

Solid State Theory: Band Structure Methods

Lilia Boeri

Wed., 12:00-13:30

HS P3 (PH02112)

<http://itp.tugraz.at/LV/boeri/ELE/>

	12/3 Intro	19/3 DFT1	26/3 DFT2	
2/4 DFT3	9/4 DFT4	16/4 BREAK	23/4 BREAK	30/4 BREAK
7/5 ADV1	13/5 P1	21/5 ADV2	23/5 P2	
30/5 P3	4/6 ADV3	11/6 ADV4/ QA		

- **DFT1+2: Hohenberg-Kohn Theorem and Kohn and Sham equations.**
- **DFT3+4: Solving K-S in practice; basis functions, augmented methods and psp theory.**
- **DFT5: Practical problems in DFT (k space integration, convergence etc)**
- **P1: EOS and band structure of silicon.**
- **ADV1+2: Linear Response theory (mostly for phonons).**
- **P2: Phonons of silicon**
- **ADV3: Wannier Functions and TB approximation.**
- **P3: Wannier Functions and BOM for silicon.**

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2/4 DFT3	9/4 DFT4	16/4 BREAK	23/4 BREAK	30/4 BREAK
7/5 ADV1	13/5 P1	21/5 ADV2	23/5 P2	
30/5 P3	4/6 ADV3	11/6 ADV4/ QA		

Important Dates (exercises):

13/5 (Tuesday, next week): 14-15:30 (Electronic structure, *pw.x*)

23/5 (Friday): 14-> 17 (Phonons, *ph.x*)

30/5 (Friday): 14-> 17 (Wannier Functions, *wannier90.x*).

We will employ quantum espresso: <http://www.quantum-espresso.org/>

Before the break:

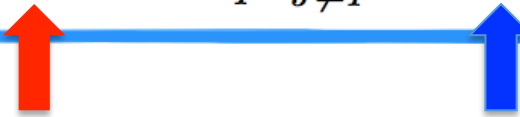
- Density Functional Theory: Hohenberg and Kohn Theorem, Kohn-Sham equations (Density is the basic variable).
- Density Functional Theory: practical problems (convergence, basis functions).
- Pseudopotential Theory.

“A primer in Density Functional Theory” (Springer), chapter 1 and 6.

- Pseudopotential Theory.

Pseudopotential Method, G.B. Bachelet and A. Filippetti (notes).

Solids: Quantum Mechanical Problem

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_i \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$


➤ Density functional theory:

- “Smart” method to approximate the electron-electron interaction: the interacting many-body wavefunction for electrons is replaced by the electron density (function of one variable).

➤ Pseudopotential Method:

- Approximate the electron-nuclei term: DFT equations in plane waves can be practically implemented.

Main Concepts of Density Functional Theory:

The quantum-mechanical many-electron problem can be greatly simplified if we are only interested in its ground-state properties.

$$\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \quad \longrightarrow \quad n_0^\sigma(\mathbf{r}) = \sum_{\sigma_2 \dots \sigma_N} \int d^3r_2 \dots d^3r_N |\Psi_0(\mathbf{r}\sigma, \dots, \mathbf{r}_N\sigma_N)|^2$$

➔ **Hohenberg-Kohn Theorem:** The ground-state energy of a system of interacting electrons is a function of its ground-state density only. The complications induced by the electron-electron interaction are "dumped" into an effective exchange and correlation energy, whose exact form is unknown (but good approximation exists).

➔ **Kohn-Sham Equations:** It is possible to find the ground-state density of the interacting system solving self-consistently a system of single-particle equations for the **auxiliary (effective) Kohn-Sham quasi-particles**.

Kohn-Sham Equations:

The Schrodinger's equation for the Kohn-Sham quasi-particles depends on the **ground-state density**; on the other hand, the ground-state density is obtained summing over the occupied **K-S orbitals**.

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + u([n]; \mathbf{r}) + v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \mathbf{r}) \right) \psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma} \psi_{\alpha\sigma}(\mathbf{r})$$

$$n_\sigma(\mathbf{r}) = \sum_{\alpha} \theta(\mu - \epsilon_{\alpha\sigma}) |\psi_{\alpha\sigma}(\mathbf{r})|^2$$

1. Start from a set of "guess functions".
2. Calculate the corresponding charge density.
3. Compute the Hartree and xc potentials
4. Insert into the Schrodinger equations.

Iterate until the charge densities at step t and $(t+1)$ differ by less than a given threshold

Kohn-Sham Equations (plane waves):

The most convenient way to solve K-S equations is to expand the K-S Bloch orbitals on given basis functions. **Plane waves** are a very common choice:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\sum_{\mathbf{G}'} \left[\frac{1}{2} |\mathbf{k} + \mathbf{G}'|^2 \delta_{\mathbf{G},\mathbf{G}'} + \tilde{v}(\mathbf{G} - \mathbf{G}') \right] c_{n\mathbf{k}}(\mathbf{G}') = \varepsilon_{n\mathbf{k}} c_{n\mathbf{k}}(\mathbf{G})$$

The computational time scales exponentially with the number of plane-waves. The length-scale (number of \mathbf{G} components) of the scf potential is given by the external (lattice potential).

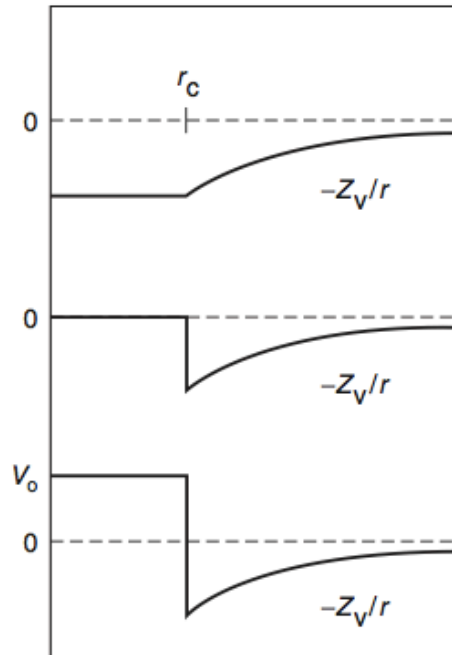
$$t_{comp} \propto (N_{pw})^3$$

$$|\mathbf{k} + \mathbf{G}|^2 < E_{cut} \quad \lambda_{min} = \frac{2\pi}{G_{cut}}$$

In order to reduce the number of plane waves, we have to “cut out” the core electrons, which have small-scale oscillations (pseudopotential).

Model Pseudopotentials:

The solid can be approximated as isolated (rigid) pseudo-atoms + valence electrons which re-arrange self-consistently due to different environment (chemical bonds). The tail of the potential of the pseudo-atoms must behave as $-Z_v/r$.



A model pseudopotential has two important physical parameters:

$$Z_v$$

Valence charge

$$r_c$$

Core radius

Figure 3 Model bare pseudopotentials. Lower panel: two-parameter pseudopotential. Upper and middle panels: one-parameter pseudopotentials, where the only parameter is the core radius r_c , roughly corresponding to the spatial extent of the outermost core orbitals, or to the outermost radial node of the true valence orbitals (see **Figure 2** and text).

Good agreement for charge density distributions (defects, impurities), bad results for total energy.

Valence charge



Periodic Table

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	* *	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	** **	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium
*		57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium	
**		89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium	

- Alkali
- Alkaline
- Transition
- Lanthanoid
- Actinoid
- Post-transition
- Metalloid
- Nonmetal
- Halogen
- Noble gas
- Unknown

Core Radius



Ab-initio Pseudopotentials:

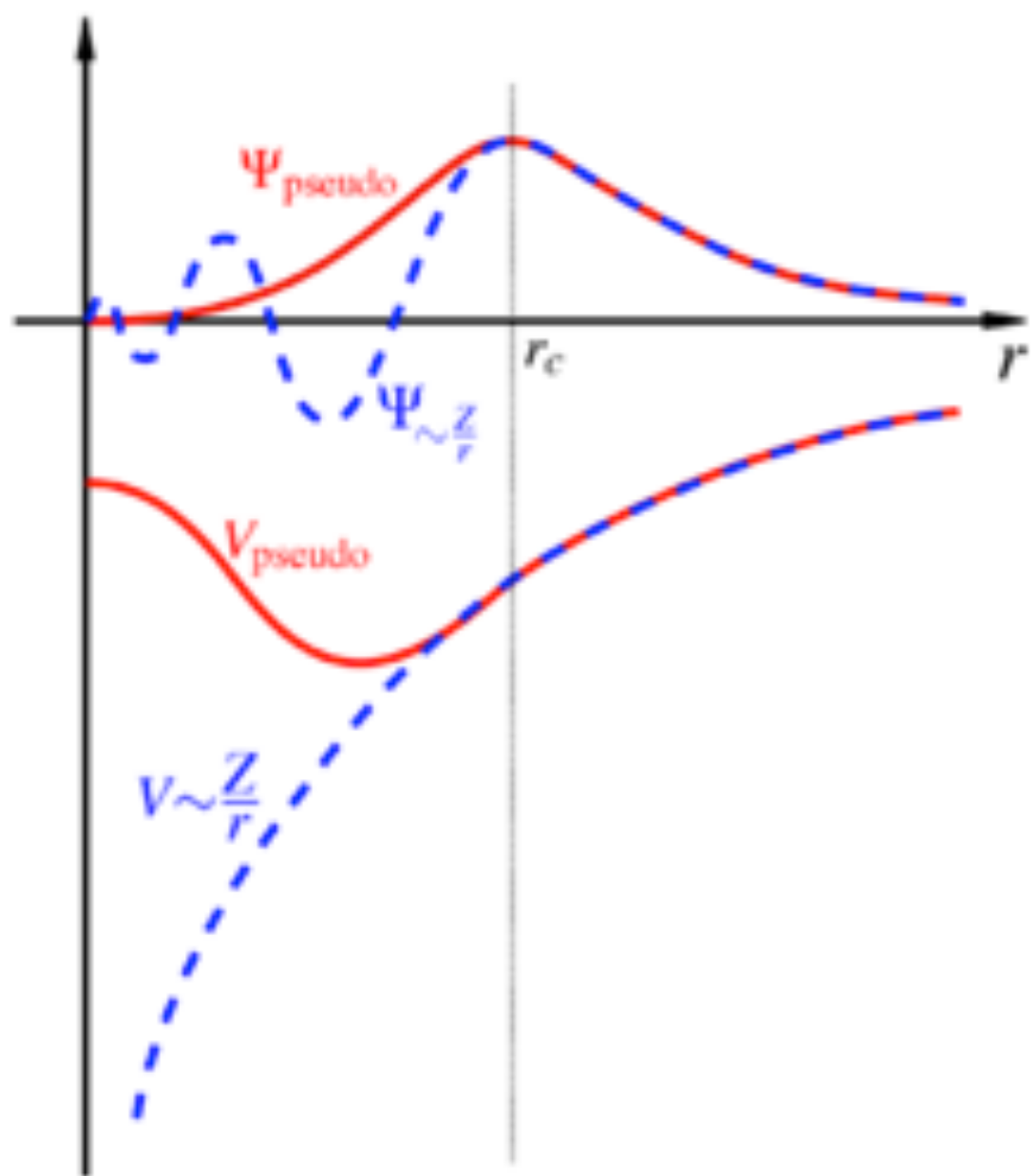
Hamann-Schlüter-Chiang (1979): A fully *ab-initio* pseudopotential can be constructed, requiring that the solution of the radial Schrödinger equation for the full and the pseudo atoms are the same, above a cut-off radius r_c :

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + v_{screen}(r) \right] \chi_{nl} = \epsilon_{nl} \chi_{nl}$$

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_l^{ps,screened}(r) \right] \chi_l^{ps} = \epsilon_l \chi_l^{ps}$$

The pseudo wave function is a **smooth** function **without nodes**. **Norm conservation** ensures optimal **transferability**.

$$\int_0^{r_c} |\chi_l^{ps}(r)|^2 dr = \int_0^{r_c} |\chi_{nl}(r)|^2 dr$$



Second Part (Advanced Topics)

PHONONS AND DENSITY FUNCTIONAL PERTURBATION THEORY

Outline:

- Phonons: Physical Properties, experiments and theory (history).
- *Ab-initio* Methods for Phonons: from the quantum many-body problem to linear response.
- *Ab-initio* Methods for Phonons: direct approaches (frozen-phonon with supercells).
- Phonon Eigenvectors and Supercells.
- Limitations of the supercell method (Kohn Anomalies in metals).

S. Baroni, S. de Gironcoli, A. del Corso, P. Giannozzi, Review of Modern Physics 73, 515 (2001).

Phonons:

☐ Physical Properties:

- Specific heat, lattice expansion, heat conduction, melting.
- Electron-Phonon interaction (metals): transport (resistivity), superconductivity, optical spectra.

☐ Experimental Methods:

- Γ point (Raman/IR spectroscopy)
- Inelastic scattering (full dispersion): neutrons, X-ray, Helium.

Phonons:

☐ Theory (early approaches):

- Quantum theory of lattice vibrations (*Born et al, 30's*): dynamical properties, relation to crystal symmetries
- Empirical Force Constant Models.
- Shell Model: semi-empirical model to account for the effect of electrons on lattice properties.

☐ Modern Approaches (*Ab-initio*):

- Based on the total energy of the quantum-mechanical problem of the crystal (electrons+ions): include self-consistently the effect of electrons on phonon properties. (*De Cicco et al, Pick et al; with DFT: Cohen et al,... + many others*).

Lattice Dynamics from electronic-structure Theory:

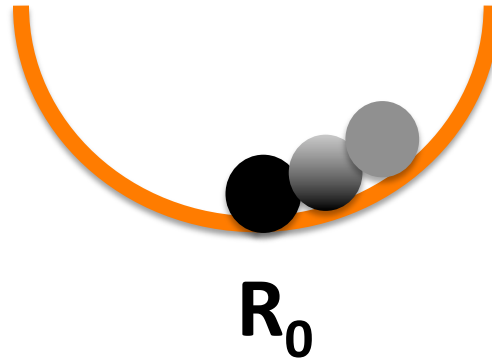
The Schroedinger equation for the nuclei reads:

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} + E(\mathbf{R}) \right] \Phi(\mathbf{R}) = \varepsilon \Phi(\mathbf{R})$$

$E(\mathbf{R})$ is the Born-Oppenheimer energy surface (solution of the electronic Schroedinger's equation for *clamped ions*).

$$H_{BO}(\mathbf{R}) = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + E_N(\mathbf{R})$$

$$E_N(\mathbf{R}) = \frac{e^2}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$



The equilibrium geometry is given by the condition that the forces on individual nuclei vanish:

$$\mathbf{F}_I = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0$$

While Phonon Frequencies can be calculated from the determinant of the Hessian matrix:

$$\det \left| \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} - \omega^2 \right| = 0$$

***Ab-initio* Lattice Dynamics:**

To calculate the *phonon* frequencies of a given system we have to compute the *second-order* variations of the energy. There are two methods for this:

- 1) ***Frozen-phonon***: Direct method (brute-force). Calculate the total energy for (small) finite displacements using **supercells**.



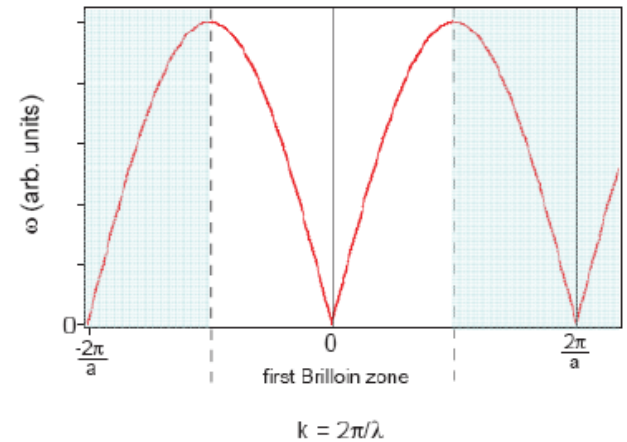
- 2) ***Linear Response***: “Elegant” Method: perturbations are “monochromatic”, all q points can be calculated with the same computational effort.



Lattice dynamics (linear chain)

$$\omega(k) = \sqrt{\frac{2k(1 - \cos(ka))}{M}} = 2\sqrt{\frac{k}{M}} \left| \sin \frac{ka}{2} \right|$$

$$u(na) = e^{i(kna - \omega t)}$$



Linear chain with 2 force constants:

$$\omega_{\pm}^2(k) = \frac{K + G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos(ka)}$$

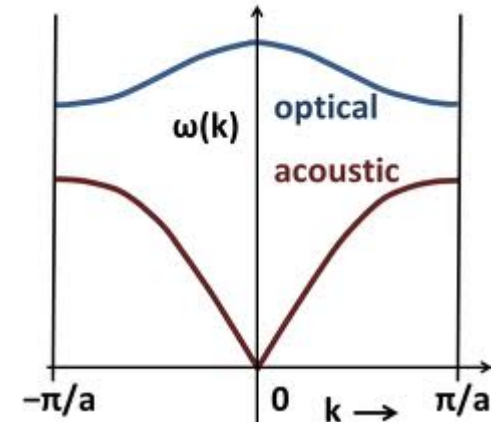
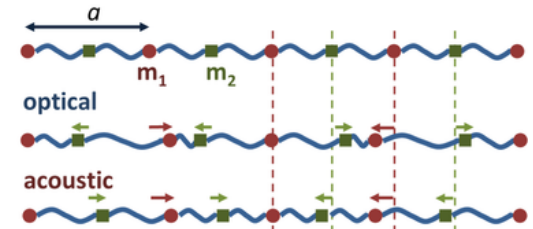
+ = optical

- = acoustical

Eigenvector:

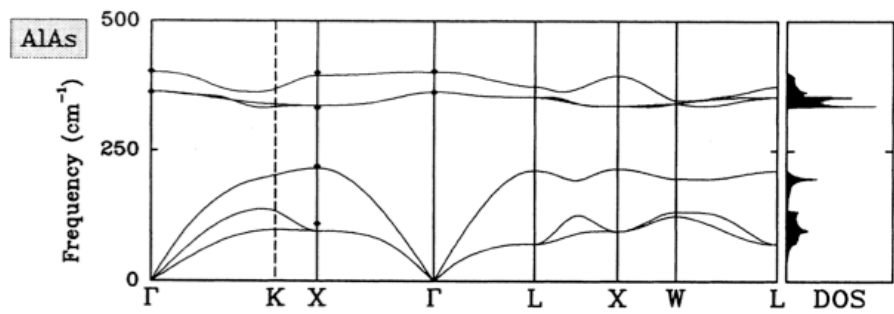
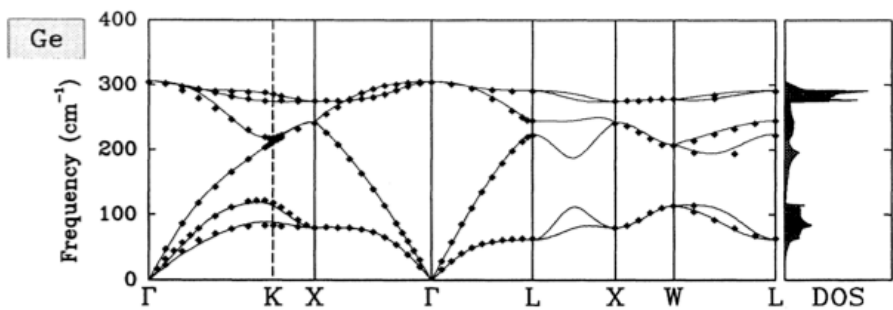
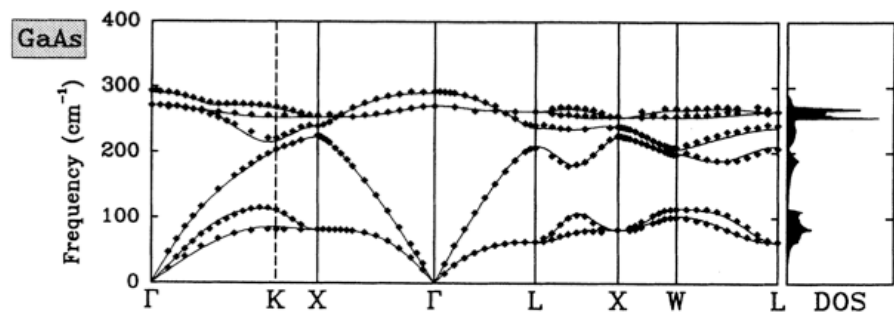
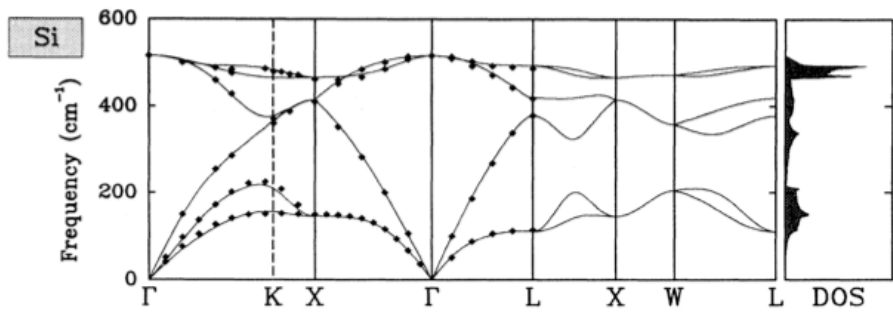
$$\frac{\varepsilon_2}{\varepsilon_1} = \mp \frac{K + Ge^{ika}}{|K + Ge^{ika}|}$$

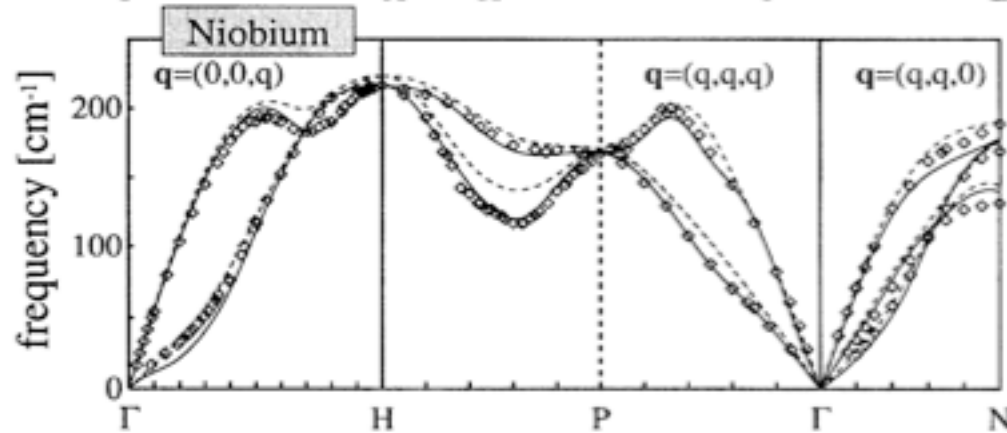
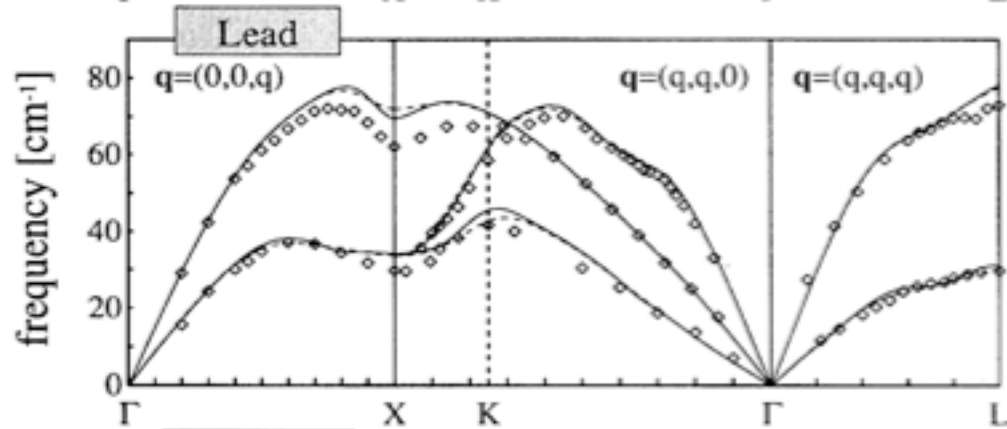
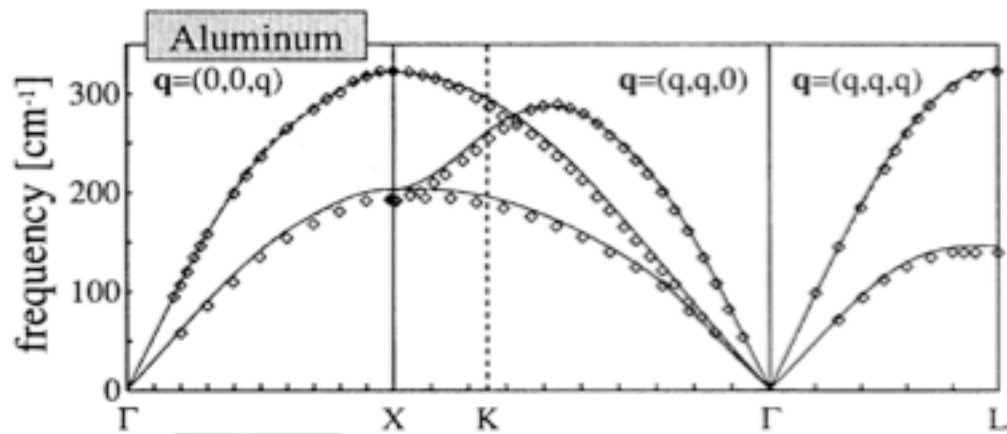
$$u_i(na) = \varepsilon_i e^{i(kna - \omega t)}$$



How to construct supercells?

EXERCISE





Metals have many small-scale structures due to electron-phonon coupling (Kohn anomalies).

Energy Gaps and Kohn Anomalies in Elemental Superconductors

P. Aynajian,¹ T. Keller,^{1,2} L. Boeri,¹ S. M. Shapiro,³ K. Habicht,⁴ B. Keimer^{1*}

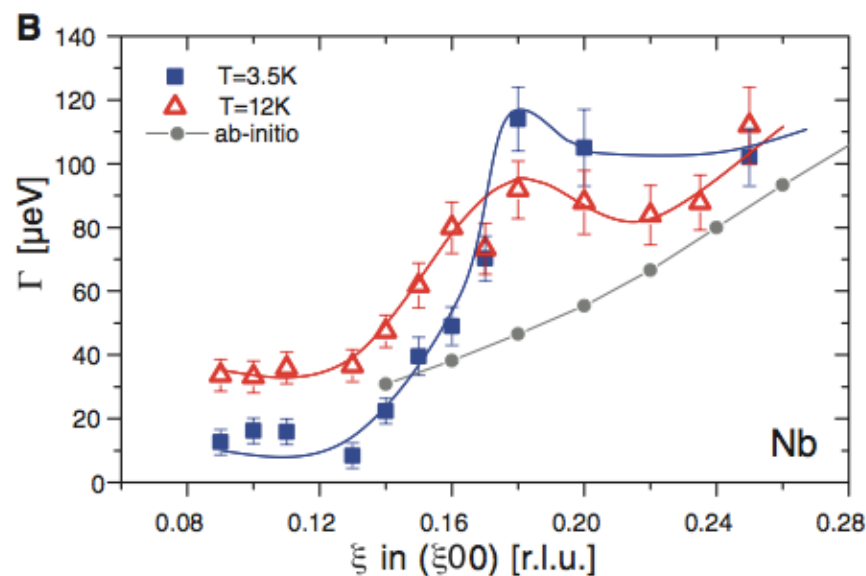
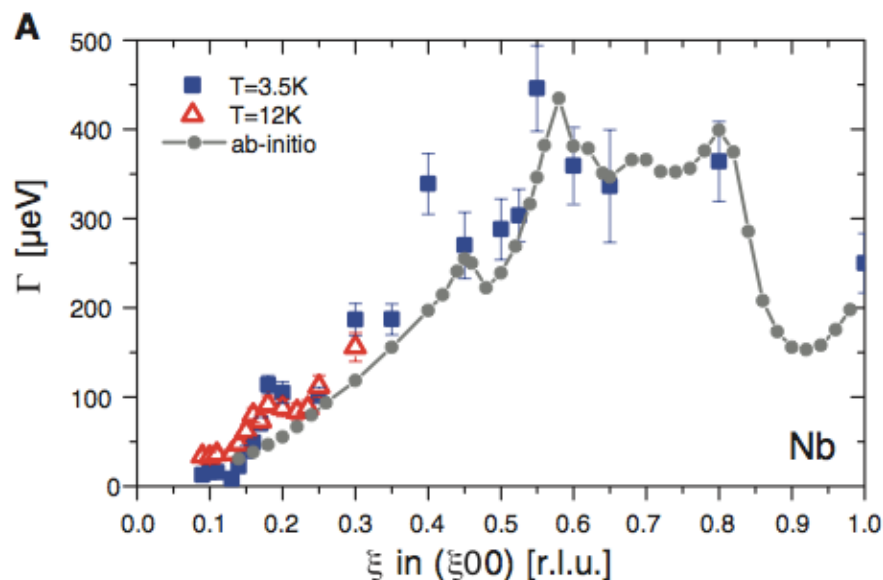


Fig. 4. (A) Linewidths of transverse acoustic phonons along $q = (\xi, 0, 0)$ in Nb at two different temperatures. The gray symbols are the results of lattice-dynamical calculations, as described in the text. **(B)** Blowup

of the low- q segment of (A). The corresponding E is provided by the scale at the top. The lines are guides to the eye. Error bars indicate the statistical errors.