

PHONON

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Phonon



- Phonon fundamentals
 - Part 1
- Phonon calculation in quantum espresso
 - Part 2
- Program files and results
 - Part 3

PHONON

- Concept introduced -**IGOR TAMM** –Russian physicst (1932)
- Greek word –**sound** or voice,because **long-wavelength** phonons give rise to **sound**.
- The study of phonons is an important part of condensed matter physics.
- **Major Role** – physical properties such as **thermal conductivity** and **electrical conductivity**.

**Photon -quantization of energy that
travels light speed .**

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PHONON

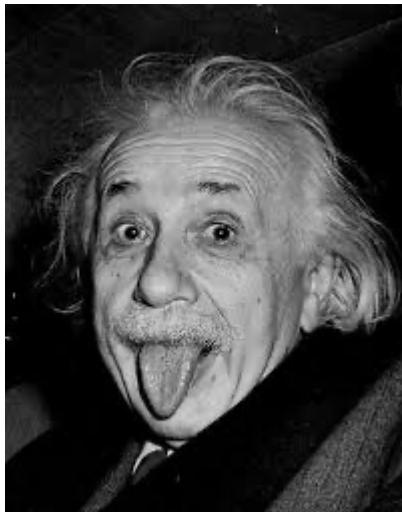
- quantization of vibrational energy.
- quantized lattice waves (collective oscillations of atoms)travels sound speed.

- If ω is the frequency of a phonon.
- Energy is in integer multiples of $\hbar\omega$

Definition

- ▶ a **phonon** is a **collective excitation** in a periodic, elastic **arrangement of atoms** or molecules in condensed matter, such as **solids** and some **liquids**.
- ▶ A phonon is a quantum mechanical description of an elementary **vibrational motion** in which a lattice **of atoms** or molecules uniformly **oscillates** at a single frequency.

Einstein and Debye – (already)introduced quantization of energy in specific heat of solid.



phonon



**LATTICE ITSELF CONSIDER AS KIND OF
CONTINUUM**

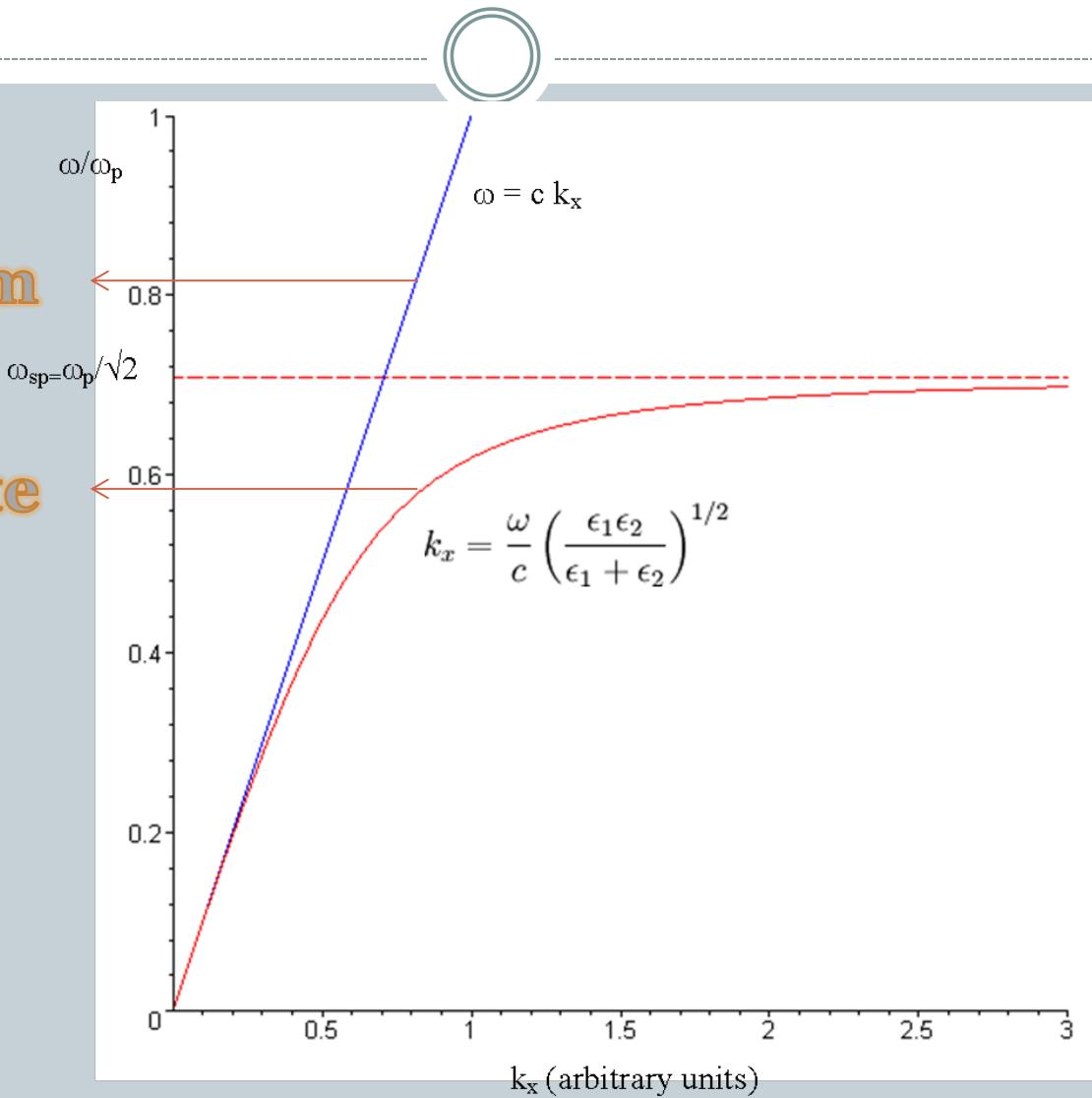
Dispersion relation

- ▶ The connection between frequency and wave-vector, $\omega=\omega'(k)$, is known as a dispersion relation.
- ▶ frequency- ω
- ▶ Wave-vector - k ,
- ▶ Velocity of sound- ω'

Dispersion relation

Continuum

discrete



Questions?

- 1.why do we expect this type of deviation?

- 2.This dispersion relation of frequency and wave no are not occur small or large value of the wave no.....why?

Answer for 2nd question.

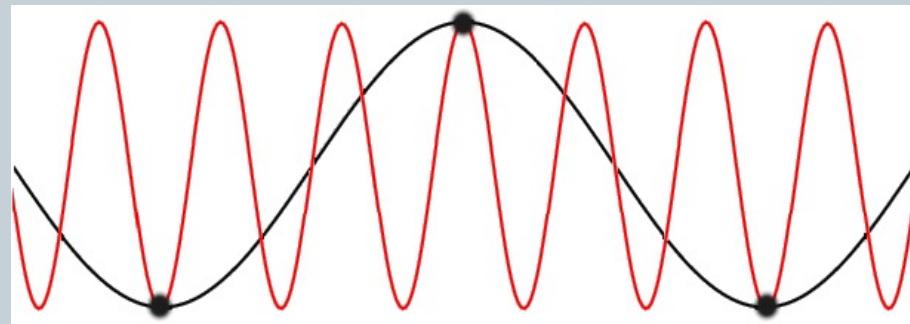
- ▶ Due to this relation....

$$|\vec{k}| = \frac{2\pi}{\lambda}$$

Some large number of k the wave length approaches interatomic distance.

- ▶ So wavelength of the wave going through the solid cant be smaller than interatomic distance. So it has upper cutoff.

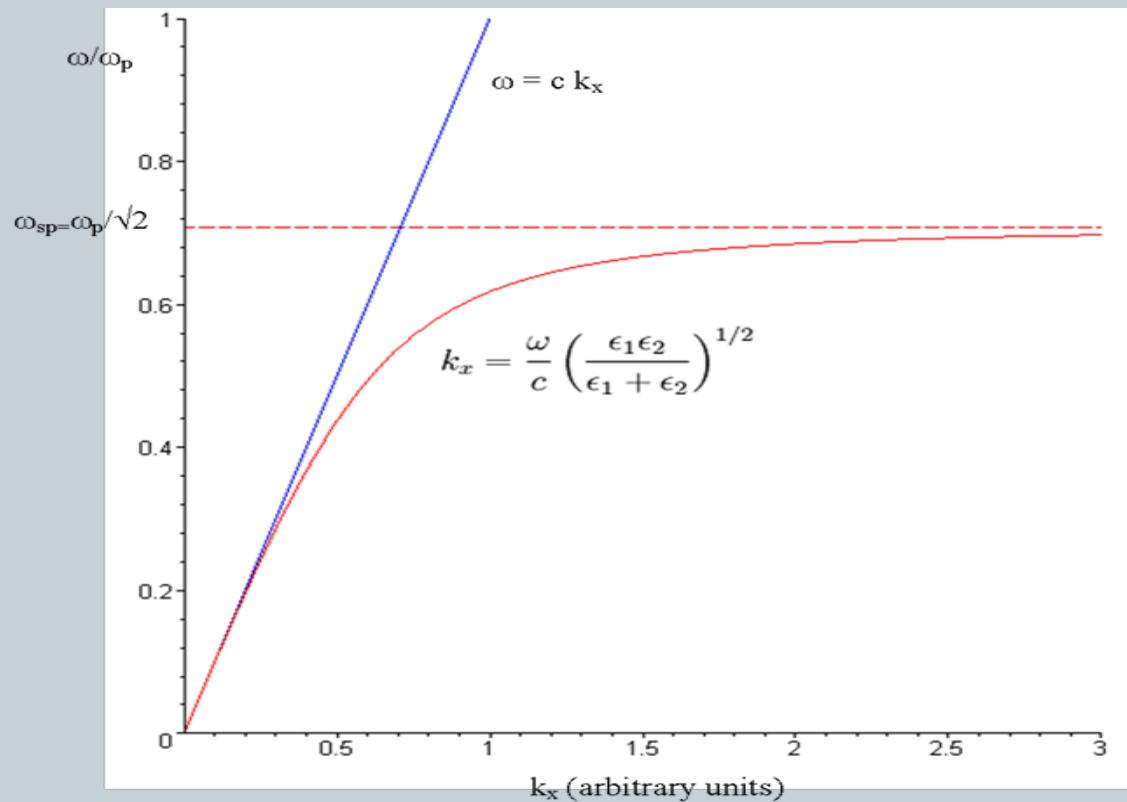
This is how....



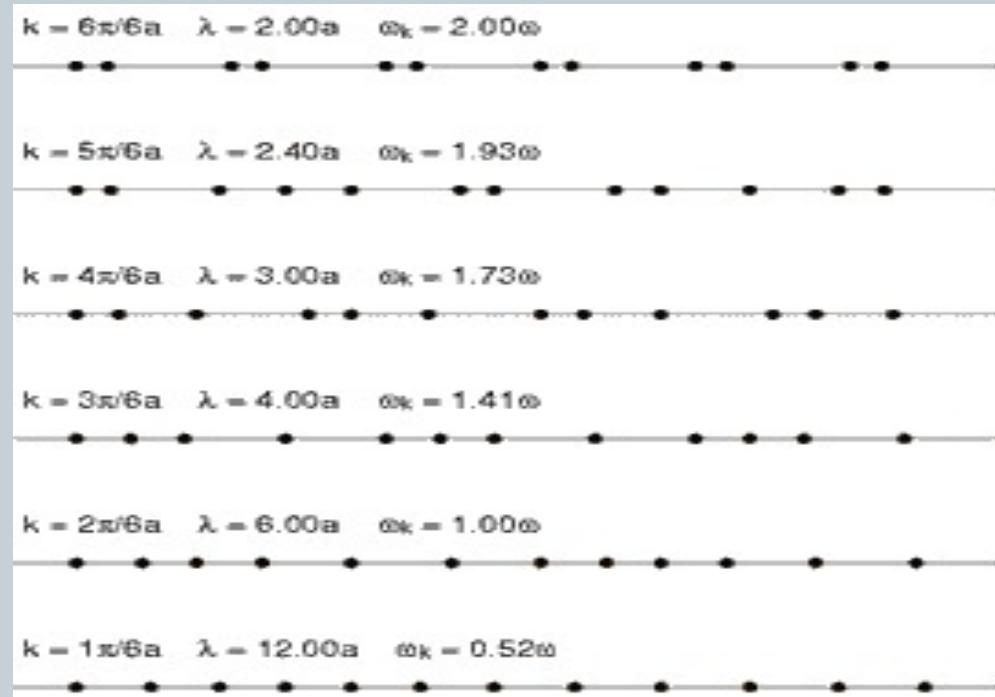
Answer for 1st question



- Large number of the k and small value of the wavelength, we expect the continuum of the picture breakdown.

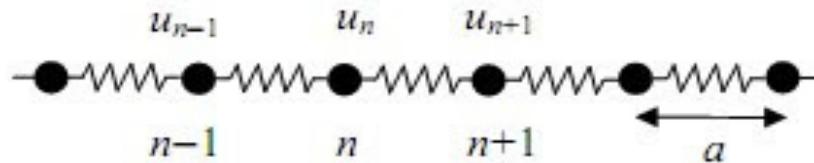


1d-Monoatomic lattice



- This is gonna help us to understand the deviation relation of frequency and wave vector.

1d-Monoatomic lattice



Newton force on atom

$$F = m \frac{\partial^2 u_n}{\partial t^2} = C \{ (u_{n+1} - u_n) - (u_n - u_{n-1}) \}$$

$$m \frac{\partial^2 u_n}{\partial t^2} = C \{ u_{n+1} - 2u_n + u_{n-1} \}$$

If we wanted to include more distant neighbour interactions (up to the Nth), our equation at this point would have the form

$$m \frac{\partial^2 u_n}{\partial t^2} = \sum_{p=1}^N C_p \{ u_{n+p} - 2u_n + u_{n-p} \}$$

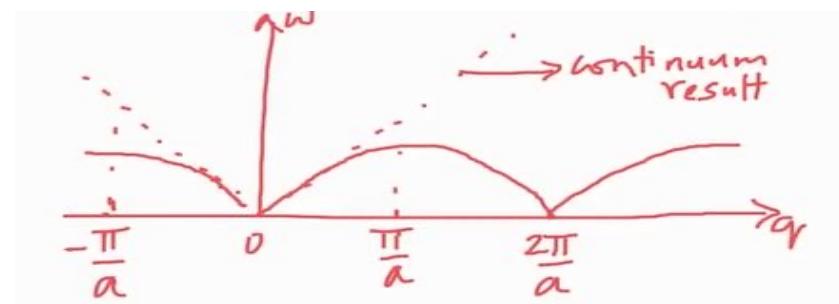
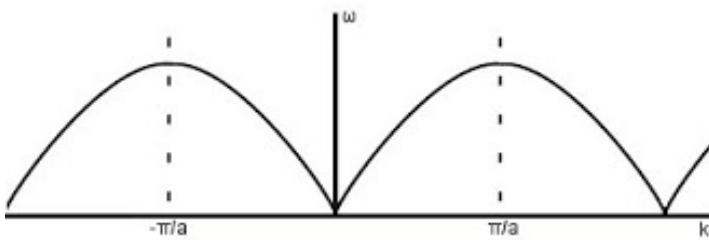
Going back to nearest neighbours, try a solution of the form

$$u_n = A e^{i(kna - \omega t)}$$

Mono Atomic lattice-final result

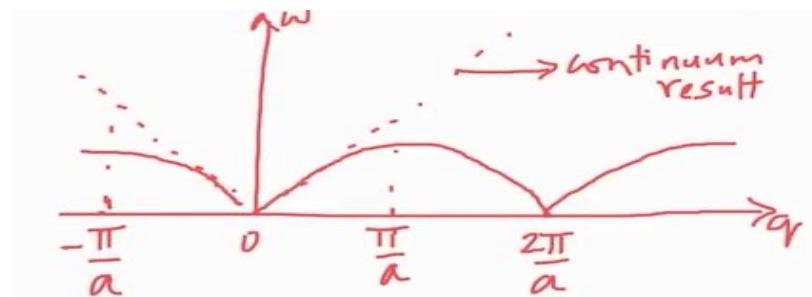
$$\omega = 2\sqrt{\frac{C}{m}} \sin \frac{ka}{2}$$

dispersion relation-nearest neighbours only



Mono atomic lattice–final result

- ▶ The continuum and discrete result are identical at small value of the q .
- ▶ When $q=\pi/a$ different. There is deviation those value of q .
- ▶ Periodicity because of sin function, region betn $-\pi/a$ and π/a is called brillouine zone.



Observations

1. In the long wavelength limit (small k),

$$\sin \frac{ka}{2} \rightarrow \frac{ka}{2}$$

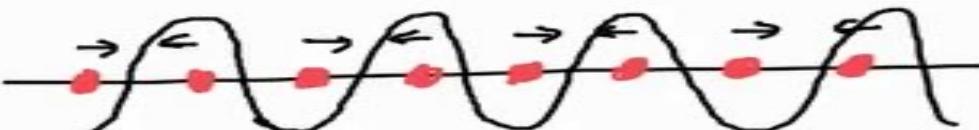
$$\omega = a \sqrt{\frac{C}{m}} k$$

Linear dispersion = continuous description is applicable

$$\frac{d\omega}{dk} = \frac{\omega}{k} = a \sqrt{\frac{C}{m}} \quad \text{speed of sound}$$

Observations- what happens ?

As $q \rightarrow \frac{\pi}{a}$ ($\lambda \rightarrow 2a$), group velocity
 $(\frac{dw}{dq}) \rightarrow 0$
⇒ Bragg scattering !



standing wave

- Slope of wvs q curve is wave velocity precisely group velocity and the value becomes zero.
- Essentially its Bragg scattering.
- pattern of vibration is called standing wave. Left going wave exactly canceling the right going wave.
- At brillouine zone boundary we can expect scattering .

Observations

- The 1-d lattice can support only frequencies below ω_m (cut-off frequency)

$$\omega_m = \sqrt{\frac{4\alpha}{M}} = \sqrt{\frac{4\alpha Y}{M}} \approx 10^{13} \text{ Hz}$$

(infra-red
regime)

- Frequency of phonon can't keep rising infinitely. There is upper cutoff which corresponds to the infra-red region.
- we use infrared rays to map out the vibrational density of states of solids in Raman spectroscopy

What happens when you have more than one atom associated with lattice points?

- ▶ This question gonna make us to add a new feature to this dispersion relationship.
- ▶ I,e 1d Mono atomic lattice to 1d Diatomic lattice

Diatomeric lattice

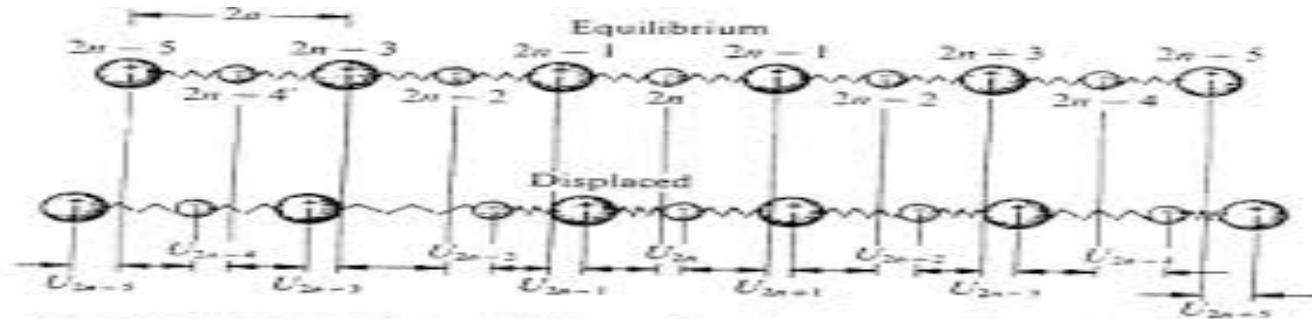


Fig. 3.10 Linear diatomic lattice of lattice constant $2a$. As in the monoatomic case, only nearest neighbor interactions need be considered.

- What if two atoms have same masses. ie $m_1 = m_2$

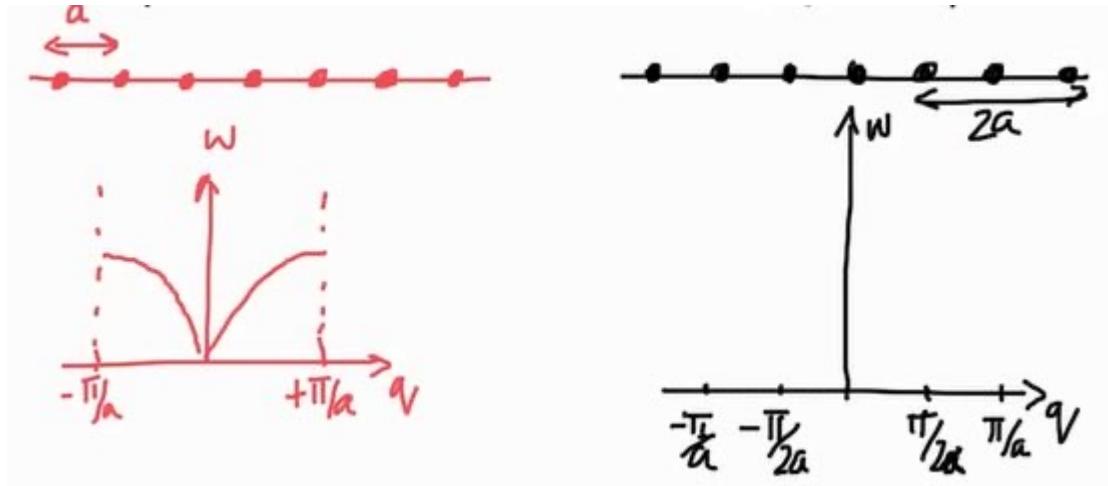
- What would be the dispersion relationship?

Diatomc lattice

Case 2:

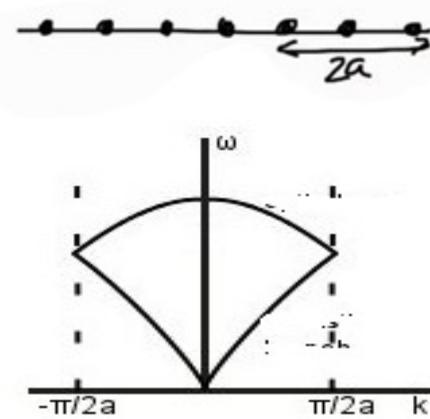
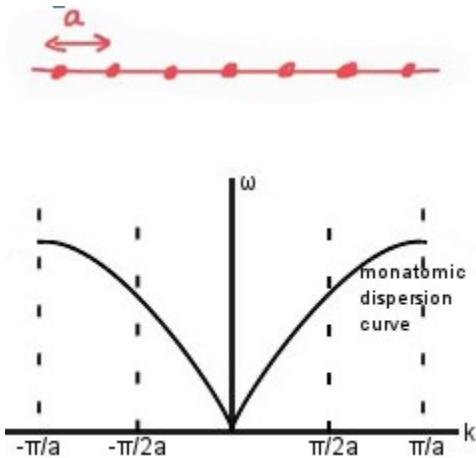
- ▶ $m_1 = m_2$, but lattice parameter is $2a$. It means two atoms per basis we have 1d lattice with $2a$ lattice parameter.
- ▶ What would be the dispersion relationship?

One dimensional Diatomic lattice



- In this two cases 'a' is physically equivalent to '2a'.
- In addition $-\pi/2a$ and $\pi/2a$.
- Reciprocal lattice is $a^*=2\pi/2a$.
- Brillouine zone in this case 0 to π/a ie $-\pi/2a$ and $\pi/2a$.

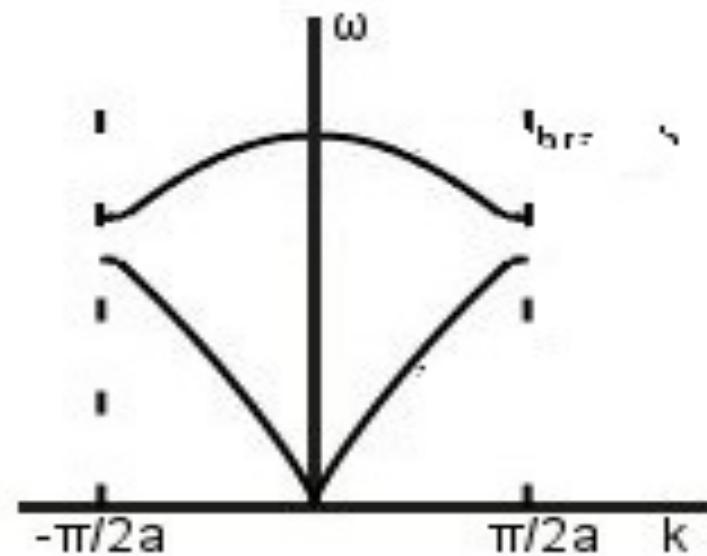
One dimensional Diatomic lattice



Zone folding

One dimensional Diatomic lattice

If the two types of atom have different masses, a gap opens up between the two branches.



One dimensional Diatomic lattice

The equation of motion

$$m \frac{\partial^2 U_{2n}}{\partial^2 t} = \beta(U_{2n+1} - 2U_{2n} + U_{2n-1})$$

$$M \frac{\partial^2 U_{2n+1}}{\partial^2 t} = \beta(U_{2n+2} - 2U_{2n+1} + U_{2n})$$

With wave solution

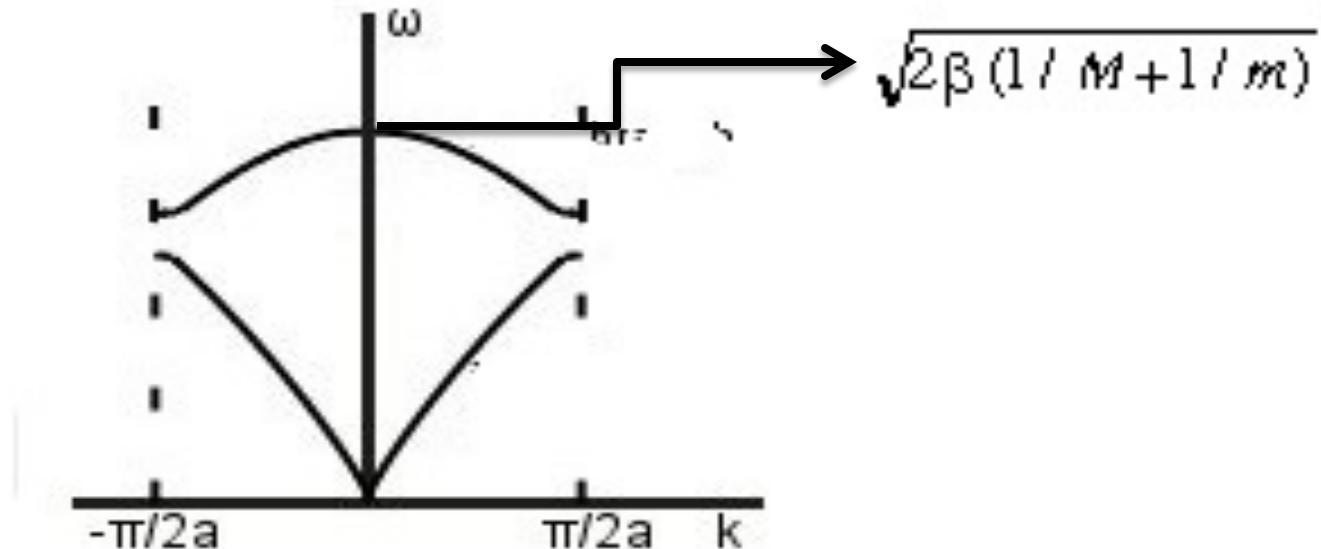
$$U_{2n} = A \exp[i(2nka \pm \omega t)]$$

$$U_{2n+1} = B \exp[i((2n+1)ka \pm \omega t)]$$

One dimensional Diatomic lattice

The solution of the diatomic lattice is

$$\omega^2 = \beta \left(\frac{1}{m} + \frac{1}{M} \right) \pm \beta \sqrt{\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2 ka}{Mm}}$$

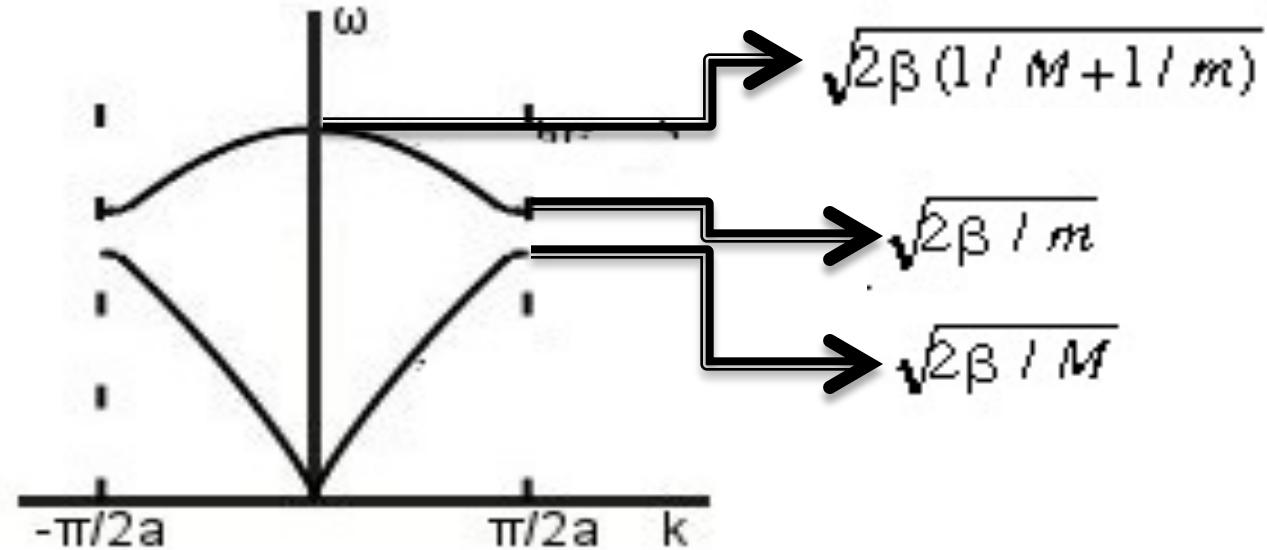


- When $k=0, \omega = 0$ in lower soln and upper soln is non zero.
- When $k=\pi/2a$, we get different soln.

One dimensional Diatomic lattice

The solution of the diatomic lattice is

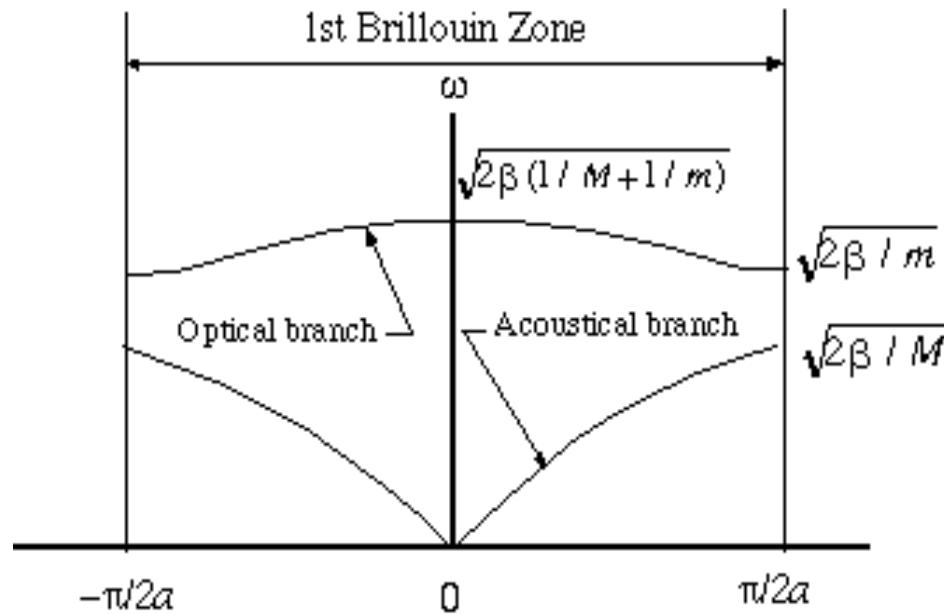
$$\omega^2 = \beta \left(\frac{1}{m} + \frac{1}{M} \right) \pm \beta \sqrt{\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2 ka}{Mm}}$$



- When $k=0, \omega = 0$ in lower soln and upper soln is non zero.
- When $q=\pi/2a$, we get different soln.

One dimensional Diatomic lattice

Now we have two branches acoustic(lower) and optical (upper)



Why it is acoustic and optical mode? How?

Acoustic branch :setting $\omega=0$ in
this{mentioned} equation. This equation will
be satisfied only if $A=B$

$$u_n = Ae^{i(kna - \omega t)}$$

$$u_{n-1} = Be^{i(k(n-1)a - \omega t)}$$

$$\begin{aligned}-Bm_2\omega^2 &= 2C(A \cos ka - B) \\ -Am_1\omega^2 &= 2C(B \cos ka - A)\end{aligned}$$

$$\left[\begin{array}{cc} 2C - m_1\omega^2 & -2C \cos ka \\ -2C \cos ka & 2C - m_2\omega^2 \end{array} \right] \begin{bmatrix} A \\ B \end{bmatrix} = 0 \quad \boxed{\quad}$$

Optical branch :setting $\omega=$
this{mentioned} equation.
We get ,

$$A_1M_1 + A_2M_2 = 0$$

$$\left[2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2}$$

.....

.....

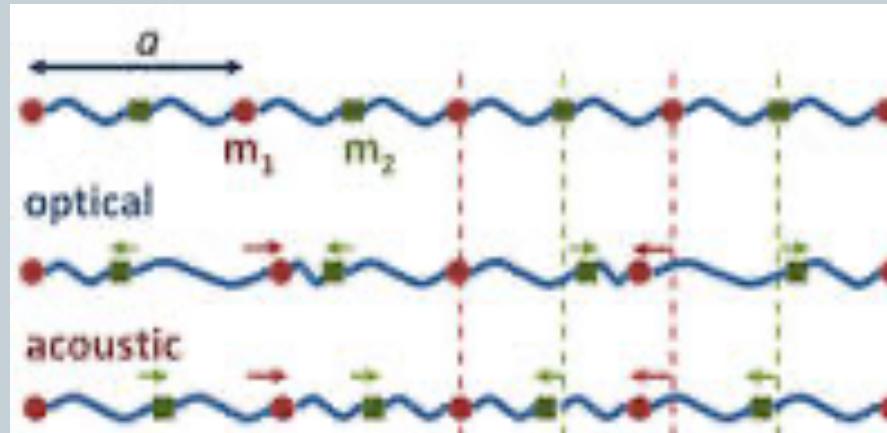
$$\omega^2 = \beta \left(\frac{1}{m} + \frac{1}{M} \right) \pm \beta \sqrt{\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2 k\alpha}{Mm}}$$

Why its is acoustic and optical mode? How?



In the case of **Acoustic branch**

if $A=B$ atoms are moving in the **same direction**. The **Net Dipole Moment** does **not change** that much..



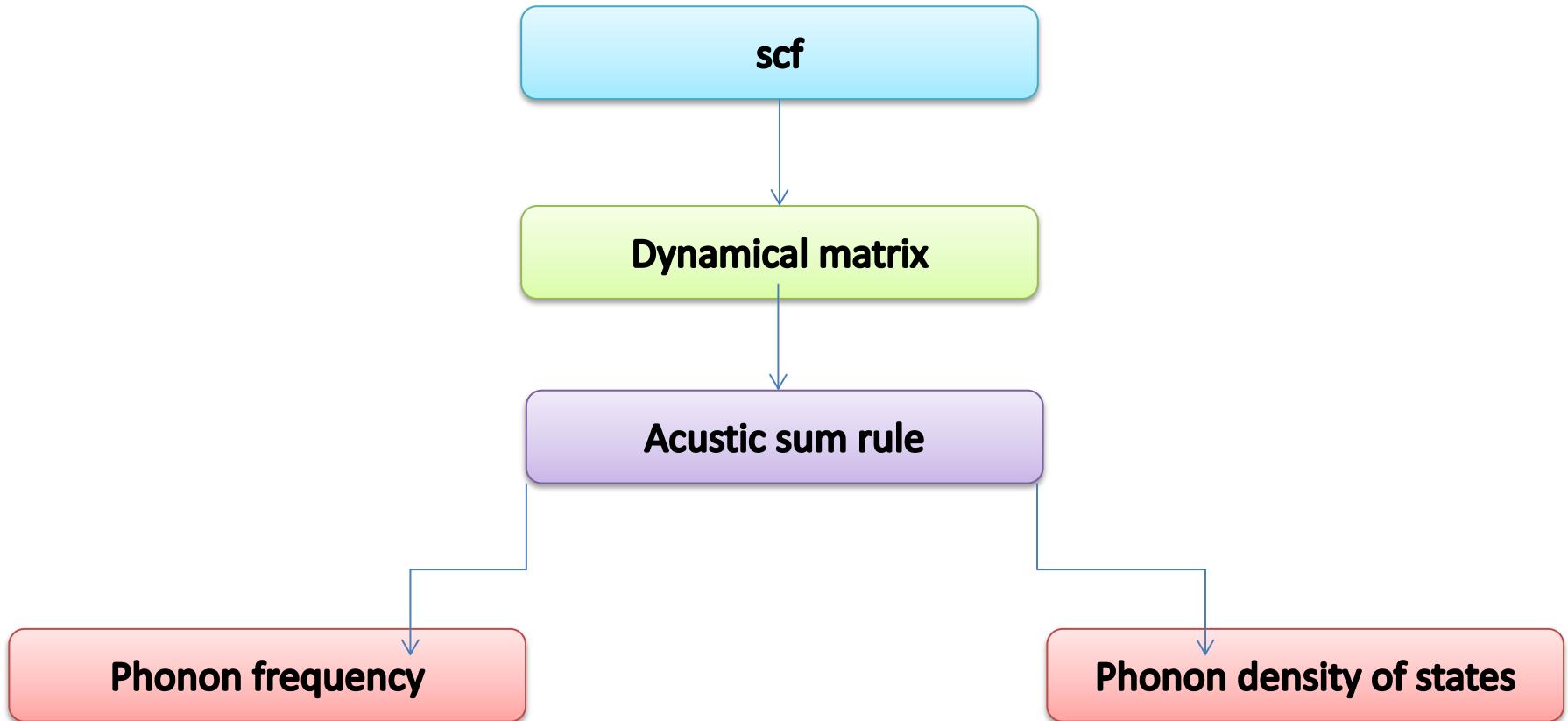
In the case of **Optical branch**

- $A_1M_1 + B_2M_2=0$ which represents atoms are moving in **opposite direction**.
So, the Net Dipole Moment **changes drastically**.
- If **Net Dipole Moment** oscillating quite **violently**, this type of vibration pattern exited by a electromagnetic wave.
- That why it is called **Optical branch**.

Part-2

Phonon calculation in quantum
espresso

Phonon calculation in quantum espresso



Phonon calculation in quantum espresso

- ▶ Aim – find dispersion relation ie relationship betn w and k.
 - Density of states
- ▶ How to find frequency w?

Phonon calculation in quantum espresso

DFT

- Phonon frozen method
- drawback large supercells are needed
- accurately calculate the force constant matrix–
- cause problems
- large time of calculation.

Frozen Phonons

- The forces between every atom construct the force constant matrix in the crystal. This force constant matrix then allows us to calculate the normal modes of at any particular wavevector \mathbf{q} .
- DFT to calculate the forces on every atom using the Hellman-Feynman theorem.
- This method of calculating the force constant matrix by explicitly displacing atoms is called the Frozen-Phonon method.

Frozen Phonons

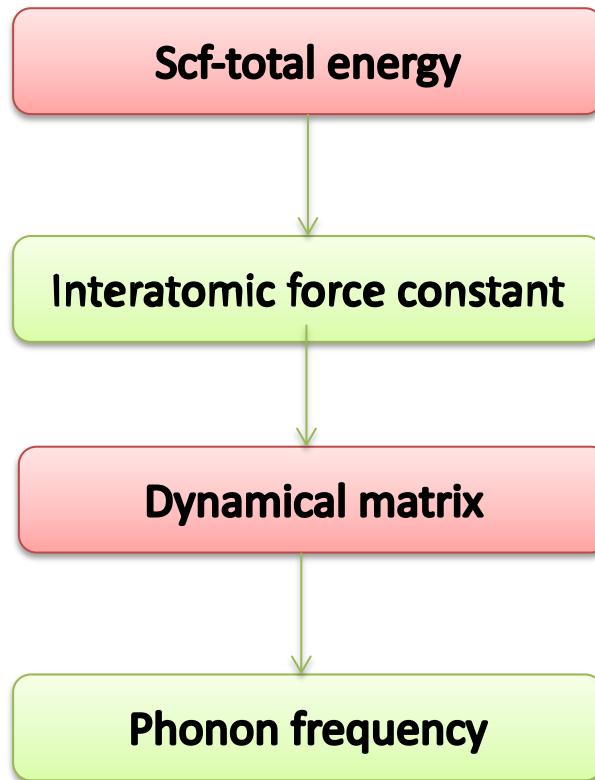
Advantage

- Quicker and computationally cheaper than the **Linear Response method**, which utilizes **DFPT** to calculate forces.

Drawback

- Large super cells - needed to accurately calculate the **Force constant matrix**.
- **Boundary conditions** used in DFT calculations cause problems -frozen phonon method.

Phonon calculation in quantum espresso



Dynamical matrix

III. DYNAMICAL MATRIX AND PHONON FREQUENCIES

The total energy of a periodic crystal with small lattice distortions from the equilibrium positions can be expressed as

$$E_{\text{tot}}(\{\Delta \tau\}) = E_{\text{tot}}^{(0)} + \sum_{a\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left(\frac{\partial^2 E_{\text{tot}}}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right) \Delta \tau_{\kappa\alpha}^a \Delta \tau_{\kappa'\beta}^b + \dots, \quad (8)$$

where $\Delta \tau_{\kappa\alpha}^a$ is the displacement along direction α of the atom κ in the cell labeled a (with vector \mathbf{R}_a), from its equilibrium position τ_κ .

The matrix of the IFC's is defined as

$$C_{\kappa\alpha,\kappa'\beta}(a,b) = \left(\frac{\partial^2 E_{\text{tot}}}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right), \quad (9)$$

its Fourier transform is

$$\begin{aligned} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) &= \frac{1}{N} \sum_{ab} C_{\kappa\alpha,\kappa'\beta}(a,b) e^{-i\mathbf{q}\cdot(\mathbf{R}_a - \mathbf{R}_b)} \\ &= \sum_b C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\mathbf{q}\cdot\mathbf{R}_b}, \end{aligned} \quad (10)$$

where N is the number of cells of the crystal in the Born-von Karman approach.³² It is connected to the dynamical matrix $\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$ by

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) / (M_\kappa M_{\kappa'})^{1/2}. \quad (11)$$

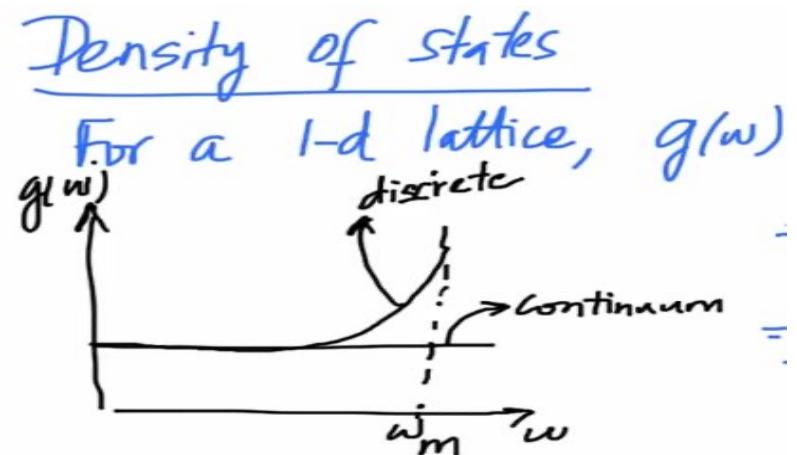
The squares of the phonon frequencies $\omega_{m\mathbf{q}}^2$ at \mathbf{q} are obtained as eigenvalues of the dynamical matrix $\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$, or as solutions of the following generalized eigenvalue problem:

This is what DFPT.....

- **Dynamical matrices** are known – can generate easily **IFC** using **Fourier transformation** and **phonon frequencies** interpolated for any wave vectors.

Phonon density of states

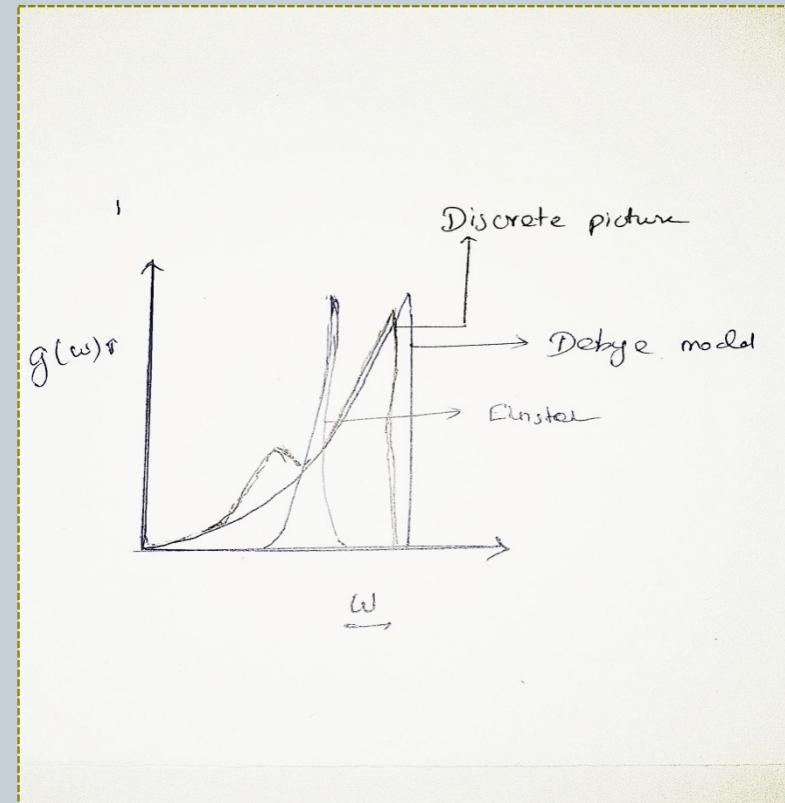
Its same as the density of states in DFT.



Einstein and Debye model



- Debye model almost same as Discrete picture.
- Debye model gives very good agreement in treating of specific heat of solid.



Part-3

Program files and results

Simulation

The Multiple Phonon simulation in Quantum Espresso consists of four steps:

- ▶ **Step 1.** **PW**Self consistent calculation of electron density. Outputs are wave functions.
- ▶ **Step 2.** **PH**Phonon calculation from linear response, with output on a rough grid.
- ▶ **Step 3.** **Q2R**Fourier transform to real space and obtain force constants by interpolation.
- ▶ **Step 4.** **MATDYN**Calculation of all phonons from dynamical matrix, given the force constants.

Self consistent calculation

- &control
 calculation='scf'

.....

.....
outdir='/home/k
/
&system

.....

.....

/
&electrons

.....

/
ATOMIC_SPECIES

.....

ATOMIC_POSITIONS

.....

K_POINTS AUTOMATIC

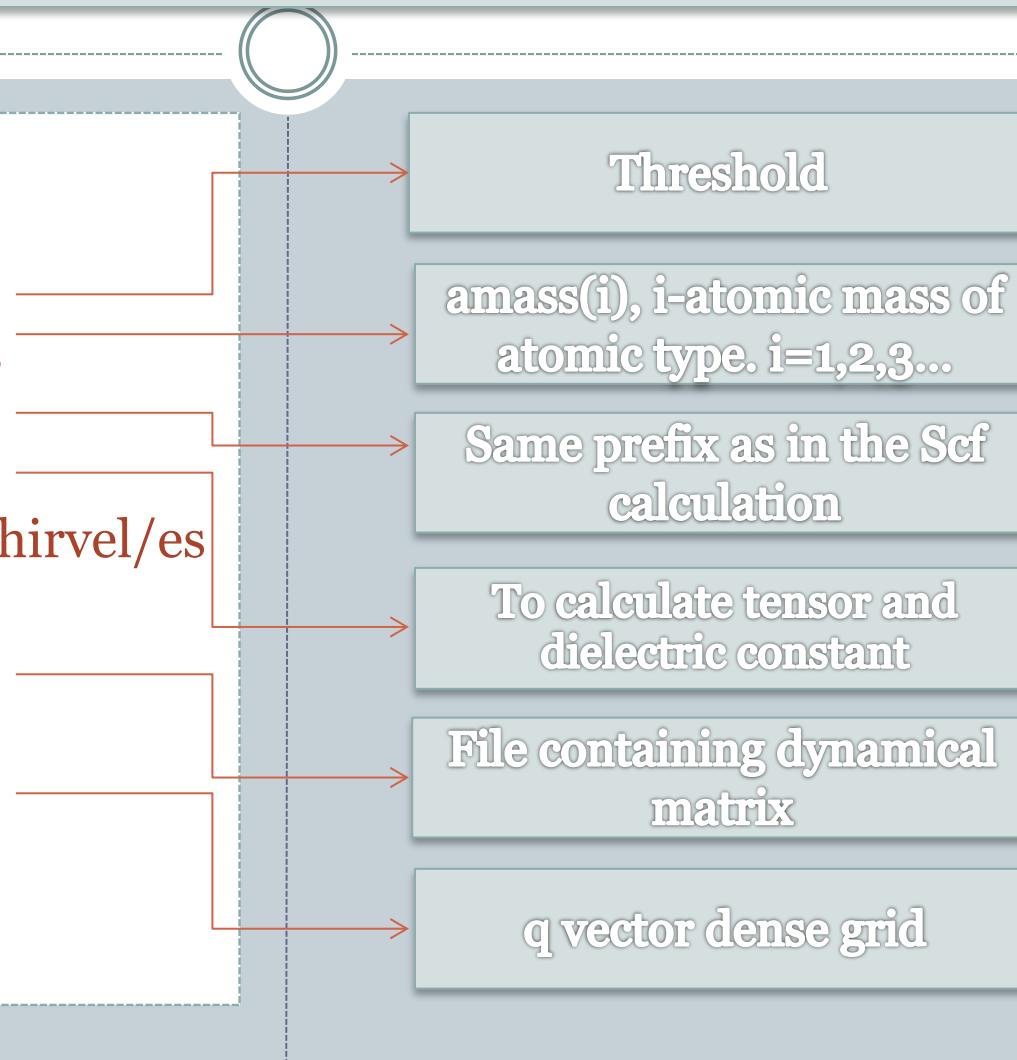
4 4 4 1 1 1

- It calculates the **total energy** of a periodic crystal from its equilibrium position.

- This total energy help us to find IFC

Calculation of Dynamical matrices on a grid of **q**-vectors (will require several minutes).

- Phonons of Si at X
&inputph
tr2_ph=1.0d-14,
amass(1)=28.0855,
prefix='SIPH',
ldisp=.true
outdir='/home/kathirvel/es'
presso/tmp/'
fildyn='si.dynX',
/
4.0 4.0 4.0



Prompt> mpirun -np 8 ph.x < si.ph.in > si.ph.out

Calculation of IFC's in real space.

- &input
fildyn='si.dynX',
zasr='simple',
flfrc='si444.fc'
/
-
- file containing dynamical matrix
- To impose acoustic sum rules
- File containing the IFC's, and a list of **q**-points for which the frequencies are to be calculated

```
prompt> mpirun -np 8 matdyn.x <input file> output file
```

The calculation of Phonon dispersions along selected high-symmetry lines

```
• &input  
asr='simple',  
amass(1)=58.6934,  
flfrc='ni444.fc',  
flfrq='ni.freq'  
/  
36  
0.0 0.0 0.0 0.0  
0.1 0.0 0.0 0.0  
.....
```

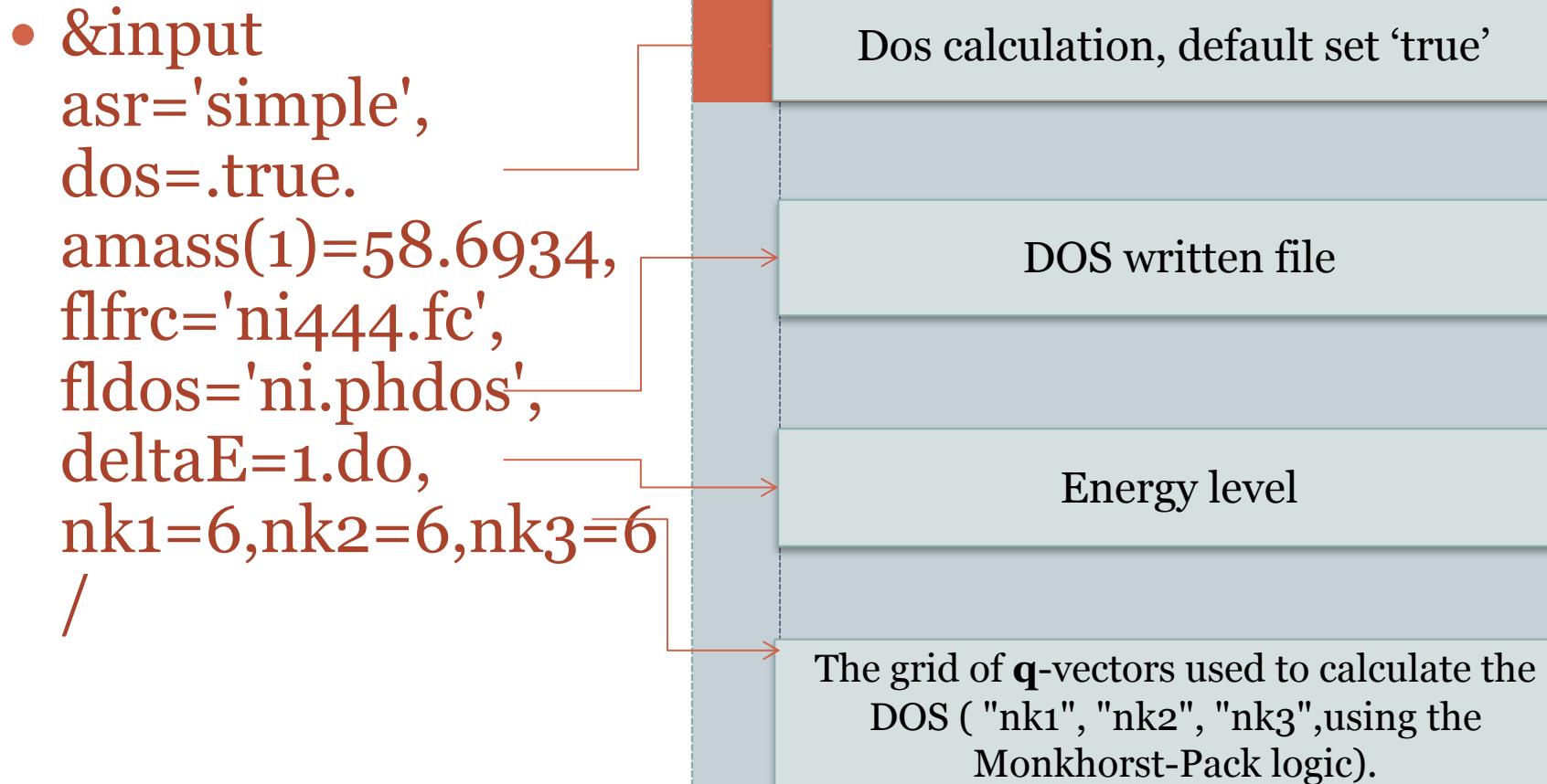
Indicate type of Acoustic Sum Rules used for the Born effective charges

File where matdyn writes the interpolated frequencies

High symmetry k points

prompt> matdyn.x <input file> output file

The calculation of Phonon DOS



Prompt> matdyn.x < phdos.in > phdos.out

Things you need to know.....



Self-consistent field

- **Scf** step as usual.
- Prefix of the **Scf** and all **ph,q2r,freq,phdos** should be same.
- Note : **relaxation** prefix would be visible to phonon calculation so, prefix of **relax** and **Scf** must be different if you do sequence calculation of Phonon. As per my experience it happened when I did **dynamical matrix** calculation, It took Energy values with '**K**' points from **relax** calculation not from **Scf**.

Dynamical matrix

- In the calculation of **Dynamical matrix** If grid of **q-vectors** increases, program running time will also increases.(not to specify more than 4).
- Form the output of **Dynamical matrix** calculation (flfrc='grap.fc'-contains force constant)we can calculate **Acoustic Sum Rule**.

In matdyn calculation we can proceed to two different types of calculations which are mentioned below.



1. Phonon dispersions

- In this `matdyn.in` calculation we must to specify the list of **q-points** for which the frequencies are to be calculated. These q points can be generate from `X-crysden` which are in **crystal co-ordinates**,actual need is **Cartesian co-ordinates** in the units of $2\pi/a$.
- To get this **Cartesian co-ordinates** we calculated band structure for given atom using high symmetry points in **crystal co-ordinates** which is generated from `X-crysden`. From the output file of band structure calculation,we could extract **Cartesian co-ordinates** which is in the units of $2\pi/a$.
- we can use these co-ordinates as a high symmetry q points for which the frequencies are to be calculated(`matdyn.in`).
- The file selected in flfrc, "`si.freq`", contains a list of frequencies in a format that can be further processed by another auxiliary code, "`plotband.x`", the same used for **band structure** plotting.

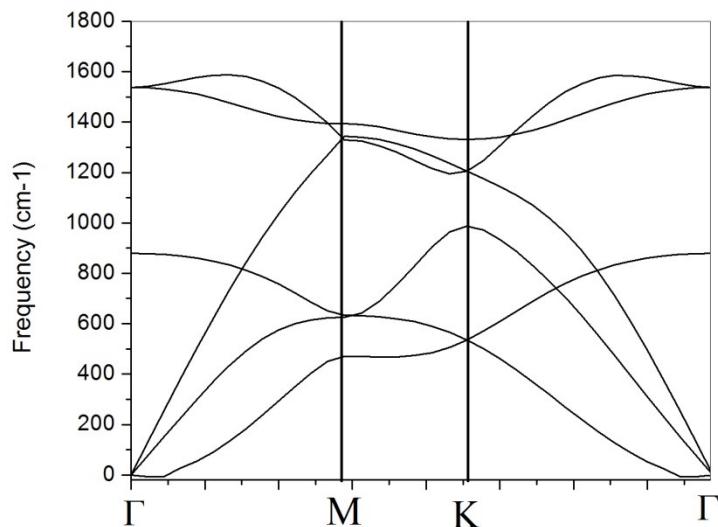
2. Phonon DOS

- If you choose option "`dos=.true.`" you must specify the grid of **q-vectors** used to calculate the **DOS**.

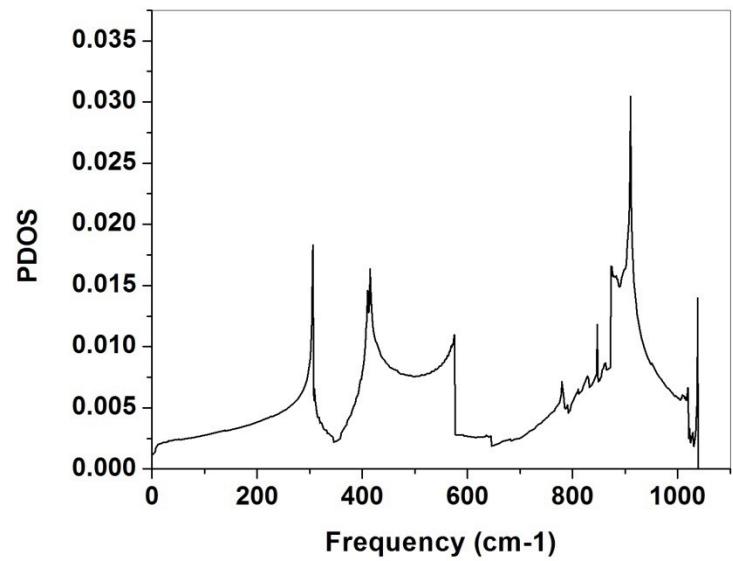
Phonon calculation for Graphene



Phonon dispersion



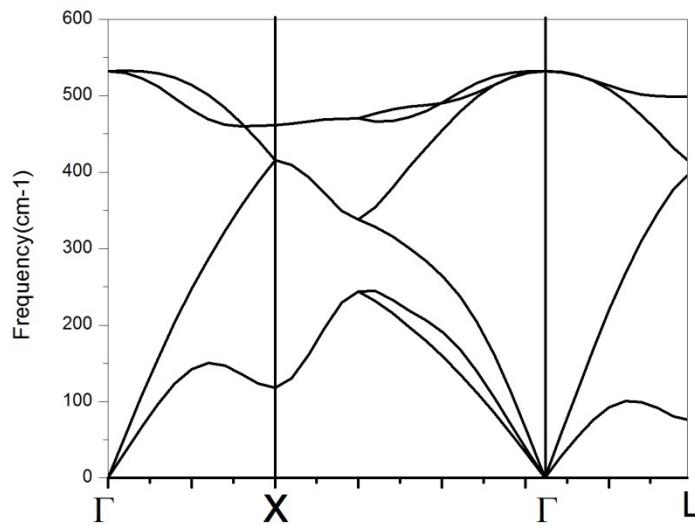
Phonon density of states



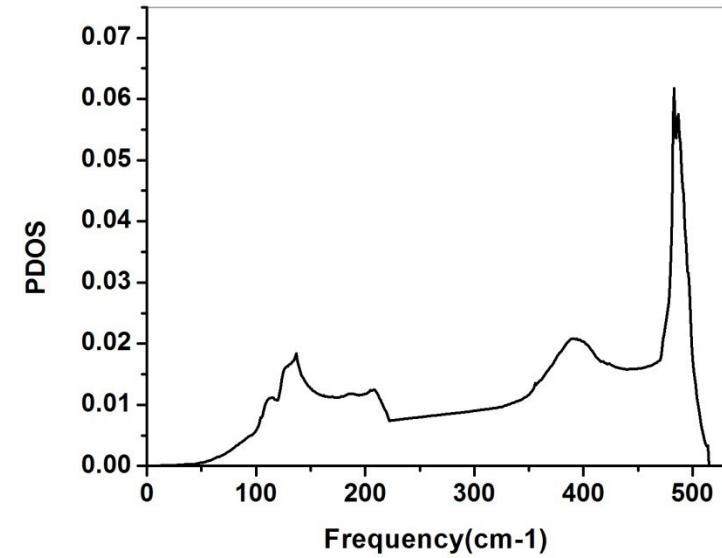
Phonon calculation for Silicon



Phonon dispersion



Phonon density of states



Thank you....