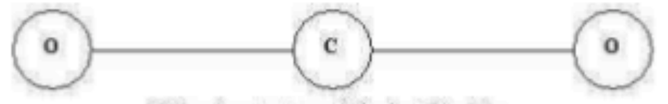
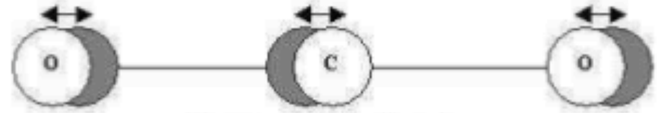
Lattice Dynamics

Classical Theory of the Harmonic Crystal

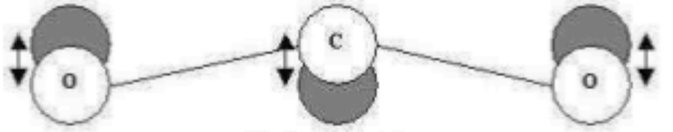
3: CO_2 molecular vibrations



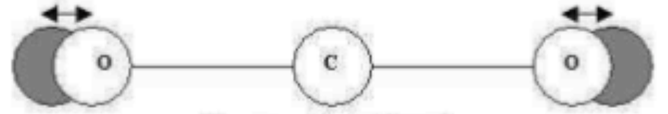
Molecular structure of Carbon Dioxide



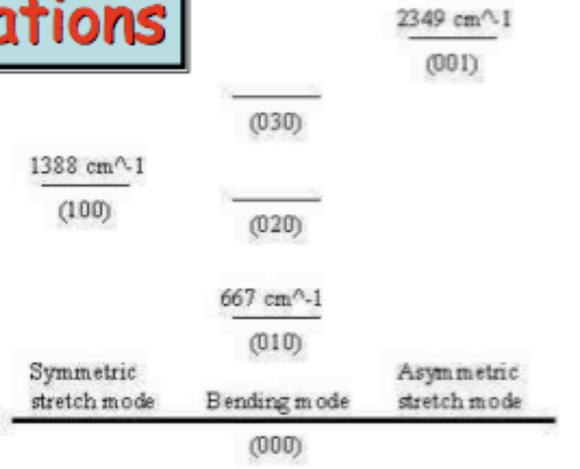
The asymmetric stretch mode



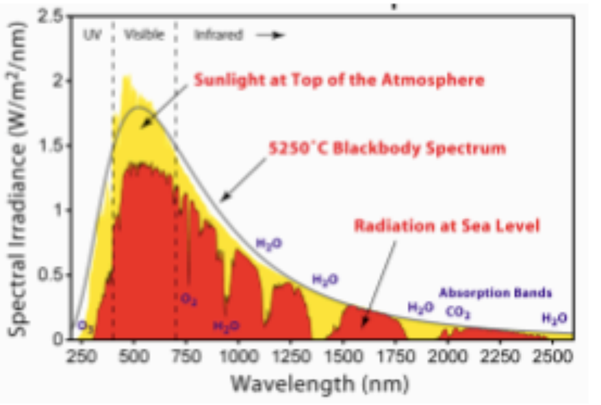
The bending mode



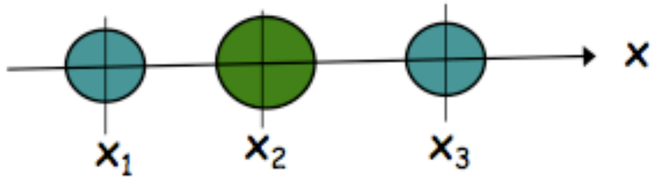
The symmetric stretch mode



The first few vibrational energy levels of the CO2 molecule



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 $m_1 = m_3$.

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

Approximate V by nearest neighbor central spring model.

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

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

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

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

The Newtonian equation of motion becomes

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

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

$$\hat{D}=M^{-\frac{1}{2}}KM^{-\frac{1}{2}}=\begin{pmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1m_2}} & 0 \\ -\frac{k}{\sqrt{m_1m_2}} & 2\frac{k}{m_2} & -\frac{k}{\sqrt{m_2m_3}} \\ 0 & -\frac{k}{\sqrt{m_2m_3}} & \frac{k}{m_3} \end{pmatrix}$$

$\hat{K}$ 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>

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

There is always a "null eigenvector,"

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

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

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

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

$|2\rangle = \begin{pmatrix} 1/\sqrt{m_1} \\ -2/\sqrt{m_2} \\ 1/\sqrt{m_1} \end{pmatrix}$ 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.)

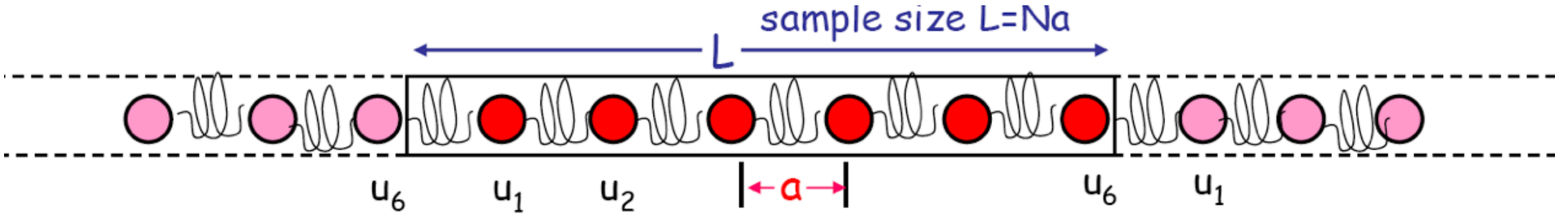
What is special about eigenvectors |i> of D?

$|s\rangle = A\cos(\omega t+\varphi)|i\rangle$ 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.)



lattice constant a

A finite system can't be truly periodic. Solution -**Born-von Karman** (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.

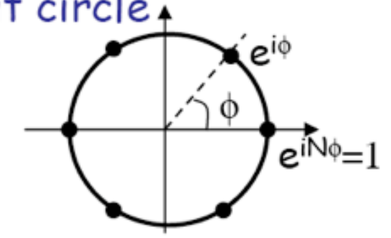
Look for eigenstates of T_1

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

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

Provided $e^{iN\phi}=1$ (here N=6)

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



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

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

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

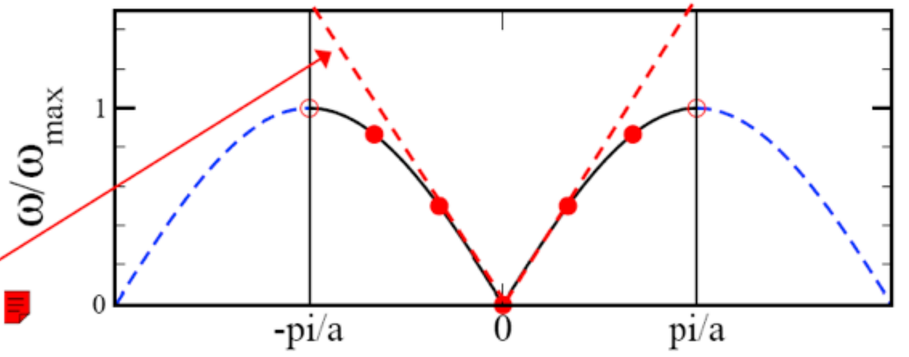
$$\hat{T}_1 \mid k >= e^{ika} \mid k > \qquad \hat{D} = \frac{k}{m}\left(2\hat{T}_0 - \hat{T}_1 - \hat{T}_{-1}\right) \rightarrow \frac{k}{m}\left(2 - e^{ika} - e^{-ika}\right)$$

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

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

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

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



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 $\langle k'|k\rangle=(1/N)\sum_R e^{i(k-k')R} = \delta(k,k')$ ***modulo G***
3. The states |k> are complete in the N-dimensional space:

   $\sum_k |k\rangle\langle k| = (1/N)\sum_k e^{ik(R-R')} = \delta(R-R')$ [R runs over the discrete lattice points.]
4. Sums become integrals: $\sum_k f(k) = \left(\frac{L}{2\pi}\right)^d \int_{BZ} d^d k \; f(k)$

Ziman's notation

I will use ω instead of ν.

Same linear chain, lattice constant a, spring constant α, alternating masses M_1 and M_2.

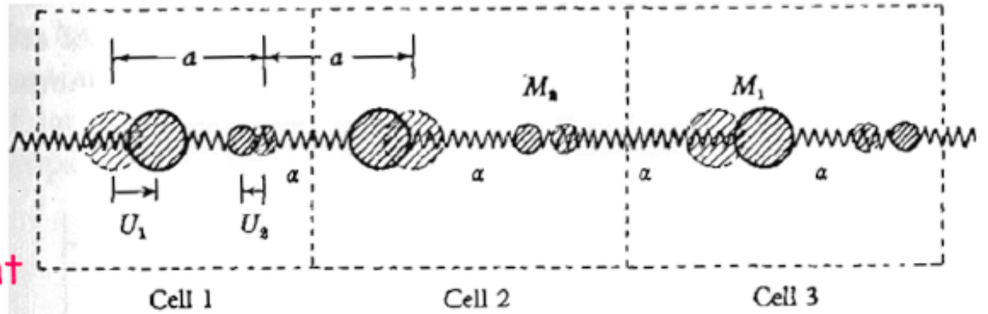


Fig. 17. Diatomic linear chain.

spring constant $K \rightarrow \alpha$

$$\left.\begin{aligned} M_1 \ddot{U}_1 &= -2\alpha U_1 + 2\alpha \cos qa \cdot U_2, \\ M_2 \ddot{U}_2 &= -2\alpha U_2 + 2\alpha \cos qa \cdot U_1. \end{aligned}\right\} \qquad (2.22)$$

substitution

$u_l = U_q e^{iql}$

has been generalized:

$u_{n1} = U_1(t)\exp(iq(2n)a)$

$u_{n2} = U_2(t)\exp(iq(2n+1)a)$

To find the frequency ν, we must solve the determinantal equation

$$\begin{vmatrix} 2\alpha - M_1\nu^2 & -2\alpha\cos qa \\ -2\alpha\cos qa & 2\alpha - M_2\nu^2 \end{vmatrix} = 0, \qquad (2.23)$$

which has the two roots

$$\nu_\pm^2 = \alpha\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \alpha\sqrt{\left\{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2 qa}{M_1 M_2}\right\}}. \qquad (2.24)$$

using mass-scaled variables:

$$\begin{pmatrix} 2\alpha/M_1 & -2\alpha\cos(qa)/\sqrt{M_1M_2} \\ -2\alpha\cos(qa)/\sqrt{M_1M_2} & 2\alpha/M_2 \end{pmatrix}\begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = \omega^2\begin{pmatrix} U_1 \\ U_2 \end{pmatrix}$$

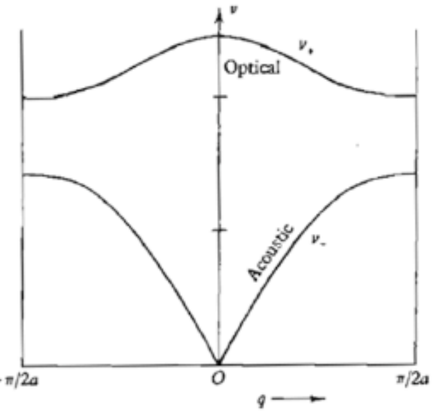


Fig. 18. Vibration frequencies of diatomic chain.

end of recycled lecture:

$$\mathscr{V} = \mathscr{V}_0 + \sum_{slj} u^j_{sl}\left[\frac{\partial \mathscr{V}}{\partial u^j_{sl}}\right]_0 + \tfrac{1}{2}\sum_{ss',ll',jj'} u^j_{sl}\,u^{j'}_{s'l'}\left[\frac{\partial^2 \mathscr{V}}{\partial u^j_{sl}\,\partial u^{j'}_{s'l'}}\right]_0 + \ldots. \quad (2.2)$$

$$M_s \ddot{u}^j_{sl} = -\sum_{s'l'j'}\left[\frac{\partial^2 \mathscr{V}}{\partial u^j_{sl}\,\partial u^{j'}_{s'l'}}\right]_0 u^{j'}_{s'l'}$$

counting: N values of ℓ, n values of s, 3 values of j

N = # cells in crystal; n = # atoms in unit cell, 3 = # dimensions of space.

3nN x 3nN matrix eigen problem ("generalized Hermitean eigenvalue problem; convert to ordinary Hermitean eigenvalue problem using mass-weighted coordinates.

$$\hat{M}\frac{d^2}{dt^2}|u\rangle = -\hat{K}|u\rangle \qquad |s\rangle = \hat{M}^{1/2}|u\rangle \qquad \hat{D} = \hat{M}^{-1/2}\hat{K}\hat{M}^{-1/2} \qquad \frac{d^2}{dt^2}|s\rangle = -\hat{D}|s\rangle$$

$$\hat{D}|s_\lambda\rangle = \omega_\lambda{}^2|s_\lambda\rangle$$

$$|u(t)\rangle = \sum_\lambda A_\lambda \cos(\omega_\lambda t + \phi_\lambda)\hat{M}^{-1/2}|s_\lambda\rangle$$

the general solution of Newton's law

Bloch-wave transformation: 3nN-vector |s> as direct product of 3n-vector |ε> and N-vector |**Q**>

$$s_{s\ell}{}^j = \varepsilon_{sj} e^{i\vec{Q}\cdot\vec{\ell}}/\sqrt{N}$$

$$|s\rangle = |\varepsilon(\vec{Q})\rangle \otimes |\vec{Q}\rangle$$

} eigenvectors of T_{op}

$$|\varepsilon(\vec{Q})\rangle = \begin{pmatrix} \varepsilon_{1x} \\ \varepsilon_{1y} \\ \vdots \\ \varepsilon_{nz} \end{pmatrix} \qquad |\vec{Q}\rangle = \frac{1}{\sqrt{N}}\begin{pmatrix} \exp(i\vec{Q}\cdot\ell_1) \\ \exp(i\vec{Q}\cdot\ell_2) \\ \vdots \\ \exp(i\vec{Q}\cdot\ell_N) \end{pmatrix}$$

Translational invariance: $\left\langle \vec{\ell}', s'\alpha' \middle| \hat{D} \middle| \vec{\ell}, s\alpha \right\rangle = \left\langle 0, s'\alpha' \middle| \hat{D} \middle| \vec{\ell} - \vec{\ell}', s\alpha \right\rangle$

Transform from one orthonormal basis to another *via* a unitary matrix:

$$\left\langle \vec{Q} \middle| \hat{U} \middle| \vec{\ell} \right\rangle = \left\langle \vec{Q} \middle| \vec{\ell} \right\rangle = \exp(-i\vec{Q}\cdot\vec{\ell})/\sqrt{N}$$

$$\hat{U}\hat{U}^{+} = \hat{U}^{+}\hat{U} = 1$$

$$\frac{1}{N}\sum_{\vec{\ell}} e^{i(\vec{Q}-\vec{Q}')\vec{\ell}} = \delta_{\vec{Q},\vec{Q}'} \quad \text{and} \quad \frac{1}{N}\sum_{\vec{Q}} e^{i\vec{Q}\cdot(\vec{\ell}-\vec{\ell}')} = \delta_{\vec{\ell},\vec{\ell}'}$$

The dynamical matrix is "block-diagonalized":

$$\sum_{\vec{\ell},\vec{\ell}'} \left\langle \vec{Q}' \middle| \vec{\ell}' \right\rangle \left\langle \vec{\ell}', s'\alpha' \middle| \hat{D} \middle| \vec{\ell}, s\alpha \right\rangle \left\langle \vec{\ell} \middle| \vec{Q} \right\rangle = \left\langle s'\alpha' \middle| \hat{D}\left(\vec{Q}\right) s\alpha \right\rangle \delta_{\vec{Q},\vec{Q}'}$$

$$\left\langle s'\alpha' \middle| \hat{D}\left(\vec{Q}\right) s\alpha \right\rangle = \sum_{\vec{\ell},\vec{\ell}'} \left\langle \vec{\ell}', s'\alpha' \middle| \hat{D} \middle| \vec{\ell} s\alpha \right\rangle e^{i\vec{Q}\cdot(\vec{\ell}-\vec{\ell}')}/N$$

$$\sum_{\vec{\ell},\vec{\ell}'} \left\langle \vec{Q} \middle| \vec{\ell} \right\rangle \left\langle \vec{\ell}, s\alpha \middle| u \right\rangle = \varepsilon_{s\alpha}\left(\vec{Q}\right)$$

$$\hat{D}\left(\vec{Q}\right)\left|\varepsilon_{\lambda}\left(\vec{Q}\right)\right\rangle = \omega_{\lambda}^{2}\left(\vec{Q}\right)\left|\varepsilon_{\lambda}\left(\vec{Q}\right)\right\rangle$$

$\hat{D}\left(\vec{Q}\right)$ is the 3n x 3n dynamical matrix, $\varepsilon_{\lambda}\left(\vec{Q}\right)$ is the 3n-eigenvector or "polarization vector" (mass-weighted)