

# Ab initio methods in solid state physics

## IX. Lattice dynamics - harmonic approximation

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April 26, 2023

- Atoms vibrate  $\rightarrow$  lattice vibrations  $\rightarrow$  thermodynamics
- Lattice dynamics:<sup>12</sup>
  - heat conductance
  - heat capacity
  - thermodynamic stability
  - mechanical stability
  - phase transitions
  - thermoelectricity

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<sup>1</sup>A. A. Maradudin, *Theory of Lattice Dynamics in the Harmonic Approximation* / (New York :, 1963.).

<sup>2</sup>M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, 1988).

# Energy of the crystal

Atomic positions in crystal lattice are described by the position vector  $\mathbf{R}(\mathbf{n}, i)$ :

$$\mathbf{R}(\mathbf{n}, i) = n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c} + \mathbf{r}_i$$

where  $i$  numbers atoms in the primitive unit cell and vector of integers  $\mathbf{n} = [n_a, n_b, n_c]$  numbers unit cells in the lattice while  $\mathbf{r}_i$  is a position of the  $i$ -th atom relative to the origin of the unit cell with cell vectors  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ . Symmetry operations of the lattice act only on indexes  $i$ , while the periodicity is encapsulated in the integer vector  $\mathbf{n}$  and lattice vectors  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ .

Potential energy of the lattice can be expanded as a function of the atomic displacements  $s_{ni\alpha}$ , where  $\alpha = x, y, z$ , (assuming small vibrations and negligible quantum effects):

$$V(s) = V_0 + \sum_{ni\alpha} \left. \frac{\partial V}{\partial s_{ni\alpha}} \right|_{s=0} s_{ni\alpha} + \frac{1}{2} \sum_{ni\alpha} \sum_{n'i'\alpha'} \left. \frac{\partial^2 V}{\partial s_{ni\alpha} \partial s_{n'i'\alpha'}} \right|_{s=0} s_{ni\alpha} s_{n'i'\alpha'} + O(s^3)$$

The linear term vanishes due to the equilibrium point assumption and we neglect higher order terms assuming they are small.

# Equation of motion

We can now write the Lagrangean  $L = T - V$  and the Euler-Lagrange equation:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{s}_{ni\alpha}} = \frac{\partial L}{\partial s_{ni\alpha}}$$

resulting in the equation of motion:

$$m_i \ddot{s}_{ni\alpha} = - \sum_{n'i'\alpha'} \Phi_{ni\alpha}^{n'i'\alpha'} s_{n'i'\alpha'}$$

where we have introduced force constants matrix  $\Phi$  denoting the second derivative term:

$$\Phi_{ni\alpha}^{n'i'\alpha'} = \left. \frac{\partial^2 V(s)}{\partial s_{ni\alpha} \partial s_{n'i'\alpha'}} \right|_{s_{ni\alpha}=0}$$

Obviously,  $\Phi_{ni\alpha}^{n'i'\alpha'} = \Phi_{n'i'\alpha'}^{ni\alpha}$  is symmetric.

# Solution of EOM

We can search for the solution of EOM with the standard oscillating ansatz:

$$s_{ni\alpha}(t) = \frac{1}{\sqrt{m_i}} u_{ni\alpha} e^{-i\omega t}$$

The equation of motion now takes form of eigen-equation:

$$\omega^2 u_{ni\alpha} = \sum_{n'i'\alpha'} \Phi_{ni\alpha}^{n'i'\alpha'} u_{n'i'\alpha'}$$

Note that the interaction between atoms  $ni\alpha$  and  $n'i'\alpha'$  depend only on relative positions of unit cells  $n$  and  $n'$ . Thus, we can select arbitrary unit cell for the origin and consider one of the indexes constant  $n' = 0$  and replace  $\Phi_{ni\alpha}^{n'i'\alpha'}$  with  $\Phi_{i\alpha}^{i'\alpha'}(n)$  taking care of the translational symmetry of the crystal.

# Dynamical matrix

We can further simplify the solution by taking into account the periodicity of the crystal lattice and taking another ansatz for a solution – this time oscillating in spatial coordinates with wave vector  $\mathbf{q}$ :

$$u_{ni\alpha} = \varepsilon_{i\alpha} e^{i\mathbf{q} \cdot \mathbf{R}_n}$$

where  $\mathbf{R}_n$  denotes relative positional vector of the  $n^{\text{th}}$  unit cell and  $\mathbf{q}$  is the point in the first Brillouin zone.

Finally, the equation of motion takes form of eigenequation:

$$\omega^2(\mathbf{q}) \varepsilon_{i\alpha} = \sum_{i'\alpha'} D_{i\alpha}^{i'\alpha'}(\mathbf{q}) \varepsilon_{i'\alpha'}$$

where dynamical matrix  $D$  is defined by the equation:

$$D_{i\alpha}^{i'\alpha'}(\mathbf{q}) = \sum_n \frac{\Phi_{i\alpha}^{i'\alpha'}(n)}{\sqrt{m_i m_{i'}}} e^{i\mathbf{q} \cdot \mathbf{R}_n}$$

above and  $\varepsilon_{i\alpha}$  present themselves as eigenvectors of the dynamical matrix – i.e. polarisation vectors or normal base vectors.

Atomic displacements  $s_{ni\alpha}$  are connected with forces acting on atoms  $F_{ni\alpha}$  with linear relation:

$$F_{ni\alpha} = -\frac{\partial V}{\partial s_{ni\alpha}} = -\sum_{mj\beta} \Phi_{ni\alpha}^{mj\beta} s_{mj\beta}$$

This is again a linear force-displacement relation similar to the one we encountered while calculating elastic tensor in Lecture 8. And we can use similar trick to derive matrix  $\Phi$  from sets of forces and displacements

Similar to the elastic tensor case the  $\Phi$  matrix is subject to symmetries of a particular crystal. Unfortunately, here it is much more complicated. But still we can symbolically rewrite above relation as following large set  $N$  of linear equations ( $a = 1 \dots N$ ):

$$F^a = S(s^a) I_\Phi$$

Where  $a$  numbers set of displacements,  $S(s^a)$  is a symmetry-encoding matrix which is a function of displacements and  $I_\Phi$  is a set of independent parameters of  $\Phi$ .

# Direct (Finite Displacements) method

The force-displacement relation can be approximately solved by fitting the  $I_\Phi$  parameters to make the sides of the equation as close as possible in the least-squares sense.<sup>3</sup> Again, we often use SVD for this, but this is by far not the only method of solving this problem (e.g. Elastic-net regression, Adaptive LASSO).<sup>4 5</sup>

The remaining problems are:

- Construction of the matrix  $S(s^a)$  and vector  $I_\Phi$
- Selection of displacement sets  $s^a$
- Multiple subtle issues (supercell selection, exact points, etc.)

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<sup>3</sup>K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997)

<sup>4</sup>T. Tadano, Y. Gohda, and S. Tsuneyuki, J. Phys.: Condens. Matter 26, 225402 (2014)

<sup>5</sup>ALAMODE manual



- Construction of  $S(s)$  is coded in multiple phonon-calculation programs (ALAMODE, PhonoPy, Phonon, Phon, GULP, ...)
- Selection of  $I_{\mathbf{q}}$  follows directly from the  $S$  matrix
- The same goes for the rest of computational details
- Selection of displacements:
  - Elementary displacements (minimal set: PhonoPy, Phonon, ...)
  - Random or thermodynamic displacements (ALAMODE, HECSS)
- Selection of the supercell:
  - Smallest cell containing interaction range
  - Preferably commensurate with important points in reciprocal space
  - Preferably not breaking symmetry of the crystal

# Goals

- Frequencies  $\omega(\mathbf{q})$
- Polarization vectors  $\varepsilon$
- Density of states  $p(\omega)$
- Structure stability
- Phase transitions
- Phonon heat capacity