Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation Lecture 2: Classical theory of lattice vibrations

Ion Errea

Dept. Applied Physics, University of the Basque Country (UPV/EHU), San Sebastian, Spain

Centro de Fśica de Materiales (CSIC-UPV/EHU), San Sebastian, Spain

Donostia International Physics Center, San Sebastian, Spain

University of Science and Technology Beijing

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Universidad del País Vasco Euskal Herriko Unibertsitatea







Outline



The Born-Oppenheimer potential

- Force constants
- Properties of the force constants
- Space group symmetries

The harmonic approximation

- Classical solution of the harmonic problem
- The dynamical matrix in reciprocal space
- The ionic displacements in the crystal
- Acoustic and optical modes
- Dispersion of acoustic modes in 3D and 2D

Symmetries of the dynamcial matrix in reciprocal space

- Symmetrization of the dynamical matrix
- Irreducible representations and degeneracies

Elastic properties of solids Sound waves



The Born-Oppenheimer approximation and the ionic problem

• Solve the electronic part of the Hamiltonian:

$$\begin{array}{lll} H_e(\boldsymbol{R}) &= & T_e + V_{e-e} + V_{e-i}(\boldsymbol{R}) + V_{i-i}(\boldsymbol{R}) \\ H_e(\boldsymbol{R}) |\Psi_{\alpha}^e(\boldsymbol{R})\rangle &= & E_{\alpha}^e(\boldsymbol{R}) |\Psi_{\alpha}^e(\boldsymbol{R})\rangle \end{array}$$

• Define the Born-Oppenheimer potential from the ground state of the solution:

$$V(\boldsymbol{R})=E_0(\boldsymbol{R})$$

• Solve the ionic problem:

$$H_i |\Psi_{\beta}^i\rangle = [T_i + V(R)] |\Psi_{\beta}^i\rangle = E_{\beta} |\Psi_{\beta}^i\rangle$$

• The BO potential is a complex many-body object that depends on $3Nn_{at}$ variables, where N is the total number of unit cells in the crystal and n_{at} the number ions in the unit cell

Taylor expansion of the V(R) potential

- In solids, ionic displacements from the lattice sites τ_s(T) are usually small compared to the interionic distance: |u| << a
- *R*₀ are the ionic positions that correspond to the minimum of *V*(*R*)
- The *classical* ionic forces vanish at **R**₀:

$$f_a = -\left[rac{\partial V(\boldsymbol{R})}{\partial R_a}
ight]_{\boldsymbol{R}=\boldsymbol{R}_0} = 0,$$

where *a* labels both an ion and a Cartesian index.



Are the R_0 positions the lattice sites $\tau_s(T)$? • The BO potential $V(\mathbf{R})$ can be Taylor-expanded around \mathbf{R}_0 as

$$V(\mathbf{R}) = V(\mathbf{R}_0) + V_2(\mathbf{R}) + V_3(\mathbf{R}) + V_4(\mathbf{R}) + \cdots,$$

$$V_n(\mathbf{R}) = \frac{1}{n!} \sum_{a_1 \cdots a_n} \phi^{(n)}_{a_1 \cdots a_n} (R_{a_1} - R_{a_10}) \cdots (R_{a_n} - R_{a_n0})$$

• The *n*-th order force-constants are given by

$$\stackrel{(n)}{\phi}_{a_1\cdots a_n} = \left[\frac{\partial^n V(\boldsymbol{R})}{\partial R_{a_1}\cdots \partial R_{a_n}}\right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

Does the Taylor expansion reflect the total potential?

Does the Taylor expansion reflect the total potential?



Fourier transformed force constants

• The force constants can be written also explicitly indexing the unit cell, so that each atom (and Cartesian index) runs for atoms in the unit cell

$$\phi_{a_1\cdots a_n}^{(n)}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_n)$$

• This allows to Fourier transform the force constants as

$$\phi_{a_1\cdots a_n}^{(n)}(\boldsymbol{q}_1,\cdots,\boldsymbol{q}_n) = \sum_{\boldsymbol{T}_1\cdots\boldsymbol{T}_n} \phi_{a_1\cdots a_n}^{(n)}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_n) e^{i\boldsymbol{q}_1\cdot\boldsymbol{T}_1}\cdots e^{i\boldsymbol{q}_n\cdot\boldsymbol{T}_n}$$

where N is the total number of cells in the crystal

• The anti transform is

$$\overset{(n)}{\phi}_{a_1\cdots a_n}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_n) = \frac{1}{N^n} \sum_{\boldsymbol{q}_1\cdots \boldsymbol{q}_n} \overset{(n)}{\phi}_{a_1\cdots a_n}(\boldsymbol{q}_1,\cdots,\boldsymbol{q}_n) e^{-i\boldsymbol{q}_1\cdot\boldsymbol{T}_1}\cdots e^{-i\boldsymbol{q}_n\cdot\boldsymbol{T}_n}$$

due to the relation (q in the first BZ)

$$\sum_{\boldsymbol{T}} e^{i\boldsymbol{q}\cdot\boldsymbol{T}} = N\delta_{\boldsymbol{q},0} \qquad \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{T}} = N\delta_{\boldsymbol{T},0}$$

• Considering that translating the crystal by a lattice vector it must remain invariant

$$\phi_{\sigma_1\cdots\sigma_n}^{(n)}(\boldsymbol{T}_1+\boldsymbol{T},\cdots,\boldsymbol{T}_n+\boldsymbol{T}) = \phi_{\sigma_1\cdots\sigma_n}^{(n)}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_n)$$

• This implies that all the *q* points in the Fourier transform are not independent and must satisfy

$$\boldsymbol{q}_1 + \cdots + \boldsymbol{q}_n = \boldsymbol{G}$$

where \boldsymbol{G} is a reciprocal lattice vector

• This can be seen by plugging the condition above in the Fourier anti transform, which yields the condition

$$e^{-i(\boldsymbol{q}_1+\cdots+\boldsymbol{q}_n)\boldsymbol{T}}=1$$

 In a crystal with atoms at equilibrium lattice positions τ_s(T), a space group operation G leaves the crystal invariant:

$$\begin{aligned} \mathcal{G} &= \{S|\boldsymbol{v}(S) + \boldsymbol{T}\} \\ \mathcal{G}\boldsymbol{\tau}_s(\boldsymbol{T}) &= S\boldsymbol{\tau}_s(\boldsymbol{T}) + \boldsymbol{v}(S) + \boldsymbol{T} \\ \mathcal{G}\boldsymbol{\tau}_s(\boldsymbol{T}) &= \boldsymbol{\tau}_{s'}(\boldsymbol{T}') \end{aligned}$$

Here, S is the point group matrix, v(S) the fractional translation, T a lattice vector

 The crystal looks exactly the same in the non-transformed τ(T) and transformed τ'(T') sites



- NbSe₂ ($P6_3/mmc$) invariant under 120° rotation around z axis
- The BO energy must be invariant under *G*:

$$V(\mathcal{G} oldsymbol{ au}(oldsymbol{T})) = V(oldsymbol{ au}(oldsymbol{T}))$$

Translation:

$$\phi_{a_1\cdots a_n}^{(n)}(\boldsymbol{T}_1+\boldsymbol{T},\cdots,\boldsymbol{T}_n+\boldsymbol{T}) = \phi_{a_1\cdots a_n}^{(n)}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_n)$$

Permutation:

$$\phi_{a_1\cdots a_j\cdots a_j\cdots a_n}^{(n)}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_i,\cdots,\boldsymbol{T}_j,\boldsymbol{T}_n) = \phi_{a_1\cdots a_j\cdots a_j\cdots a_n}^{(n)}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_j,\cdots,\boldsymbol{T}_i,\boldsymbol{T}_n)$$

• Space group symmetries: For $\mathcal{G} = \{S | v(S)\}$ space group operation

$$\phi_{s_1'\cdots s_n'}^{(n)^{\beta_1\cdots\beta_n}}(\boldsymbol{T}_1',\cdots,\boldsymbol{T}_n')=\sum_{\alpha_1\cdots \alpha_n}S^{\beta_1\alpha_1}\cdots S^{\beta_n\alpha_n}\phi_{s_1\cdots s_n}^{(n)^{\alpha_1\cdots\alpha_n}}(\boldsymbol{T}_1,\cdots,\boldsymbol{T}_n)$$

where the operation $\mathcal{G} = \{S | \mathbf{v}(S)\}$ transforms the ion at $\tau_{s_i}(\mathbf{T})$ into ion at $\tau_{s_i'}(\mathbf{T}')$. In this case we have divided the combined *a* index into a Cartesian index α_i and a ion index *s*

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The harmonic approximation

- The first non-trivial approximation we can do to the vibrational problem is to assume the harmonic approximation
- We assume that atoms oscillate around the **R**₀ positions (classical approximation) and oscillate around them
- The potential is truncated at second order



$$V(R) = V(R_0) + V_2(R) + V_3(R) + V_4(R) + \dots$$

The classical solution of the harmonic problem

• The BO potential in the harmonic approximation is

$$V(\boldsymbol{R}) = \frac{1}{2} \sum_{ab} \phi^{(2)}_{ab} u_a u_b$$

where $u_a = R_a - R_{a0}$ is the displacement from the reference position with vanishing classical forces

• The Newton equation to be solved for the motion of the ions is

$$M_{a}\frac{d^{2}u_{a}(t)}{dt^{2}} = -\left[\frac{\partial V(\boldsymbol{R})}{\partial u_{a}}\right]_{u=0} = -\sum_{b} \phi_{ab}^{(2)}u_{b}^{2}$$

• This type of differential equation is solved with oscillatory functions, so we can seek solutions of the type

$$u_a(t) = \frac{e^a}{\sqrt{M_a}} e^{-i\omega t}$$

where e is a vector that determines how each atom is moving

• Plugging this we obtain the following equation

$$\sum_{b} \frac{\phi_{ab}}{\sqrt{M_a M_b}} e^b = \omega^2 e^a$$

The classical solution of the harmonic problem

- This means that the eigenvalues of the matrix $\frac{\binom{2}{\phi}}{\sqrt{M_a M_b}}$ (the dynamical matrix) will determine the ω frequencies of the ionic oscillations and the displacements of the ions will be determined by the eigenvectors e of the same matrix
- The number of eigenvalues of the matrix will be $3N_{at} = 3n_{at}N$, 3 times the total number of ions in the crystal
- We will label with μ each eigenmode

$$\sum_{b} \frac{\overset{(2)}{\phi_{ab}}}{\sqrt{M_a M_b}} e^b_\mu = \omega^2_\mu e^a_\mu$$

• The ionic displacements will be a sum of all eigenmodes

$$u_a(t) = \sum_{\mu} rac{e^a_{\mu}}{\sqrt{M_a}} \mathrm{Re}\left[e^{-i\omega_{\mu}t}
ight]$$

The classical solution of the harmonic problem

• The polarization vectors are orthonormal

$$\sum_{\mu} e^{a}_{\mu} e^{b}_{\mu} = \delta_{ab}$$
$$\sum_{a} e^{a}_{\mu} e^{a}_{\nu} = \delta_{\mu\nu}$$

• The dynamical matrix can be constructed as

$$\frac{\overset{(2)}{\phi_{ab}}}{\sqrt{M_a M_b}} = \sum_{\mu} \omega_{\mu}^2 e_{\mu}^a e_{\mu}^b$$

• The force constants matrix can be written in the reciprocal space as

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{q}) = \sum_{\boldsymbol{\tau}} \overset{(2)}{\phi}_{ab}(\boldsymbol{\tau}) e^{i\boldsymbol{q}\cdot\boldsymbol{\tau}}$$

Alternatively

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{T}) = rac{1}{N} \sum_{\boldsymbol{q}} \overset{(2)}{\phi}_{ab}(\boldsymbol{q}) e^{-i\boldsymbol{q}\cdot\boldsymbol{T}}$$

• In order to write so we have noted that the the harmonic force constants can only depend on the difference between two lattice vectors

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{T}_{a},\boldsymbol{T}_{b}) = \overset{(2)}{\phi}_{ab}(\boldsymbol{T}_{a}-\boldsymbol{T}_{b})$$

The dynamical matrix in reciprocal space

• The dynamical matrix can thus be defined in reciprocal space as

$$D_{ab}(\boldsymbol{q}) = rac{\phi_{ab}^{(2)}(\boldsymbol{q})}{\sqrt{M_a M_b}}$$

• The eigenvalue problem in reciprocal space is thus solved at each \boldsymbol{q} in the first BZ

$$\sum_{b} D_{ab}(\boldsymbol{q}) e^{b}_{\mu}(\boldsymbol{q}) = \omega^{2}(\boldsymbol{q}) e^{a}_{\mu}(\boldsymbol{q})$$

- For each q point there are $3n_{at}$ eigenvalues. As there are N q points in the first BZ, in total $3Nn_{at}$ modes
- Polarization vectors are in general complex and fulfill the following relations $(e_{\mu}^{a*}(q) = e_{\mu}^{a}(-q))$

$$\sum_{\mu} e_{\mu}^{a*}(\boldsymbol{q}) e_{\mu}^{b}(\boldsymbol{q}) = \delta_{ab}$$

$$\sum_{a} e_{\mu}^{a*}(\boldsymbol{q}) e_{\nu}^{a}(\boldsymbol{q}) = \delta_{\mu\nu}$$

$$\frac{{}^{(2)}_{\phi}}{\sqrt{M_{a}M_{b}}} = \sum_{\mu} \omega_{\mu}^{2}(\boldsymbol{q}) e_{\mu}^{a*}(\boldsymbol{q}) e_{\mu}^{b}(\boldsymbol{q})$$

The harmonic potential in the normal mode basis

 In real space let's assume the following transformation of the displacements into the normal mode basis (Q_μ)

$$u_{a}=\sum_{\mu}rac{\mathrm{e}_{\mu}^{a}}{\sqrt{M_{a}}}Q_{\mu}$$

The potential can be written as an independent sum of harmonic oscillators

$$V(\mathbf{R}) = \frac{1}{2} \sum_{ab} \phi^{(2)}_{ab} u_a u_b = \frac{1}{2} \sum_{\mu} \omega^2_{\mu} Q^2_{\mu}$$

• In Fourier space, assuming the relation

$$u_{a}(\boldsymbol{T}_{a}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q}\mu} \frac{e_{\mu}^{a}(\boldsymbol{q})}{\sqrt{M_{a}}} Q_{\mu}(\boldsymbol{q}) e^{-i\boldsymbol{q}\cdot\boldsymbol{T}_{a}}$$

The potential becomes $(Q_{\mu}(-\boldsymbol{q}) = Q^*_{\mu}(\boldsymbol{q}))$

$$V(oldsymbol{R}) = rac{1}{2} \sum_{oldsymbol{q} \mu} \omega_{\mu}^2(oldsymbol{q}) |Q_{\mu}(oldsymbol{q})|^2$$

The harmonic potential in the normal mode basis

- The ionic displacements are a linear combination of oscillating harmonic oscillators
- The kinetic of each oscillator is proportional to $\sim k_B T$



How much do the atoms move if the mechanical energy is 0 (0 temperature)?

Energy

Normal coordinate Q

 $V_2(\mathbf{R})$

$$u_{a}(\boldsymbol{T}_{a}) = rac{1}{\sqrt{N}}\sum_{\boldsymbol{q}\mu}rac{e^{a}_{\mu}(\boldsymbol{q})}{\sqrt{M_{a}}}Q_{\mu}(\boldsymbol{q})e^{-i\boldsymbol{q}\cdot\boldsymbol{T}_{a}}$$

• As the displacements are real we need to assume that

$$egin{array}{rcl} e^{a}_{\mu}(-m{q}) &=& e^{a*}_{\mu}(m{q}) \ Q_{\mu}(-m{q}) &=& Q^{*}_{\mu}(m{q}) \end{array}$$

• The wave-like $e^{-iq\cdot T}$ factor tells us how the ionic displacements are modulated from cell to cell

The ionic displacements: an example

We take a crystal in 2D with one atom in the unit cell and a mode with $e_{\mu} = (1, 0)$. Each ion in the crystal is at a lattice site $T = n_1 a + n_2 b = (n_1, n_2)$. The displacements for different q modes are the following



The ionic displacements: an example

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Acoustic and optical modes

- At *q* = 0 point (Γ) there are always three modes in which all ions move together, translational modes
- If we displace the ions according to any of these normal modes, the harmonic potential will be parametrized as

$$V({m R}) = rac{1}{2} \omega_{\mu}^2(0) |Q_{\mu}(0)|^2$$

- The energy cannot be modified by a translational mode
- The frequency of the translational modes must be 0. These are the acoustic modes



• If there is more than an atom in the unit cell there will be other non-zero frequency modes. These are the optical modes

Acoustic and optical modes



Linear dispersion of acoustic modes

• The frequency of any mode can be obtained from

$$\omega_{\mu}^{2}(\boldsymbol{q}) = \sum_{\alpha\beta st} e_{\mu s}^{\alpha}(\boldsymbol{q}) \frac{\overset{(2)}{\phi}_{st}^{\alpha}(\boldsymbol{q})}{\sqrt{M_{s}M_{t}}} e_{\mu t}^{\beta *}(\boldsymbol{q}) = \sum_{\alpha\beta st} \sum_{\boldsymbol{T}} e_{\mu s}^{\alpha}(\boldsymbol{q}) \frac{\overset{(2)}{\phi}_{st}^{\alpha}(\boldsymbol{T})}{\sqrt{M_{s}M_{t}}} e^{i\boldsymbol{q}\cdot\boldsymbol{T}} e_{\mu t}^{\beta *}(\boldsymbol{q})$$

• As $\sum_{t \, T} \phi_{st}^{(2)^{\alpha \beta}}(T) = 0$, this can be written as

$$\omega_{\mu}^{2}(\boldsymbol{q}) = -2\sum_{\alpha\beta st}\sum_{\boldsymbol{T}}e_{\mu s}^{\alpha}(\boldsymbol{q})\frac{\overset{(2)^{\alpha\beta}}{\phi_{st}}(\boldsymbol{T})}{\sqrt{M_{s}M_{t}}}\sin^{2}(\boldsymbol{q}\cdot\boldsymbol{T}/2)e_{\mu t}^{\beta*}(\boldsymbol{q})$$

• In the $\boldsymbol{q} \rightarrow 0$ limit

$$\omega_{\mu}^{2}(\boldsymbol{q})\sim-rac{1}{2}\sum_{lphaeta st}\sum_{\boldsymbol{T}}e_{\mu s}^{lpha}(0)rac{\phi_{st}^{(2)}(\boldsymbol{T})}{\sqrt{M_{s}M_{t}}}(\boldsymbol{q}\cdot\boldsymbol{T})^{2}e_{\mu t}^{eta *}(0)$$

• This implies that acoustic modes will have a linear dispersion with *q*

Phonon spectrum

- The $\omega_{\mu}(\boldsymbol{q})$ frequencies form the honon spectrum
- Usually plotted for $q \in 1BZ$ along high-symmetry lines



NbSe₂ crystal with $P6_3/mmc$ space group

- Nb: 2b Wyckoff positions
- Se: 4f Wyckoff positions

Quadratic dispersion of out-of-plane acoustic modes in 2D materials

- Apart from the translational invariance solids are also invariant to rotational symmetry
- In a strictly 2D material this has special consequences
- Let's assume that we rotate the atoms in the 2D plane by an infinitesimal rotation $u_s^{\alpha}(\mathbf{T}) = \delta\theta \mathbf{n} \times \mathbf{R}_{s0}(\mathbf{T})$, where the rotation axis \mathbf{n} is in the 2D plane
- As this rotation cannot create any force

$$\sum_{\boldsymbol{\tau}} \phi_{st}^{(2)^{zz}}(\boldsymbol{\tau}) \boldsymbol{\tau}^{\alpha} = \mathbf{0} \quad \forall \alpha = x, y$$

• This implies that the out-of-plane flexural acoustic mode (ZA) in 2D materials is quadratic

$$\omega_{ZA}^2(\boldsymbol{q}) \sim \boldsymbol{q}^2$$

- M. I. Katsnelson and A. Fasolino, Acc. Chem. Res. 46, 97 (2013)
 - J. Carrete et al., Mater. Res. Lett. 4, 204 (2016)

Quadratic dispersion of out-of-plane acoustic modes in 2D materials

Graphene



M. I. Katsnelson and A. Fasolino, Acc. Chem. Res. 46, 97 (2013)

Lecture 2

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Transformation of the dynamical matrix

Symmetry properties of the dynamical matrix

$$D_{ab}(\boldsymbol{q}) = \sum_{\boldsymbol{\tau}} \frac{\overset{(2)}{\phi}_{ab}(\boldsymbol{\tau})}{\sqrt{M_a M_b}} e^{i\boldsymbol{q}\cdot\boldsymbol{\tau}}$$

 Permutation: Implies that D(q) is Hermitian

$$D_{ab}(\boldsymbol{q})=D^*_{ab}(\boldsymbol{q})$$

and has, thus, real eigenvalues ($\omega_{\mu}^2(\boldsymbol{q})$ is real)

• Space group: Fourier transforming the real space relation for a symmetry operation $\mathcal{G} = \{S | \mathbf{v}(S)\}$ $D(Sq) = \Gamma(q, \mathcal{G})D(q)\Gamma^{\dagger}(q, \mathcal{G})$

where $\Gamma(q, G)$ is a unitary matrix given by

$$\Gamma_{s_1s_2}^{\alpha_1\alpha_2}(\boldsymbol{q},\mathcal{G}) = S^{\alpha_1\alpha_2} \delta_{s_2s_1'} e^{iS\boldsymbol{q}\cdot(\boldsymbol{\tau}_{s_1}-\mathcal{G}\boldsymbol{\tau}_{s_1'})}$$

Consequences of

 $D(Sq) = \Gamma(q, \mathcal{G})D(q)\Gamma^{\dagger}(q, \mathcal{G})$

- Knowing D(q) the dynamical matrix can be obtained for all the q points related by a point group matrix: Sq
- The set formed by all the transformed *q* points, {*Sq*}, is called the star of *q*
- Knowing D(q) for the points not related by Sq is sufficient to generate the dynamical matrix for the whole 1BZ
- These points form the asymmetric cell, sometimes called, the irreducible BZ



1BZ and asymmetric cell of $P6_3/mmc$

Symmetrizing the dynamical matrix

• If a given point group matrix S leaves invariant a q point,

$$S \boldsymbol{q} = \boldsymbol{q} + \mathsf{G}_{\boldsymbol{q}},$$

where G_q is the reciprocal lattice vector that brings q into the 1BZ, then

$$D(\boldsymbol{q}) = \Gamma(\boldsymbol{q}, \mathcal{G}) D(\boldsymbol{q}) \Gamma^{\dagger}(\boldsymbol{q}, \mathcal{G})$$

- This imposes symmetry conditions to the dynamical matrix
- The point group operations that satisfy the above equation form the **little co-group of** *q*
- In case time-reversal symmetry is present, if a given point group matrix S brings q into -q

$$S \boldsymbol{q} = -\boldsymbol{q} + \mathbf{G}_{-\boldsymbol{q}},$$

then

$$D^*(\boldsymbol{q}) = \Gamma(\boldsymbol{q}, \mathcal{G}) D(\boldsymbol{q}) \Gamma^{\dagger}(\boldsymbol{q}, \mathcal{G})$$

because if time-reversal symmetry is present $D^*(\boldsymbol{q}) = D(-\boldsymbol{q})$

• This imposes further symmetry conditions to the dynamical matrix

An example: D(q) for FCC crystal at X (0, 1, 0)

- The FCC lattice belongs to the *Fm*3*m* space group with atoms in 4*a* Wyckoff positions
- It has 48 symmetry operations in the point group
- 16 of them (4/mmn) leave the X point invariant, $Sq = q + G_q$ (e.g. 4^+_{010})
- There are also symmetries for which
 Sq = -q + G_{-q} (e.g. -1)
- As in the FCC primitive unit cell there is only one atom, Γ(q, G) = S



Obilbao crystallographic serve. http://www.cryst.ehu.es

An example:
$$D(q) = \begin{pmatrix} A_{11} + iB_{11} & A_{12} + iB_{12} & A_{13} + iB_{13} \\ A_{12} - iB_{12} & A_{22} + iB_{22} & A_{23} + iB_{23} \\ A_{13} - iB_{13} & A_{23} - iB_{23} & A_{33} + iB_{33} \end{pmatrix}$$
 for FCC crystal at X
(0, 1, 0)

• The effect of the inversion through $D^*(q) = SD(q)S^T$ with

$$S_{-1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \text{ yields}$$

$$\begin{pmatrix} A_{11} - iB_{11} & A_{12} - iB_{12} & A_{13} - iB_{13} \\ A_{12} + iB_{12} & A_{22} - iB_{22} & A_{23} - iB_{23} \\ A_{13} + iB_{13} & A_{23} + iB_{23} & A_{33} - iB_{33} \end{pmatrix} = \begin{pmatrix} A_{11} + iB_{11} & A_{12} + iB_{12} & A_{13} + iB_{13} \\ A_{12} - iB_{12} & A_{22} + iB_{22} & A_{23} + iB_{23} \\ A_{13} - iB_{13} & A_{23} - iB_{23} & A_{33} + iB_{33} \end{pmatrix}$$

• Thus, $D^*(q) = D(q)$, which means that D(q) at X is real

Symmetrizing the dynamical matrix

An example:
$$D(q) = \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{12} & A_{22} & A_{23} \\ A_{13} & A_{23} & A_{33} \end{pmatrix}$$
 for FCC crystal at X (0, 1, 0)

• The effect of the 4^+_{010} rotation through $D(\mathbf{q}) = SD(\mathbf{q})S^T$ with $S_{4^+_{010}} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$ yields

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{12} & A_{22} & A_{23} \\ A_{13} & A_{23} & A_{33} \end{pmatrix} = \begin{pmatrix} A_{33} & A_{23} & -A_{13} \\ A_{23} & A_{22} & -A_{12} \\ -A_{13} & -A_{12} & A_{11} \end{pmatrix}$$

• Thus, $A_{33} = A_{11}$, $A_{23} = A_{12}$, $A_{13} = 0$, and $A_{23} = -A_{12}$

• Applying the same procedure with all 16 operations of 4/mmm

$$D(\mathbf{q}) = \begin{pmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{11} \end{pmatrix} \longrightarrow \begin{cases} \omega_1^2(\mathbf{q} = X) = \omega_2^2(\mathbf{q} = X) = A_{11} \\ \omega_3^2(\mathbf{q} = X) = A_{22} \end{cases}$$

Irreducible representations and degeneracies

- Crystal symmetries determine the degeneracies of the phonon modes
- The number of different frequencies coincides with the number of (**irreps**) of the little co-group of **q** in which the atomic displacements are decomposed
- The dimension of each irrep determines the number of degenerate modes associated to it



Decomposition of the mechanical representation of the space group (N. 225)

Wave-vector: X:(0,1,0),(1,0,0),(0,0,1)

Wyckoff position	Decomposition into irreps
192I:(x,y,z)	9 X1+(3) 9 X2+(3) 9 X3+(3) 9 X4+(3) 18 X5+(6) 9 X1-(3) 9 X2-(3) 9 X3-(3) 9 X4-(3) 18 X5-(6)
96k:(x,x,z)	5 X1+(3) ⊕ 4 X2+(3) ⊕ 4 X3+(3) ⊕ 5 X4+(3) ⊕ 9 X5+(6) ⊕ 4 X1-(3) ⊕ 5 X2-(3) ⊕ 5 X3-(3) ⊕ 4 X4-(3) ⊕ 9 X5-(6)
96j:(0,y,z)	6 X1+(3) ⊗ 6 X2+(3) ⊗ 4 X3+(3) ⊗ 4 X4+(3) ⊗ 8 X5+(6) ⊗ 3 X1-(3) ⊗ 3 X2-(3) ⊗ 5 X3-(3) ⊗ 5 X4-(3) ⊗ 10 X5-(6)
48i:(1/2,y,y)	3 X1+(3) © 3 X2+(3) © 2 X3+(3) © 2 X4+(3) © 4 X5+(6) © X1-(3) © 2 X2-(3) © 3 X3-(3) © 2 X4-(3) © 5 X5-(6)
48h:(0,y,y)	3 X1+(3) ⊕ 3 X2+(3) ⊕ 2 X3+(3) ⊕ 2 X4+(3) ⊕ 4 X5+(6) ⊕ X1-(3) ⊕ 2 X2-(3) ⊕ 3 X3-(3) ⊕ 2 X4-(3) ⊕ 5 X5-(6)
48g:(x,1/4,1/4)	3 X1+(3) ⊕ 2 X2+(3) ⊕ X3+(3) ⊕ 2 X4+(3) ⊕ 5 X5+(6) ⊕ 2 X1-(3) ⊕ 3 X2-(3) ⊕ 2 X3-(3) ⊕ X4-(3) ⊕ 5 X5-(6)
32f:(x,x,x) k	2 X1+(3) X2+(3) X3+(3) 2 X4+(3) 3 X5+(6) X1-(3) 2 X2-(3) 2 X3-(3) X4-(3) 3 X5-(6)
24e:(x,0,0)	2 X1+(3) ⊕ X2+(3) ⊕ X3+(3) ⊕ X4+(3) ⊕ 2 X5+(6) ⊕ 2 X3-(3) ⊕ X4-(3) ⊕ 3 X5-(6)
24d:(0,1/4,1/4)	2 X1+(3) ⊕ 2 X2+(3) ⊕ X3+(3) ⊕ X4+(3) ⊕ 3 X5+(6) ⊕ X2-(3) ⊕ X3-(3) ⊕ 2 X5-(6)
8c:(1/4,1/4,1/4)	X1+(3) © X5+(6) © X2-(3) © X5-(6)
4b:(1/2,1/2,1/2)	X3-(3) ⊕ X5-(6)
4a:(0,0,0)	X3-(3) ⊕ X5-(6)

In parenthesis the dimension of the irreducible representation

Irreducible representations and degeneracies

- Crystal symmetries determine the degeneracies of the phonon modes
- The number of different frequencies coincides with the number of (**irreps**) of the little co-group of **q** in which the atomic displacements are decomposed
- The dimension of each irrep determines the number of degenerate modes associated to it
- The number or irreps for the *q* points in a high-symmetry line is the same



Outline



The Born-Oppenheimer potential

- Force constants
- Properties of the force constants
- Space group symmetries

The harmonic approximation

- Classical solution of the harmonic problem
- The dynamical matrix in reciprocal space
- The ionic displacements in the crystal
- Acoustic and optical modes
- Dispersion of acoustic modes in 3D and 2D

Symmetries of the dynamcial matrix in reciprocal space

- Symmetrization of the dynamical matrix
- Irreducible representations and degeneracies

Elastic properties of solids Sound waves



The elastic theory

- In the theory of elasticity, there is no crystal, but the material is described as a continuum at position r = (x, y, z)
- A deformation of the material is described with the field u(r)
- In the harmonic approximation the equation of motion are

$$\rho \frac{\partial^2 u^{\alpha}}{\partial t^2} = \sum_{\beta \gamma \sigma} c^{\alpha \beta \gamma \sigma} \frac{\partial^2 u^{\sigma}}{\partial r^{\beta} r^{\gamma}}$$

where $c^{lphaeta\gamma\sigma}$ is the elastic tensor

• Plugging here plane wave solutions

$$\boldsymbol{u}(\boldsymbol{r},t)=e^{i(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)}\boldsymbol{e}$$

we obtain the following equation

$$\rho\omega^{2}\boldsymbol{e}_{\alpha}=\sum_{\beta\gamma\sigma}\boldsymbol{c}^{\alpha\beta\gamma\sigma}\boldsymbol{q}^{\beta}\boldsymbol{q}^{\gamma}\boldsymbol{e}^{\sigma}$$

Ashcroft & Mermin, Thomson Learning Born & Huang, Oxford University Press

Lecture 2

• Comparing the

$$ho \omega^2 e_lpha = \sum_{eta\gamma\sigma} c^{lphaeta\gamma\sigma} q^eta q^\gamma e^\sigma$$

equation with the equation we obtained for the ${m q}
ightarrow 0$ limit of the acoustic modes

$$\omega_{\mu}^{2}(\boldsymbol{q})\sim-rac{1}{2}\sum_{lphaeta st}\sum_{\boldsymbol{T}}e_{\mu s}^{lpha}(0)rac{\phi_{st}^{(2)^{lphaeta}}}{\sqrt{M_{s}M_{t}}}(\boldsymbol{q}\cdot\boldsymbol{T})^{2}e_{\mu t}^{eta st}(0),$$

it seems that the frequencies are the same

- Indeed the polarization vectors of the elastic waves are homogeneous translations
- $\bullet\,$ This means that the frequency of the elastic wave is the ${\it q} \rightarrow 0$ limit of the acoustic modes

The elastic theory and acoustic modes



The elastic theory and sound propagation

- As sound is an elastic wave, the velocity of sound is the velocity of the phonon propagation
- In analogy to the photon speed

 (c = λ/T → ω = cq, with q the wave number), the velocity of sound of a wave propagating with wave number q is

$$m{v}_{\mu}(m{q}) = rac{\partial \omega_{\mu}(m{q})}{\partial |m{q}|}$$

when ${m q}
ightarrow 0$

There will be three acoustic velocities, one for the longitudinal mode
 (e_{LA} || q) and two for the transversal
 modes (e_{TA} ∦ q)



Show that due to translational symmetry

$$\sum_{s_n \boldsymbol{T}_n} \phi_{s_1 \cdots s_n}^{(n)^{\alpha_1 \cdots \alpha_n}} (\boldsymbol{T}_1, \cdots, \boldsymbol{T}_n) = 0$$

and that the same holds for the sum over any index n

- Show that the dynamical matrix in reciprocal space is Hermitian
- Show that applying symmetries for a FCC crystal the dynamical matrix at the X point is

$$D(\boldsymbol{q}) = egin{pmatrix} A_{11} & 0 & 0 \ 0 & A_{22} & 0 \ 0 & 0 & A_{11} \end{pmatrix}$$