* NOTES ON PHONONS

PASQUALE PAVONE (HU BERLIN)

* NOTATION

$\underline{R}$ BRAVAIS LATTICE VECTORS.
TOTAL NUMBER IS N IN AGREEMENT WITH BORN-VON KARMAN BOUNDARY CONDITIONS.
IN THE FOLLOWING WE USE THE CONVENTION:

$$\underline{R} \rightarrow R$$

q PHONON WAVE-VECTOR $\quad q \rightarrow q$

$\underline{\tau}_\alpha$ POSITION OF THE ATOM α ($\alpha = 1 \ldots N_{AT}$) IN THE UNIT CELL OF THE CRYSTAL.

EXAMPLE:

DIAMOND CRYSTAL (ALSO ZINC BLENDE)

$$\underline{\tau}_1 = a(0,0,0)$$

$$\underline{\tau}_2 = a\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$$

$\underline{u}_{R\alpha}$ DISPLACEMENT OUT OF EQUILIBRIUM OF ATOM α IN THE UNIT CELL R

k ($k = 1,2,3$) INDEX OF CARTESIAN COMPONENT

* EXPANSION OF TOTAL ENERGY PER UNIT CELL IN THE HARMONIC APPROXIMATION

$$E^{UC} = E^{EQUILIBRIUM} + \frac{1}{2}\frac{1}{N}\sum_{R\alpha K}\sum_{R'\alpha'K'} u_{R\alpha K}\,\Phi^{R\alpha K}_{R'\alpha'K'}\,u_{R'\alpha'K'} \qquad (1)$$

NOTE:

- EQUILIBRIUM $\rightarrow$ $u_{R\alpha K} = 0 \quad \forall_{R\alpha K}$

- EXPRESSION ABOVE IS VALID FOR REAL DISPLACEMENTS, IF COMPLEX DISPLACEMENTS ARE CONSIDERED, THEN THE SECOND TERM IN TH R.H.S. MUST BE WRITTEN AS

$$\frac{1}{2}\frac{1}{N}\sum_{R\alpha K}\sum_{R'\alpha'K'} u^{*}_{R\alpha K}\,\Phi^{R\alpha K}_{R'\alpha'K'}\,u_{R'\alpha'K'} \qquad (2)$$

- THE LINEAR TERM IN THE $\{u_{R\alpha K}\}$ IS MISSING BECAUSE FORCES ON ATOMS ARE VANISCHING AT EQUILIBRIUM

- THE INTERATOMIC FORCE CONSTANTS $\Phi^{R\alpha K}_{R'\alpha'K'}$ ARE DEFINED AS

$$\Phi^{R\alpha K}_{R'\alpha'K'} = \left.\frac{\partial^2 E^{UC}}{\partial u_{R\alpha K}\,\partial u_{R'\alpha'K'}}\right|_{EQUILIBRIUM}$$

* GENERAL PHONON-DISPLACEMENT PATTERN AT A GIVEN WAVE-VECTOR q

$$u_{R\alpha k} = w_{\alpha k} e^{iq\cdot R}$$

LET US INSERT THIS IN EQ. (1) USING THE CONDITION GIVEN IN EQ. (2):

$$\Delta E^{UC} = E^{UC} - E^{EQUILIBRIUM}$$

$$= \frac{1}{2}\frac{1}{N}\sum_{R\alpha k}\sum_{R'\alpha' k'} \Phi^{R\alpha k}_{R'\alpha' k'} e^{iq(R'-R)} w^{*}_{\alpha k} w_{\alpha k}$$

LET US RECALL THE DEFINITION OF THE DYNAMICAL MATRIX:

$$D^{\alpha k}_{\alpha' k'}(q) = \frac{1}{N}\frac{1}{\sqrt{M_\alpha M_{\alpha'}}}\sum_{RR'} \Phi^{Rkk}_{R'\alpha' k'} e^{iq(R'-R)}$$

WHERE M_α IS THE MASS OF THE ATOM α. THEN WE CAN WRITE:

$$\Delta E^{UC} = \frac{1}{2}\sum_{\alpha k}\sum_{\alpha' k'} \sqrt{M_\alpha}\, w^{*}_{\alpha k}\, D^{\alpha k}_{\alpha' k'}(q)\, \sqrt{M_{\alpha'}}\, w_{\alpha' k'}$$

UP TO NOW:

$\{W_{\alpha k}\}$ ARE GENERAL VECTORS.

NOW:

$\{W_{\alpha k}\}$ ARE CHOOSEN TO BE EXPRESSED IN TERMS OF THE EIGENVECTORS OF THE DYNAMICAL MATRIX $\{\varepsilon^n_{\alpha k}(q)\}$ AS

$$\varepsilon^n_{\alpha k}(q) = \sqrt{M_\alpha}\, W_{\alpha k}$$

AT A GIVEN q AND FOR A GIVEN MODE n

THEN, WE CAN WRITE:

$$\Delta E^{UC} = \frac{1}{2} \sum_{\alpha k} \sum_{\alpha' k'} \varepsilon^n_{\alpha k}(q)^* \; D^{\alpha k}_{\alpha' k'}(q) \; \varepsilon^n_{\alpha' k'}(q)$$

HOWEVER, FOR THE DEFINITION OF $\{\varepsilon^n_{\alpha k}(q)\}$:

$$\sum_{\alpha' k'} D^{\alpha k}_{\alpha' k'}(q) \; \varepsilon^n_{\alpha' k'}(q) = \omega^2_n(q) \; \varepsilon^n_{\alpha k}(q)$$

(EIGENVALUE EQUATION)

THEN:

$$\Delta E^{UC} = \frac{1}{2} \sum_{\alpha k} \varepsilon^{m}_{\alpha k}(q)^{*} \, \omega^{2}_{m}(q) \, \varepsilon^{m}_{\alpha k}(q)$$

$$\boxed{\Delta E^{UC} = \frac{1}{2} \, \omega^{2}_{m}(q) \sum_{\alpha k} \left| \varepsilon^{m}_{\alpha k}(q) \right|^{2}} \qquad (3)$$

THIS EXPRESSION CAN BE USED FOR THE CALCULATION OF THE PHONON FREQUENCIES $\omega_m(q)$ AT "SPECIAL" VALUES OF q WITHIN THE "FROZE-PHONON" METHOD, FOR THOSE CASES WHERE THE EIGEN-VECTORS ARE KNOWN BY SYMMETRY.

* APPLICATION:

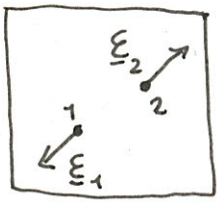
LO MODE AT M IN THE DIAMOND STRUCTURE

DIAMOND STRUCTURE:
ONLY 2 ATOMS IN THE UNIT CELL

$$\left.\begin{aligned} \underline{\tau}_1 &= a\,(0,0,0) \\ \underline{\tau}_2 &= a\left(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}\right) \end{aligned}\right\} \quad a = \text{LATTICE CONSTANT}$$

THE 2 ATOMS HAVE THE SAME MASS $M_\alpha = M$.
DUE TO THE SYMMETRY, THE EIGENVECTORS OF THE LO MODE AT M ARE EQUAL IN MAGNITUDE AND POINTS OPPOSITE DIRECTIONS

SCHEMATICALLY:



ONE POSSIBLE CHOICE IS:

$$\underline{\varepsilon}_1 = (-\varepsilon, -\varepsilon, -\varepsilon)$$

$$\underline{\varepsilon}_2 = (\varepsilon, \varepsilon, \varepsilon)$$

WE NEED NOW TO CONVERT THE EIGENVECTORS INTO REAL DISPLACEMENTS:

WE OBTAIN:

$$\begin{cases} \underline{w}_1 = \dfrac{1}{\sqrt{M}}\,\underline{\varepsilon}_1 \\ \underline{w}_2 = \dfrac{1}{\sqrt{M}}\,\underline{\varepsilon}_2 \end{cases} \quad \text{AND} \quad \begin{cases} \underline{u}_1 = \dfrac{1}{\sqrt{M}}\,\underline{\varepsilon}_1 \\ \underline{u}_2 = \dfrac{1}{\sqrt{M}}\,\underline{\varepsilon}_2 \end{cases}$$

THEN

$$\begin{cases} \underline{u}_1 = -\dfrac{\varepsilon}{\sqrt{M}}\,(1,1,1) \\ \underline{u}_2 = \dfrac{\varepsilon}{\sqrt{M}}\,(1,1,1) \end{cases} \tag{4}$$

IT IS CONVENIENT TO EXPRESS THE DISPLACEMETS IN A WAY THAT:

$$\underline{u}_2 - \underline{u}_1 = a\,U\,(1,1,1) \tag{5}$$

AND EXPRESSING ε IN TERMS OF THE PARAMETER U.

BY COMPARING EQS. (4) AND (5)

$$\boxed{a\,U = \frac{2\,\varepsilon}{\sqrt{M}}} \quad \Rightarrow \quad \boxed{\varepsilon = a\sqrt{M}\,\frac{U}{2}}$$

FINALLY, USING EQ. (3), WE FIND:

$$\Delta E^{UC} = \frac{1}{2}\,\omega_{LO}^2(M)\left[\,3\,\varepsilon^2 + 3\,\varepsilon^2\,\right]$$

$$= \frac{1}{2}\,\omega_{LO}^2(M)\;6\,\varepsilon^2$$

$$= \frac{1}{2}\,\omega_{LO}^2(M)\;a^2\,M\,\frac{U^2}{4}\,6$$

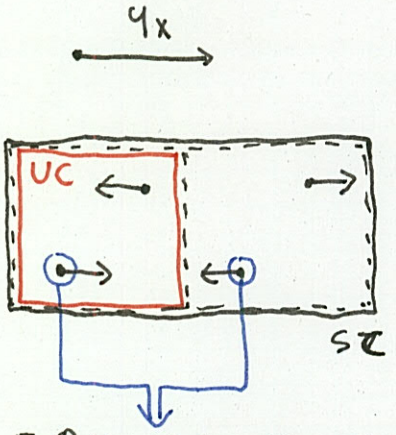
$$\boxed{\Delta E^{UC} = \frac{3}{4}\,M\,\omega_{LO}^2(M)\,a^2\,U^2}$$

* APPLICATION:

MODES AT X IN THE DIAMOND STRUCTURE

$q_X \equiv X = \frac{2\pi}{a}(0,0,1)$ (AMONG THE EQUIVALENT X_S)

THE SUPERCELL (SC) COMPATIBLE WITH PHONON DISPLACEMENTS WITH PERIODICITY GIVEN BY THE FACTOR $e^{i q_X \cdot R}$ IS TWICE AS LARGE THAN THE UNIT CELL (UC



EQUIVALENT ATOMS HAVE OPPOSITE DISPLACEMENTS

AT THE X POINT THE DYNAMICAL MATRIX AND ITS EIGENVECTORS CAN BE CHOOSEN TO BE REAL

EIGENVECTORS ARE COMPLETELY DETERMINED BY SYMMETRY

LA MODE

$$\begin{cases} \underline{\varepsilon}_1 = (0,0,\varepsilon) \\ \underline{\varepsilon}_2 = (0,0,\varepsilon) \end{cases}$$

LO MODE

$$\begin{cases} \underline{\varepsilon}_1 = (0,0,\varepsilon) \\ \underline{\varepsilon}_2 = (0,0,-\varepsilon) \end{cases}$$

TA MODE (ONE OF 2 DEGENERATE MODES)

$$\begin{cases} \underline{\varepsilon}_1 = (0,\varepsilon,0) \\ \underline{\varepsilon}_2 = (0,\varepsilon,0) \end{cases}$$

TO MODE (ONE OF 2 DEGENERATE MODES)

$$\begin{cases} \underline{\varepsilon}_1 = (0,\varepsilon,0) \\ \underline{\varepsilon}_2 = (0,-\varepsilon,0) \end{cases}$$

* WE CONSIDER HERE THE LA MODE (EASY EXTENSION TO THE OTHER MODES)

IN THIS CASE, THE DISPLACEMENTS ARE

$$\begin{cases} \underline{u}_1 = \frac{1}{\sqrt{M}}\,\underline{\varepsilon}_1 \\ \underline{u}_2 = \frac{1}{\sqrt{M}}\,\underline{\varepsilon}_2 \end{cases}$$

WE CAN WRITE DISPLACEMENTS AS, e.g.:

$$\underline{u}_1 = a\,U\,(0,0,1)$$

WITH

$$aU = \frac{\varepsilon}{\sqrt{M}} \qquad \Rightarrow \qquad \boxed{\varepsilon = \sqrt{M}\, a\, U}$$

THEN, USING EQ. (3):

$$\Delta E^{UC} = \frac{1}{2}\,\omega_{LA}^2(X)\left[\varepsilon^2 + \varepsilon^2\right]$$

$$= \frac{1}{2}\,\omega_{LA}^2(x)\;2\varepsilon^2$$

$$\boxed{\Delta E^{UC} = M\,\omega_{LA}^2(x)\,a^2\,U^2}$$

BY USING:

$$\Delta E^{UC} = \frac{\Delta E^{SC}}{2} \qquad \left(V_{UC} = \frac{V_{SC}}{2}\right)$$

WE OBTAIN

$$\boxed{\Delta E^{SC} = 2M\,\omega_{LA}^2(x)\,a^2\,U^2}$$