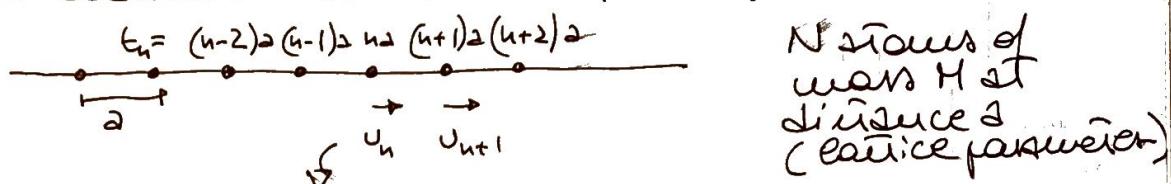


Crystal Vibrations

From the quantum mechanical theory of electrons and nuclei \rightarrow Born-Oppenheimer approx: electronic and nuclear degrees of freedom are discretely related: electrons remain in their ground state upon movement of the nuclei \rightarrow small displacements from their equilibrium position: harmonic approximation

Propagation of the normal modes: natural vibrations of the lattice \rightarrow phonons.

Simple case: 1 dim. monatomic lattice (like the TB model for electrons with 1 orbital per site).



u_n = (longitudinal) displacement of atom n at t_n from its equilibrium position (t_n)

From the energy point of view

$$\left[\begin{array}{l} E_0(0) = \text{ground state of the system with the nuclei at equilibrium position} \\ E_0(\{u_n\}) = \text{ground state of the system with nuclei displaced by } u_n \rightarrow R_n = t_n + u_n = n a + u_n = \text{static lattice energy} \end{array} \right.$$

NB These come from the total energy of electrons + nuclei with the nuclei in fixed positions \equiv potential energy of nuclear motion.

In these configurations, the forces on the nuclei will be

$$F_i = \frac{\partial E_0(\{u_n\})}{\partial u_i}, \text{ dependent on the instantaneous nuclear positions.}$$

In the ~~harmonic approximation~~ case \rightarrow expand the total energy $E_0(\{u_n\})$ in powers of the displacements:

$$E_0(\{u_n\}) = E_0(0) + \frac{1}{2} \sum_{nn'} \left(\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}} \right)_0 u_n u_{n'} + \frac{1}{3!} \sum_{nn'mm'} \left(\frac{\partial^3 E_0}{\partial u_n \partial u_{n'} \partial u_{m'}} \right)_0 u_n u_{n'} u_{m'} + \dots$$

(at the equilibrium position !!)

Note that $\frac{\partial E_0}{\partial u_n}$ is always zero, since at the equilibrium configuration.

Truncation of the sum to the second order term defines the "harmonic approximation".

$$E_0^{\text{har}}(\{u_n\}) = E_0(0) + \frac{1}{2} \sum_{nn'} D_{nn'} u_n u_{n'}, \text{ with}$$

$$D_{nn'} = \left(\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}} \right)_0 = \begin{matrix} \text{force} \\ \downarrow \\ \text{coefficient} \end{matrix}$$

it is \rightarrow matrix = force coefficient matrix.

$$\text{Force coefficients: } F_n = - \frac{\partial E_0^{\text{har}}}{\partial u_n} = - \sum_{n'} D_{nn'} u_{n'}$$

REH $F = -kx$: They describe the crystal as a system of balls + springs!

A crystal is \rightarrow very symmetric environment \Rightarrow consequences on the properties of the force coefficient matrix:

1. Force coefficient matrix is real (forces are real)
2. $D_{nn'} = D_{n'n}$ (symmetric) \Rightarrow Newton's III principle
3. $D_{nn'} = D_{m'm'}$ if $t_n - t_{n'} = t_m - t_{m'}$ for the translational symmetry of the lattice
4. Forces can be zero only if all displacements are 0, or if all displacements are equal (rigid translation of the lattice) \Rightarrow

$$\sum_{n'} D_{nn'} = 0 \text{ for any } n \text{ (scarcity rule).}$$



Equations of motion

REH $F = -kx \Rightarrow m\ddot{x} = -kx$

ALL CLASSICAL!

so for the n -th nucleus this becomes

$$m\ddot{u}_n = - \sum_{n'} D_{nn'} u_{n'} \quad \text{for any } n = 1 \dots N$$

This is a set of coupled differential equations. To look for their solutions, consider:

1. in general, one looks for solution. They are periodic in time (it's a pendulum!!!):

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

2. since the system is translationally symmetric, and so is the force constant matrix \mathbf{D} \Rightarrow one can add a specific periodicity to the solution and look for functions

$$u_n(t) = A_n e^{i(qa - \omega t)}$$

periodic in space
and time
(Traveling wave)
plane

Replacing in the equations of motion one gets:

$$-M\omega^2 A = - \sum_{nn'} D_{nn'} e^{-iq(na-n'a)} A$$

This can be rewritten as

$$\frac{M\omega^2(q)}{D(q)} = D(q) \text{ where} \\ \boxed{D(q) = \sum_{nn'} D_{nn'} e^{-iq(na-n'a)}} \equiv \text{Dynamical matrix} \equiv$$

\equiv Fourier Transform of the matrix of interatomic force constants.

The above equation provides the dispersion relation

$$\omega = \omega(q) \text{ for the modes (phonons),}$$

connecting frequency ω to the wave vector of the travelling plane wave.

Note 1. $u_n(t) = A_n e^{i(qa - \omega t)}$ are not affected by changes in q by multiples of $2\pi/a \Rightarrow$ also note, the relevant values of q are confined to the first Brillouin zone

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}$$

2. if the system is periodic \Rightarrow subject to Both-Von Karman PBC \Rightarrow

$$u_n(t) = u_{n+N}(t) \text{ and the allowed values of } q \text{ become discretized } \left(m \frac{2\pi}{N a} \right).$$

Example Linear monostinic chain with nearest neighbor interaction

Assume that the only non zero force constants are between nearest neighbor atoms. That is only D_{nn} , $D_{n,n+1}$ and $D_{n,n-1}$ are non zero.

Since $D_{n,n} = D_{n,n}$, it follows that the IFC are described by a single parameter, C :

$$D_{nn} = 2C \quad D_{n,n+1} = D_{n,n-1} = -C.$$

In the harmonic approximation

$$E_0^{\text{har}} = \frac{1}{2} C \sum_n (2v_n^2 - v_n v_{n+1} - v_n v_{n-1}) =$$

$$= \frac{1}{2} C \sum_n (v_n - v_{n+1})^2 \quad = \text{elastic energy of a chain of atoms connected by springs of spring constant } C$$

REM $E = \frac{1}{2} k x^2$

The equation of motion becomes

$$M\ddot{v}_n = -C(2v_n - v_{n+1} - v_{n-1}) \text{ for any } n.$$

Again, we look for solution as a travelling plane wave

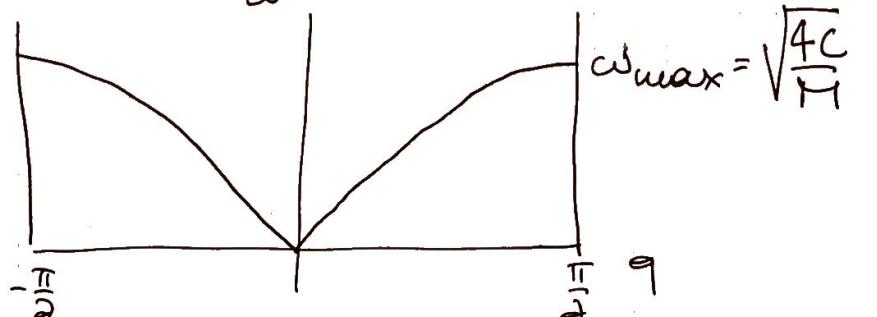
$$v_n(t) = A e^{i(qn - \omega t)} \quad \text{and by}$$

substituting in the eqn we get

$$-M\omega^2 = -C(2e^{iqn} - e^{i(n+1)q} - e^{-i(n-1)q}) = -4C \sin^2 \frac{1}{2}qn.$$

This expression gives us the dispersion relation

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{1}{2}qn \right|$$



In the long wavelength limit ($q \gg 0$), the dispersion is linear

$$\omega = \sqrt{\frac{4C}{M}} \cdot 2q \equiv v_s q \quad \text{where } v_s = \sqrt{\frac{C}{M}} \text{ is}$$

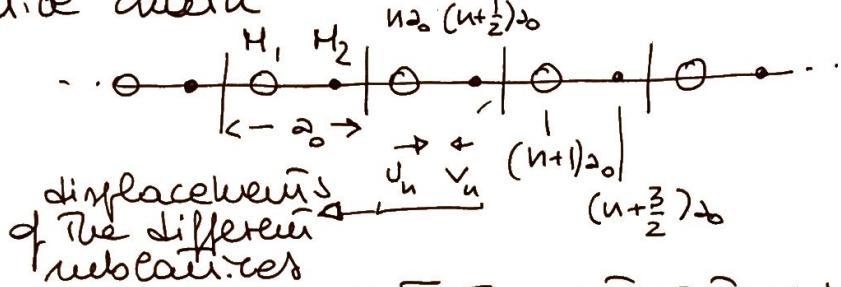
The sound velocity (velocity of sound in the medium).

Since we can measure $v_s \Rightarrow$ estimate of ω_{max} :

$$\omega_{max} = \frac{2v_s}{\lambda} \sim \frac{10^5 \text{ cm/sec}}{10^{-8} \text{ cm}} \sim 10^{13} \text{ sec}^{-1}.$$

Ditatomic & linear lattice.

Extend the previous example to the case of a ditatomic lattice chain



prototype of
2 lattice
with bands

Assuming again that the interaction is up to first nearest neighbor, we need now to write the classical equations of motion for the two types of particles:

Note

- Particles of species 1 have mass M_1 and occupy positions $R_n^{(1)} = n_2_0$
- particles of species 2 have mass M_2 and occupy positions $R_n^{(2)} = (n + \frac{1}{2})_0$.

With these definitions, the equations of motion become:

$$\begin{cases} M_1 \ddot{u}_n = -C(2v_n - v_{n-1} - v_{n+1}) \\ M_2 \ddot{v}_n = -C(2u_n - u_{n-1} - u_{n+1}) \end{cases} \text{ for any } n.$$

Set of coupled differential equations, for which we look for solutions of the form

$$u_n(t) = A_1 e^{i(qn_2_0 - \omega t)}, \quad v_n(t) = A_2 e^{i(qn_2_0 + q\frac{1}{2} - \omega t)}$$

By replacing $u_n(t)$ and $v_n(t)$ in the form we obtain
The ~~homogeneous~~ linear system

$$\begin{cases} -M_1 \omega^2 A_1 = -C(2A_1 - A_2 e^{-iq\frac{1}{2}} - A_2 e^{iq\frac{1}{2}}) \\ -M_2 \omega^2 A_2 = -C(2A_2 - A_1 e^{-iq\frac{1}{2}} - A_1 e^{iq\frac{1}{2}}) \end{cases}$$

This has a nontrivial solution only if the determinant of the coefficient is zero.

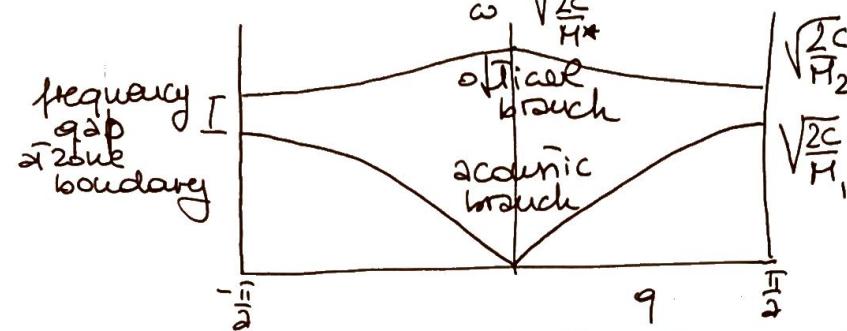
$$\begin{vmatrix} 2C - M_1\omega^2 & -2C \cos \frac{q\pi}{2} \\ -2C \cos \frac{q\pi}{2} & 2C - M_2\omega^2 \end{vmatrix} = 0 \quad \text{That}$$

gives the following dispersion relations:

$$\omega^2 = C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm C \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4M\mu^2 q^2}{M_1 M_2}}$$

with the amplitudes remaining

$$\frac{A_1}{A_2} = \frac{2C \cos \frac{q\pi}{2}}{2C - M_1\omega^2}$$



assuming
 $M_1 > M_2$

If we consider again the long wavelength limit $q \rightarrow 0$
we get

$$1. \omega^2 = \frac{2C}{M_1 + M_2} \left(\frac{\omega_0}{2} \right)^2 q^2 + O(q^4) \quad \text{and} \quad A_1 = A_2 \approx$$

\approx acoustic branch. Here stones vibrate in phase and with the same amplitude. The frequency is proportional to the wave number q and the sound velocity is

$$v_s = \sqrt{\frac{C}{(M_1 + M_2)/2}} \cdot \frac{\omega_0}{2}$$

recovers the same as the monatomic lattice for $M_1 = M_2$

$$2. \omega^2 = \frac{2C}{M^*} + O(q^2) \quad \text{and} \quad M_1 A_1 = -M_2 A_2 \approx$$

\approx optical branch

The two stones move in opposite directions while their center of mass remains fixed.

As $q \rightarrow 0$ the frequency of the optical branch tends to a finite value, $\omega_0 = \sqrt{\frac{2C}{M^*}}$.

Quantization of ~~mechanical~~ elastic waves: phonons.

Back to The 1D line chain of stones (or circular ring in PBC). Be u_n The displacement of stone n and p_n its momentum.

The Hamiltonian can be written as

$$H = \sum_n \left[\frac{1}{2M} p_n^2 + \frac{1}{2} C (u_{n+1} - u_n)^2 \right]. \quad (1)$$

REM:

The harmonic oscillator H_{HO} is

$$\text{eigenvalues } H = \frac{1}{2M} p^2 + \frac{1}{2} C x^2 \text{ with energy} \\ E_n = \left(n + \frac{1}{2}\right) \hbar \omega$$

similar to the haro. osc. case.

- Transformation of variables from particle coordinates u_n, p_n to phonon coordinates, P_q and U_q

Note: The transformation must be canonical \Leftrightarrow satisfy the quantum commutation relations for canonical variables.

Let's define

$$U_q = \frac{1}{\sqrt{N}} \sum_n u_n e^{-iqna}, \text{ that is The}$$

inverse of $u_n = \frac{1}{\sqrt{N}} \sum_q U_q e^{iqna}$. The transformation from p_n to P_q that is canonically conjugate to U_q , is

$$P_n = \frac{1}{\sqrt{N}} \sum_q P_q e^{-iqna} \text{ and } P_q = \frac{1}{\sqrt{N}} \sum_n p_n e^{iqna}$$

Note: not just a substitution of p for u in the def. above, since q and $-q$ in the exponent have interchanged.

Proof Verify that P_q and U_q satisfy the quantum commutation relation for canonical variables

~~(*)~~ p_n and u_n are conjugate variables that obey

$$[u_n, p_n] = i\hbar \delta_{n,n}, [u_n, u_n] = [p_n, p_n] = 0.$$

\rightarrow Let's verify this also for ~~(*)~~ $[U_q, P_q]$:

$$\begin{aligned}
 [U_q, P_{q'}] &= \frac{1}{N} [\bar{\sum}_n U_n e^{-iqna}, \bar{\sum}_n P_n e^{iq'n'a}] = \\
 &= \frac{1}{N} \bar{\sum}_n \bar{\sum}_n \underbrace{[U_n, P_n]}_{ik\delta_{nn'}} e^{-i(qn - q'n')a} = \\
 &= \frac{1}{N} ik \bar{\sum}_n e^{-i(q-q')na} = ik S_{q,q'} \quad \text{by definition of } S(x). \quad \text{QED.}
 \end{aligned}$$

Let's now rewrite the Hamiltonian in terms of the phonon coordinates:

$$\begin{aligned}
 \bar{\sum}_n P_n^2 &= \frac{1}{N} \bar{\sum}_n \bar{\sum}_{q'} P_q P_{q'} e^{-i(q+q')na} = \\
 &= \bar{\sum}_q \bar{\sum}_{q'} P_q P_{q'} \delta(-q, q) = \bar{\sum}_q P_q P_{-q}
 \end{aligned}$$

$$\begin{aligned}
 \bar{\sum}_n (U_{n+1} - U_n)^2 &= \frac{1}{N} \bar{\sum}_n \bar{\sum}_q \bar{\sum}_{q'} U_q U_{q'} e^{iqna} (e^{iq'a} - 1) \times \\
 &\quad \times e^{iq'n'a} (e^{iq'a} - 1) = 2 \bar{\sum}_q U_q U_{-q} (1 - \cos k_a)
 \end{aligned}$$

so the Hamiltonian becomes

$$H = \bar{\sum}_q \left[\frac{1}{2M} P_q P_{-q} + \frac{1}{2} M \omega_q^2 U_q U_{-q} \right] \quad \text{with}$$

$$\omega_q^2 = \left(\frac{2C}{M} \right)^{1/2} (1 - \cos k_a)^{1/2}.$$

If we want to get the equations of motion for the phonon coordinate U_q we just follow the quantum mechanical prescription

$$ik \dot{U}_q = [U_q, H] = \frac{ik}{M} P_{-q} \quad \text{and again:}$$

$$ik \ddot{U}_q = [\dot{U}_q, H] = \frac{1}{M} [P_{-q}, H] = ik \omega_q^2 U_q$$

$$\boxed{\ddot{U}_q + \omega_q^2 U_q = 0} \quad \text{quantum harmonic oscillator}$$

Energies are $\epsilon_q = \hbar \omega_q (n_q + \frac{1}{2})$ and the total energy of all phonons

$$\bullet E = \bar{\sum}_q \left(n_q + \frac{1}{2} \right) \hbar \omega_q.$$

|| Quantization of the phonons for a solid. etc. ||

The phonon Hamiltonian in U_q and P_q can be rewritten as the linear superposition of harmonic oscillators by introducing the creation and annihilation operators a and a^\dagger :

$$H = \sum_q \hbar\omega_q (a_q^\dagger a_q + \frac{1}{2}) \quad (3)$$

Proof:

$a^\dagger = a^\dagger |n\rangle = (n+1)^{1/2} |n+1\rangle$ creates a phonon when acting on a harmonic oscillator state of quantum number n .

Similarly:

$a = a |n\rangle = n^{1/2} |n-1\rangle$ annihilates (destroys) a phonon.

It follows that

$$a^\dagger a |n\rangle = a^\dagger n^{1/2} |n-1\rangle = n |n\rangle$$

↑ quantum number of occupancy.

In the phonon picture, we have $u_q \equiv$ There are u_q phonons in that mode, and the eigenvalues of the phonon Hamiltonian are still such that: $U = \sum_q \hbar\omega_q (u_q + \frac{1}{2})$.

Let's prove the equivalence of the two Hamiltonians:

Express a and a^\dagger in terms of the global variables U_q and P_q :

$$a^\dagger = \frac{1}{\sqrt{2\hbar}} [\sqrt{\hbar\omega_q} U_q - i \frac{1}{\sqrt{\hbar\omega_q}} P_q]$$

$$a = \frac{1}{\sqrt{2\hbar}} [\sqrt{\hbar\omega_q} U_q + i \frac{1}{\sqrt{\hbar\omega_q}} P_q]$$

$$U_q = \left(\frac{\hbar}{2\hbar\omega_q}\right)^{1/2} (a_q + a_q^\dagger)$$

$$P_q = \left(\frac{\hbar}{2\hbar\omega_q}\right)^{1/2} (a_q^\dagger - a_q)$$

To which it corresponds:

Then the particle position operator is

$$u_n = \frac{1}{\sqrt{2\hbar\omega_q}} \left[a_q e^{iqn} + a_q^\dagger e^{-iqn} \right]$$

Work with (1) and (3) \Rightarrow

a and a^\dagger can be expressed in terms of the particles coordinates u_n and momenta p_n :

$$\begin{cases} \hat{\alpha}_q = \frac{1}{\sqrt{N}} \sum_n e^{-iqt_n} \left[\sqrt{\frac{M\omega_q}{2\hbar}} u_n + i \sqrt{\frac{1}{2\hbar M\omega_q}} p_n \right] \\ \hat{\alpha}_q^+ = \frac{1}{\sqrt{N}} \sum_n e^{iqt_n} \left[\sqrt{\frac{M\omega_q}{2\hbar}} u_n - i \sqrt{\frac{1}{2\hbar M\omega_q}} p_n \right] \end{cases}$$

It is easy to verify that these transformations are canonical \Leftrightarrow commutation rules are preserved.

Noting that $\frac{1}{N} \sum_n e^{-i(q-q')t_n} = \delta_{q,q'}$, and $\frac{1}{N} \sum_n e^{-i(q-t_n)} = \delta_{q,n}$,

it is immediate to verify that

$$[\hat{\alpha}_q, \hat{\alpha}_q^+] = \delta_{q,q}, \text{ and } [\hat{\alpha}_q, \hat{\alpha}_{q'}^+] = [\hat{\alpha}_q^+, \hat{\alpha}_{q'}] = 0.$$

We can then invert the above relations to obtain

$$\begin{cases} u_n = \frac{1}{\sqrt{N}} \sum_q \sqrt{\frac{\hbar}{2M\omega_q}} e^{iqt_n} (\hat{\alpha}_q + \hat{\alpha}_q^+) \\ p_n = \frac{-i}{\sqrt{N}} \sum_q \sqrt{\frac{\hbar}{2M\omega_q}} e^{iqt_n} (\hat{\alpha}_q - \hat{\alpha}_q^+). \end{cases} \text{ Inverting}$$

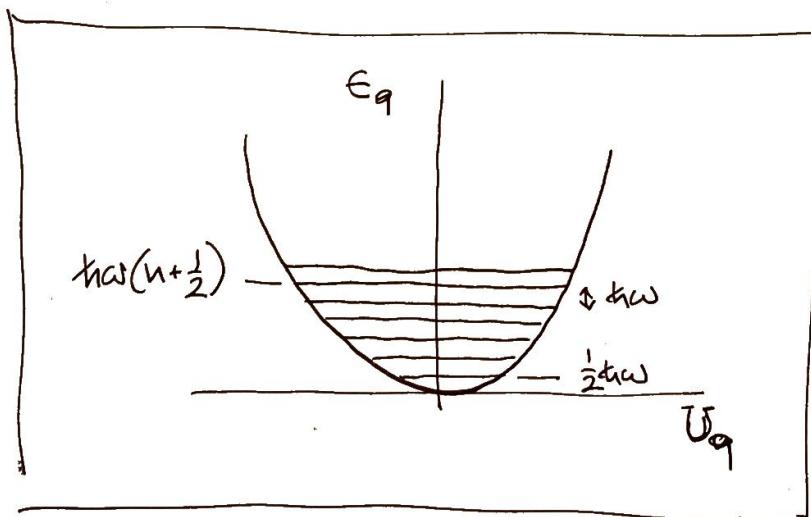
These in the Hamiltonian (1) yields

$$H = -\frac{1}{4} \sum_q \hbar \omega_q (\hat{\alpha}_q - \hat{\alpha}_q^+) (\hat{\alpha}_q - \hat{\alpha}_q^+) + \\ + \frac{1}{4} \sum_q \frac{\hbar}{\omega_q} \frac{C}{M} (\hat{\alpha}_q + \hat{\alpha}_q^+) (\hat{\alpha}_q + \hat{\alpha}_q^+) (2 - e^{iq^2} - e^{-iq^2}).$$

If we define $\frac{1}{\omega_q} \frac{C}{M} (2 - e^{iq^2} - e^{-iq^2}) = \omega_q$ we obtain

The Hamiltonian (3)

$$H = \sum_q \hbar \omega_q \left(\hat{\alpha}_q \hat{\alpha}_q^+ + \frac{1}{2} \right).$$



Generalization To 3dim - atomic motion

- 1 dim + 1 atom \rightarrow 1 phonon mode: acoustical
- 1 dim + 2 atoms \rightarrow 2 phonon modes: 1 acoustical + 1 optical
- 1 dim + 4 atoms: 4 combinations of motion
(limit of $q \rightarrow 0$)

$\underbrace{+++}_{\text{acoustic}}$; $\underbrace{++--}_{\text{sum of the displacements}};$ $\underbrace{+-+-}_{\text{is zero}}$; $\underbrace{---+}_{\text{= optic modes}}$

\therefore generalization to 2 atoms 3
 1 acoustical $(2-1)$ optical

- generalization to 3 dim:
 - 3 acoustic
 - $(3^2 - 3)$ optical
- In 3-dim, the motion of the atoms can be either
 - || or \perp to the wave vector (direction of propagation)
 - || displacements: longitudinal modes (1)
 - \perp : transverse modes (2)

Elementary introduction To Deutify Function

Perturbation Theory

Perturbation Theory: Properties of the system with an hamiltonian

$$H = H_0 + \lambda \Delta V = H_0 + \sum_i \lambda_i V_i$$

In this case, the energies (and wavefunctions) can be expressed as power series in λ_i :

$$E[\lambda] = E_0 - \sum_i \lambda_i f_i + \frac{1}{2} \sum_{i,j} h_{ij} \lambda_i \lambda_j + \dots$$

$$f_i = \left. \frac{\partial E}{\partial \lambda_i} \right|_{\lambda_i=0} = \text{Force}$$

$$h_{ij} = \left. \frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} \right|_{\lambda_{ij}=0} = \text{Interatomic force constants}$$

→ I order perturbation theory requires the knowledge of the unperturbed wavefunctions:

$$E_1 = E_0 + \langle \Psi_0 | \Delta V | \Psi_0 \rangle$$

→ II order perturbations require the knowledge of the I order variations in the wavefunctions:

$$\Delta \Psi_i = \sum_j \Psi_j \frac{\langle \Psi_j | \Delta V | \Psi_i \rangle}{\varepsilon_j - \varepsilon_i} \quad \text{and any generic operator } \hat{O} \text{ can be expressed as}$$

$$\begin{aligned} \Delta \hat{O} &= \sum_{i=1}^{\text{occ}} \langle \Psi_i | \Delta \hat{O} | \Psi_i \rangle + \\ &= \sum_{i=\text{occ}}^{\text{occ}} \sum_{j=\text{empty}}^{\text{empty}} \langle \Psi_j | \hat{O} | \Psi_i \rangle \langle \Psi_i | \Delta V | \Psi_j \rangle + \text{c.c.} \end{aligned}$$

Note: contribution from pairs of occupied states cancel the. In particular, for the variation of the deutify, one can write

$$\Delta n = 2 \sum_i^{\text{occupied}} \sum_j^{\text{empty}} \Psi_i \Psi_j \frac{\langle \Psi_j | \Delta V | \Psi_i \rangle}{\varepsilon_i - \varepsilon_j}$$

Problem
sum over all unoccupied states!

Note that this matrix elements couple empty empty states and occupied states → diagonal matrix!

DFT

$$\boxed{V_{KS} \xrightarrow{\text{perturbations}} V_{ext}(\vec{r}) + \int \frac{u(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + V_{xc}(\vec{r})}$$

$$V_{KS} = V_{ext}(\vec{r}) + \int \frac{u(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + V_{xc}(\vec{r})$$

$$(-\nabla^2 + V_{KS}) \Psi_i = \varepsilon_i \Psi_i$$

$$n(\vec{r}) = \sum_{\varepsilon_i < E_F} |\Psi_i|^2$$

DFPT

$$\Delta V_{ext} \xrightarrow{\text{perturbations}} \Delta n$$

perturbations in a
perturbative

perturbation in the
density

see The Hohenberg-Kohn
Theorem!

$$\Delta V_{KS} = \Delta V_{ext} + \int \frac{\Delta n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + \int d\vec{r}' \frac{dV_{xc}}{dn} \Delta n(\vec{r}')$$

and

$$\Delta n = 2 \operatorname{Re} \sum_i^{\text{occ}} \Psi_i^* |\Delta \Psi_i|$$

from first order
perturbation theory

see Hirsch,
pg. 687!!!

$$(H_{KS} - \varepsilon_i) |\Delta \Psi_i\rangle = - (\Delta V - \Delta \varepsilon_i) |\Psi_i\rangle$$

$$\Delta \varepsilon_i = \langle \Psi_i | \Delta V | \Psi_i \rangle \equiv \text{first order variation}$$

Treat these as a set of self-consistent equations
for $\Delta \Psi_i$. This is the core of DFPT.

Since the ~~perturbations~~ response of the system depends
only on the component of the perturbation that
coupling the occupied states to the empty states,
we can safely project the rhs onto the empty
state manifold:

$$(H_{KS} - \varepsilon_i) |\Delta \Psi_i\rangle = - P_{\text{empty}} \Delta V |\Psi_i\rangle \quad \text{with}$$

$$P_{\text{empty}} = 1 - P_{\text{occ}} = 1 - \sum_i^{\text{occ}} |\Psi_i\rangle \langle \Psi_i|$$