M. Fox: Ch. 10 (ignore 10.4 - 10.5)

- Phonon Dispersion (Ag & M, Zinan, etc.)
- IR active modes (modes that carry a dipole)
  Lyddane-Sachs-Teller
- Two-Phonon Absorption
- IR modes in metals & doped semiconductors
- ⇒ Coupled modes; Fano Resonances & Interf.-induced transparency (EIT-like)
- Polaritons + LO (carries a field)
- Phonon Lifetime (anharmonicity)
  Molecular crystals
  Internal modes

Motion of nuclei in the adiabatic approx. is described by

$$H_{ions} = \sum \frac{\hat{P}_i^2}{2M_i} + \underbrace{V_T(\{r_i\})}_{\text{includes direct + } e^- \text{-mediated interaction}}$$

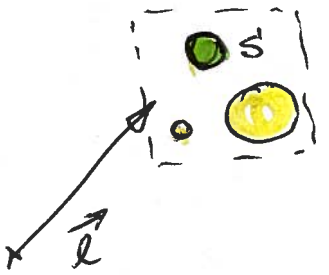
To lowest order, system of coupled oscillators

⇒ normal modes

Ω vs. $\vec{q}$ (Bloch wavevector) of these modes is known as phonon dispersion

EXPAND V_T:

V_T = CONSTANT + FIRST-ORDER TERMS + $\sum \frac{\partial^2 V_T}{\partial \vec{u}_{\vec{l},s}\, \partial \vec{u}_{\vec{l}',s'}} \vec{u}_{\vec{l},s}\, \vec{u}_{\vec{l}',s'}$ + HIGHER-ORDER TERMS



$\vec{l}, s$ labels the cell

$\vec{l}', s'$ labels ion in cell

HIGHER-ORDER TERMS → ANHARMONICITY

CLASSICAL EQS.:

$$M_s \ddot{\vec{u}}_{\vec{l},s} = -\sum_{\vec{l}',s'} \frac{\partial^2 V_T}{\partial \vec{u}_{\vec{l},s}\, \partial \vec{u}_{\vec{l}',s'}} \vec{u}_{\vec{l}',s'}$$

equilibrium

DEFINE DYNAMIC MATRIX

$$G_{\vec{l}s,\vec{l}'s'} = \frac{\partial^2 V_T}{\partial \vec{u}_{\vec{l}s}\, \partial \vec{u}_{\vec{l}',s'}}$$

equilibrium

$$M_s \ddot{\vec{u}}_{\vec{l},s} = -\sum_{\vec{l}',s'} G_{\vec{l}s,\vec{l}'s'} \vec{u}_{\vec{l}'s'}$$

$G_{\vec{l}s,\vec{l}'s'}$: FORCE ON $\vec{l},s$ due to displac. of s'th ion @ $\vec{l}'$

Solutions must satisfy Bloch Theorem

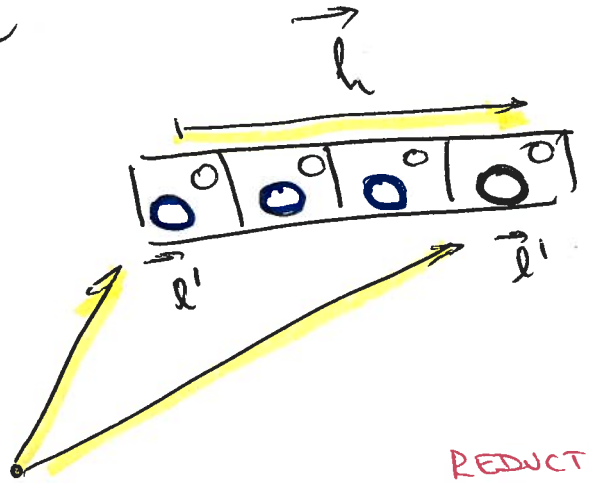
$$\vec{u}_{s\vec{l}}(t) = e^{i\vec{q}\cdot\vec{l}}\,\vec{u}_{s0}(t)$$

$\vec{q}$: Bloch

$\vec{u}_{s0}$: arbitrary cell chosen as the (0,0,0) origin

$$\Rightarrow M_s e^{i\vec{q}\cdot\vec{l}}\,\ddot{\vec{u}}_{0,s} = -\sum_{l',s'} G_{\vec{l}s,\vec{l}'s'}\,\vec{u}_{0,s'}\,e^{i\vec{q}\vec{l}'}$$

WRITE $\vec{l}' = \vec{l} + \vec{h}$



REDUCTION TO A SINGLE CELL

$$\Rightarrow M_s\,\ddot{\vec{u}}_{0,s} = -\sum_{s'} G_{ss'}(\vec{q})\,\vec{u}_{0s'}$$

WHERE

$$G_{s,s'}(\vec{q}) = \sum_{\vec{h}} G_{\vec{l}s,\vec{l}'s'}\,e^{i\vec{q}\cdot\vec{h}}$$

$G_{0s,\vec{h}s'}$

depends only on $\vec{l}'-\vec{l}$

ACCOUNTING FOR THE FACT THAT $\vec{u}_{ls}$ IS A VECTOR:

$$M_s \ddot{u}_i^{(s)} = -M_s \Omega^2 u_i^{(s)} = -\sum_{s',j} G_{i,j}^{s,s'}(\vec{q})\, u_j^{(s')} \qquad i,j = 1,2,3$$

HOW DO WE SOLVE THIS?

$$\left| M_s \Omega^2 \delta_{i,j} \delta_{s,s'} - G_{i,j}^{s,s'}(\vec{q}) \right| = 0$$

(DETERMINANT)

IF THERE ARE n IONS/CELL $\Rightarrow$ $3n \times 3n$

FOR EACH VALUE OF $\vec{q}$ (N ALLOWED VALUES)

WE GET $3n$ SOLUTIONS, SOME OF WHICH CAN BE DEGENERATE

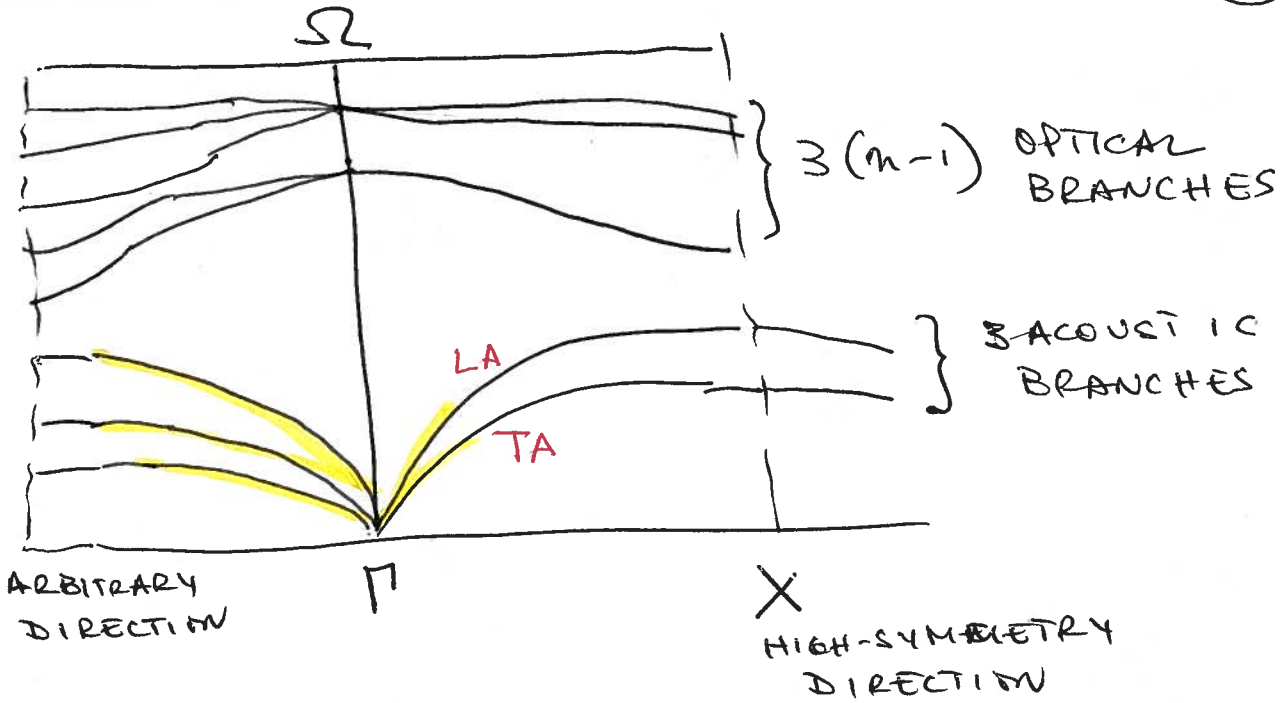
OUT OF THE $3n$, 3 SOLUTIONS HAVE THE PROPERTY THAT

$$\Omega(\vec{q}) \xrightarrow[\vec{q}=0]{} 0$$

ACOUSTIC MODES

(energy can't change if we displace the solid as a whole)

PHONON DISPERSION



THE ONLY MODES THAT COUPLE TO LIGHT ARE THOSE @ $q=0$ THAT CARRY AN ELECTRIC DIPOLE (MODES THAT TRANSFORM LIKE A VECTOR)

EVEN IF YOU DON'T KNOW GROUP THEORY, THIS IS EASY:

- POINT GROUP of CRYSTAL (32 GROUPS) → CHARACTER TABLE
  - O_h (DIAMOND)
  - T_d (ZINC-BLENDE)
  - C_{4v}
  - D_{3d}
  - ⋮

IRREDUCIBLE REPS. FOR (x, y, z) → PHONON SYMMETRY

IN T_d (ZINC-BLEND) THE REP. IS "T_2"

3-FOLD DEGENERATE

IN C_{6v} (WURZITE), THE REPS ARE "A_1" & "E_1"

"A_1": 1-FOLD "z"

"E_1": 2-FOLD "x, y"

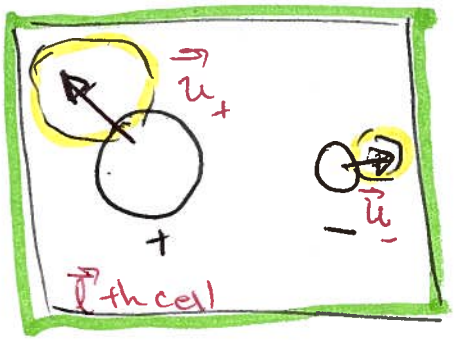
IF CRYSTAL HAS INVERSION SYMMETRY, ONLY ODD MODES CAN COUPLE TO LIGHT. THEN, LOOK FOR "UNGERADE" REPS.

AT THE END OF THIS PROCESS, WE END UP WITH A SMALL SET OF OPTICAL MODES THAT ARE "IR ACTIVE"

Lecture #9

MICROSCOPIC MODEL

CONSIDER CRYSTAL WITH TWO IONS/CELL & ASSUME STRUCTURE IS CUBIC & MATERIAL IS AN INSULATOR



SZIGETI EFF. CHARGE

$$\delta\vec{P}_D = Z^* e\left(\vec{u}_+ - \vec{u}_-\right)$$

$\delta\vec{P}_D$: electric dipole moment

$\vec{u}_+ - \vec{u}_-$: normal mode coordinate, 3-fold degenerate

INSTEAD OF $\vec{u}_+ - \vec{u}_- \equiv \vec{Q}$, IT'S CONVENIENT TO USE THE VARIABLE

$$\vec{W} = \left[\frac{M_+ M_-}{M_+ + M_-}\right]^{1/2} \frac{1}{\sqrt{v_c}} \left(\vec{u}_+ - \vec{u}_-\right)$$

($M_+ M_- / (M_+ + M_-)$: reduced mass; v_c: volume of cell)

THE ION HAMILTONIAN IS

- $H_{ION} = \frac{V}{2}\left[|\vec{P}_W|^2 + \Omega_0^2 |\vec{W}|^2\right]$ (V: VOLUME OF CRYSTAL; energy density)

COUPLING OF EM FIELD TO NORMAL MODE IS

- $H_{EM-LATTICE} = -\frac{\vec{P}_D}{V_C} \cdot \int_{CRYSTAL} \vec{E}\, dV$ (LOCAL ELECTRIC FIELD; see later)

$$= -\frac{Z^* e}{\sqrt{T_C M_R}}\, \vec{W} \cdot \int_{CRYSTAL} \vec{E}\, dV$$

($\vec{W}$: SAME FOR EACH CELL)

- FINALLY, WE HAVE THE TERM

$$H_{ELECTRON-EM} = \frac{1}{4\pi}\int \vec{D}\cdot\vec{E}\, dV = \int \frac{|E|^2}{4\pi} dV + \int \vec{P}_{electronic}\cdot\vec{E}\, dV$$

WHAT IS $\vec{P}_{electronic}$?

$\vec{P}_D$ INDUCED BY DISPLACEMENT OF ELECTRONIC CLOUD ASSOCIATED W/EACH ION

THEN, WE GET

$$\frac{d^2\vec{w}}{dt^2} = -\Omega_0^2 \vec{w} + \frac{Z^* e}{(M_R V_C)^{1/2}} \vec{E} = b_{11}\vec{w} + b_{12}\vec{E}$$

(SHORT RANGE; LONG RANGE FORCES DUE TO $\vec{E}$)

$$\vec{P} = \frac{Z^* e}{(M_R V_C)^{1/2}} \vec{w} + \frac{(\alpha_e^+ + \alpha_e^-)}{V_C} \vec{E}$$

($\vec{P}$: POLARIZ.; b_{12}: IONIC; b_{22}: ELECTRONIC)

FOR TIME-DEPENDENCE $\sim e^{-i\Omega t}$

$$\begin{cases} -(\Omega^2 - \Omega_0^2)\vec{w} = \dfrac{Z^* e}{[M_R V_C]^{1/2}} \vec{E} \\ \vec{P} = \left[\dfrac{(\alpha^+ + \alpha^-)}{V_C} - \dfrac{Z^{*2} e^2 / M_R V_C}{\Omega^2 - \Omega_0^2}\right] \vec{E} \end{cases}$$

WHAT IS THE RELATIONSHIP BETWEEN

$\vec{P} \overset{?}{\propto} \vec{E}$?

FOR STANDARD, TRANSVERSE WAVES

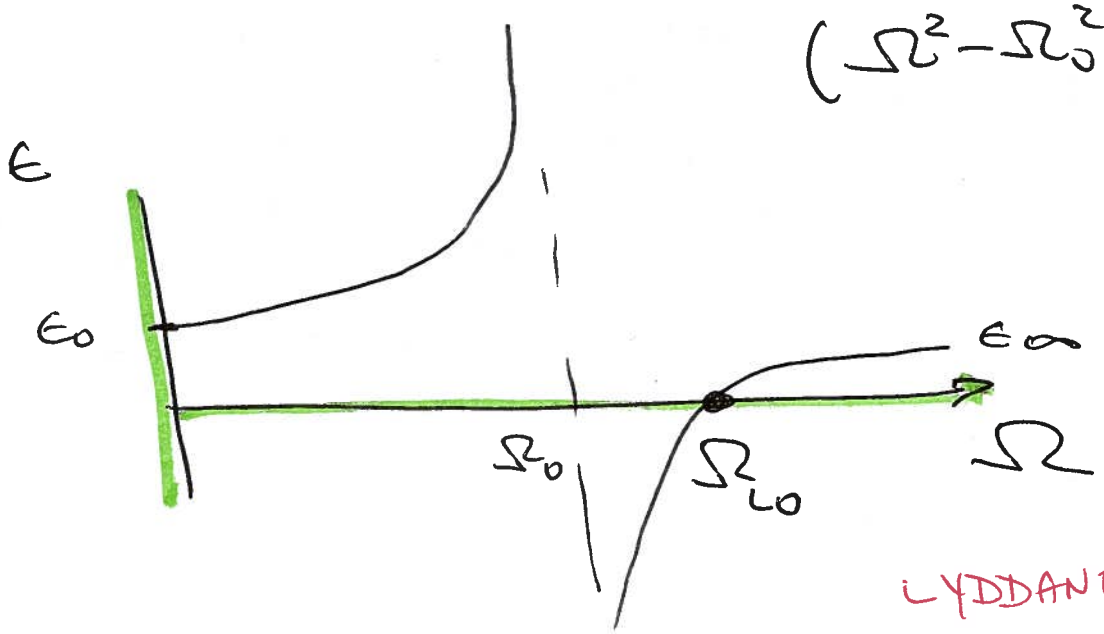
$$\vec{P} = \chi_T \vec{E} = \frac{(\epsilon_T - 1)}{4\pi} \vec{E}$$

AND WE GOT

$$\epsilon(\Omega) = \underbrace{1 + \frac{4\pi(\alpha^+ + \alpha^-)}{V_c}}_{\epsilon(\Omega \gg \Omega_0) \equiv \epsilon_\infty} - \frac{4\pi Z^{*2} e^2 / M_R V_c}{(\Omega^2 - \Omega_0^2)}$$

$$1 + \frac{4\pi(\alpha^+ + \alpha^-)}{V_c} + \frac{4\pi Z^{*2} e^2 / M_R V_c}{\Omega_0^2} = \epsilon(\Omega=0) \equiv \epsilon_0$$

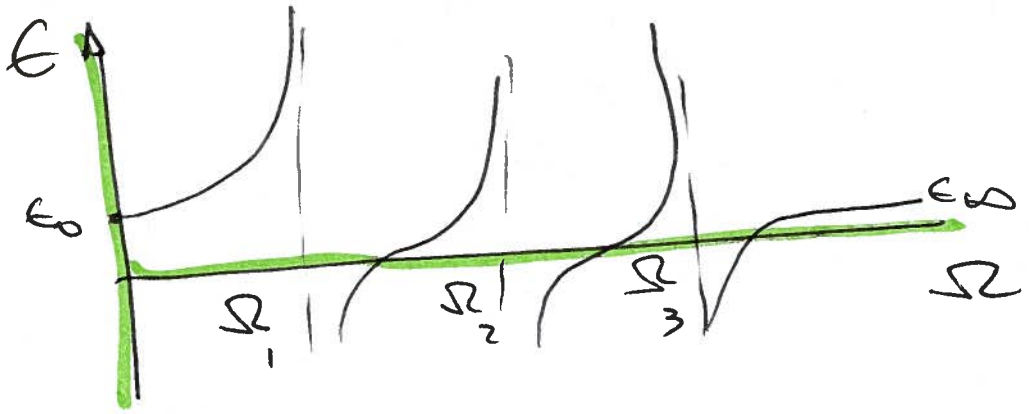
$$\Rightarrow \epsilon(\Omega) = \epsilon_\infty - \frac{(\epsilon_0 - \epsilon_\infty)\Omega_0^2}{(\Omega^2 - \Omega_0^2)}$$



LYDDANE-SACHS-TELLER

$$\epsilon_\infty(\Omega_{LO}^2 - \Omega_0^2) = (\epsilon_0 - \epsilon_\infty)\Omega_0^2 \Rightarrow \frac{\Omega_{LO}}{\Omega_0} = \left(\frac{\epsilon_0}{\epsilon_\infty}\right)^{1/2}$$

MORE THAN ONE MODE ?



GENERALIZED LST

$$\frac{\epsilon_0}{\epsilon_\infty} = \prod_{j=1}^{N} \frac{\Omega_{LO,j}^2}{\Omega_{TO,j}^2}$$

CHAVES & PORTO, SSC. 13, 865 (1973)
SIEVERS & PAGE, PRB 41, 3455

NOTE ON LOCAL FIELDS

$$\vec{E}_{LOCAL} = \vec{E} + \frac{4\pi}{3}\vec{P}$$

KITTEL, INTROSS. 5th., P 406

$$b_{12} = \frac{Z^* e}{\sqrt{M_R V_C}} \left[1 - \frac{4\pi}{3}\frac{(\alpha^+ + \alpha^-)}{V_C}\right]^{-1}$$

$$b_{22} = \frac{(\alpha^+ + \alpha^-)}{V_C} \left[1 - \frac{4\pi}{3}\frac{(\alpha^+ + \alpha^-)}{V_C}\right]^{-1}$$

LOCAL FIELD CORRECTION.

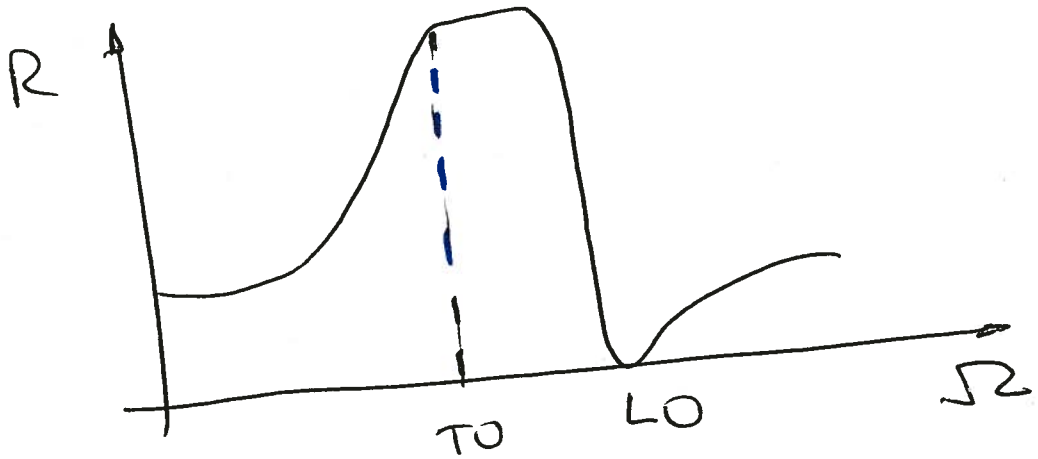
AFTER SOME ALGEBRA

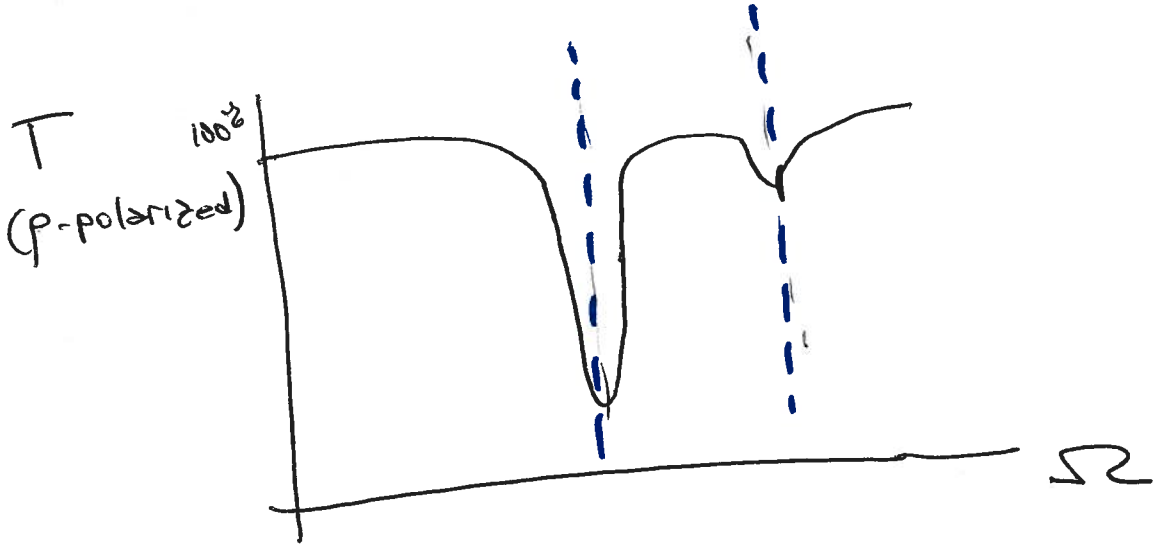
$$\frac{4\pi (Z^* e)^2}{M_R V_c} \equiv \omega_{TO}^2 \frac{(\epsilon_0 - \epsilon_\infty)}{(\epsilon_\infty + 2)^2}$$

ALSO ENTERS IN FRÖHLICH INTERACTION

Z^* IS A MEASURE OF IONICITY

	NaCl	MgO	ZnS	GaAs
Z^*	0.74	1.76	0.96	0.51





PHYSICAL MEANING OF Ω_{LO}

$$\vec{\nabla}\cdot\vec{D}=0 \quad \Rightarrow \quad \epsilon\,\vec{k}\cdot\vec{D}=0$$

LONGITUDINAL SOLUTIONS ARE OK IF $\epsilon=0$ $\left(\vec{E}=-4\pi\vec{P}\right)$

$\vec{\nabla}\cdot\vec{E}=0$ Coulomb-like

LO MODES CARRY A LONGITUDINAL (COULOMB-LIKE) ELECTRIC FIELD

BUT TIME VARYING

THIS IS WHY THEY INTERACT STRONGLY WITH CARRIERS ... FRÖHLICH INTER.

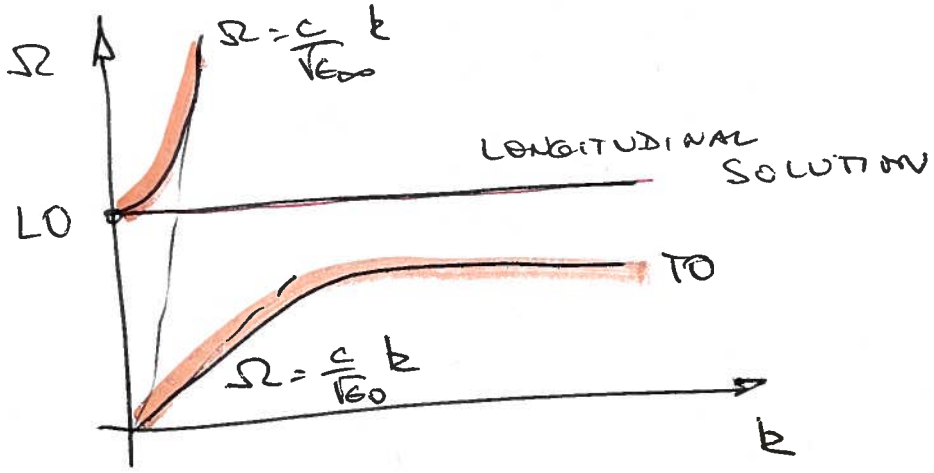
$$\frac{\vec{r}}{r^3} \equiv \frac{i}{(2\pi)^2}\int e^{i\vec{q}\cdot\vec{r}}\,\frac{\vec{q}}{q^2}\,d^3q$$

LONGITUDINAL

TRANSVERSE SOLUTIONS

$$\omega^2 = \frac{c^2}{\epsilon(\omega)}\,k^2 = \frac{c^2}{n^2(\omega)}\,k^2$$

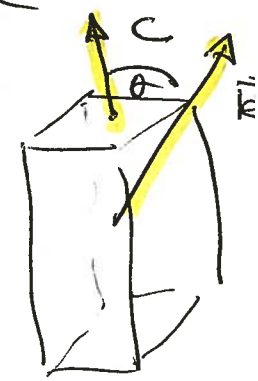
$$\epsilon = \epsilon_\infty\,\frac{(\omega^2-\omega_{LO}^2)}{(\omega^2-\omega_{TO}^2)}$$



COUPLED MODES

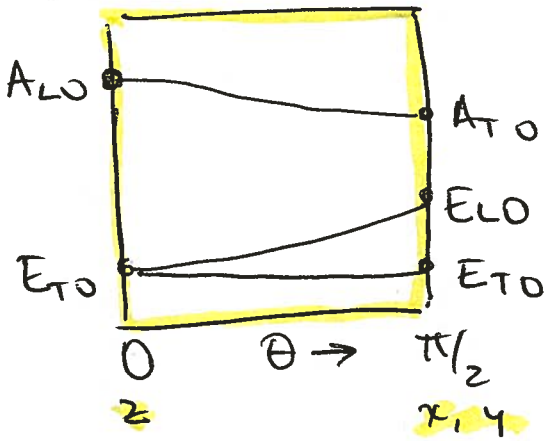
POLARITONS

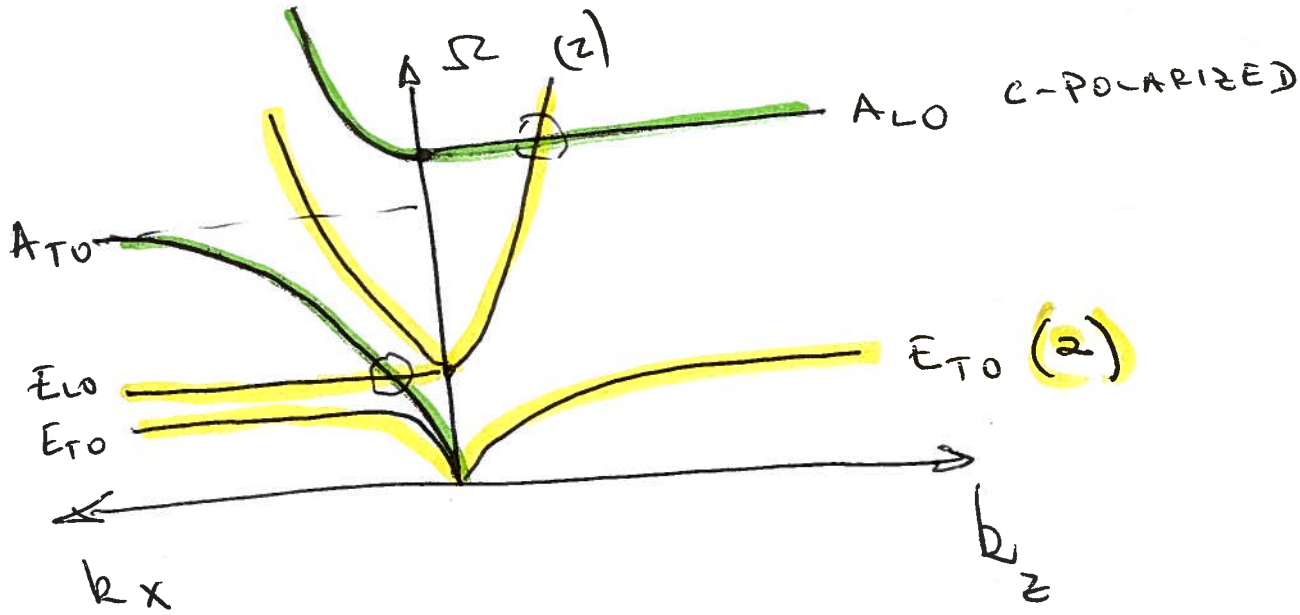
- EMPHASIZE SPLITTING & LACIC OF SPONTANEOUS DECAY



TETRAGONAL CRYSTAL

- ROLE OF ANISOTROPY





TWO-PHONON ABSORPTION

$\vec{P}$ = FIRST-ORDER TERMS

LABELS PHONON BRANCH

$$+ \sum_{\substack{bb' \\ \vec{q}}} C_{bb'}(\vec{q})\, u_{\vec{q}}^{b}\, u_{-\vec{q}}^{b'}$$

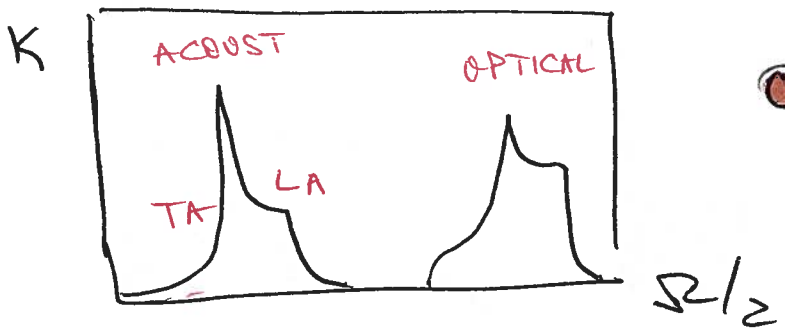
NOISE

CONSTANTS

WEAKER SELECTION RULES

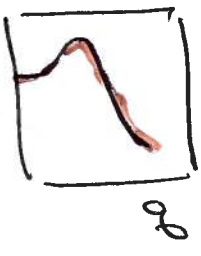
SINCE EVERY CELL MUST UNDERGO SAME DISPLACEMENTS, LIGHT COUPLES TO PAIR OF MODES, SO THAT $\vec{q}_1 + \vec{q}_2 = 0$

SPECTRUM DOMINATED USUALLY BY OVERTONES ⇒ $\propto$ DENSITY OF STATES



WEIGHTING FACTORS

DISCUSS NON-ANALYTICAL VAN HOVE SINGULARITIES — DIAMOND



WHY IS H_2O BLUE ?

4-5 PHONON ABSORPTION

O–H BOND

IR MODES IN METALS AND DOPED SEMICONDUCTORS

PHONONS ALONE:

$$\epsilon_{PH} = \epsilon_\infty \frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2}$$

CARRIERS ALONE

$$\epsilon_C = 1 - \frac{\omega_p^2}{\omega^2} \qquad \omega_p^2 = \frac{4\pi n e^2}{m^* \epsilon_B}$$

ϵ_0 OR ϵ_∞

$$\epsilon_{TOTAL} \equiv \epsilon_{PH} + \epsilon_C - 1$$

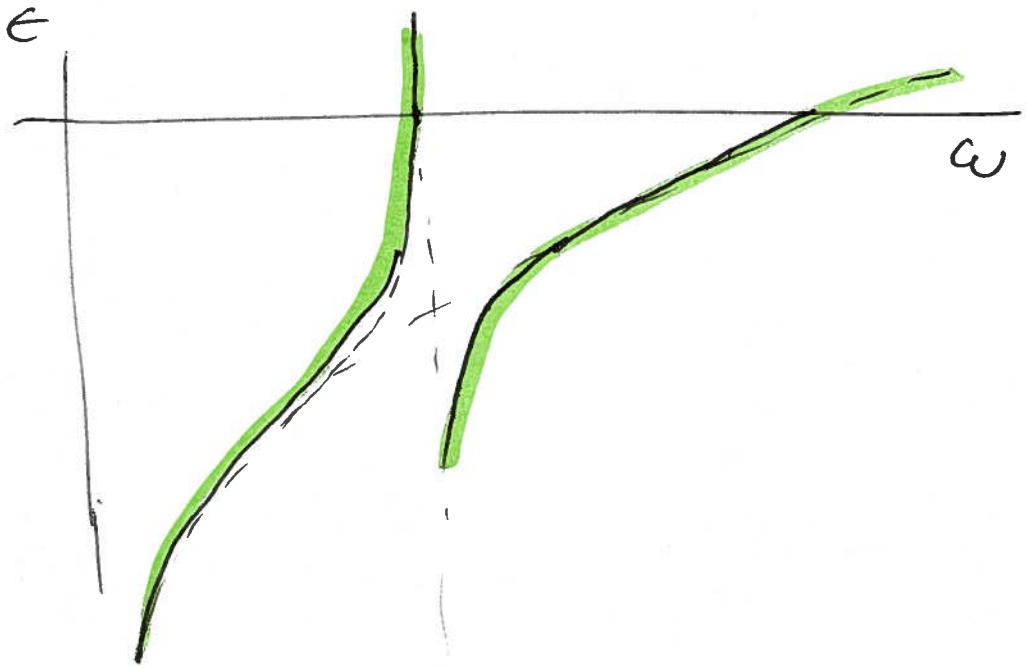
$$= \epsilon_\infty \left[\frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2} \right] - \frac{\omega_p^2}{\omega^2}$$

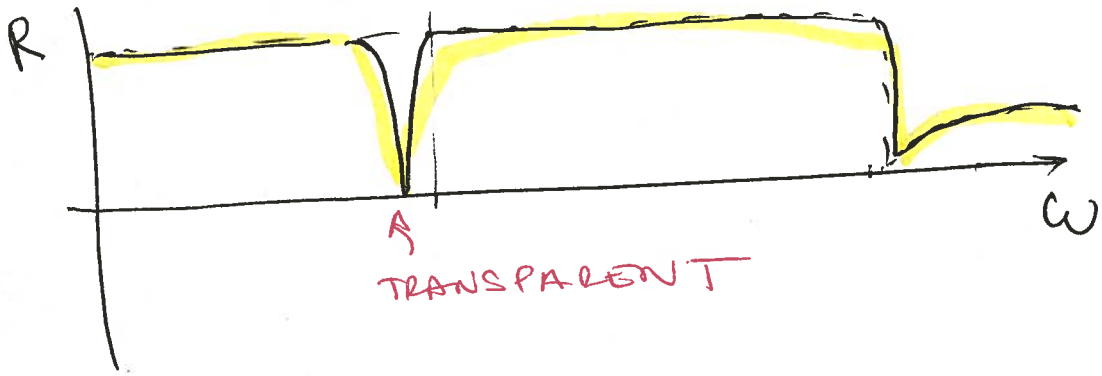
PROOF IS EQUIVALENT TO SHOW THAT

$$\chi_{TOTAL} = \chi_{PH} + \chi_C$$

WHICH FOLLOWS FROM THE GENERAL EXPRESSION FOR ϵ IF PHONONS & CARRIERS

For $\omega_p >> \omega_{LO}$





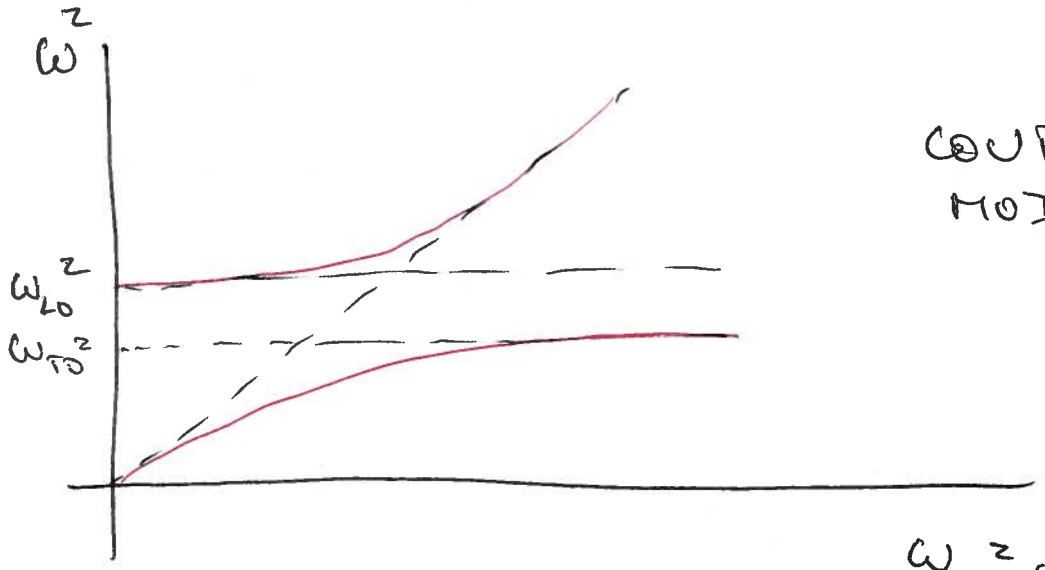
NEW MODES

$\epsilon_{PHONON} = 0 \Rightarrow \omega_{LO}$

$\epsilon_{CARRIER} = 0 \Rightarrow \omega_p$

$\epsilon_{TOTAL} = 0$ LO-PLASMON COUPLED MODES

$$\epsilon_\infty \omega^2(\omega^2 - \omega_{LO}^2) = \omega_p^2(\omega^2 - \omega_{TO}^2)$$



COUPLED MODES

$\omega_p^2 \propto$ CARRIER DENSITY

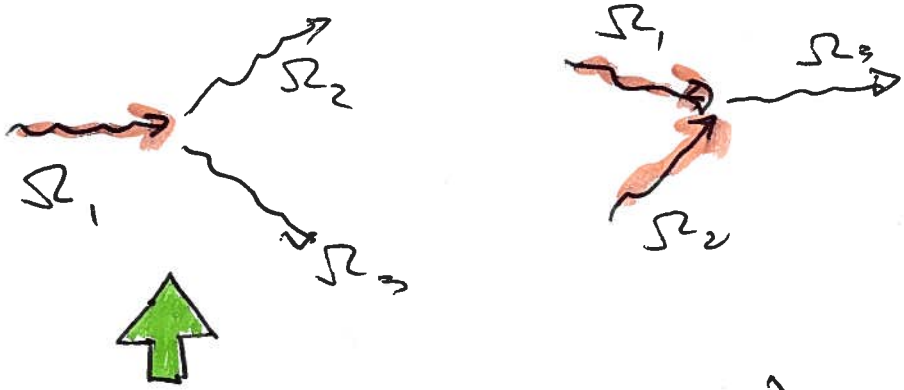
$$\omega^4 - \left(\frac{\omega_p^2}{\epsilon_\infty} + \omega_{LO}^2\right)\omega^2 + \omega_p^2 \frac{\omega_{TO}^2}{\epsilon_\infty} = 0$$

ANHARMONICITY

$$H_{ION} = \frac{1}{2}\left[P_k^{b\,2} + \Omega_{kb}^2 Q_{kc}^{b\,2}\right] + \text{THIRD-ORDER} +$$

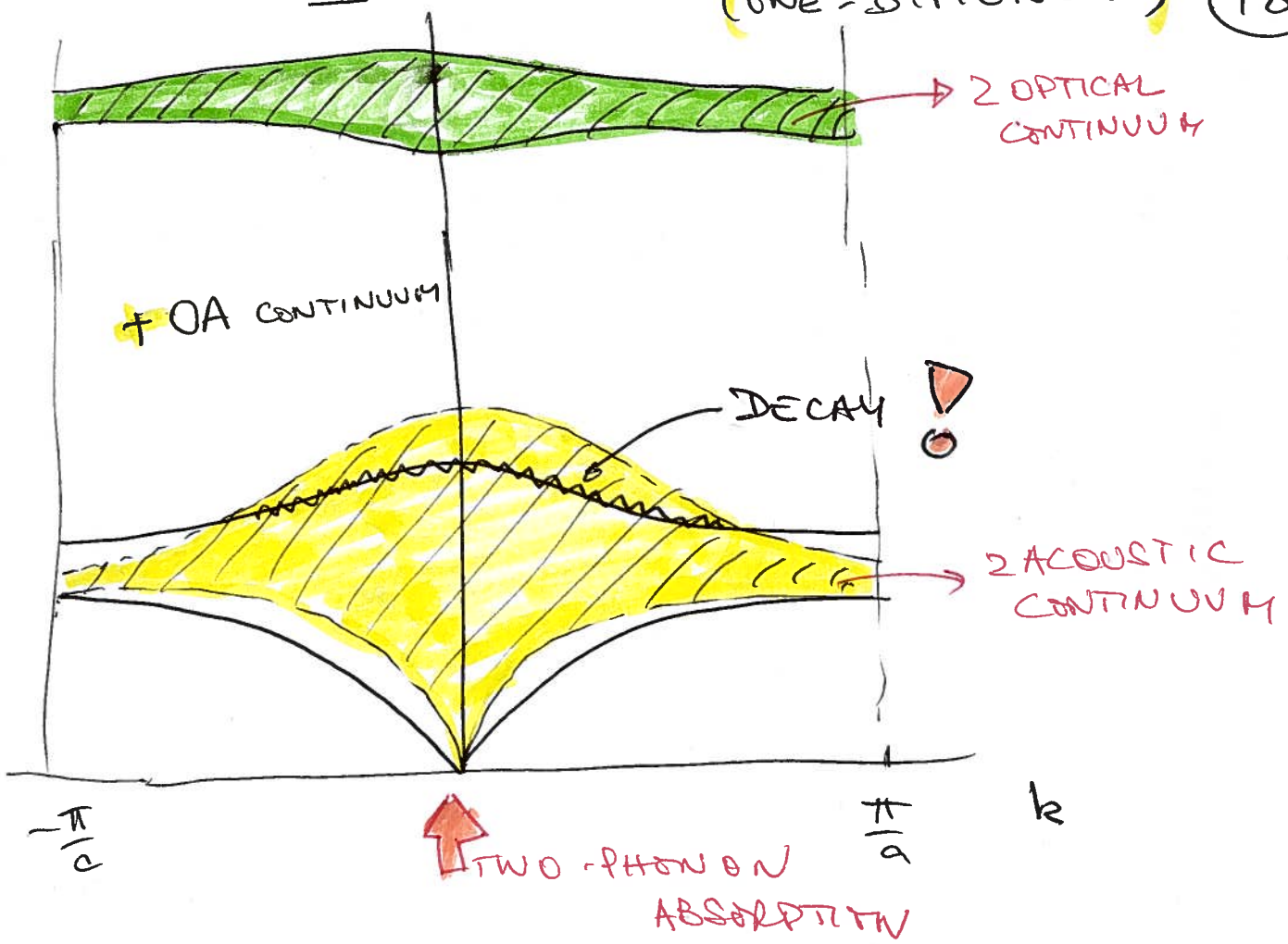
+ FOURTH-ORDER TERMS + ...

THIRD-ORDER $\sum_{k_1 k_2 k_3}^{b_1 b_2 b_3} C\, Q_{k_1}^{b_1} Q_{k_2}^{b_2} Q_{k_3}^{b_3}$ $\quad k_1 \pm k_2 \pm k_3 = 0$

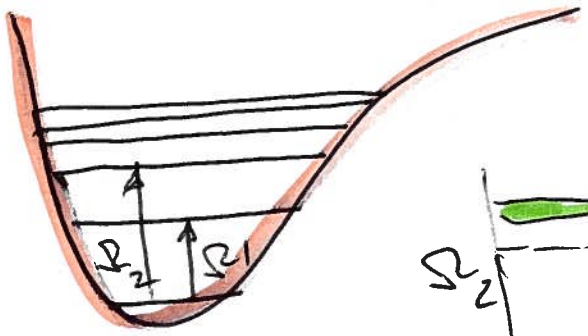


DECAY (IF $\Omega_1 = \Omega_2 + \Omega_3$)

TWO-PHONON DISPERSION (ONE-DIMENSION)



COMPARE WITH MOLECULES



MOLECULAR SOLIDS: