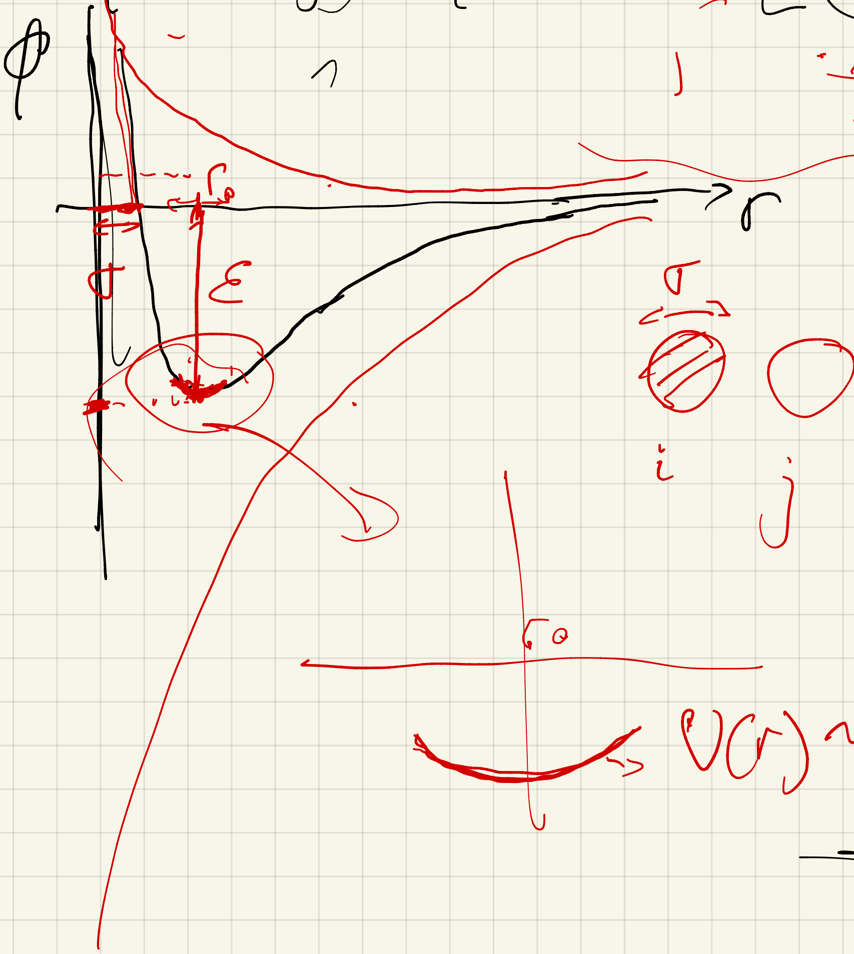
$$\phi(r_i - r_j) = \phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



$$\boxed{k = \frac{\partial^2 \phi}{\partial r^2}\Big|_{r_0}}$$

$$V(r) \sim V_0 + \frac{1}{2} k r^2$$

$$U = \frac{1}{2}\sum_{RR'} \phi(R - R') = \frac{N}{2}\sum_{R \neq 0} \phi(R) \qquad T = 0$$

$T \neq 0$

$$U = \frac{1}{2}\sum_{RR'} \phi(r(R) - r(R')) = \frac{1}{2}\sum_{RR'} \phi(\vec{R} - \vec{R}' + u(\vec{R}) + u(\vec{R}'))$$

$$H_{ion} = \sum_{R} \frac{\vec{P}(R)}{2M} + U$$

· Taylor expansion of $U(R)$ → potential energy.

$$f(\vec{r}+\underbrace{\vec{a}}_{\text{small parameter}}) = f(\vec{r}) + \vec{a}\vec{\nabla} f(\vec{r}) + \frac{1}{2}(\vec{a}\vec{\nabla})^2 f(r) + \frac{1}{3!}(\vec{a}\vec{\nabla})^3 f(r) + \dots$$

$$\vec{r} = \vec{R} - \vec{R}' \qquad \vec{a} = \underbrace{u(R) - u(R')}_{\text{very small}}$$

$$U = \underbrace{\frac{N}{2}\sum_{R\neq 0}\phi(R)}_{U_{eq}} + \cancel{\frac{1}{2}\sum_{RR'}\left(u(\vec{R}) - u(R')\right)\cdot\vec{\nabla}\phi(R-R')}^{\,0} + \underbrace{\frac{1}{4}\sum_{RR'}\left[\left(u(R) - u(R')\right)\cdot\vec{\nabla}\right]^2\phi(R-R')}_{U^{\text{harmonic}}}$$

$$+\,O(u^3)$$

$$U^{\text{harmonic}} = \frac{1}{4} \sum_{\substack{RR' \\ \mu, \nu = x, y, z}} \left[U_\mu(R) - U_\mu(R') \right] \phi_{\mu\nu}(R - R') \left[U_\nu(R) - U_\nu(R') \right]$$

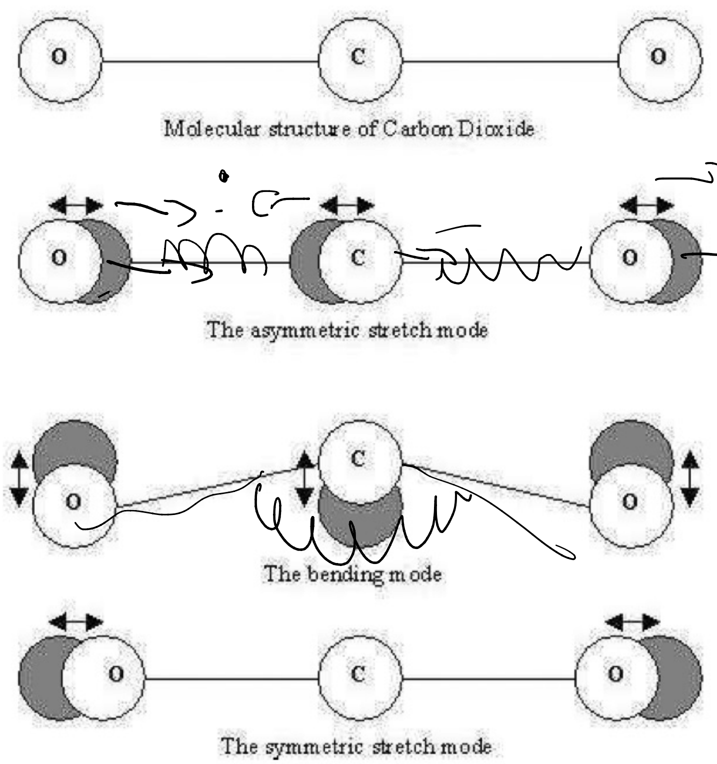
$$\boxed{\phi_{\mu\nu}(r) = \frac{\partial^2 \phi(r)}{\partial r_\mu \partial r_\nu}}$$

$$U^{\text{harm}} = \frac{1}{2} \sum_{\substack{RR' \\ \mu\nu}} U_\mu(R) D_{\mu\nu}(R - R') U_\nu(R')$$

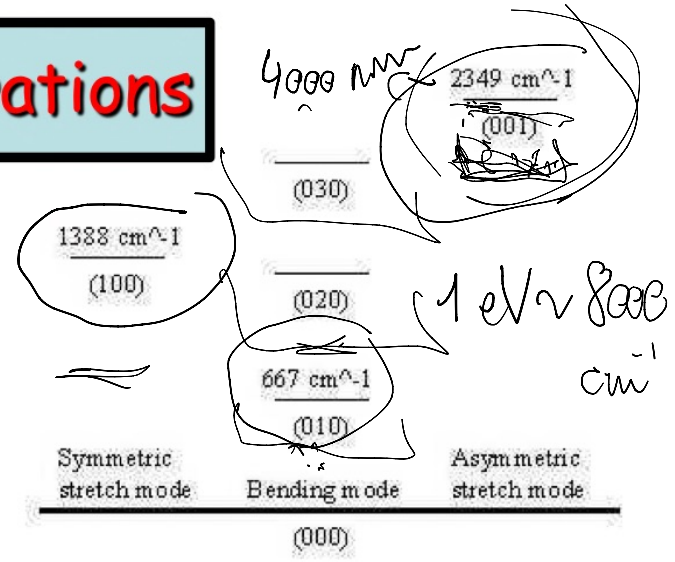
$$D_{\mu\nu}(\vec{R} - \vec{R}') = \delta_{RR'} \sum_{R''} \phi_{\mu\nu}(\vec{R} - \vec{R}'') - \phi_{\mu\nu}(R - R')$$

Matrix Tensor = Dynamical matrix.

3: CO_2 molecular vibrations

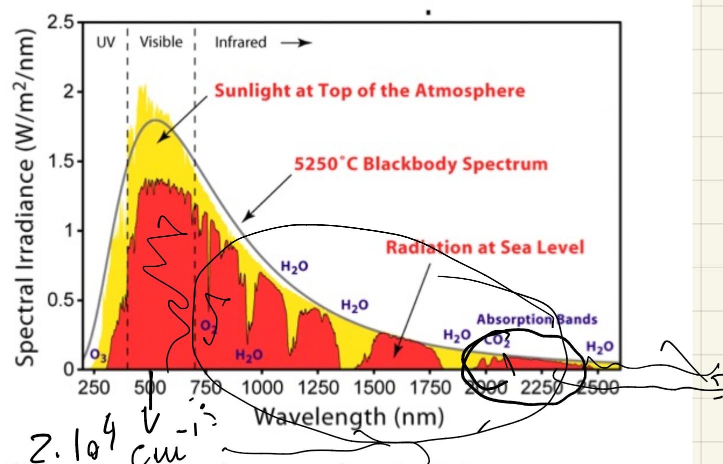


4000 nm



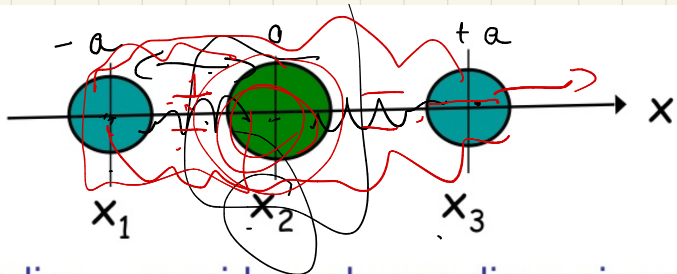
The first few vibrational energy levels of the CO2 molecule

$1\ eV \sim 8000\ cm^{-1}$



$2 \cdot 10^4\ cm^{-1}$

Derek Kverno, Davidson College
http://www.phy.davidson.edu/StuHome/derekk/Resonance/pages/main.htm



Neglect bending – consider only one dimensional motions. Choose the origin at the center of mass; define displacement coordinates u_i

$$u_1=x_1+a \quad u_2=x_2 \quad u_3=x_3-a \quad \langle u_1\rangle=\langle u_2\rangle=\langle u_3\rangle=0$$

a = equilibrium C – O distance; mass $m_1 = m_3$.

$$H = p_1^2/2m_1 + p_2^2/2m_2 + p_3^2/2m_3 + V(u_1,u_2,u_3)$$

Approximate V by nearest neighbor central spring model.

$$V(u_1,u_2,u_3) = ½k(u_1-u_2)^2 + ½k(u_3-u_2)^2$$

Newtonian equations of motion

$$m_1\ddot{u}_1 = -\partial V/\partial u_1 = -k(u_1-u_2)$$
$$m_2\ddot{u}_2 = -\partial V/\partial u_2 = -k(u_2-u_1) - k(u_2-u_3)$$
$$m_3\ddot{u}_3 = -\partial V/\partial u_3 = -k(u_3-u_2)$$

Matrix form of equation of motion (note: $m_1 = m_3$ for CO_2)

$$-\frac{d^2}{dt^2}\begin{pmatrix} m_1 & 0 & 0 \\ 0 & m_2 & 0 \\ 0 & 0 & m_3 \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix}$$

Abstract (Dirac) notation for matrix and vector

$$\boxed{-\frac{d^2}{dt^2}\hat{M}\,|u> = \hat{K}\,|u>}$$

where $|u> = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix}$ and $\hat{M}$ is the (diagonal) mass matrix

and $\hat{K}$ is the (real symmetric) force constant matrix

Define $|s> = M^{\frac{1}{2}}\,|u>$ or $\begin{pmatrix} s_1 \\ s_2 \\ s_3 \end{pmatrix} = \begin{pmatrix} u_1\sqrt{m_1} \\ u_2\sqrt{m_2} \\ u_3\sqrt{m_3} \end{pmatrix}$ mass-weighted coordinates

S

The Newtonian equation of motion becomes

$$\boxed{-\frac{d^2}{dt^2}|s> = \hat{D}|s>}$$

where $\hat{D}$ is the (real-symmetric) "dynamical matrix."

$$\hat{D} = M^{-\frac{1}{2}} K M^{-\frac{1}{2}} = \begin{pmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} & 0 \\ -\frac{k}{\sqrt{m_1 m_2}} & 2\frac{k}{m_2} & -\frac{k}{\sqrt{m_2 m_3}} \\ 0 & -\frac{k}{\sqrt{m_2 m_3}} & \frac{k}{m_3} \end{pmatrix}$$

$\hat{K}$ and $\hat{D}$ are both "non-negative." This follows from the fact that

$$\frac{1}{2} < u|\hat{K}|u> = V(u_1, u_2, u_3)$$

and the potential energy of a stable oscillator is never negative.

$\hat{D}$ has non-negative eigenvalues (call them ω_i^2, i=1,2,3) and orthonormal eigenvectors |i>

$$\boxed{\hat{D}|i> = \omega_i^2 |i>}$$

There is always a "null eigenvector," → in 1D

$$\hat{D}\,|\,0>=\begin{pmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} & 0 \\ -\frac{k}{\sqrt{m_1 m_2}} & 2\frac{k}{m_2} & -\frac{k}{\sqrt{m_2 m_3}} \\ 0 & -\frac{k}{\sqrt{m_2 m_3}} & \frac{k}{m_3} \end{pmatrix}|\,0>=0$$ where $$|\,0>=\begin{pmatrix} \sqrt{m_1} \\ \sqrt{m_2} \\ \sqrt{m_3} \end{pmatrix}$$

The vector |s>=|0> corresponds to $|\,u>=\begin{pmatrix} c \\ c \\ c \end{pmatrix}$ a uniform translation – all atoms have the same displacement.

Because $\boxed{m_1=m_3}$, the matrix D has an extra symmetry which allows eigenvectors to be found by "guessing."

$|\,1>=\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$ is an eigenvector with eigenvalue $\omega_1^2=k/m_1$ symmetric stretch

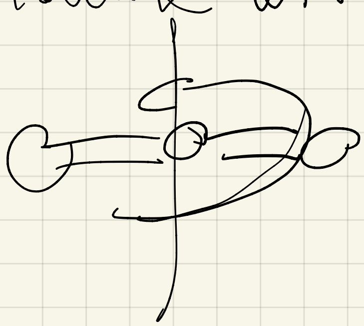
$|\,2>=\begin{pmatrix} 1/\sqrt{m_1} \\ -2/\sqrt{m_2} \\ 1/\sqrt{m_1} \end{pmatrix}$ is an eigenvector with eigenvalue $\omega_2^2=k/m_1+2k/m_2$ antisymmetric stretch

prediction: $\omega_2/\omega_1=\sqrt{1+2m_1/m_2}$ =1.9 (1.7 is found experimentally.)

3N → 3 x 3 individual solutions.

3N → 3 x 3 Normal modes { Molecular systems. (3N - 6) zero modes

Molecule with 3 atoms { 3 Translations = 0, 3 Rotations = 0, 3 vibrations = { S.S, A.S, B



What is special about eigenvectors |i> of D?

$|s\rangle = A\cos(\omega t+\varphi)|i\rangle$ is a solution of Newton's laws provided ω is chosen as the eigenvalue ω_i. It is a "stationary solution" or "normal mode." The "pattern" of oscillation is fixed in time.

The normal modes are "complete." All solutions of Newton's laws can be built from them. They also generate corresponding quantum results, i.e. solutions of the Schrödinger equation.
A simple way to designate a complete set of stationary (many body) quantum states is $|n_1, n_2, \ldots, n_i, \ldots\rangle$. This specifies, for each normal mode, the integer level n_i of excitation of the i^{th} mode. **Reinterpretation**:
Instead of the excitation level of a normal mode, we regard $\mathbf{n_i}$ as its "occupancy." That is, we ask how many quanta of vibration are "in the i^{th} mode."

The different normal modes are "independent" (in Harmonic approximation.) All extensive thermodynamic functions are sums over the thermodynamics of the independent normal modes.
There are 3N normal modes for a bound system of N atoms in d=3
(actually 3N-6 when we separate uniform translations and rotations.)

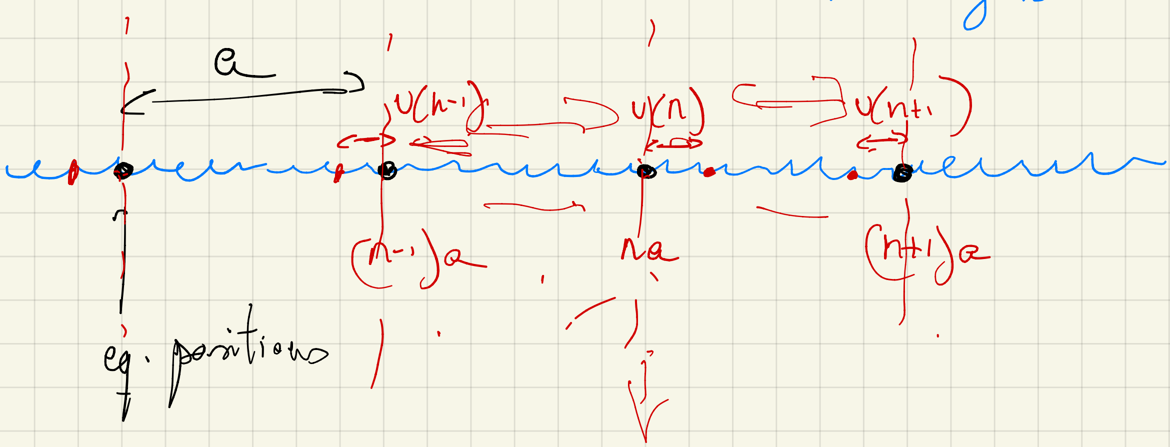
. Let's now look at a periodic, infinite system.

. Most simple version: 1D chain of atoms, with lattice constant a, springs of force constant K.

displacement from equilibrium

$$U^{harm} = \frac{1}{2} K \left[s(n) - s(n+1) \right]^2$$

$\longrightarrow$ only springs among 1st neighbors



$$K = \frac{\partial^2}{\partial x^2} \Phi(x) \quad ; \quad \Phi(x) = \frac{1}{2} k (x - x_0)^2$$

$$M \ddot{s}(n) = -K \left(s(n) - s(n-1)\right) - K \left(s(n) - s(n+1)\right)$$

$$= -K \left[2 s(n) - s(n-1) - s(n+1) \right]$$

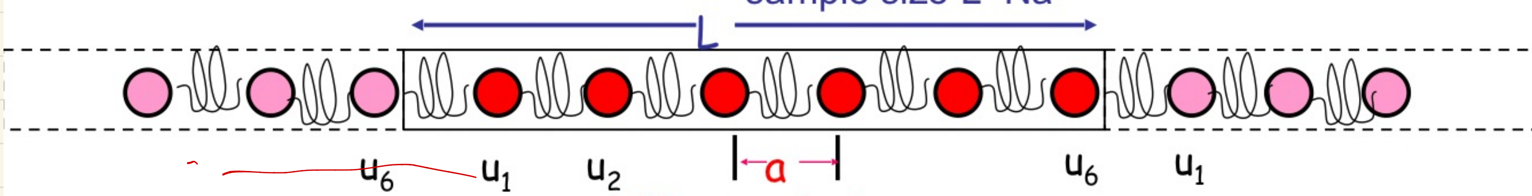
Eq. of motion:

$$M \ddot{s}(n) = - \frac{\partial U^{harm}}{\partial s(n)}$$

Boundary Conditions $\Rightarrow$ BVK (closed chain).

$S(N+1) = S(1)$; $S(0) = S(N)$

Periodic systems and Bloch's theorem

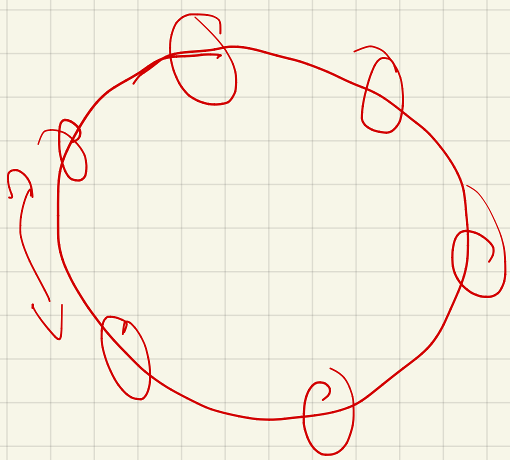


A finite system can't be truly periodic. Solution – (periodic) boundary conditions. Attach periodic replicas which copy the N-atom finite system.

$$V = \tfrac{1}{2}k(u_1-u_2)^2 + \tfrac{1}{2}k(u_2-u_3)^2 + \ldots + \tfrac{1}{2}k(u_N-u_1)^2$$

Finite and periodic

$$-m\frac{d^2}{dt^2}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix} = \begin{pmatrix} 2k & -k & 0 & 0 & 0 & -k \\ -k & 2k & -k & 0 & 0 & 0 \\ 0 & -k & 2k & -k & 0 & 0 \\ 0 & 0 & -k & 2k & -k & 0 \\ 0 & 0 & 0 & -k & 2k & -k \\ -k & 0 & 0 & 0 & -k & 2k \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix}$$



Translation operators $\hat{T}_n$

$$\hat{T}_1 \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix} = \begin{pmatrix} u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \\ u_1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix}$$

Multiplication rules: T_i form an Abelian group

$T_1^2 = T_2$, $T_1^N = T_N = T_0 = 1$

$T_1^{-1} = T_{-1}$, $T_m T_n = T_{m+n}$

$T_m T_n = T_n T_m$

Newton equation of motion in matrix form using translation matrices

$$-\frac{d^2}{dt^2} | u > = \frac{k}{m} \left(2\hat{T}_0 - \hat{T}_1 - \hat{T}_{-1} \right) | u > = \hat{D} | u >$$

Dynamical matrix D is built from translation matrices T, and commutes with them. Therefore, we can build eigenstates of the dynamical matrix using eigenstates of translations. These are traveling waves.

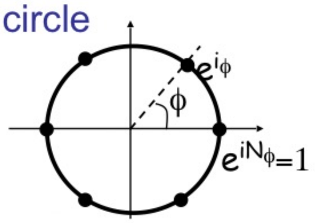
Look for eigenstates of T_1

$$|\phi> = \begin{pmatrix} e^{i\phi} \\ e^{i2\phi} \\ e^{i3\phi} \\ e^{i4\phi} \\ e^{i5\phi} \\ e^{i6\phi} \end{pmatrix} \qquad \hat{T}_1 |\phi> = \begin{pmatrix} e^{i2\phi} \\ e^{i3\phi} \\ e^{i4\phi} \\ e^{i5\phi} \\ e^{i6\phi} \\ e^{i\phi} \end{pmatrix} = e^{i\phi} |\phi>$$

If $|\varphi>$ is an eigenstate of T_1 with eigenvalue $e^{i\varphi}$, then it is an eigenstate of T_2 with eigenvalue $e^{i2\varphi}$, etc.

$\boxed{\text{Provided } e^{iN\varphi}=1 \text{ (here N=6)}}$

$e^{i\varphi}$ must be one of the N roots of unity. There are N such roots, on the unit circle



$$\phi = \frac{2\pi m}{N} = \frac{2\pi m a}{Na = L} \equiv ka \qquad k \equiv \frac{2\pi m}{L} = \frac{2\pi}{\lambda}$$

q

q -> k

$$|\phi> = |k> = \begin{pmatrix} e^{ika} \\ e^{i2ka} \\ e^{3ika} \\ e^{i4ka} \\ e^{i5ka} \\ e^{i6ka} \end{pmatrix}$$

Mathematical meaning of the – the eigenvalue of T_1 =T(a) is e^{ika}

Therefore, k and $k+2\pi/a$ have exactly the same meaning.

Warning – notation!
k is used for wave vector and for spring constant!

Bloch's Theorem

Operators like H and D for a periodic system commute with the translations. Therefore, we can choose eigenstates of H and D to be simultaneously eigenstates of all T_i. These eigenstates are labeled by their wavevector $\vec{k}$.

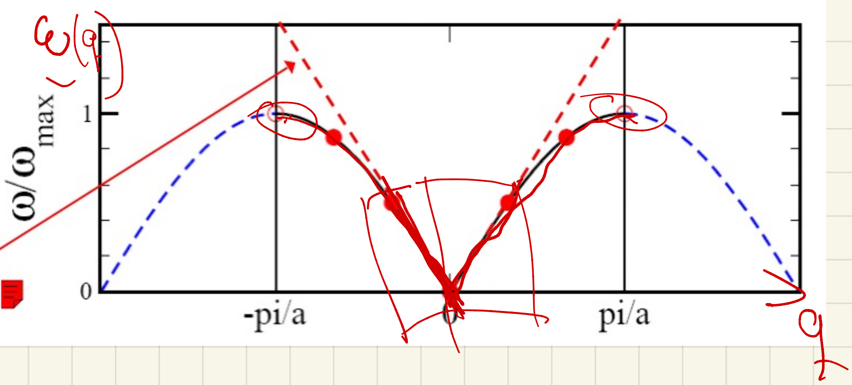
$$\hat{T}_1 \,|\, k \rangle = e^{ika} \,|\, k \rangle \qquad \hat{D} = \frac{k}{m}\left(2\hat{T}_0 - \hat{T}_1 - \hat{T}_{-1}\right) \rightarrow \frac{k}{m}\left(2 - e^{ika} - e^{-ika}\right)$$

$\omega^2(k)$ = eigenvalue of D = $\boxed{\frac{k}{m}}\left(2 - 2\cos(ka)\right) = 4\boxed{\frac{k}{m}}\sin^2(ka/2)$

$$\omega(k) = \omega_{max}\left|\sin(ka/2)\right|$$

$$\omega_{max} = 2\sqrt{\frac{k}{m}}$$

Continuum ("Debye") limit:
propagating sound waves $\omega = v|k|$



phase velocity $= \cancel{q/\omega}$ $c_v = q/\omega$

group velocity $= \dfrac{\partial \omega}{\partial q}$

Counting rules in k-space.

1. There are exactly N k-vectors $\vec{k}$ which label the inequivalent eigenvectors |k> of T. These N k-vectors lie in the Brillouin zone.
2. Bloch states |k> with inequivalent $\vec{k}$'s are orthogonal. Norm = 1. Thus $\langle k'|k\rangle = (1/N)\Sigma_R e^{i(k-k')R} = \delta(k,k')$ **modulo G**
3. The states |k> are complete in the N-dimensional space: $\Sigma_k |k\rangle\langle k| = (1/N)\Sigma_k e^{ik(R-R')} = \delta(R-R')$ [R runs over the discrete lattice points.]
4. Sums become integrals: $$\sum_k f(k) = \left(\frac{L}{2\pi}\right)^d \int^{BZ} d^d k\, f(k)$$

PBC $\rightarrow S(0) = S(N) \rightarrow$ ~~e~~

$S(n,t) \propto e^{iqna-\omega t}$ (2nd order differential eq.)

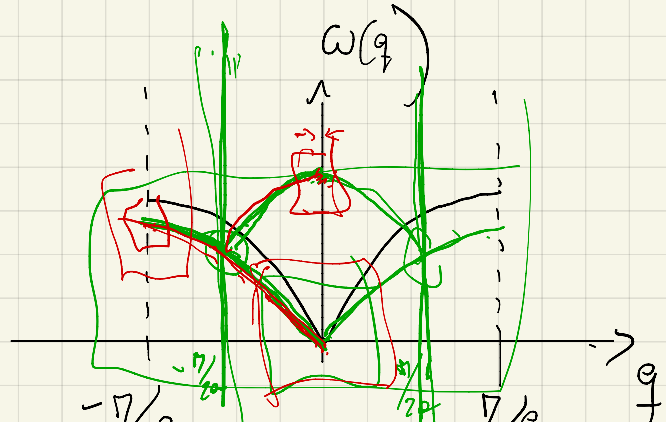
$e^{iqNa} = 1 \Rightarrow q = \frac{2\pi}{a}\frac{n}{N}$, n integer

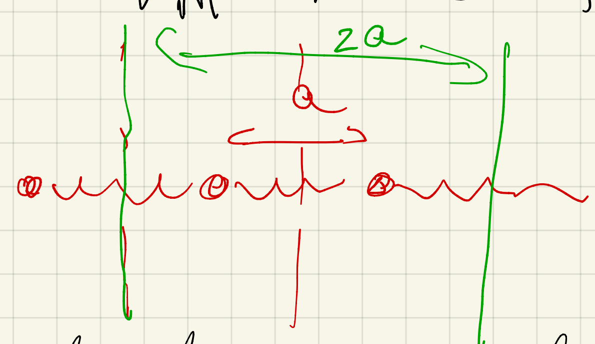
The solution is periodic, only N values of q yield distinct solutions, $\Rightarrow$ choose q in 1st BZ $\left[\frac{-\pi}{a}, \pi/a\right]$

$$-M\omega^2 e^{i(qna-\omega t)} = -K\left(2 - e^{-iqa} - e^{iqa}\right) e^{i(qna-\omega t)}$$

$$-M\omega^2 = -2K(1-\cos qa) \Rightarrow \omega(q) = \left(\sqrt{\frac{2K}{M}}(1-\cos qa)\right)^{1/2}$$

$$= 2\sqrt{\frac{K}{M}}\left|\sin\frac{1}{2}qa\right|$$





How are the solutions that describe the atomic displacements

$$S(n,t) \propto \begin{cases} \cos(qna-\omega t) \\ \sin(qna-\omega t) \end{cases}$$ $\rightarrow$ given by either the real or imaginary part of the PW.

How many solutions are there in Total ?

N values of q, each with a characteristic frequency $\omega(q)$

We have 2N independent solutions, N normal modes

$$\left(s \propto \sin(qna - \omega t) = \cos\left(qna - \omega\left(t + \frac{\pi}{2\omega}\right)\right) \right)$$

shift in Time, same normal mode

Any arbitrary motion of The chain can be specified by giving a set of $\begin{cases} N \text{ initial positions} \\ N \text{ initial velocities} \end{cases}$

$\Rightarrow$ They can be expressed as linear combinations of The 2N solutions.

Normal modes are complete $\Rightarrow$ All solutions of Newton's Law can be built from them.

$s(n, t)$ = Waves propagating along the chain

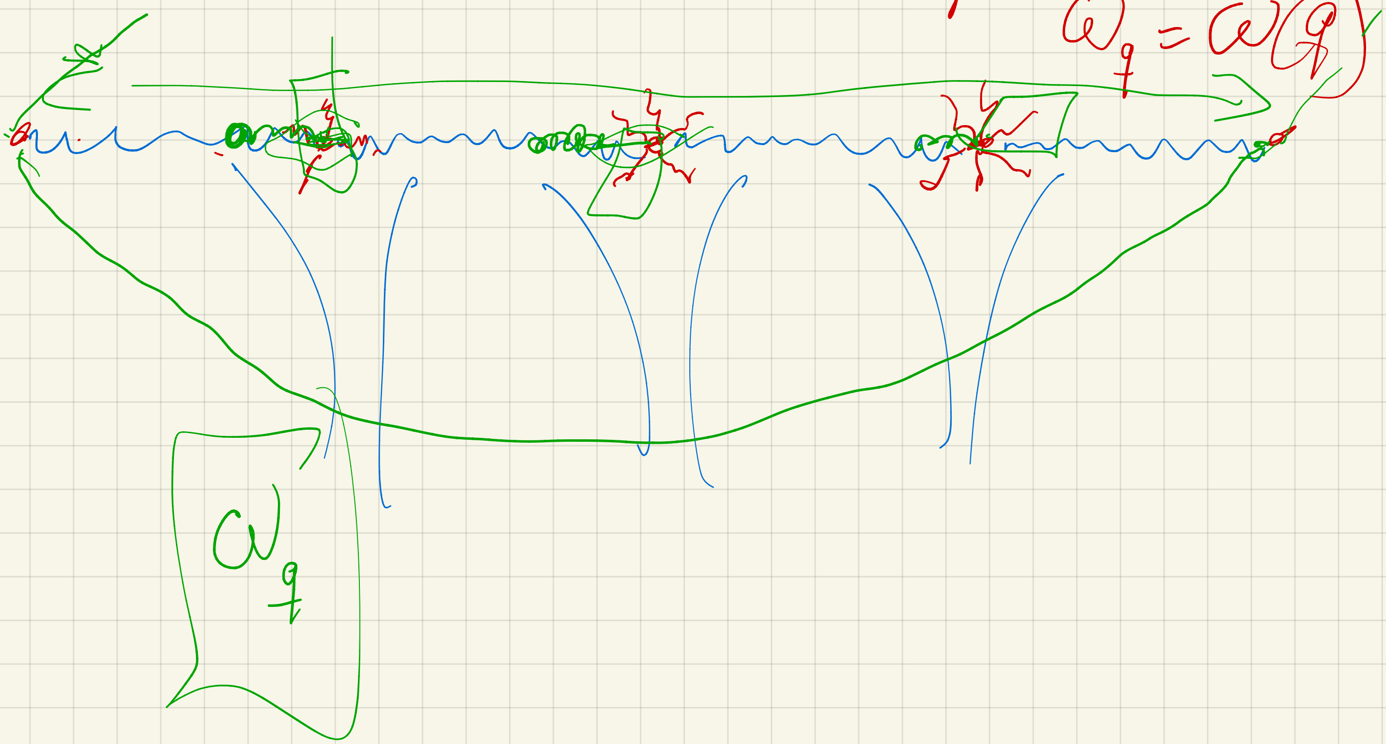
$\begin{cases} \text{phase velocity} : c = \omega/q \\ \text{group velocity} : v = \partial\omega/\partial q \end{cases}$ } They are equal in The linear regime for q small $\Rightarrow$ $\omega = \left(a\sqrt{\frac{K}{M}}\right)|q|$ $\to$ linear relation.

$$\lim_{q\to 0} 2\sqrt{\frac{K}{M}}\,\left|\sin \frac{q}{2} a\right|$$

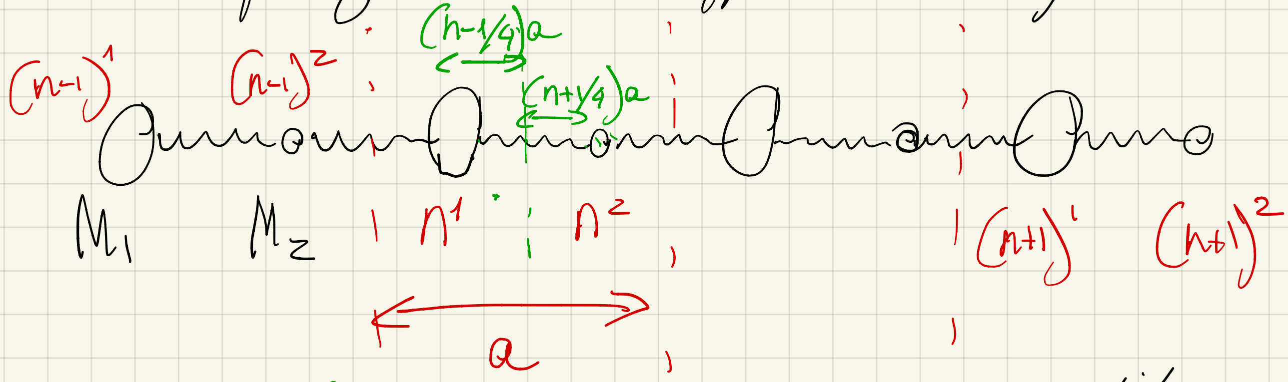
In the linear (elastic) regime the group and phase velocity are the same, but the group velocity goes to zero at the zone boundaries.

$$H = \sum_{\alpha=1}^{N} h_\alpha(R_\alpha) \to H = \sum_{q=1}^{N} H_q(R_1, \dots R_d)$$

$$\omega_q = \omega(q)$$



• 2 Atoms per unit cell (chain of 2 different springs or same spring constant, different mass).



This is the general eq (more at end of lecture). $\longrightarrow$ $$M_\alpha \ddot{S}_{\alpha n i} = -\sum_{n'\alpha' i'} \phi_{n\alpha i}^{n'\alpha' i'} S_{n'\alpha' i'}$$

$$M_1 \ddot{S}_n^1 = -K\left(S_n^1 - S_n^2\right) - K\left(S_n^1 - S_{n-1}^2\right) = -K\left(2S_n^1 - S_n^2 - S_{n-1}^2\right)$$

$$M_2 \ddot{S}_n^2 = -K\left(S_n^2 - S_n^1\right) - K\left(S_n^2 - S_{n+1}^1\right) = -K\left(2S_n^2 - S_n^1 - S_{n+1}^1\right)$$

$$S_1 = \frac{1}{\sqrt{M_1}} C_1 e^{i\left(q\underbrace{(n-1/4)}a - \omega t\right)}$$

$\vec{R}_n^1 = \underbrace{\vec{R}_n}_{\text{DLV}} + \underbrace{\vec{d}_1}_{\text{basis vector}}$

$$S_2 = \frac{1}{\sqrt{M_2}} C_2 e^{i\left(q\overbrace{(n+1/4)}a - \omega t\right)}$$

$$\boxed{\frac{S_2}{S_1} = \frac{\sqrt{M_1}}{\sqrt{M_2}} \frac{C_2}{C_1} e^{i\frac{qa}{2}}} ; \quad S_2 = S_n^1 e^{i\frac{qa}{2}} \frac{C_2}{C_1} \sqrt{\frac{M_1}{M_2}}$$

$$\dot{S}_n^1 = -i\omega S_n^1 ; \quad \ddot{S}_n^1 = -\omega^2 S_n^1$$

$$-M_1\omega^2 S_n^1 = -K\left(2S_n^1 - S_n^2 - S_{n-1}^2\right)$$

$$-M_1\omega^2 \frac{1}{\sqrt{M_1}} C_1 e^{i(q(n-1/4)a} \times e^{-i(q(n-1/4))a} = -K\left(\frac{2C_1}{\sqrt{M_1}} e^{iq(n-1/4)a} - \frac{C_2}{\sqrt{M_2}} e^{iq(n+1/4)a} - \frac{C_2}{\sqrt{M_2}} e^{iq\overbrace{(n-1+1/4)}^{\vec{R}_{n-1}}a}\right) \times e^{-i(q(n-1/4))a}$$

$$(n-3/4)a$$

$$-M_1\omega^2 \frac{C_1}{\sqrt{M_1}} = -K\left(\frac{2C_1}{\sqrt{M_1}} - \frac{C_2}{\sqrt{M_2}} e^{\frac{iqa}{2}} - \frac{C_2}{\sqrt{M_2}} e^{-\frac{iqa}{2}}\right)$$

$$\begin{cases} -\omega^2\sqrt{M_1}\, C_1 = -\dfrac{2KC_1}{\sqrt{M_1}} + \dfrac{2K}{\sqrt{M_2}} C_2 \cos\left(\dfrac{qa}{2}\right) \\ \text{and the same for } S_n^2 \\ -\omega^2\sqrt{M_2}\, C_2 = -\dfrac{2K}{\sqrt{M_2}} C_2 + \dfrac{2K}{\sqrt{M_1}} C_1 \cos\left(\dfrac{qa}{2}\right) \end{cases}$$

Secular equation. To find C_1 and C_2 we make the determinant of coeficients equal to zero

$$\begin{vmatrix} \frac{2K}{\sqrt{M_1}} - \omega^2\sqrt{M_1} & -\frac{2K}{\sqrt{M_2}}\cos\left(\frac{qa}{2}\right) \\ -\frac{2K}{\sqrt{M_2}}\cos\left(\frac{qa}{2}\right) & \frac{2K}{\sqrt{M_2}} - \omega^2\sqrt{M_2} \end{vmatrix} = 0$$

$$\omega_\pm^2 = K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm K\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4}{M_1M_2}\sin^2\frac{qa}{2}}$$

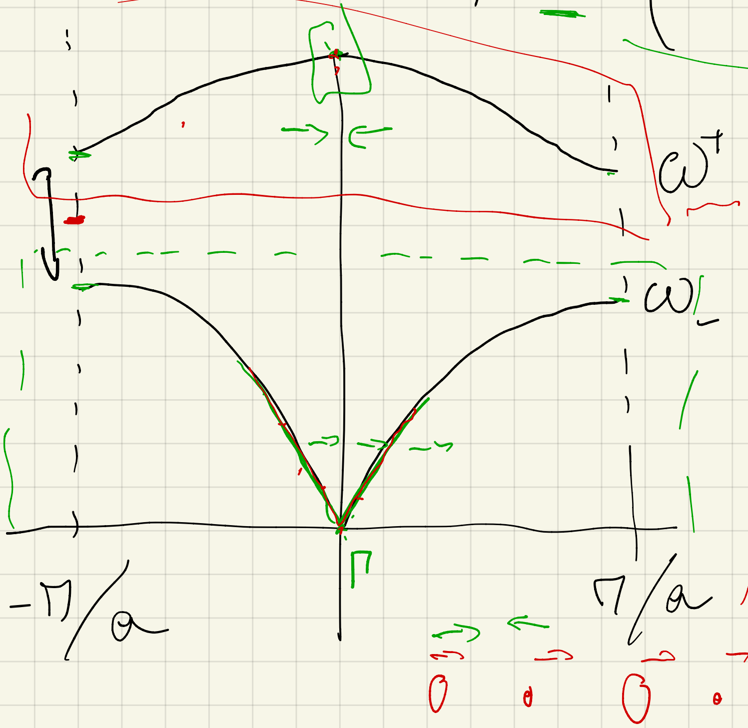
We obtain 2 different Branches

$\omega_+(q)$ $\quad$ $\omega_-(q)$

If $M_1 = M_2$ at $q = \pi/a$

$$\begin{cases} \omega^+(\pi/a) = \frac{2K}{M} + K\sqrt{\frac{4}{M^2} - \frac{4}{M^2}} \\ \omega^-(\pi/a) = \frac{2K}{M} - K\sqrt{\frac{4}{M^2} - \frac{4}{M^2}} \end{cases}$$

at $q=0$ (Γ) $\begin{cases} \omega_- = 0 \\ \omega_+ = \left(2K\frac{M_1+M_2}{M_1M_2}\right)^{1/2} = \left(2K\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right)^{1/2} \end{cases}$



$q=0$ $\left(|q| = \frac{2\pi}{\lambda}\right)$, oscillations of infinite wave length

$\omega = \omega_-$ 2 atoms move in the same direction.

$\omega = \omega_+$ => opposite directions

$q=0$, $\omega=0$ $\Rightarrow$ acoustic branch

$q=0$, $\omega\neq 0$ $\Rightarrow$ optical branch

if r basis atoms $\Rightarrow$ $\boxed{r-1}$ optical branches in 1D, in 3D

$3(r-1)$ optical branches . 3 acoustic branches

We can look at the ratios C_2/C_1 at $\begin{cases} q=0 \\ q=\pm\pi/a \end{cases}$

$(C_2 \longrightarrow S_2$ motions of atoms of mass $M_2)$

$(C_1 \longrightarrow S_1$ motions of atoms of mass $M_1)$

Within unit cell

$$q=0 \begin{cases} C_2/C_1 = +(M_2/M_1)^{1/2} & \omega=\omega_- \Rightarrow \text{Atoms move in same direction} \\ C_2/C_1 = -(M_2/M_1)^{1/2} & \omega=\omega_+ \Rightarrow \text{Atoms move in opposite directions} \end{cases}$$

$$q=\pm\pi/a \begin{cases} C_2/C_1 = \infty & \omega=\omega_- \\ C_2/C_1 = 0 & \omega=\omega_+ \end{cases} \Rightarrow \lambda = 2a$$

atoms M_1 or M_2 located at the nodes of vibrations with $\lambda=2a$

Note: Only vibrations in phase for ω_- near $q=0$ and out of phase for ω_+ near $q=0$

Classical equations of Motion

General case, Crystal with N cells, r atoms (basis) per unit cell

Equilibrium positions $\vec{R}_{n\alpha} = \vec{R}_n + \vec{R}_\alpha$ → basis vector

lattice vector

- Atoms vibrate around equilibrium positions

→ displacement $\vec{S}_{n\alpha}(t)$ → Time dependent vector

Build the classical hamiltonian :

1.- Kinetic Energy $T = \sum_{n\alpha i} \frac{M_\alpha}{2} \dot{S}_{n\alpha i}^2$ $\begin{cases} n = 1 \dots N \\ \alpha = 1 \dots r \\ i = 1, 2, 3 \end{cases}$

cartesian coordinates

2.- Potential Energy ⇒ Expand the potential energy $V\{R\}$ in a Taylor series of the displacements $S_{n\alpha i}$

1st Term ⇒ Potential energy of the lattice in equilibrium (does not contribute to the dynamics).

2nd Term ⇒ $\left.\frac{\partial V}{\partial R}\right|_{R=R_0} = 0$ ($V\{R_0\}$ is a minimum)

3rd Term: $\frac{1}{2} \sum_{\substack{n\alpha i \\ n'\alpha' i'}} \underbrace{\frac{\partial^2 V}{\partial R_{n\alpha i} \partial R_{n'\alpha' i'}}}_{\Phi_{n\alpha i}^{n'\alpha' i'}} S_{n\alpha i} S_{n'\alpha' i'}$

$\Phi_{n\alpha i}^{n'\alpha' i'} \Longrightarrow$ Matrix with $3rN$ rows and columns

Eq of Motion: $M_\alpha \ddot{S}_{n\alpha i} = -\frac{\partial V}{\partial S_{n\alpha i}} = -\sum_{n'\alpha' i'} \Phi_{n\alpha i}^{n'\alpha' i'} S_{n'\alpha' i'}$

$\longrightarrow \Phi_{n\alpha i}^{n'\alpha' i'}$ = force in the i-direction on the αth ion in the nth cell when the α'th ion in the n'th cell is displaced by unit distance in the i'-direction

$\downarrow$

These are the atomic force constants, related by many symmetry relations.

1.- Force constants are symmetric $\Rightarrow \frac{\partial^2 V}{\partial R_i \partial R_j} = \frac{\partial^2 V}{\partial R_j \partial R_i}$

$\Phi_{n\alpha i}^{n'\alpha' i'} = \Phi_{n'\alpha' i'}^{n\alpha i}$

2.- Φ's are real (V is real)

3.- V must be invariant to an infinitesimal translation or rotation of the crystal

$\delta T_i\, S_{n\alpha i} = \delta s_i$ for all n, α, i

$$R\, S_{n\alpha i} = \sum_{k=1,3} \delta\omega_{ik}\, R_{n\alpha k} \quad \left(\delta\omega_{ik} = -\delta\omega_{ki}\right)$$

These operations should not result in forces on the ions

$$\sum_{i'} \delta s_{i'} \sum_{n'\alpha'}^{n\alpha} \Phi_{n\alpha i}^{n'\alpha' i'} = 0 \qquad \text{(let } S_{n\alpha i} = \delta s_i \text{ for all } n, \alpha, i\text{)}$$

$$\boxed{\sum_{n\alpha} \Phi_{n\alpha i}^{n'\alpha' i'} = 0} \Rightarrow F \text{ sum rule, acoustic sum rule.}$$

. We look for solutions to the eq. of motion that are stationary (periodic) in time

$$S_{n\alpha i}(t) = \frac{1}{\sqrt{M_\alpha}}\, U_{n\alpha i}\, e^{-i\omega t}$$

$U_{n\alpha i}$ → time independent

$$\omega^2\, U_{n\alpha i} = \sum_{n'\alpha' i'} D_{n\alpha i}^{n'\alpha' i'}\, U_{n'\alpha' i'} \qquad D = \frac{\Phi}{\sqrt{M_\alpha M_{\alpha'}}}$$

This is the eigenvalue equation for the real, symmetric Matrix $D_{n\alpha i}^{n'\alpha' i'}$

with $3rN$ eigenvalues ω_j^2 ; ω_j either real or pure imaginary

only possible if $S_{n\alpha i}$ is not periodic.

The eigenvectors $U_{n\alpha i}$ are characterized by the index j

$U^j_{n\alpha i}$, for each ω_j There are $3rN$ $U^j_{n\alpha i}$ $\Rightarrow$ normal modes

Now we apply the Translational symmetry of the lattice

$D_{n\alpha i}^{n'\alpha' i'}$ can not depend on n, n' separatelly, but on the difference $n-n'$

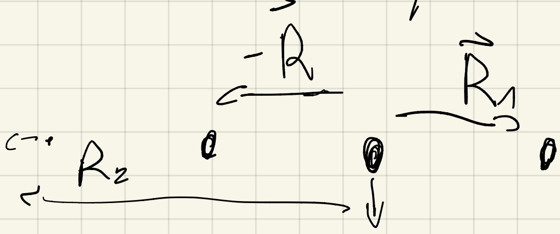
$$\Phi_{n\alpha i}^{n'\alpha' i'} = \Phi_{\alpha i}^{\alpha' i'}(n-n')$$

$\Rightarrow$ Solutions to the equations of motion $\Rightarrow$ plane waves, eigenstates of the Translation operator

$$U_{n\alpha i} = C_{\alpha i}\, e^{iqR_n}$$

$$\omega^2 C_{\alpha i} = \sum_{\alpha' i'} \left\{ \sum_{n'} \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \Phi_{\alpha i}^{\alpha' i'}(n-n')\, e^{iq(R_n - R_{n'})} \right\} C_{\alpha' i'}$$

$$\rightarrow \sum_{n'} \rightarrow \sum_{n'-n} \rightarrow \sum_{\vec{R}}$$



$$\boxed{\omega^2 C_{\alpha i} = \sum_{\alpha' i'} D_{\alpha i}^{\alpha' i'}(q)\, C_{\alpha' i'}}$$

$\rightarrow$ Dynamical matrix $$D_{\alpha i}^{\alpha' i'}(q) = \sum_{\vec{R}} \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \Phi_{\alpha i}^{\alpha' i'}(\vec{R})\, e^{iq\vec{R}}$$

with $\vec{R} \rightarrow$ all lattice vectors

So, by applying the lattice periodicity we have reduced a system of $3rN$ eq. to a system of $3r$ equations

The system has now $3r$ eigen values, $3r$ ω_j's which now are functions of the vector q

$$\omega = \omega_j(q) \quad j = 1 \ldots 3r$$

For each ω_j The eq. of motion has a solution

$$C^j_{\alpha i} = e^j_{\alpha i}(q) \Longrightarrow i = 1,3 \rightarrow \text{form a 3D vector}$$

$$\overbrace{\vec{e}_\alpha^{\,j}(q)}^{\rightarrow \text{ polarization vector}} \rightarrow \text{vector, describes The direction in which}$$

The ions move. $e_\alpha^j(q)$ are normalized and orthogonal To each other

So, finally The displacements (solutions of The eq. of motion)

$$\underbrace{\vec{S}_{n\alpha}^{\,j}(q,t)}_{\downarrow \text{ cartesian NoTation.}} = \underbrace{\frac{1}{\sqrt{M_\alpha}}\, \underbrace{\vec{e}_\alpha^{\,j}(q)}_{\text{3D vector}}}^{\text{Normal mode NoTation}} e^{i\left(q R_n - \omega(q) t\right)}$$

For each of The $j = 1 \ldots 3r$ solutions we obtain a collective motion $\{ S_{n\alpha}(q,t) \}$ for all The atoms in The system

Note: $\omega_j(\vec{q})$ is equivalent for lattice vibrations to $E_n(k)$ The energy dispersion for e^-

$\hbar\omega_j$ = energy $\vec{q}$ ⇝ Reciprocal vector in The 1st BZ

1) $\omega_j(\underline{q}) \to$ periodic in $\underline{q}$, only 1st BZ needed

2) As with e^-, only finite values of $\underline{q}$ are allowed (PBC)

N values of $\underline{q}$ in The Brillouin zone, $j = 1 \dots 3r$

$\Rightarrow 3rN$ different $\omega_j(\underline{q}) \Rightarrow$ as many as The crystal's internal degrees of freedom.

3) Note in $E_n(k)$ $n = 1 \dots \infty$ (or as many as basis...)

but $\omega_j(\underline{q})$ $j = 1 \dots 3r \Rightarrow$ Only $3r$ Branches

4) $\omega_j(\underline{q}) \to$ same symmetries as The band structure $E_n(k)$. We always have Time reversal sym.

$\omega_j(\underline{q}) = \omega_j(-\underline{q})$