the phonon dispersion and the delta functions restrict the two summations to states at the Fermi energy, as only these electrons can partake in the interactions (The Fermi level is assumed be at energy zero, $E_F = 0$). The subscripts include wavevector and band index, therefore the above formula is general. Furthermore, the matrix element M in principle includes all information about the electron phonon scattering process such as the actual (measured) phonon dispersion, screening effects, vertex corrections etc. This is important to note, as it implies that to obtain the full M, which would yield the "real" λ, one needs detailed information about all kinds of things that are difficult to measure and impossible to calculate in full detail. In this project, we will attempt to obtain knowledge about the behavior of λ based on a higly theoretical , apporximate M. This is the topic of the next section. [2]
It is useful also to define $\mathbf{q}$ dependent λ as

$$\lambda_{\mathbf{q}} = \frac{2}{\omega_{\mathbf{q}} N(0)} \sum_{\mathbf{k}} |M_{\mathbf{k},\mathbf{k}+\mathbf{q}}|^2 \delta(\varepsilon_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}}), \tag{2.3}$$

so that $\lambda = \sum_{\mathbf{q}} \lambda_{\mathbf{q}}$. This $\lambda_{\mathbf{q}}$ will often be plotted against the Brillouin zone for diagnostics purposes [4].
The parameter λ replaces the BCS parameter $N(0)V$ in 2.1 and substitution yields

$$k_B T_c = 1.13\hbar\omega_D e^{\frac{-1}{\lambda}}. \tag{2.4}$$

2.2 The BLF Hamiltonian

The idea in this project is to simulate λ based on a highly simplified theoretical matrix element M which arises from a model Hamiltonian based on tight bind-

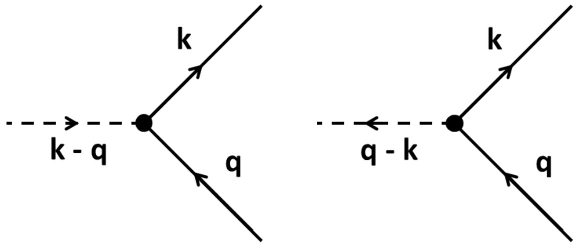

Figure 2.2: *Feynmann diagrams for the electron phonon scattering processes as they appear in equation 2.6, both of which occur with amplitude* $g(\mathbf{k},\mathbf{q})$.

ing electrons modulated by atomic displacements. This Hamiltonian is the BLF Hamiltonian:

$$H = \overbrace{\sum_i \frac{\vec{p}_i^{\,2}}{2m_i} + \sum_{<ij>} \frac{1}{2}\kappa\left(\vec{u}_i - \vec{u}_j\right)^2}^{\text{phonons}} - \overbrace{\sum_{<ij>\sigma} \underbrace{\left(t - \vec{\alpha}\cdot\left(\vec{u}_i - \vec{u}_j\right)\right)}_{\text{hopping parameter}} \Big(c^\dagger_{i\sigma}c_{j\sigma} + h.c.\Big)}^{\text{electrons + electron−phonon coupling}} . \tag{2.5}$$

The first two sums in the BLF Hamiltonian are the kinetic and potential energies of the atoms, the $\vec{p}_i$ and $\vec{u}_i$ represent the momentum and displacement from equilibrium of atom i, m_i is its mass and κ the spring constant of the "spring" connecting nearest neighbors. The third sum appearing in the Hamiltonian 2.5 is the electron part, it is based on tight binding (hopping amplitude t) but modulated with atomic displacements ($\vec{\alpha}\cdot\left(\vec{u}_i - \vec{u}_j\right)$). The vector $\vec{\alpha}$ quantifies the strength of the coupling to atomic displacement. The $c^\dagger_{i\sigma}$ and $c_{j\sigma}$ are electron creation and annihilation operators respectively.

If we transfer to momentum space, the BLF Hamiltonian becomes

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} c^\dagger_{\mathbf{k}} c_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} a^\dagger_{\mathbf{q}} a_{\mathbf{q}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{kq}} g(\mathbf{k},\mathbf{q}) \Big(a_{\mathbf{k}-\mathbf{q}} + a^\dagger_{-(\mathbf{k}-\mathbf{q})}\Big) c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{q}\sigma}. \tag{2.6}$$

Here, the $a_{\mathbf{k}}$'s are boson oscillator operators that diagonalize the phonon part of the Hamiltonian and the $c_{\mathbf{k}}$ and $c^\dagger_{\mathbf{k}}$ are fermion creation and annihilation operators which diagonalize the thight binding electron Hamiltonian, and the subscripts again contain wavector and band index information. The third sum in 2.6 represents the electron phonon coupling, with amplitude $g(\mathbf{k},\mathbf{q})$ for electron-phonon scattering processes. These processes can be graphically represented by diagrams as in figure 2.2.
Thus the amplitude $g(\mathbf{k},\mathbf{q})$ in the Hamiltonian 2.6 is the matrix element for the electron phonon scattering processes we are interested in, as *calculated* based on the BLF Hamiltonian 2.5. A glance at the formula for λ in 2.2 reveals that

the Hamiltonian in equation 2.6 contains all information necessary to calculate λ. With the identification $g(\mathbf{k},\mathbf{q}) = M_{\mathbf{k},\mathbf{k}+\mathbf{q}}$ we see that it contains M and the phonon dispersion explicitely, and the electron dispersion $\epsilon_{\mathbf{k}\sigma}$ can be used to calculate the electronic density of states $N(0)$.
With this, we are in principle in a position to calculate λ. The problem is that the calculation bringing Hamiltonian 2.5 to the Hamiltonian 2.6 can only be done analytically for some simple cases, such as the one dimesional monoatomic and diatomic chains. These two cases are worked out analytically in the next chapter.
For a general case, the dispersions and g-function cannot be found analytically and we use a numerical calculation written in the programing language MATLAB.

Milan Allan and Mark Fischer recently wrote down a procedure for relating the general matrix element M back to the matrix element for the monoatomic case. This procedure is worked out in detail in chapter 3 of this document. Here we state without calculation only the formula relating the general case to the monoatomic case:

$$M^{\nu}_{\vec{k},\vec{k}+\vec{q}} = \frac{1}{\sqrt{L}} \frac{g(\vec{k},\vec{q})}{\sqrt{2\omega^{\nu}_{\vec{q}}}} \sum_{\alpha} l^{\alpha}_{\vec{q}} C^{\alpha\nu}_{\vec{q}}. \tag{2.7}$$

The band index is now included explicitely and appears as a superscript, and the subscrips represent only wavevectors taken from the Brillouin zone defined by the problem. The $g(\vec{k},\vec{q})$ is the matrix element for the monoatomic case and therefore only has one band, so no superscript. The sum appearing in 2.7 runs over all bands and $l^{\alpha}_{\vec{q}}$ is given by

$$l^{\alpha}_{\vec{q}} = \frac{e^{i\vec{q}\cdot\vec{r}_{\alpha}}}{\sqrt{m_{\alpha}}}.$$

.
$C^{\alpha\nu}_{\vec{q}}$ is an element of the matrix of eigenvectors of the interaction matrix that needs to be diagonalized in order to find the phonon dispersion and oscillator operators. The origin of this factor is explained in chapter 3.
With all of this, we have a complete procedure for finding our theoretical λ parameter:

1. Write down the BLF Hamiltonian in real space, for the situation we wish to calculate λ for.

2. Diagonalize the bare electron and phonon Hamiltonian and extract the phonon dispersion, consisting of the eigenvalues of interaction matrices. In order to relate the general coupling function to the monoatomic one,

we also need the transformation matrix $C^{\alpha\nu}_{\vec{q}}$ consisting of the eigenvectors of these interaction matrices. The MATLAB code therefore stores this information at this stage.

3. Calculate the general coupling function $M_{\vec{k},\vec{k}+\vec{q}}$ using formula 2.7 and compute λ via equation 2.2.

The MATLAB code, which is the subject of chapter 4 of this thesis, will use this procedure to obtain the λ parameter.

2.3 Possible realisation using nanofabrication

The first experimental test we intend to conduct will be done on thin sheets of material with a periodic array of holes acting as a supermodulation that influences the phonon dispersion of the material. Such devices have not been built yet, and we do not have concrete details at this point, but some general considerations can be stated. The devices will be built from elemental superconductors such as lead and the sheets will have the supermodulation imposed in the form of a perforated sheet of material, with preiodically recurring holes. Since we want the electron dispersion to remain unchanged while changing the phonons, the holes will not be made directly in the superconducting material. Rather, another layer will be grown on top and holes will be made in that material so that the phonons of the underlying superconducting layer will be influenced by the presence or lack of material on top. Figure 2.3 shows several steps of a possible nanofabrication procedure, We will test the setup with varying hole sizes. In principle we want the smallest holes to be as small as we can possibly produce, so the limit is determined only by the nanofabrication facilities at our disposal. Once these devices are produced, the critcal temperature will most likely be detemined by measuring the critical magnetic field of the devices.

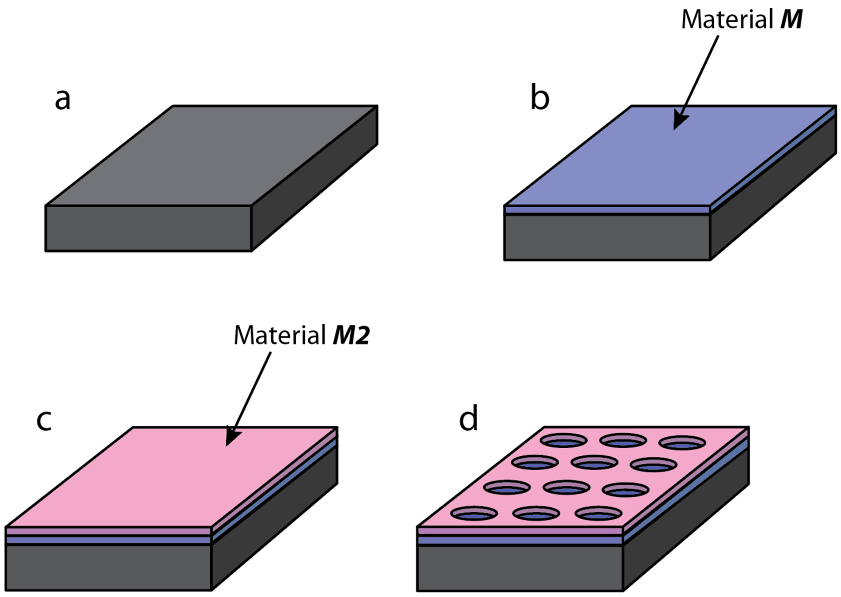

Figure 2.3: *Possible realization of the theory using nanofabrication, several steps are shown: a) a substrate, b) grow superconducting material on top of substrate, c) grow a sheet of material on top of the superconductor, d) introduce supermodulation by making holes in the topmost material, without making holes in the superconductor. Due to the different rigidity in the superconducting layer arising from presence or lack of material on top, we only influence the phonons in the superconductor without affecting the electron dispersion.*

Chapter 3

Calculating λ from the BLF Hamiltonian

This chapter presents an example of the procedure used to find the electron phonon coupling function necessary for the calculation of the λ parameter. The example is that of the monoatomic one dimensional chain, and the full calclulation leading up to finding the coupling function $g(k, q)$ is worked out in detail for the monoatomic case. The diatomic chain is computed up to finding the variables which diagonalize the electrons and phonons. In the end, the atomic displacement variables that diagonalize the phonon Hamiltonian describing the diatomic chain are written in terms of the variables that diagonalize the monoatomic chain Hamiltonian, so the first step is to recap the calculation for the monoatomic chain. The final section of this chapter describes the procedure to relate the exactly solvable case of the monoatomic chain to an arbitrary supermodulation. This is used later in the code.

3.1 Notation

Since this chapter is rather math-intensive, we start with a summary of all the commonly occuring symbols and their meaning as used in the remainder of this chapter.

a		Periodicity of atomic positions (lattice constant)
t		Electron hopping parameter
m_n		Mass of atom n
κ		Spring constant between neighbouring atoms
α		Electron-phonon coupling parameter
N	$\in \mathbb{N}$	Number of atoms in the chain
L	$\in \mathbb{N}$	Periodicity of supermodulation, $L \ll N$
M	$= N/L$	Number of unit cells, assumed to be $\in \mathbb{N}$
n, m	$\in \{1...N\}$	Enumerators denoting position on the chain
k, q		The wavevector for the FT w.r.t. a
α, β	$\in \{1...L\}$	Enumerators denoting position within unit cell
R, R'	$\in \{1...M\}$	Indicator of Unit cell
u_n		Displacement of ion n
u_q		The FT of the displacemetns u_n with respect to a
Q, Q'		The wavevector for the FT with respect to $L \cdot a$
x_n, x_R		Position of atom or unit cell. Has dimension of length.
ν	$\in \{1...L\}$	Band index.

3.2 Monoatomic chain: $L = 1$

This section contains a calculation of the bare electron and phonon dispersions as well as the calculation of the coupling function $g(k, q)$, for the one dimensional monoatomic chain. The monoatomic chain is worked out in detail because the general case, which will be treated later, turns out to require some results from the monoatomic case.

The monoatomic chain consists of N atoms, with lattice constant a and ionic mass m, making the realspace BLF Hamiltonian for the one dimensional monoatomic chain:

$$H = \sum_n \frac{p_n^2}{2m} + \frac{\kappa}{2}(u_n - u_{n+1})^2 - \sum_{n\sigma}(t - \alpha(u_n - u_{n+1}))\left(c^\dagger_{(n+1)\sigma}c_{n\sigma} + h.c\right). \quad (3.1)$$

The summation over nearest neighbors has been written explicitly in the above expression. m is the mass of the atoms and κ the spring constant of the "spring" connecting each neighbor.

3.2.1 The electron part

Starting with the realspace BLF Hamiltonian, 2.5, the first step is to find variables which diagonalize the bare electron and phonon parts of the Hamiltonian. We start with the electron part,

$$H_{electron} = -t \sum_{i\sigma} c^\dagger_{(i+1)\sigma}c_{i\sigma} + c^\dagger_{i\sigma}c_{(i+1)\sigma}. \quad (3.2)$$

The sum over the spin index σ will be ommited from now on.
The electron Hamiltonian 3.5 is diagonalized by the Fourier transform

$$\begin{aligned} c_j &= \frac{1}{\sqrt{N}} \sum_k c_k e^{ikx_j}, \\ c_j^\dagger &= \frac{1}{\sqrt{N}} \sum_k c_k^\dagger e^{-ikx_j}. \end{aligned} \tag{3.3}$$

Substituting these expressions into 3.5 gives

$$\begin{aligned} H &= -t \sum_k (e^{ika} + e^{-ika}) c_k^\dagger c_k \\ &= -2t \sum_k \cos{(ka)} c_k^\dagger c_k, \end{aligned} \tag{3.4}$$

where the standard tight binding electron dispersion relation is recognized:

$$\epsilon_k = -2t \cos ka. \tag{3.5}$$

3.2.2 The phonons

The phonon part of the realspace BLF Hamiltonian can be written as

$$H_{phonon} = \sum_n \frac{p_n^2}{2m} + \frac{\kappa}{2} (u_n - u_{n+1})^2. \tag{3.6}$$

The p's and u's are atomic momentum and displacement variables.
The procedure for finding the oscillator operators required to bring our Hamiltonian into the form 2.6 begins by introducing the Fourier transforms:

$$\begin{aligned} u_n &= \frac{1}{\sqrt{N}} \sum_k u_k e^{ikx_n}, \\ p_n &= \frac{1}{\sqrt{N}} \sum_k p_k e^{ikx_n}. \end{aligned} \tag{3.7}$$

Substituting into the Hamiltonian 3.6 yields, for the first term

$$\begin{aligned} \sum_n \frac{p_n^2}{2m} &= \frac{1}{2mN} \sum_n^N \sum_k p_k e^{ikx_n} \sum_q p_q e^{iqx_n} \\ &= \frac{1}{2mN} \sum_n^N \sum_{k,q} p_k p_q e^{ix_n(k+q)} \\ &= \frac{1}{2m} \sum_{k,q} p_k p_q \delta_{k,-q} \\ &= \frac{1}{2m} \sum_k p_k p_{-k}. \end{aligned}$$

And for the second term

$$\begin{aligned}
\sum_n \frac{\kappa}{2}(u_n - u_{n+1})^2 &= \frac{\kappa}{2N}\sum_n^N \sum_k u_k e^{ikx_n} - u_k e^{ik(x_n+a)} \sum_q u_q e^{iqx_n} - u_q e^{iq(x_n+a)} \\
&= \frac{\kappa}{2N}\sum_n^N \sum_{k,q} u_k u_q e^{i(k+q)x_n}(1 - e^{ika} - e^{iqa} + e^{i(k+q)a}) \\
&= \frac{\kappa}{2}\sum_{k,q} u_k u_q \delta_{k,-q}(1 - e^{ika} - e^{iqa} + e^{i(k+q)a}) \\
&= \frac{\kappa}{2}\sum_{k} u_k u_{-k}(1 - e^{ika} - e^{i-ka} + 1) \\
&= \kappa \sum_k (1 - \cos ka) u_k u_{-k}.
\end{aligned}$$

Using $1 - \cos\theta = 2\sin^2\theta/2$ and putting together the terms gives the Hamiltonian in terms of the u_ks and p_ks:

$$H_{phonon} = \sum_k \frac{1}{2m} p_k p_{-k} + 2\kappa \sin^2\left(\frac{ka}{2}\right) u_k u_{-k}. \tag{3.8}$$

At this point it is convenient to define the dimensionless variables $\tilde{p}_k$ and $\tilde{u}_k$ by

$$\begin{aligned}
u_k &= \ell_k \tilde{u}_k, \\
p_k &= \frac{\hbar}{\ell_k}\tilde{p}_k,
\end{aligned} \tag{3.9}$$

with ℓ_k given by

$$\ell_k^2 = \frac{\hbar}{2\sqrt{\kappa m \sin^2(ka/2)}}. \tag{3.10}$$

With this substitution the Hamiltonian becomes

$$H_{phonon} = \sum_k \hbar \sqrt{\frac{\kappa}{m}\sin^2\left(\frac{ka}{2}\right)}(\tilde{p}_k \tilde{p}_{-k} + \tilde{u}_k \tilde{u}_{-k}). \tag{3.11}$$

The oscillator operators can be defined in terms of $\tilde{p}_k$ and $\tilde{u}_k$:

$$\begin{aligned}
a_k &= \frac{1}{\sqrt{2}}(\tilde{u}_k + i\tilde{p}_k), \\
a_k^\dagger &= \frac{1}{\sqrt{2}}(\tilde{u}_{-k} - i\tilde{p}_{-k}).
\end{aligned} \tag{3.12}$$

The second equation (the phonon creation operator) follows from $\tilde{u}_k^* = \tilde{u}_{-k}$ and $\tilde{p}_k^* = \tilde{p}_{-k}$. These relations are implied by the definitions of the u_k and p_k in equation 3.7.

The inverses are given by

$$\begin{aligned} \tilde{u}_k &= \frac{1}{\sqrt{2}}(a_k + a^\dagger_{-k}), \\ \tilde{p}_k &= \frac{1}{i\sqrt{2}}(a_k - a^\dagger_{-k}). \end{aligned} \tag{3.13}$$

With this, we have

$$\begin{aligned} \tilde{p}_k\tilde{p}_{-k} &= -\frac{1}{2}\left(a_k - a^\dagger_{-k}\right)\left(a_{-k} - a^\dagger_k\right) \\ &= -\frac{1}{2}\left(a_k a_{-k} - a_k a^\dagger_k - a^\dagger_{-k}a_{-k} + a^\dagger_{-k}a^\dagger_k\right), \\ \tilde{u}_k\tilde{u}_{-k} &= \frac{1}{2}\left(a_k + a^\dagger_{-k}\right)\left(a_{-k} + a^\dagger_k\right) \\ &= \frac{1}{2}\left(a_k a_{-k} + a_k a^\dagger_k + a^\dagger_{-k}a_{-k} + a^\dagger_{-k}a^\dagger_k\right), \end{aligned}$$

and therefore

$$\begin{aligned} \tilde{p}_k\tilde{p}_{-k} + \tilde{u}_k\tilde{u}_{-k} &= a_k a^\dagger_k + a^\dagger_{-k}a_{-k} \\ &= 1 + a^\dagger_k a_k + a^\dagger_{-k}a_{-k}. \end{aligned} \tag{3.14}$$

The second line follows from the fact that the operators a and $a^\dagger$ obey the Boson-Heisenberg algebra, $[a_k, a^\dagger_k] = 1 \Rightarrow a_k a^\dagger_k = 1 + a^\dagger_k a_k$.
Since the expression in equation 3.14 appears in a sum over the Brillouin zone, which can be chosen symmetric around $k = 0$, we have that

$$\sum_k a^\dagger_k a_k + a^\dagger_{-k}a_{-k} = \sum_k 2a^\dagger_k a_k.$$

With this, the Hamiltonian in 3.11 becomes

$$\begin{aligned} H_{phonon} &= \sum_k \hbar\sqrt{\frac{\kappa}{m}\sin^2\left(\frac{ka}{2}\right)}(1 + 2a^\dagger_k a_k) \\ &= \sum_k 2\hbar\sqrt{\frac{\kappa}{m}\sin^2\left(\frac{ka}{2}\right)}\left(a^\dagger_k a_k + \frac{1}{2}\right) \\ &= \sum_k \hbar\omega_k\left(a^\dagger_k a_k + \frac{1}{2}\right), \end{aligned}$$

which is the Hamiltonian of N independent harmonic oscillators, the normal modes, with the dispersion relation

$$\omega_k = 2\sqrt{\frac{\kappa}{m}\sin^2\left(\frac{ka}{2}\right)}.$$

3.2.3 Electron phonon coupling

Now that the variables which diagonalize the bare electron and phonon parts of the Hamiltonian have been found, they can be substituted into the electron phonon part given by

$$H_{el-ph} = \sum_n \alpha(u_n - u_{n+1})\left(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n\right). \tag{3.15}$$

The parameter α is the electron-phonon coupling strength. The other variables are the same as before, and the transfer to Fourier space is again achieved by the substitutions 3.3 and 3.7.
We will work out the two factors in the sum individually:

$$\begin{aligned} u_n - u_{n+1} &= \frac{1}{\sqrt{N}} \sum_k u_k e^{ikx_n} - u_k e^{ikx_{n+1}} \\ &= \frac{1}{\sqrt{N}} \sum_k u_k e^{ikx_n} - u_k e^{ikx_n} e^{ika} \\ &= \frac{1}{\sqrt{N}} \sum_k \left(1 - e^{ika}\right) u_k e^{ikx_n}. \end{aligned}$$

And:

$$\begin{aligned} c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n &= \frac{1}{N} \sum_{p,q} c_p^\dagger e^{-ipx_n} c_q e^{iqx_{n+1}} + c_p^\dagger e^{-ipx_{n+1}} c_q e^{iqx_n} \\ &= \frac{1}{N} \sum_{p,q} c_p^\dagger c_q e^{-i(p-q)x_n} e^{iqa} + c_p^\dagger c_q e^{-i(p-q)x_n} e^{-ipa} \\ &= \frac{1}{N} \sum_{p,q} \left(e^{iqa} - e^{-ipa}\right) c_p^\dagger c_q e^{-i(p-q)x_n}. \end{aligned}$$

Putting this into the Hamiltonian gives:

$$\begin{aligned} H_{el-ph} &= \frac{\alpha}{N^{3/2}} \sum_n \sum_{k,p,q} \left(1 - e^{ika}\right) u_k e^{ikx_n} \times \left(e^{iqa} - e^{-ipa}\right) c_p^\dagger c_q e^{-i(p-q)x_n} \\ &= \frac{\alpha}{N^{3/2}} \sum_n \sum_{k,p,q} \left(1 - e^{ika}\right)\left(e^{iqa} - e^{-ipa}\right) u_k c_p^\dagger c_q e^{-i(p-q-k)x_n} \\ &= \frac{\alpha}{\sqrt{N}} \sum_{k,p,q} \left(1 - e^{ika}\right)\left(e^{iqa} - e^{-ipa}\right) u_k c_p^\dagger c_q \ \delta_{k,p-q} \\ &= \frac{\alpha}{\sqrt{N}} \sum_{p,q} \left(1 - e^{i(p-q)a}\right)\left(e^{iqa} - e^{-ipa}\right) u_{p-q} c_p^\dagger c_q \\ &= \frac{\alpha}{\sqrt{N}} \sum_{p,q} \left(e^{iqa} + e^{-ipa} - e^{iqa} - e^{-ipa}\right) u_{p-q} c_p^\dagger c_q \\ &= -\frac{2i\alpha}{\sqrt{N}} \sum_{p,q} (\sin pa - \sin qa) u_{p-q} c_p^\dagger c_q. \end{aligned}$$

At this point the u_{p-q} can be written in terms of the oscillator operators from the previous section to give Hamiltonian in the form 2.6. The present form is more useful for our purposes though, as we will be need the variable u_q for the general case later. To bring the Hamiltonian into a form containg u_q explicitly, the substitutions $p = k + \tilde{q}/2$ and $q = k - \tilde{q}/2$ are made, this gives

$$H_{el-ph} = -\frac{4i\alpha}{\sqrt{N}} \sum_{k,\tilde{q}} \sin\left(\frac{\tilde{q}a}{2}\right) \cos\left(ka\right) u_q c^{\dagger}_{k+\tilde{q}/2} c_{k-\tilde{q}/2}. \tag{3.16}$$

The coupling amplitude for the process of momentum exchange between the electronic part of the system and atomic displacements has been found to be:

$$\tilde{g}(k,q) = -4i\alpha \sin\left(\frac{qa}{2}\right) \cos\left(ka\right). \tag{3.17}$$

The tilde on the $\tilde{g}(k,q)$ is there to differentiate this coupling amplitude, which does not include the actual phonon operators, from the $g(\mathbf{k},\mathbf{q})$ in equation 2.6. We will later use this $\tilde{g}(k,q)$ and not the actual $g(k,q)$, so we can consider the calculation finished at this stage.

3.3 Diatomic chain: $L = 2$

The above calculation is done in this section for the diatomic chain. It is assumed that the electron part of the Hamiltonian is the same as in the monoatomic case, as well as the electron phonon coupling strenght α. Therefore, the calculation for the bare electron part is exactly the same, with the substitution 3.3 diagonalizing the electronic part of the Hamiltonian. This calculation done here is closer to the way the theory is implemented in code later for a general supermodulation and is meant to serve as an example of the general procedure. It is also meant to provide some intuition for the concepts treated in the general formalism and the implementation in the code.

The diatomic chain consists of a unit cell with two masses m_1 and m_2 which repeats M times. As in the monoatomic case, the chain contains N atoms in total, so $N = 2M$. The phonon part of the Hamiltonian can now be written in the general form

$$H_{phonon} = \sum_n \frac{p_n^2}{2m_n} + \sum_{m,n} u_n V_{mn} u_m. \tag{3.18}$$

Nearest neighbor coupling is still assumed, and with the same spring constant κ, so it is possible to write the interaction matrix element V_{mn} explicitly at this stage and proceed along the same lines as in the previous chapter, i.e substitute the Fourier transforms and go from there. The alternative calculation in this chapter is closer to the algorithm the code uses to find the phonon dispersion however, and it requires the more general form for now.

First, the variables are redefined in order to shift the variable mass to the potential energy part

$$\begin{aligned} p_n &= \sqrt{\frac{m_n}{m}}\pi_n, \\ u_n &= \sqrt{\frac{m}{m_n}}\xi_n. \end{aligned} \tag{3.19}$$

The mass m is artificial and could be any number. Substituting these into the phonon Hamiltonian 3.21 results in

$$\begin{aligned} H_{phonon} &= \sum_n \frac{\pi_n^2}{2m} + m\sum_{m,n}\frac{\xi_n}{\sqrt{m_n}}V_{mn}\frac{\xi_m}{\sqrt{m_m}} \\ &= \sum_n \frac{\pi_n^2}{2m} + \sum_{m,n}\xi_n K_{mn}\xi_m, \end{aligned} \tag{3.20}$$

with $K_{mn} = \frac{m}{\sqrt{m_n m_m}}V_{mn}$.

Assuming the same lattice constant, a, makes the periodicity of this diatomic chain $2a$. To avoid confusion, the letter R is introduced to run over this new periodicity, so now $x_{R+1} = x_R + 2a$. Later, in the general case when the periodicity of the supermodulation becomes some general length L, we will have $x_{R+1} = x_R + L$. In order to still be able to account for each atom in the chain, the letters α and β will be used to denote atom 1 or 2 in unit cell R. Furthermore, Q will be used to denote elements from the Brillouin zone defined by this new periodicity. The following sums up the notation for this section:

$$\begin{aligned} R, R' &\in \{1, \ldots, M\}, \\ \alpha, \beta &\in \{1, 2\}, \\ Q, Q' &\in \{-\frac{\pi}{2a}, \ldots, \frac{\pi}{2a}\}. \end{aligned}$$

Relabelling the variables as π_R^α and ξ_R^α makes the Hamiltonian

$$H_{phonon} = \sum_{R,\alpha}\frac{(\pi_R^\alpha)^2}{2m} + \sum_{R,R'}\sum_{\alpha,\beta}^{2}\xi_R^\alpha K_{RR'}^{\alpha\beta}\xi_{R'}^\beta. \tag{3.21}$$

All steps so far are completely general and can be copied for the case of general supermodulation.
The specific $K_{RR'}^{\alpha\beta}$ for the diatomic chain reads

$$\begin{aligned} K_{RR'}^{\alpha\beta} = \frac{m\kappa}{\sqrt{m_\alpha m_\beta}}\Big[&\delta_{R,R'}\big(2\delta_{\alpha,\beta} - \delta_{\alpha,\beta+1} - \delta_{\alpha,\beta-1}\big) \\ &- \delta_{R-1,R'}\delta_{\alpha,1}\delta_{\beta,2} - \delta_{R+1,R'}\delta_{\alpha,2}\delta_{\beta,1}\Big]. \end{aligned} \tag{3.22}$$

The first term in the square brackets forms the connections within the unit cell. The second and third are the connections to the unit cell left and right respectively. The picture in figure 3.1 should clarify the form of the matrix element $K^{\alpha\beta}_{RR'}$.

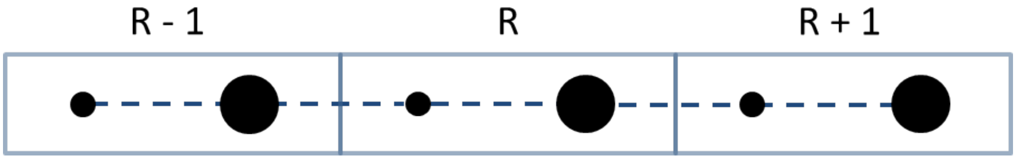

Figure 3.1: *Three unit cells of the diatomic chain, with the small atom having mass m_1 and the big one m_2. The dotted blue lines represent springs with spring constant κ. To make sure the sum in 3.21 runs over all springs, the matrix element $K^{\alpha\beta}_{RR'}$ must contain the interactions within a unit cell, which is ensured by the term containing $\delta_{R,R'}$, as well as connections to the unit cells left and right, ensured by the terms with $\delta_{R-1,R'}$ and $\delta_{R+1,R'}$ respectively. These connection terms are always between the first and last atoms in the unit cell, hence the factors like $\delta_{\alpha,2}\delta_{\beta,1}$.*

Introducing the Fourier transforms with respect to the periodicity of the supermodulation;

$$\begin{aligned}\pi^{\alpha}_{R} &= \frac{1}{\sqrt{M}}\sum_{Q} e^{iQx_R}\pi^{\alpha}_{Q},\\ \xi^{\alpha}_{R} &= \frac{1}{\sqrt{M}}\sum_{Q} e^{iQx_R}\xi^{\alpha}_{Q},\end{aligned} \tag{3.23}$$

and inputting them, as well as the explicit form of $K^{\alpha\beta}_{RR'}$ given in 3.22 into the Hamiltonian 3.21 reveals that the kinetic energy part remains diagonal, and gives a useful form for the potential energy part. First the kinetic part

$$\begin{aligned}\sum_{R,\alpha}\frac{(\pi^{\alpha}_{R})^2}{2m} &= \frac{1}{M}\frac{1}{2m}\sum_{R,\alpha}\sum_{Q,Q'}\pi^{\alpha}_{Q}\pi^{\alpha}_{Q'}e^{i(Q+Q')x_R}\\ &= \frac{1}{2m}\sum_{\alpha}\sum_{Q,Q'}\pi^{\alpha}_{Q}\pi^{\alpha}_{Q'}\delta_{Q,-Q'}\\ &= \sum_{\alpha,Q}\frac{\pi^{\alpha}_{Q}\pi^{\alpha}_{-Q}}{2m}.\end{aligned}$$

And the potential part

$$
\begin{aligned}
\sum_{R,R'}\sum_{\alpha,\beta}\xi^{\alpha}_{R}K^{\alpha\beta}_{RR'}\xi^{\beta}_{R'} &= \frac{1}{M}\sum_{R,R'}\sum_{Q,Q'}\sum_{\alpha,\beta}\xi^{\alpha}_{Q}\xi^{\beta}_{Q'}\frac{m\kappa}{\sqrt{m_\alpha m_\beta}}\Big[\dots\Big]e^{i(Q+Q')x_R+x_{R'}}\\
&= \sum_{R}\sum_{Q,Q'}\sum_{\alpha,\beta}\xi^{\alpha}_{Q}\xi^{\beta}_{Q'}\frac{m\kappa}{\sqrt{m_\alpha m_\beta}}\Big[\big(2\delta_{\alpha,\beta}-\delta_{\alpha,\beta+1}-\delta_{\alpha,\beta-1}\big)\\
&\qquad - e^{-iQ'2a}\delta_{\alpha,1}\delta_{\beta,2}-e^{iQ'2a}\delta_{\alpha,2}\delta_{\beta,1}\Big]e^{i(Q+Q')2x_R}\\
&= \sum_{Q,Q'}\sum_{\alpha,\beta}\xi^{\alpha}_{Q}\xi^{\beta}_{Q'}\frac{m\kappa}{\sqrt{m_\alpha m_\beta}}\Big[\big(2\delta_{\alpha,\beta}-\delta_{\alpha,\beta+1}-\delta_{\alpha,\beta-1}\big)\\
&\qquad - e^{-iQ'2a}\delta_{\alpha,1}\delta_{\beta,2}-e^{iQ'2a}\delta_{\alpha,2}\delta_{\beta,1}\Big]\delta_{Q,-Q'}\\
&= \sum_{Q}\sum_{\alpha,\beta}\xi^{\alpha}_{Q}\xi^{\beta}_{-Q}\frac{m\kappa}{\sqrt{m_\alpha m_\beta}}\Big[\big(2\delta_{\alpha,\beta}-\delta_{\alpha,\beta+1}-\delta_{\alpha,\beta-1}\big)\\
&\qquad - e^{iQ2a}\delta_{\alpha,1}\delta_{\beta,2}-e^{-iQ2a}\delta_{\alpha,2}\delta_{\beta,1}\Big]\\
&= \sum_{Q}\sum_{\alpha,\beta}\xi^{\alpha}_{Q}K^{\alpha\beta}_{Q}\xi^{\beta}_{-Q},
\end{aligned}
\tag{3.24}
$$

with

$$
\begin{aligned}
K^{\alpha\beta}_{Q} = {} & \frac{m\kappa}{\sqrt{m_\alpha m_\beta}}\Big[\big(2\delta_{\alpha,\beta}-\delta_{\alpha,\beta+1}-\delta_{\alpha,\beta-1}\big)\\
&\qquad - \delta_{\alpha,1}\delta_{\beta,2}e^{i2aQ}-\delta_{\alpha,2}\delta_{\beta,1}e^{-i2aQ}\Big].
\end{aligned}
\tag{3.25}
$$

This form reveals that only the parts of the matrix element which connect to the neighboring unit cells get a Q dependence. Furthermore, the final form in equations 3.24 is not quite diagonal due to the sum over α and β. But the double sum can be interpreted as a matrix product, allowing for a different way to write the final expression which is close to the way the code is built. Introducing the vector $\vec{\xi}_Q = (\xi^1_Q, \xi^2_Q)^T$ and noting that its Hermitian conjugate is given by $\vec{\xi}^\dagger_Q = (\xi^1_{-Q}, \xi^2_{-Q})$ due to the definitions 3.23 allows us to write;

$$
\sum_{Q}\sum_{\alpha,\beta}\xi^{\alpha}_{Q}K^{\alpha\beta}_{Q}\xi^{\beta}_{-Q} = \sum_{Q}\vec{\xi}^\dagger_Q\mathbf{K}_Q\vec{\xi}_Q,
$$

with the matrix $\mathbf{K}_Q$ given by

$$
\mathbf{K}_Q = m\kappa\begin{bmatrix} \frac{2}{m_1} & \frac{-1-e^{-i2aQ}}{\sqrt{m_1 m_2}} \\ \frac{-1-e^{i2aQ}}{\sqrt{m_1 m_2}} & \frac{2}{m_2} \end{bmatrix}.
$$

This matrix is Hermitian, and expressions of the kind $\vec{\xi}_Q^\dagger \mathbf{K}_Q \vec{\xi}_Q$ can always be diagonalized if the matrix is Hermitian by the basis transformation $\vec{\xi}_Q = \mathbf{C}_Q \vec{\mu}_Q$, with $\mathbf{C}_Q$ the matrix of eigenvectors (as collumns) of $\mathbf{K}_Q$.
The matrix $\mathbf{K}_Q$ has two eigenvalues in this case, λ_Q^1 and λ_Q^2, and with the matrix $\mathbf{D}_Q$ = diag$\{\lambda_Q^1, \lambda_Q^2\}$ the expression inside the sum is diagonalized as follows

$$\begin{aligned} \vec{\xi}_Q^\dagger \mathbf{K}_Q \vec{\xi}_Q &= (\mathbf{C}_Q \vec{\mu}_Q)^\dagger \mathbf{K}_Q \mathbf{C}_Q \vec{\mu}_Q \\ &= \vec{\mu}_Q^\dagger \mathbf{C}_Q^\dagger \mathbf{K}_Q \mathbf{C}_Q \vec{\mu}_Q \\ &= \vec{\mu}_Q^\dagger \mathbf{D}_Q \vec{\mu}_Q \\ &= \sum_\nu^2 \lambda_Q^\nu \mu_{-Q}^\nu \mu_Q^\nu. \end{aligned} \tag{3.26}$$

The index ν introduced here is used to denote band index. It runs over two values just like α and β but since it no longer has the meaning of position within unit cell, we opted to change the symbol in order to avoid confusion. The rest of this document uses the symbol ν to denote band index. Therefore the expression obtained in 3.24 is brought to a diagonal form by this basis transformation

$$\sum_Q \sum_{\alpha,\beta} \xi_Q^\alpha K_Q^{\alpha\beta} \xi_{-Q}^\beta = \sum_Q \sum_\nu^2 \lambda_Q^\nu \mu_{-Q}^\nu \mu_Q^\nu.$$

With this, the full Hamiltonian has been brought to a form analogous to equation 3.8:

$$H_{phonon} = \sum_{\nu,Q} \frac{\pi_Q^\nu \pi_{-Q}^\nu}{2m} + \lambda_Q^\nu \mu_Q^\nu \mu_{-Q}^\nu,$$

with the variables π_Q^ν and μ_Q^ν taking the roles of the old p_k and u_k. The calculation to find the oscillator operators and the phonon dispersion is exactly analogous to the calculation following equation 3.8, so rather than repeating that calculation we note that the factor multiplying $u_k u_{-k}$ is exactly $m\omega_k^2/2$ and provide a calculation to show that the λ_Q^ν and the diatomic dispersion ω_Q^ν are related through[*].

$$\lambda_Q^\nu = m(\omega_Q^\nu)^2 \quad \Rightarrow \quad \omega_Q^\nu = \sqrt{\frac{\lambda_Q^\nu}{m}}. \tag{3.27}$$

The eigenvalues of the matrix $\mathbf{K}_Q$ are given by

$$\lambda_Q^\pm = m\kappa \frac{m_1 + m_2 \pm \sqrt{m_1^2 + m_2^2 + 2m_1 m_2 \cos(2Qa)}}{m_1 m_2}$$

---

[*] The lack of the factor 2 is (presumably) due to the fact that we have a factor $\kappa/2$ in the monoatomic case, which is replaced by the K matrix in the diatomic case. For a full analogy, we should divide the K matrix by 2 in the beginning

and the phonon dispersion relation for the diatomic chain is known to be

$$(\omega_Q^{\pm})^2 = \kappa \frac{m_1 + m_2 \pm \sqrt{m_1^2 + m_2^2 + 2m_1 m_2 \cos(2Qa)}}{m_1 m_2}.$$

This confirms the claim in equation 3.27.

3.4 Formalism: $L \in \mathbb{N}$

This section generalizes the calculation conducted for the $L = 1$ and $L = 2$ cases in the previous sections to an arbitrary supermodulation lenght. It is still constrained to one dimensional atomic chains. This is due to the fact that the MATLAB code only implements the one dimensional calculation at the time of writing of this thesis, for details see chapter 4. The electron part of the calculation remains the same as in the monoatomic and diatomic cases, it is assumed that the periodicity of the electrons is the same as the monoatomic version for all supermodulations. This section introduces an arbitrary supermodulation "lenght" L. The accolades in the previous sentance are there to emphesize that in our notation L is *dimensionless* and just denotes the number of atoms in our supermodulation. It is *not* the length of the unit cell defined by the supermodulation, that length is La, since we still call the lattice constant a. The same notation is used as in the previous section. Here is a full overview for clarity

$$\begin{aligned}
R, R' &\in \{1, \ldots, M\}, \\
\alpha, \beta &\in \{1, \ldots, L\}, \\
Q, Q' &\in \{-\frac{\pi}{La}, \ldots, \frac{\pi}{La}\}, \\
q &\in \{-\frac{\pi}{a}, \ldots, \frac{\pi}{a}\}.
\end{aligned}$$

Note that the symbol q is used for elements of the unmodulated Brillouin zone, i.e. the Brillouin zone of the monoatomic chain. The chain still has a total of N atoms, therefore $N = LM$.

All steps leading up to equation 3.21 in the previous section are completely general (except that α and β now run over L numbers), so the starting point in this section is that equation, which is the phonon Hamiltonial in terms of the rescaled variables π and ξ:

$$H_{phonon} = \sum_{R,\alpha} \frac{(\pi_R^{\alpha})^2}{2m} + \sum_{R,R'} \sum_{\alpha,\beta}^{L} \xi_R^{\alpha} K_{RR'}^{\alpha\beta} \xi_{R'}^{\beta}. \tag{3.28}$$

For a general supermodulation, the interaction matrix is given by an expression very similar to diatomic case:

$$
\begin{aligned}
K_{RR'}^{\alpha\beta} = & \frac{m\kappa}{\sqrt{m_\alpha m_\beta}} \Big[\delta_{R,R'} \left(2\delta_{\alpha,\beta} - \delta_{\alpha,\beta+1} - \delta_{\alpha,\beta-1} \right) \\
& \qquad - \delta_{R-1,R'} \delta_{\alpha,1} \delta_{\beta,L} - \delta_{R+1,R'} \delta_{\alpha,L} \delta_{\beta,1} \Big] .
\end{aligned}
\tag{3.29}
$$

The first term, connecting atoms within the unit cell, is identical to the diatomic case. The terms connecting to neighboring unit cells have changed only in the label of the last atom, which is now L rather than 2. Thus the Fourier transformation is analogous to the calculation in 3.24 and yields:

$$
\begin{aligned}
H_{phonon} &= \sum_Q \sum_{\alpha,\beta}^{L} \xi_Q^\alpha K_Q^{\alpha\beta} \xi_{-Q}^\beta \\
K_Q^{\alpha\beta} &= \frac{m\kappa}{\sqrt{m_\alpha m_\beta}} \Big[\left(2\delta_{\alpha,\beta} - \delta_{\alpha,\beta+1} - \delta_{\alpha,\beta-1} \right) \\
& \qquad - \delta_{\alpha,1} \delta_{\beta,L} e^{iLaQ} - \delta_{\alpha,L} \delta_{\beta,1} e^{-iLaQ} \Big] .
\end{aligned}
\tag{3.30}
$$

Again, only the terms connecting neighboring unit cells (the last two terms) pick up a Q dependence and the vector $\vec{\xi}_Q$ generalizes to $\vec{\xi}_Q = (\xi_Q^1, \dots, \xi_Q^L)^T$ and the matrix $\mathbf{K}_Q$ in

$$
\sum_Q \sum_{\alpha,\beta}^{L} \xi_Q^\alpha K_Q^{\alpha\beta} \xi_{-Q}^\beta = \sum_Q \vec{\xi}_Q^\dagger \mathbf{K}_Q \vec{\xi}_Q
$$

generalizes to

$$
\mathbf{K}_Q = m\kappa \begin{bmatrix}
\frac{2}{m_1} & \frac{-1}{\sqrt{m_1 m_2}} & & & \frac{-e^{-iLaQ}}{\sqrt{m_1 m_L}} \\
\frac{-1}{\sqrt{m_2 m_1}} & \frac{2}{m_2} & & & \\
 & & \ddots & & \\
 & & & \frac{2}{m_{L-1}} & \frac{-1}{\sqrt{m_{L-1} m_L}} \\
\frac{-e^{iLaQ}}{\sqrt{m_L m_1}} & & & \frac{-1}{\sqrt{m_L m_{L-1}}} & \frac{2}{m_L} .
\end{bmatrix}
\tag{3.31}
$$

This is no longer a useful form for analytical calculations. However, it is exactly the matrix used in the MATLAB code so we mention it at this stage anyway.
The eigenvalues of this matrix correspond to the phonon dispersion as in 3.27. Since the electron and phonon dispersions are now in principle given, the only thing that remains is finiding the matrix element, or coupling function $g_{k,q}^\alpha$. There exists a procedure for relating the general $g_{k,q}^\alpha$ to the analytically obtained monoatomic $g(k,q)$ as given in 3.17.
The starting point is the one dimensional electron phonon Hamiltonian in equation 3.16:

$$H_{el-ph} = \frac{1}{\sqrt{N}} \sum_{k,q} \tilde{g}(k,q) u_q, c^{\dagger}_{k+q/2} c_{k-q/2} \tag{3.32}$$

where $g(k,q)$ is the monoatomic matrix element as in 3.17. Rather than following the whole procedure by which the monoatomic g was obtain for each supermodulation (which becomes quite impossible for large supermodulations), the trick is to rewrite u_q in terms of the displacement variables μ^{ν}_{Q} which diagonalize the supermodulated phonons.
Since u_q is a Fourier transform of u_n, the first step is to rewrite u_n in terms of μ^{ν}_{Q}:

$$\begin{aligned} u_n &= \sqrt{\frac{m}{m_n}} \xi_n \\ &= \sqrt{\frac{m}{m_\alpha}} \xi^{\alpha}_{R} \\ &= \sqrt{\frac{m}{m_\alpha}} \frac{1}{\sqrt{M}} \sum_{Q} e^{iQx_R} \xi^{\alpha}_{Q} \\ &= \sqrt{\frac{m}{m_\alpha}} \frac{1}{\sqrt{M}} \sum_{Q} e^{iQx_R} \sum_{\nu} C^{\alpha\nu}_{Q} \mu^{\nu}_{Q}. \end{aligned} \tag{3.33}$$

In the above calculation, the first step is the rescaling as in 3.19, the second is relabbeling to make use of the periodically recurring masses due to the supermodulation and the third is the Fourier transform as in 3.23. The final step is the basis transformation $\vec{\xi}_Q = \mathbf{C}_Q \vec{\mu}_Q$, with $\mathbf{C}_Q$ the matrix of eigenvectors of $\mathbf{K}_Q$, analogous to the diatomic case, but now written in terms of components rather than in matrix notation.

Next is the substitution into the inverse Fourier transform of u_n:

$$\begin{aligned}
u_q &= \frac{1}{\sqrt{N}} \sum_n e^{-iqx_n} u_n \\
&= \frac{1}{\sqrt{N}} \sum_n e^{-iqx_n} \sqrt{\frac{m}{m_\alpha}} \frac{1}{\sqrt{M}} \sum_Q e^{iQx_R} \sum_\nu C_Q^{\alpha\nu} \mu_Q^\nu \\
&= \frac{\sqrt{m}}{\sqrt{N}\sqrt{M}} \sum_R \sum_\alpha e^{-iq(x_R+\alpha a)} \sqrt{\frac{1}{m_\alpha}} \sum_Q e^{iQx_R} \sum_\nu C_Q^{\alpha\nu} \mu_Q^\nu \\
&= \frac{\sqrt{m}}{\sqrt{N}\sqrt{M}} \sum_R \sum_\alpha \sum_Q \sqrt{\frac{1}{m_\alpha}} e^{-ix_R(Q-q)} e^{-iq\alpha a} \sum_\nu C_Q^{\alpha\nu} \mu_Q^\nu \qquad (3.34) \\
&= \sqrt{m}\sqrt{\frac{M}{N}} \sum_\alpha \sum_Q \sqrt{\frac{1}{m_\alpha}} \delta_{Q,q} e^{-iq\alpha a} \sum_\nu C_Q^{\alpha\nu} \mu_Q^\nu \\
&= \sqrt{m}\sqrt{\frac{M}{N}} \sum_{\alpha,\nu} \frac{e^{-iq\alpha a}}{\sqrt{m_\alpha}} C_q^{\alpha\nu} \mu_q^\nu \\
&= \frac{1}{\sqrt{L}} \sum_{\alpha,\nu} \frac{e^{-iq\alpha a}}{\sqrt{m_\alpha}} C_q^{\alpha\nu} \mu_q^\nu .
\end{aligned}$$

Steps one through four are substitutions of previously obtained results, and the delta function in step 5 works out because the set which Q belongs to is a subset of the set which q belongs to. This means that the q appearing in the last two lines is in principle constrained to the smaller Brillouin zone, the elements of which we labelled Q until now. In the final step the arbitrary m has been set equal to one and the relation $N = LM$ was used to rewrite the square root.
For compactness, we rewrite:

$$u_q = \frac{1}{\sqrt{L}} \sum_{\alpha,\nu} \frac{e^{-iq\alpha a}}{\sqrt{m_\alpha}} C_q^{\alpha\nu} \mu_q^\nu \equiv \sum_\nu \Gamma_q^\nu \mu_q^\nu, \qquad (3.35)$$

where we defined the *weight* Γ_q^ν through:

$$\begin{aligned}
\Gamma_q^\nu &= \frac{1}{\sqrt{L}} \sum_\alpha \frac{e^{-iq\alpha a}}{\sqrt{m_\alpha}} C_q^{\alpha\nu} \\
&= \frac{1}{\sqrt{L}} \sum_\alpha l_q^\alpha C_q^{\alpha\nu} .
\end{aligned} \qquad (3.36)$$

The definition of the weight in 3.35 reveals its meaning: we write the old monoatomic states as a superposition of the proper states diagonalizing the phonon Hamiltonian, and the coefficient of each eigenstate μ_q^ν is the number we call the weight.

Now the solution for u_q can be substituted into 3.32, which yields

$$H_{el-ph} = \frac{1}{\sqrt{N}} \sum_{k,q} \tilde{g}(k,q) \left[\sum_{\nu} \Gamma_q^\nu \mu_q^\nu \right] c_{k+q/2}^\dagger c_{k-q/2}.$$

Since μ_q^ν diagonalizes the phonon Hamiltonian, it can be expressed in terms of phonon creation and annihilation operators as

$$\mu_q^\nu = \sqrt{\frac{\hbar}{2m\omega_q^\nu}} \left(a_q^\nu + a_{-q}^\nu \right). \tag{3.37}$$

Setting $\hbar$ and the arbitrary m to one makes the Hamiltonian

$$H_{el-ph} = \frac{1}{\sqrt{N}} \sum_{k,q} \sum_{\nu} \frac{\tilde{g}(k,q)}{\sqrt{2\omega_q^\nu}} \Gamma_q^\nu \left(a_q^\nu + a_{-q}^\nu \right) c_{k+q/2}^\dagger c_{k-q/2}. \tag{3.38}$$

A comparison with equation 2.6 reveals that we have found our band dependent matrix element:

$$\begin{aligned} g_{k,q}^\nu &= \frac{\tilde{g}(k,q)}{\sqrt{2\omega_q^\nu}} \Gamma_q^\nu \\ &= \frac{1}{\sqrt{L}} \frac{\tilde{g}(k,q)}{\sqrt{2\omega_q^\nu}} \sum_\alpha l_q^\alpha C_q^{\alpha\nu} \\ &= -\frac{1}{\sqrt{L}} \frac{4i\alpha \sin\left(\frac{qa}{2}\right) \cos(ka)}{\sqrt{2\omega_q^\nu}} \sum_\alpha \frac{e^{-iq\alpha a}}{\sqrt{m_\alpha}} C_q^{\alpha\nu}. \end{aligned} \tag{3.39}$$

We have obtained a formula for the coupling function for a general supermodulation. With the identification $g_{k,q}^\nu = M_{k,k+q}^\nu$ it is possible to calculate the parameter λ for an arbitrary supermodulation.

3.5 Summary

We have carried out the procedure outlined in chapter 2 for the case of the monoatomic chain in its entirity, and obtained a monoatomic coupling funciton $\tilde{g}(k,q)$ which we need for the case of general supermodulation to be

$$\tilde{g}(k,q) = -4i\alpha \sin\left(\frac{qa}{2}\right) \cos(ka). \tag{3.40}$$

The phonon dispersion for the diatomic chain has been found by a method closer to the algorithm used by the code.

The formalism by which the coupling function for the case of general supermodulation can be found has been worked out. That procedure saw the introduction of the weight Γ_q^ν which is proportional to $M_{k,k+q}^\nu$, this weight is given by

$$\Gamma_q^\nu = \frac{1}{\sqrt{L}} \sum_\alpha \frac{e^{-iq\alpha a}}{\sqrt{m_\alpha}} C_q^{\alpha\nu}. \tag{3.41}$$

Its interpretation is most clearly seen in the relation

$$u_q = \sum_\nu \Gamma_q^\nu \mu_q^\nu. \tag{3.42}$$

So we write the displacement variables u_q of the monoatomic Hamiltonian as a superposition of the variables μ_q^ν of the supermodulated Hamiltonian, with the weight Γ_q^ν giving the magnitude of each μ in the superposition.

And most importantly, we have found the formula for the matrix element $M_{k,k+q}^\nu$, which brings all these quantities together, to be given by

$$M_{k,k+q}^\nu = \frac{\tilde{g}(k,q)}{\sqrt{2\omega_q^\nu}} \Gamma_q^\nu. \tag{3.43}$$

Chapter 4

Implementation and preliminary results

Having worked out the theoretical foundation and general idea in the previous chapters, this chapter describes the procedure implemented in the MATLAB code to find the λ parameter. At the time of writing, the code was not yet able to calculate the actual λ, but all steps leading up to the final calculation had been implemented sucessfully. As the code is still in a stage of development, all parameters such as lattice constant, coupling strenght α etcetera have been set equal to one. Therefore all results presented in this chapter are in arbitrary units and have (mostly) not been tested against analytical results for correctness. The code follows the theory as much as possible, with an emphasis on using matrix operations where possible due to the fact that MATLAB is maximally efficient when doing matrix operations.

4.1 The algorithm

In its final form, the code should *output* the parameter λ and the associated T_c which it obtains through 2.4. In its current form, the focus is on outputting pictures based on which we can diagnose our progress in the code development. Therefore the current output consists primarily of diagnostic plots of things like the weight Γ_q^ν as defined in 3.36 and phonon and electron dispersions. As *input*, the code requires all relevant parameters needed to construct a model system and compute λ. The list of parameters it uses at the time of writing:

- The number of atoms in the chain, N
- Supermodulation length L
- The lattice constant a

- The spring constant κ
- The electrion hopping parameter t
- The electron-phonon interaction strength α
- Electron chemical potential $\mu_{electron}$

Most parameters have been set equal to 1 as the code is still in development and only the number of atoms and supermodulation length have actively been used.
Based on this list of parameters the code follows the following procedure:

1. Build the (extended) Brillouin zone defined by the smallest periodicity, a, and extend it to two dimensions, this is necessary because we need the electron density of states to be two dimensional in order to give physically plausible results. At this initial step, the supermodulation is created as an array of L masses, the magnitudes of which are chosen manually by the user.
2. Calculate and store the electron density of states based on analytically calculated electron dispersion for tight binding electrons.
3. Generate the Q-independent part of the Fourier space interaction matrix $\mathbf{K}_Q$ as shown in 3.31.
4. Add the Q-dependent parts and diagonalize the matrix $\mathbf{K}_Q$ for each Q in the Brillouin zone and store the eigenvalues (related to phonon dispersion through 3.27) and the corresponding eigenvector matrix $\mathbf{C}_Q$ and construct and store the weight Γ_q^ν as a vector.
5. Artificially extend the one dimensional dispersion relation and weight to two dimensions, due to the fact that the electron DOS is two dimensional.
6. Compute λ_q based on equation 2.2, using the matrix element as in 2.7. This step has not been completed at the time of writing of this thesis.

All calculations have been done on the ”extended” Brillouin zone, determined by the lattice constant a. An example plot is shown in figure 4.1, where the phonon dispersion for a supermodulation of 2 is plotted for the case of two equal masses and for two different masses with mass ratio 1 : 0.8.

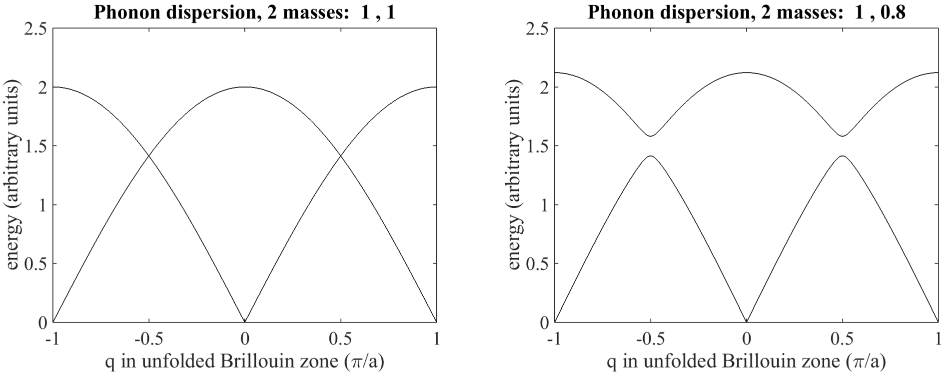

Figure 4.1: *Phonon dispersions as generated by the algorithm for the case of unit cell of two masses and if the algorithm is carried out for the extended Brillouin zone. In the right picture the mass ratio between the masses is 1:0.8, in the left picture the masses are the same and a shifted "artificial" band appears due to the fact that the interaction matrix is diagonalized for all elements of the extended Brillouin zone.*

The shadow bands present in this figure are a result of the way the code operates, it diagonalizes a matrix $\mathbf{K}_Q$ for each element of the extended Brillouin zone, resulting in two eigenvalues for each such element. This nonstandard representation is unnecessary for the phonon dispersion as all information is contained in the folded Brillouin zone, defined by the periodicty $2a$. We therefore plot them on the folded Brillouin zone, figure 4.2 shows the result of the same calculation on the folded Brillouin zone.

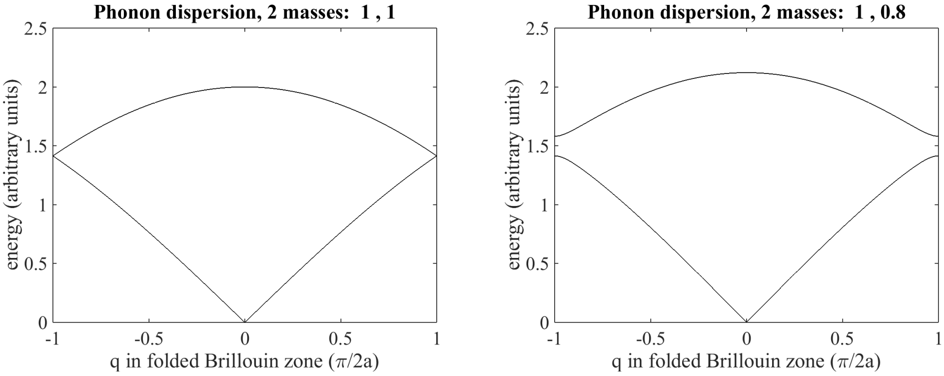

Figure 4.2: *Phonon dispersions as generated by the algorithm for the case of unit cell of two masses and if the algorithm is carried out for the* folded *Brillouin zone. The input parameters are otherwise identical to the parameters used to generate 4.1*

Quantities such as the weight Γ_q^ν as defined in 3.36 have to be computed on the extended Brillouin zone, as it "spills" out of the folded Brillouin zone for the case of a supermodulation with unequal masses. For the case of a supermodulation with equal masses, all the weight is concentrated on the real, monoatomic band. Figure 4.3 shows these two cases. The weights are superimposed in blue

on top of the phonon branches, the thickness of the band is proportional to the absolute value of the weight in that figure and all following ones.
The left memeber of figure 4.3 shows a diagnostic value of the quantity Γ_q^ν: in the case of equal masses all the weight is on the real band, corresponding to the monoatomic chain, which is the physical system with a supermodulation of equal masses.

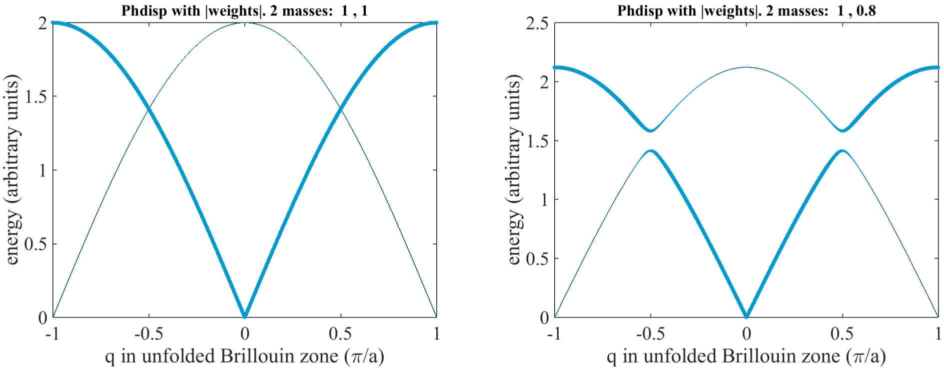

Figure 4.3: *The same parameters used to generate the folded and unfolded dispersions inprevious two figures. In addition, the absolute value of the weight, as computed by the algorihm, is shown. It is plotted in blue on top of the phonon bands, the width of the band is proportional to* $|\Gamma_q^\nu|$*. In the left figure, we see that the weight has nonzero elements on both bands spilling over into the unfolded Brillouin zone.*

We can still plot the weights on the folded Brillouin zone, we do that by folding the right member of figure 4.3. The weights which spill over are summed with the weight on the correspoing value of q. So the weight at some q in the reduced Brillouin zone is summed with the weight at $q \pm \pi/2a$. This results in figure 4.4

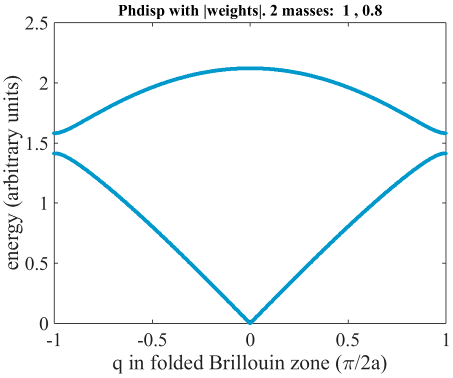

Figure 4.4: *Dispersion relation on the folded Brillouin zone with weights superimposed in blue. The width of the blue band is proportional to absolute value the weight. The values were obtained by summing the values of the weight for each* q *on the folded Brillouin zone to the values at* $q \pm \pi/2a$*.*

Another instructive plot is the difference between the weight for the case of a supermodulation with the same masses in the unit cell, so the left member of figure 4.3 and the weight for different masses, so the right memeber of that figure. The absolute values of the weights in the case of the same atomic masses are subtracted from the weights with different masses and plotted on the folded Brillouin zone. This is done to visualise the change between the monoatomic case and the case with a supermodulation where one atom in the unit cell is changed. The result is plotted in figure 4.5. We see that the weights are affected most at the edges of the Brillouin zone, where the bandgap appears.

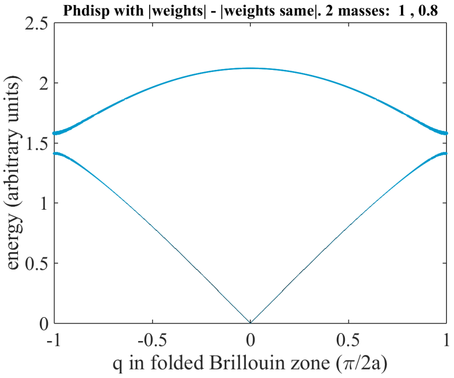

Figure 4.5: *Dispersion relation on the folded Brillouin zone with weight difference superimposed in blue. These differences are computed by subtracting the absolute value of the weights for the case of two equal masses in the supermodulation from the absolute value of the weights for different masses, i.e. the weights in the left member of figure 4.2 minus those in the right memeber. The width of the blue band is proportional to the difference of their absolute values.*
This figure therefore shows which parts of the Brilllouin zone are most affected by the introduction of a supermodulation.
To account for the possibility of the difference being negative, blue represents positive values and red represents negative. We see that in this case the difference is always positive, meaning that the weights for the case with different masses is bigger than the value for the same masses, for all values of q. *This makes sense, given the factors* $1/\sqrt{m}$ *in the definition of the weights in equation 3.36.*

Since the weight is proportial to $M^{\nu}_{k,k+q}$, making it an integral part in all our calculations, we present plots of the weight and the weight differences for several supermodulations in the next section. The rest of this section continues with a desctription and visualisation of the various aspects of the code.

As mentioned in the description of the procedure above, these phonon dispersions and weights are artificially extended to two dimensions because the electron density of states must be two dimensional to produce physically plausible results. Figure 4.6 shows the artificially extended dispersion relation for the diatomic chain in folded and unfolded mode. The same parameters are used as in the left member of figures 4.1 and 4.2, i.e. for a diatomic chain with mass ratio 1 : 0.8.

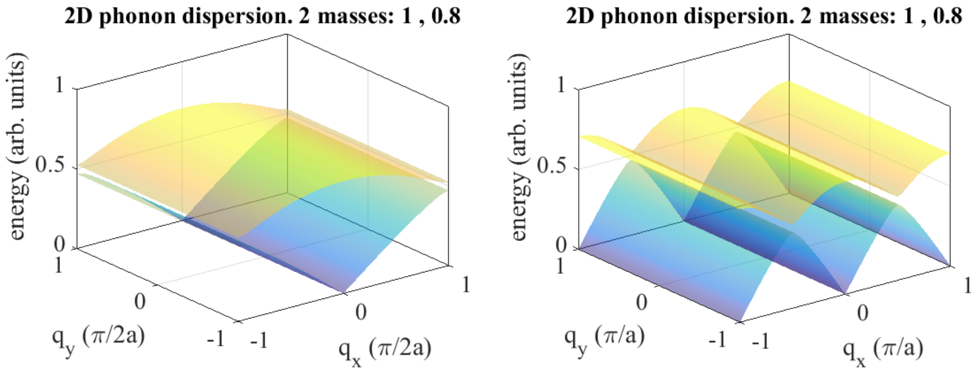

Figure 4.6: *Diatomic chain phonon dispersion with the atomic masses in the proportion* 1 : 0.8*, artificially extended to two dimensions, in folded and unfolded Brillouin zone.*

These figures show that the artificially extended phonon dispersions have a two-fold symmetry so one would expect all computations based on the phonon dispersions, such as the weights, to have the same symmetry, and this is indeed the case. This is not so with the electrons however, these have a four fold symmetry as shown in figure 4.7. Ideally, the electron dispersion would be sharp, having nonzero values only at wavevectors at the Fermi energy. Due to the fact that we have a finite number of atoms, infinite sharpness is not possible and we introduce a prameter to ”smear” the electron dispersion out over several pixels. This means extending the values of q_x and q_y for which the electron dispersion is nonzero. The electron dispersion is shown for two values of the smear parameter in figure 4.7.

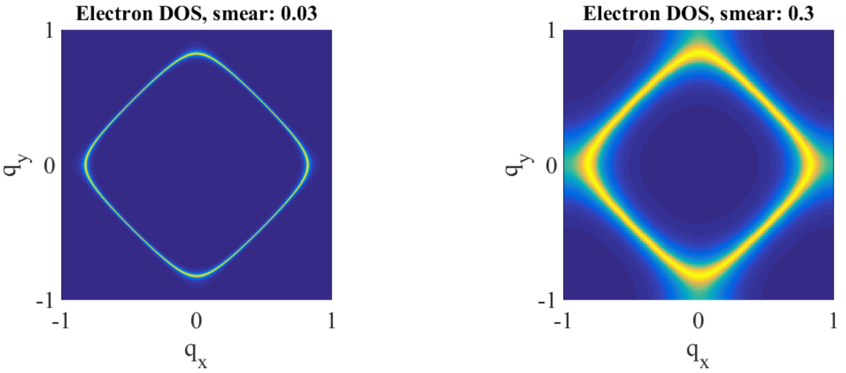

Figure 4.7: *The electron density of states for two different values of the smearing parameter. Both q_x and q_y are plotted in units of π/a.*

The four-fold symmetry of the electron dispersion means that in the eventual implementation, the $\lambda_{\mathbf{q}}$ will also have the four-fold symmetry.

4.2 Weights and weight differences for several supermodulations

This section presents plots of the weights superimposed on the phonon dispersion for the cases of a supermodulation $L = 2$ for mass ratios $1 : 1.1$, $1 : 2$ and $1 : 5$. We show the absolute value of the weights on the unfolded and on the folded Brillouin zones, as well as the weight difference on the folded Brillouin zone. In addition, the weight difference is plotted for the case $L = 3$ with mass ratios $1 : 1.2 : 1.4$ and for the case $L = 10$ for linearily increasing masses. All the differences are computed with respect to the case of a supermodulation with all masses equal to 1. In all difference plots, blue indicates positive vales of the difference and red indicates negative values. In all cases, the absolute values of the weights with same masses are subtracted from the absolute values of the weights with different masses.
Figure 4.8 shows the weights on the unfolded Brilluoin zone for the diatomic chain with mass ratios $1 : 1.1$.

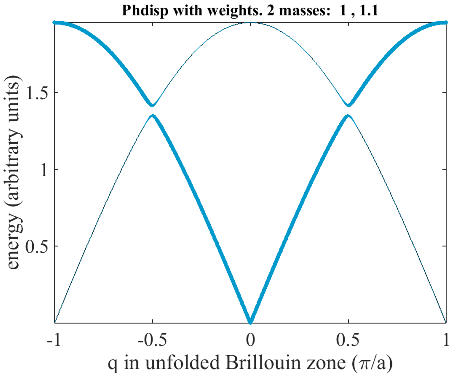

Figure 4.8: *Phonon dispersion for diatomic chain with mass ratio* $1 : 1.1$*, plotted on the unfolded Brillouin zone. The width of the superimposed band is proportional to the absolute value of the weight,* $|\Gamma_q^\nu|$.

Figure 4.9 shows the weights for the same case on the folded Brillouin zone, as well as the weight difference as described in the previous section.

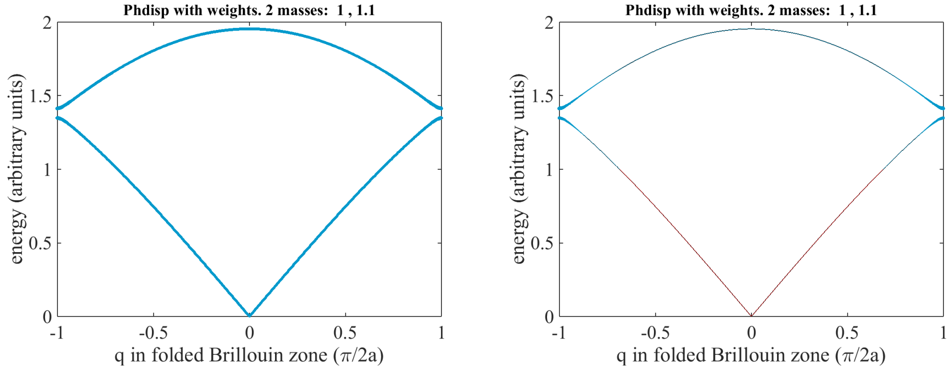

Figure 4.9: *Left: Weights on the folded Brillouin zone. Right: Weight difference on the folded Brillouin zone. Red indicates negative values and blue indicates positive values. The difference is computed by subtracting the absolute value of the weights in the case of equal masses in the supermodulation from the absolute value of the weights in the case of different masses, in this case with mass ratio* $1 : 1.1$.

We see again that the biggest difference is where the bandgap appears. Furthermore we now see negative values on the lower band. This is due to the fact that the second mass is higher than in the case of the same masses, making the value of the weight for different masses smaller than the value in the case of equal masses for some values of q, this is due to the factor $1/\sqrt{m}$ in the definition 3.36.

Next we present the plots of the folded weights and weight differences for the diatomic chain for mass ratios $1 : 2$ in figure 4.10.

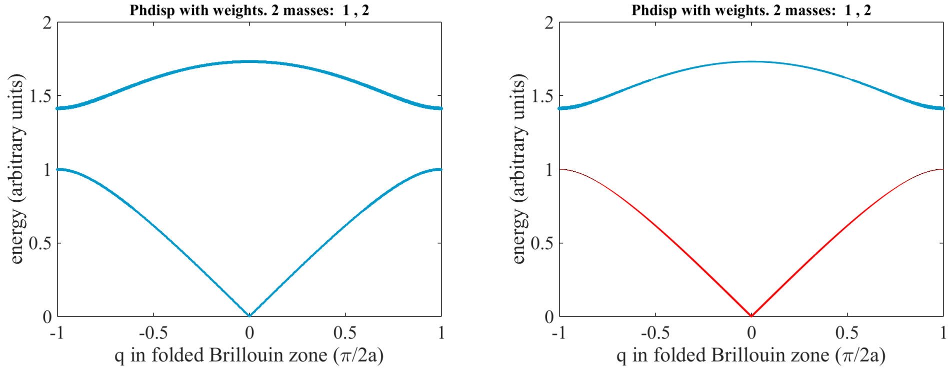

Figure 4.10: *Left: Weights on the folded Brillouin zone. Right: Weight difference on the folded Brillouin zone. Red indicates negative values and blue indicates positive values. Mass ratio* $1 : 2$.

In addition to the increased bandgap, which is expected due to the larger mass ratio, we see in the left member that the weights have a larger value on the upper band than in the case of the small mass difference. This is to be expected

given our interpretation of the weight as relating the states of the system with supermodulation to the system without. Based on that interpretaion, we would expect the weights to shift to the parts of the system most different from the monoatomic system.
The right member of figure 4.10, where the weights difference is superimposed on the phonon dispersion, underscores that point even more strongly. We see there that the entire lower band has a negative weight difference, meaning that there the weights of the modulated system are smaller than the weights in the case of the same masses. On the upper band we see the opposite, there the modulated weights are bigger for every q in the Brillouin zone.

As one would expect, this effect becomes stronger if we increase the mass difference. Figure 4.11 shows the same plot for mass ratio $1:5$

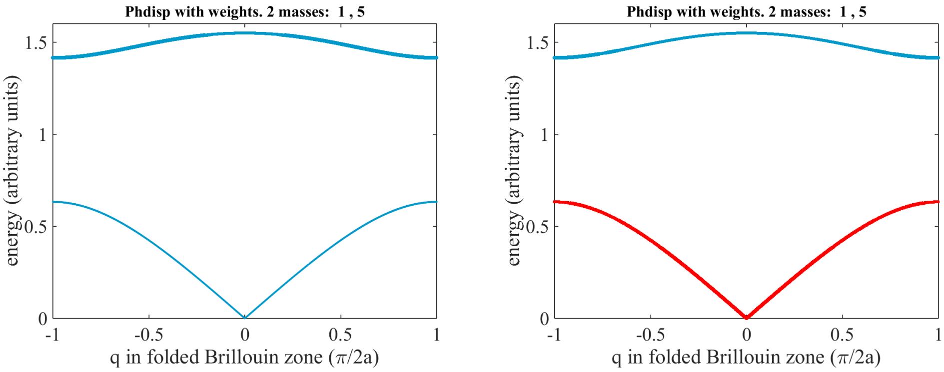

Figure 4.11: *Left: Weights on the folded Brillouin zone. Right: Weight difference on the folded Brillouin zone. Red indicates negative values and blue indicates positive values. Mass ratio* $1:5$.

As a final result, we show the weight differences for the cases of a supermodulation $L = 3$ with mass ratio $1:1.2:1.4$ and a supermodulation $L = 10$ for 10 linearly increasing masses in figure 4.12.

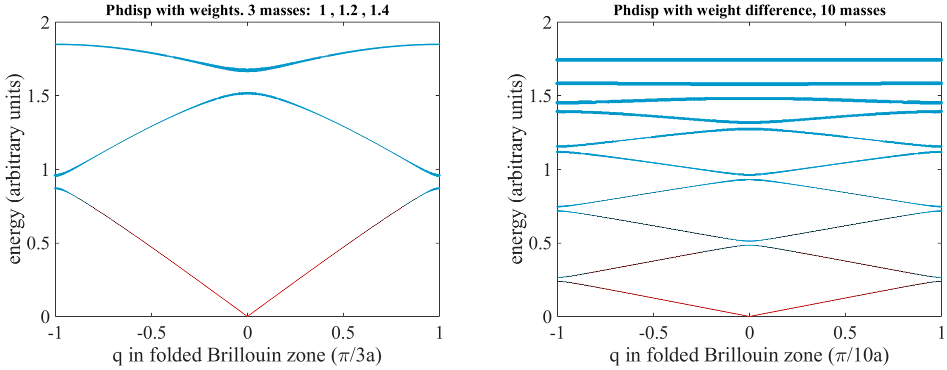

Figure 4.12: *Left: Weight difference on the folded Brillouin zone for* $L = 3$ *and mass ratios* $1 : 1.2 : 1.4$*. Right: Weight difference on the folded Brillouin zone for* $L = 10$ *and masses increasing linearily between* 1.1 *and* 2*. Red indicates negative values and blue indicates positive values.*

In the left member, for the case $L = 3$ we see the same effects we saw in the case of the diatomic chain plotted excessively above. We see again that the weight difference is largest at the places where the bandgap appears. The same effect is visible on the lower few bands of the $L = 10$ case. We also see in the right member of figure 4.11 that the magnitude of the weight difference tends to become bigger and bigger as we depart more and more from the monoatomic system, so as we go to higher and higher bands.

4.3 Outlook

At the time of writing of this thesis the final part of the calculation, the actual λ_q and λ, had not yet been implemented sucessfully. A lot of progress has been made on that in the mean time, but it was chosen not to present the results in this document as we are not yet completely sure that it is correct. Even when we are reasonably sure that the algorithm that produces the λ is correct, the code will have to be subjected to many tests to verify the validity of the results. The project has been joined by Arjo Andringa as part of his requirements for receiving the Bachelor degree in the mean time, and will be carried on by him and myself, under the supervision of Milan Allan, in the coming few months. Therefore, I will conclude this document with a list of things to be done in the further development of the code.

1. Implement λ through equation 2.2. A lot of work has been done on this by Arjo Andringa, and we are confident that this step is nearing completion.
2. Test: Density of states. We can diagnose the physical validity of our results based on some general arguments concerning the total density of phonon states. We know that introducing extra bands should not increase

the total density of states, and Arjo Andringa has been working on testing for this with positive results recently. We are currently exploring the effect of the weights on the density of states.

3. Other tests: Many other tests must be conducted that are not yet in progress. An important example is to test if the correct energies are produced by the code for known analytical results.

4. Once the testing phase is complete, we will write a script that will run this core code for many values of input parameters and invesigate the change of T_c with respect to the monoatomic case.

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