# Density functional theory in solid state physics

Lecture 11

- Electronic bandstructures and density-of-states of solid materials can be calculated effectively using non-selfconsistent calculations

- A variety of derived properties is accessible if bandstructure is calculated

- Several degrees of inclusion of spin effects are possible:

  - collinear approximation: spins are either up or down, point along common axis
  - Non-collinear spin: spins do not have to be aligned (more expensive)
  - NC spin+spin-orbit coupling: inclusion of orbital splitting from relativistic effects

- DFT quite suitable for efficient study of magnetism in materials, consistent access to atomic geometry, spin structure, electronic structure and other groundstate properties

- Local XC approximations can fail to predict correct electronic band gaps, e.g. in Mott insulators.

  → hybrid functionals help, cheaper alternative is DFT+U method

- Phonons: collective excitations of crystal atoms

- Knowledge about phonon spectra is crucial to understand several material properties

  - Charge transport, electron scattering

  - Heat transport

  - Thermal expansion

  - Electron and hole lifetimes

  - Superconductivity, e.g. through phonon-mediated electron-electron interaction
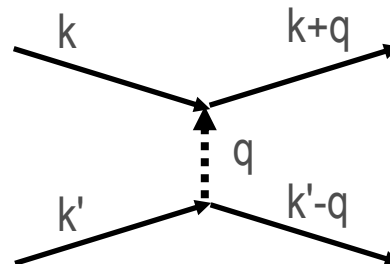
- Excitation of the lattice: increase of kinetic energy of atoms compared to potential minimum, displacement

- If displacement is sufficiently small: Harmonic approximation

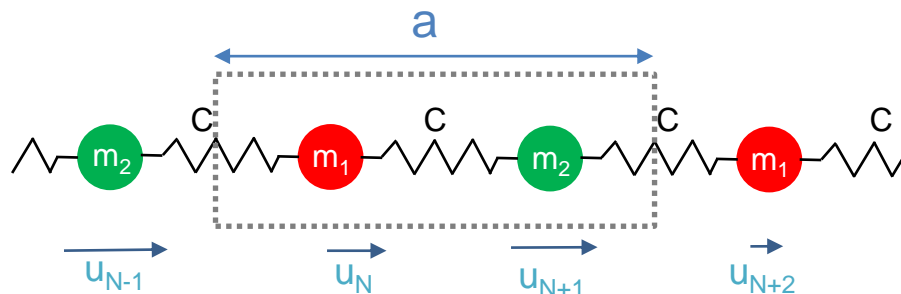$$U_{ions}(u) \approx U_{ions}(0) + \frac{1}{2}\frac{\partial^2 U_{ions}}{\partial u^2}u^2$$
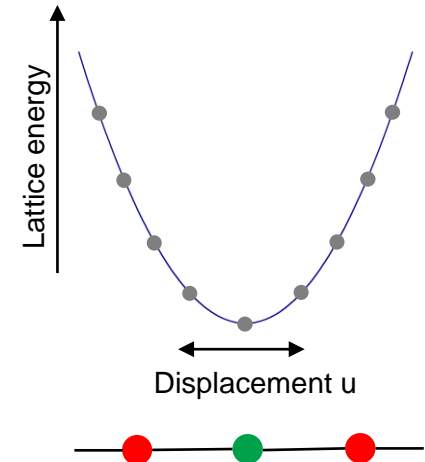
- Equation-of-motion of atom j in unit cell in 1D two-atomic chain:

$$m_j \frac{\partial^2 u_j}{\partial t^2} = F_{ext} = C(u_{j-1} - u_j) + C(u_{j+1} - u_j)$$

Ansatz:

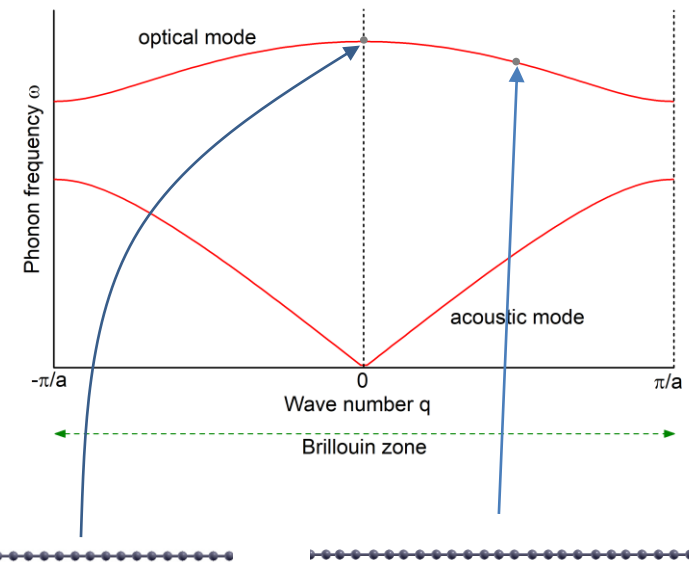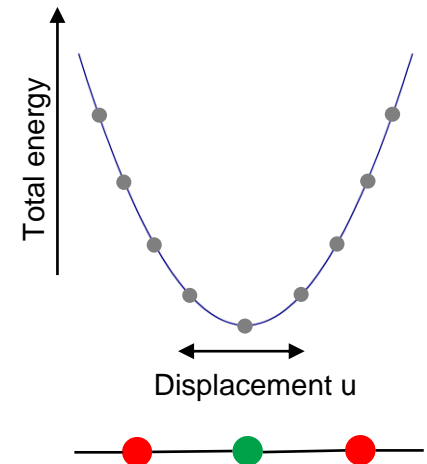$$u_j(t) = \frac{c_j(q)}{\sqrt{m_s}} e^{i\left(\frac{1}{2}q \cdot j \cdot a - \omega t\right)}$$

⋮   some algebra

$$det \left[\begin{pmatrix} \dfrac{2C}{\sqrt{m_1 m_2}} & -\dfrac{2C}{\sqrt{m_1 m_2}} cos\left(\dfrac{qa}{2}\right) \\ -\dfrac{2C}{\sqrt{m_1 m_2}} cos\left(\dfrac{qa}{2}\right) & \dfrac{2C}{\sqrt{m_1 m_2}} \end{pmatrix} - \omega^2 I \right] = 0$$

$$\underbrace{\hspace{6cm}}_{\text{dynamical matrix}}$$

$$\rightarrow \omega_{\pm}^2(q) = \frac{C}{\widetilde{m}} \pm C \sqrt{ \underbrace{\left(\frac{1}{\widetilde{m}}\right)^2}_{\frac{1}{m_1}+\frac{1}{m_2}} - \frac{4}{m_1 m_2} sin^2\left(\frac{qa}{2}\right)}$$

- Phonons: only discrete lattice excitation energies possible for specific transferred momentum transfer q

- „dispersion" in momentum space

- More general: springs between all atoms, displacements in all directions possible

$$C_{\alpha,\beta}^{i-1,i+1}$$

$$C_{\alpha,\beta}^{i,i+1}$$

i-1   *i*   *i+1*   *i+2*

$$C_{\alpha,\beta}^{i,i+2}$$

$$C_{\alpha,\beta}^{i-1,i+2}$$

- „Generalized" Hooke's Law:

$$F_{i,\alpha} = -\sum_{i'\neq i}\sum_{\beta}^{3} C_{\alpha,\beta}^{i,i'} u_{i',\beta} \qquad \left(\text{or } C_{\alpha,\beta}^{i,i'} = -\frac{\partial F_{i,\alpha}}{\partial u_{i',\beta}}\right)$$
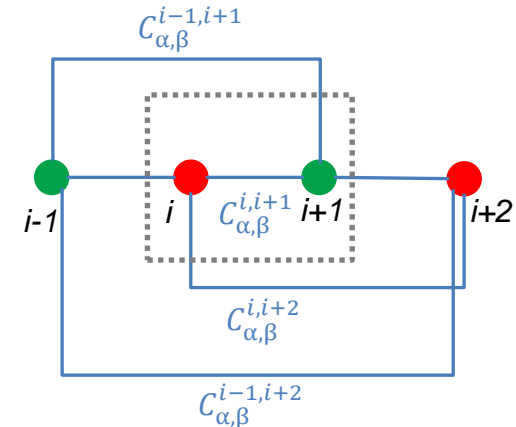
- Equation-of-motion of atom *j* in unit cell *l*

$$m_j \ddot{u}_{lj,\alpha} = -\sum_{l'=1}\sum_{j'=1}^{M}\sum_{\beta}^{3} C_{\alpha,\beta}^{lj,l'j'} u_{l'j',\beta}$$

Ansatz:

Position of unit cell

Position in unit cell

$$\vec{R}_i = \vec{t}_l + \vec{r}_j$$

$$u_{lj,\alpha}(t) = \frac{c_{j,\alpha}}{\sqrt{m_j}} e^{i(\vec{q}\cdot\vec{t}_l - \omega(\vec{q})t)}$$

- Dispersion relation

$$\omega^2(\vec{q})c_{j,\alpha} = \sum_{j'}\sum_{\beta} D_{\alpha,\beta}^{j,j'}(\vec{q})c_{j',\beta}(\vec{q})$$

$$D_{\alpha,\beta}^{j,j'}(\vec{q}) = \frac{1}{\sqrt{m_j m_{j'}}}\sum_{l'} C_{\alpha,\beta}^{0j,l'j'} e^{-i\vec{q}\cdot\vec{t}_{l'}}$$

Dynamical matrix

- Dynamical matrix has size 3Nx3N, where *N* is the number of atoms per unit cell

- Obtain dispersion relation from solving

$$det\left[D_{\alpha,\beta}^{j,j'}(\vec{q}) - \omega^2(\vec{q})\delta_{\alpha,\beta}\delta_{j,j'}\right] = 0$$

Our input

This we want for selected $\vec{q}$

- 3N eigenvalues give rise to 3N branches in the phonon dispersion

- The eigenvectors of the dynamical matrix give the atomic displacements of each phonon mode at a given wavevector $\vec{q}$

- Eigenvectors can be characterized by group theory

- Of course can also calculate phonon density-of-states, identify frequency regions with many phonon modes

- Role of DFT: Calculate the „spring constants" *C* between all (relevant) pairs of atoms to derive the dynamical matrix

- Finite displacement approach: Take ground-state geometry, displace atom j' of cell l' in direction β and derive resulting interatomic forces $F_{0j,\alpha}$:

$$C_{\alpha,\beta}^{0j,l'j'} \approx -\frac{\Delta F_{0j,\alpha}}{u_{l'j',\beta}}$$

- One displacement gives a whole row of the force constant matrix

- This is a numerical derivative, could also use *central differences* by displacing by $\pm u_{l'j',\beta}$

- But: displacement of atom in simulation cell by u also means displacement of equivalent atom in the periodic images
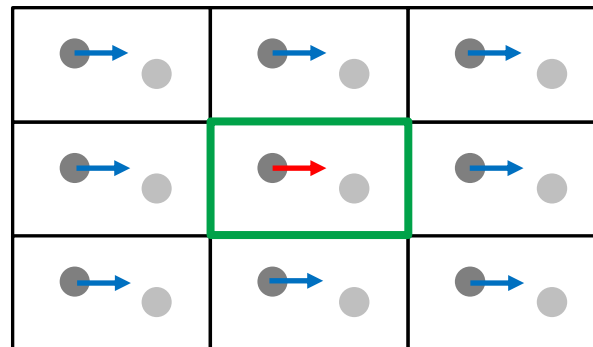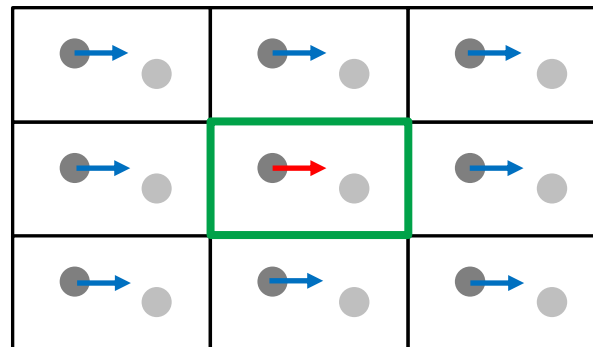
- When using the primitive cell, we don't actually calculate exact $C_{\alpha,\beta}^{lj,l'j'}$, but linear combination over periodic images
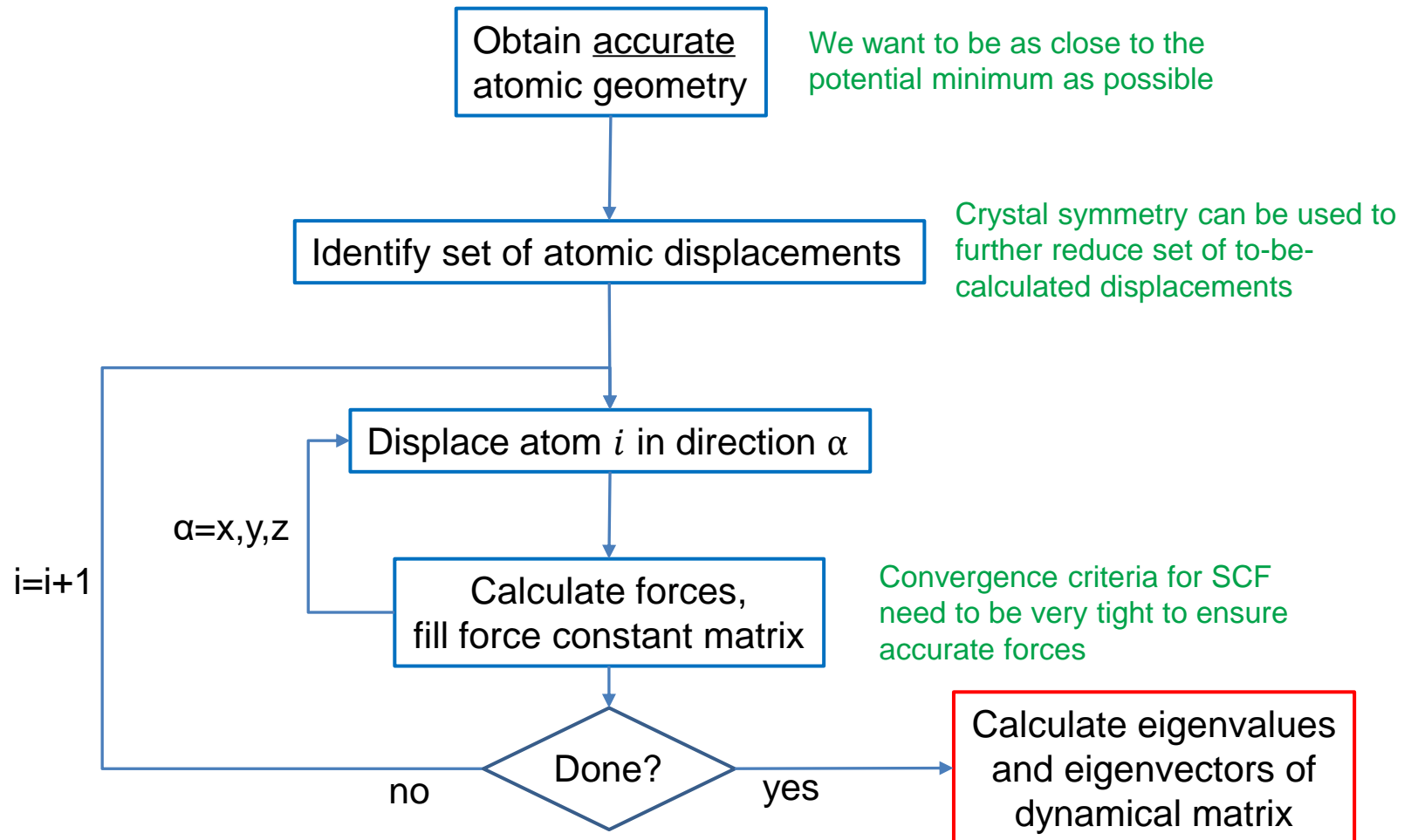
$$\tilde{C}_{\alpha,\beta}^{lj,lj'} = \sum_{l'} C_{\alpha,\beta}^{lj,l'j'} \quad \text{because } F_{0j,\alpha} = -\sum_{l'} C_{\alpha,\beta}^{lj,l'j'} u_{l'j',\beta} = u_{l'j',\beta} \sum_{l'} C_{\alpha,\beta}^{lj,l'j'}$$

i.e. we have no information about the effect of other unit cells on force constants

- Due to periodic boundary conditions, all unit cells are equivalent and we only need to displace atoms in one unit cell, i.e. consider $\tilde{C}_{\alpha,\beta}^{0j,0j'}$

- Dynamical matrix is only exact for $\vec{q} = 0$ when using primitive cell

- Scheme for FD calculation of $\vec{q} = 0$ phonons

Obtain <u>accurate</u> atomic geometry

We want to be as close to the potential minimum as possible

Identify set of atomic displacements

Crystal symmetry can be used to further reduce set of to-be-calculated displacements

Displace atom i in direction α

α=x,y,z

i=i+1

Calculate forces, fill force constant matrix

Convergence criteria for SCF need to be very tight to ensure accurate forces

Done?

no   yes

Calculate eigenvalues and eigenvectors of dynamical matrix

- Example: Monolayer MoS_2

- 3 atoms per unit cell → 9 phonon modes

Mode	Frequency (cm^{-1})
1	0
2	0
3	0
4	289.1
5	289.1
6	391.4
7	391.4
8	410.4
9	476.5
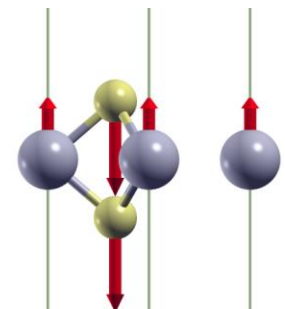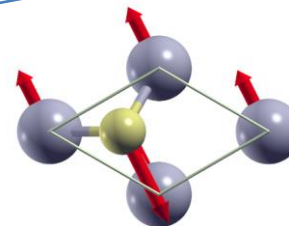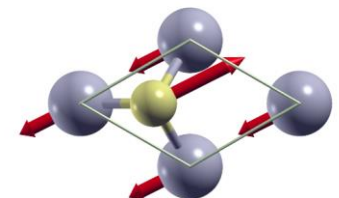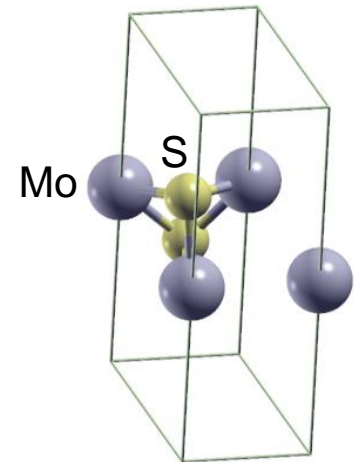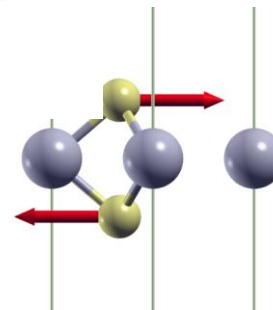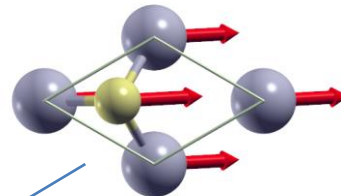
- Monolayer MoS_2: space group $P\bar{6}m2$

- Factor group analysis (q=0): $2A_2'' + 2E' + A_1' + E''$

Mode	Frequency (cm^{-1})	Symmetry
1	0	E''
2	0	E'
3	0	A_2''
4	289.1	E''
5	289.1	E''
6	391.4	E'
7	391.4	E'
8	410.4	A_1'
9	476.5	A_2''

Symmetry determines Raman or infrared activity

Raman-active

Infrared-active

- Planewave energy cutoff means that we also only have discrete sampling in real space unit cell, e.g. for electron density etc.

- Discrete sampling slightly breaks translation invariance of space

- „Eggbox" effect: total energy of system can very slightly vary with small rigid shift of atoms in unit cell

  -> can be a problem for acoustic modes, causing non-zero frequencies of up to $\pm 50 \; cm^{-1}$

- Typical approach: correct dynamical matrix to satisfy acoustic sum rule (ASR)

$$\sum_j D_{\alpha,\beta}^{j,j'}(\vec{q}=0) = 0$$

- Several schemes how to best achieve this exist, details depend on code

- Typically only correction for low-frequency modes, higher modes unaffected

- DFT (usually) quite reliable for phonons, but agreement strongly depends on v_{xc}

- Error of frequencies typically below 5%, often much lower

- LDA typically overestimates phonon frequencies, PBE and PBEsol underestimate

- Better agreement of phonon frequencies often comes at the cost of worse prediction of lattice constants

- Inclusion of van-der-Waals interactions is very beneficial in layered or molecular systems

Bulk MoS_2
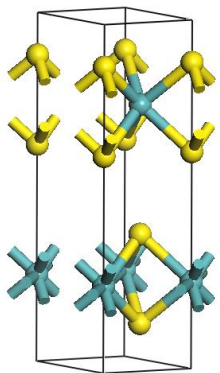
	LDA	PBE	PBE-D3	Exp.
	a=3.125, c= 12.07	a=3.19, c= 14.3	a=3.15, c= 12.09	a=3.16, c=12.3
E_{2g}	36.4	8.5	33	**32[b]**
E_{1g}	289	276	284	**286[b]**
E_{2g}	384	372.2	380.1	**383[a,b]**
E_{1u}	384.5	372.8	380.4	**384[a]**
A_{1g}	412.8	396.4	410	**408, 409[a,b]**
A_{2u}	470.0	457.4	463.3	**462[c]**

[a] Phys. Rev. Lett. 25, 362 (1970)   [c] Solid State Commun. 14, 857 (1974)   [c] Adv. Funct. Mat. 22, 1385 (2012)

- How about phonon *dispersions*?

- FD scheme: Cannot easily resolve force constants between different unit cells, due to periodic boundary conditions

- Supercell method:
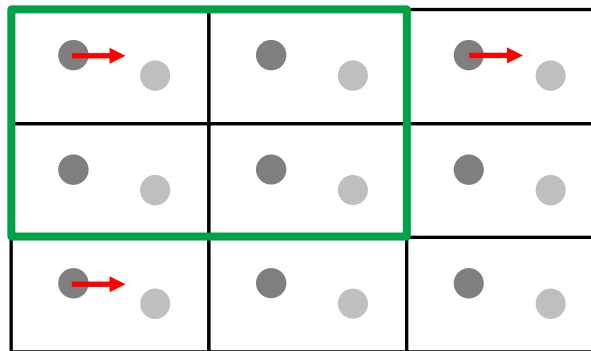

$$\tilde{C}_{\alpha,\beta}^{0j,l'j'} = \sum_L C_{\alpha,\beta}^{lj,(l'+L)j'}$$

(l' is index of unit cell within supercell, L is index of supercell)

- Now also have some info about longer-range force constants

- Using $\tilde{C}_{\alpha,\beta}^{0j,lj'}$, the dynamical matrix is only exact for phonon wavevectors $\vec{q}$ with $\vec{q} \cdot \vec{t}_L = n2\pi$

- For all other wavevectors, the dynamical matrix is Fourier interpolated

$$\omega^2(\vec{q})c_{j,\alpha} = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{j'} \sum_{\beta} \sum_{l'} \sum_L e^{i\vec{q}\cdot\vec{t}_L} C_{\alpha,\beta}^{lj,(l'+L)j'} e^{-i\vec{q}\cdot\vec{t}_{l'+L}} c_{j',\beta}(\vec{q})$$

- Supercell size has to be chosen large enough that the interpolation of the dynamical matrix is good enough (no artificial wiggles)

- Luckily: force constants decay quickly with $1/r^5$ (in non-polar solids), supercells with lattice constants of 10-15 Å usually enough, less for metals

- Example: Silicon, LDA, 5x5x5 supercell
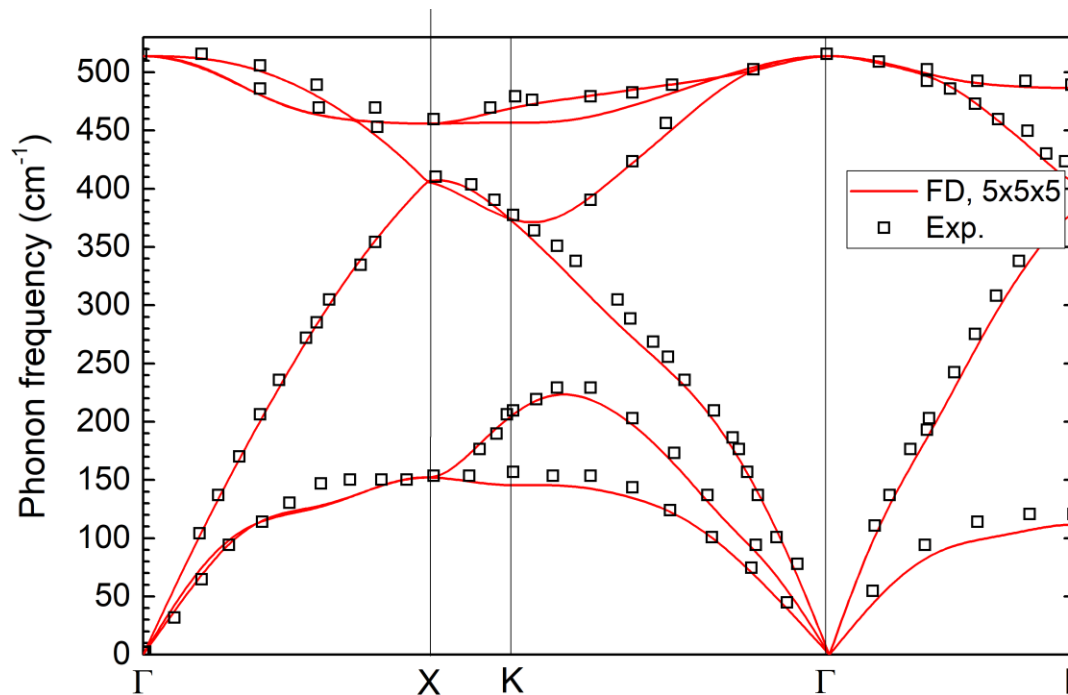
Phys. Rev. B 50, 347 (1994)

- Alternative method for phonons: Density functional perturbation theory (DFPT)

- Idea: Force constants can be written as *second derivatives of Kohn-Sham energy*

$$C_{\alpha,\beta}^{lj,l'i'} = -\frac{\partial F_{lj,\alpha}}{\partial u_{l'i',\beta}} = \frac{\partial^2 E_{KS}}{\partial u_{lj,\alpha}\partial u_{i',\beta}}$$

- Similarly, the dynamical matrix can be written as

$$D_{\alpha,\beta}^{j,i'}(\vec{q}) = -\frac{1}{\sqrt{m_j m_{j'}}}\frac{\partial^2 E_{KS}}{\partial \tilde{u}_{lj,\alpha}^*(\vec{q})\partial \tilde{u}_{i',\beta}(\vec{q})}$$

Fourier transformation of *u*

- Derivatives:

External potential from nuclei

$$\frac{\partial E_{KS}}{\partial u_i} = \int \frac{\partial v(r)}{\partial u_i}n(r)dr + \int \frac{\partial E_{KS}}{\partial n(r)}\frac{\partial n(r)}{\partial u_i}dr$$

Hellmann-Feynman forces

$$\frac{\partial^2 E_{KS}}{\partial u_i \partial u_j} = \int \frac{\partial v(r)}{\partial u_i}\frac{\partial n(r)}{\partial u_j}dr + \int n(r)\frac{\partial^2 v(r)}{\partial u_i \partial u_j}dr$$
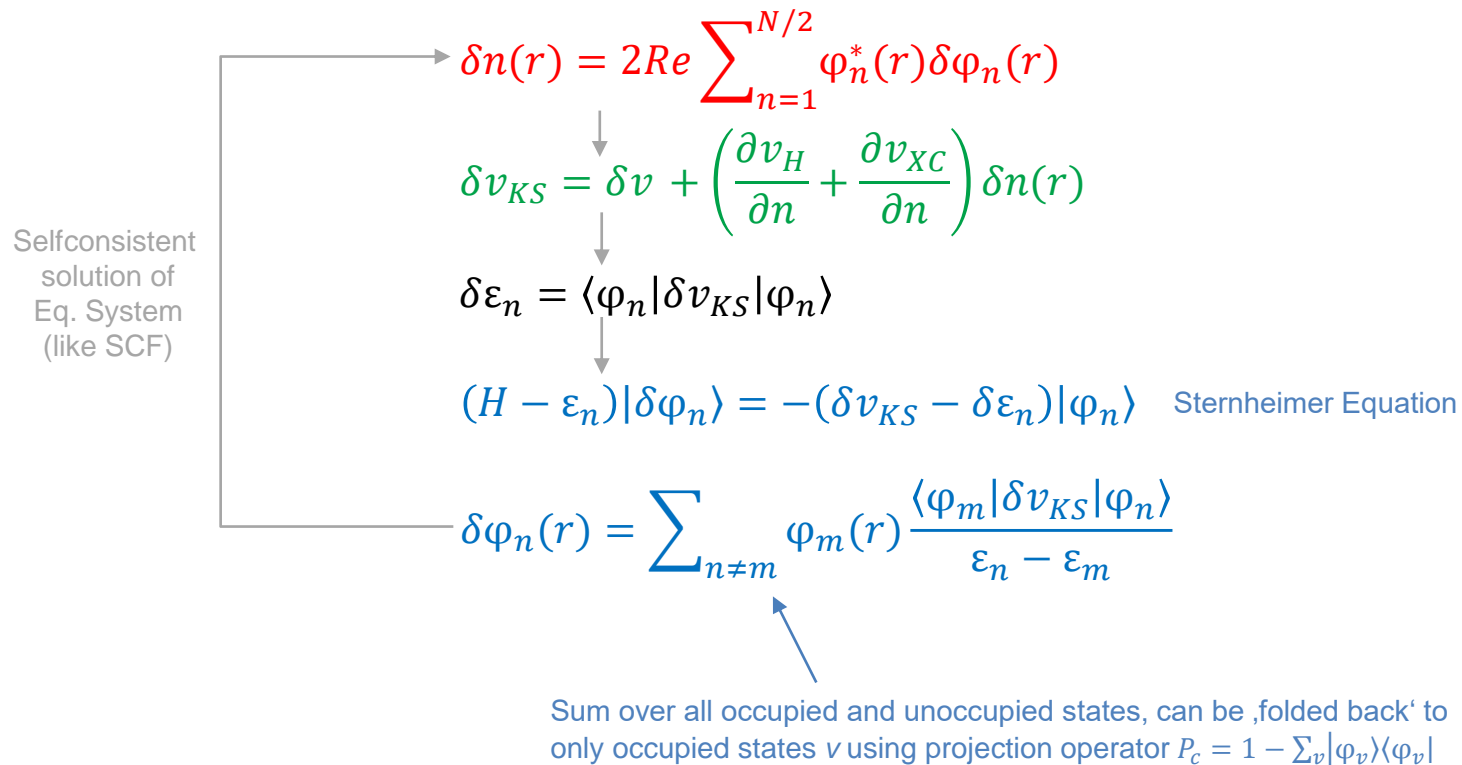
This we need   This we can easily calculate
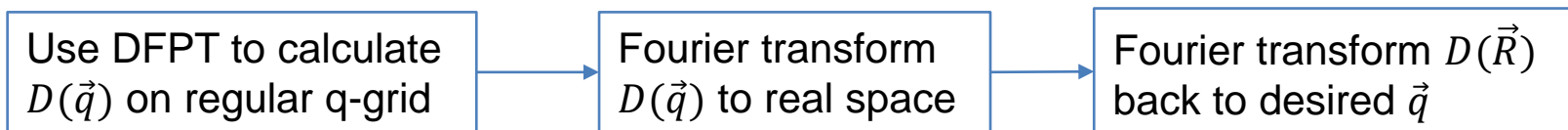
- Linear response ansatz: wavefunctions, electron density and potentials can be written as a perturbation series

$$Y(\lambda) = Y + \lambda \underbrace{\left.\frac{\partial Y}{\partial \lambda}\right|_{\lambda=0}}_{\delta Y} + \cdots$$

λ : Small perturbation parameter

- For semiconductors/insulators:

$$\delta n(r) = 2Re \sum_{n=1}^{N/2} \varphi_n^*(r)\delta\varphi_n(r)$$

$$\delta v_{KS} = \delta v + \left(\frac{\partial v_H}{\partial n} + \frac{\partial v_{XC}}{\partial n}\right)\delta n(r)$$

$$\delta\varepsilon_n = \langle\varphi_n|\delta v_{KS}|\varphi_n\rangle$$

$$(H - \varepsilon_n)|\delta\varphi_n\rangle = -(\delta v_{KS} - \delta\varepsilon_n)|\varphi_n\rangle \quad \text{Sternheimer Equation}$$

$$\delta\varphi_n(r) = \sum_{n \neq m} \varphi_m(r)\frac{\langle\varphi_m|\delta v_{KS}|\varphi_n\rangle}{\varepsilon_n - \varepsilon_m}$$

Selfconsistent solution of Eq. System (like SCF)

Sum over all occupied and unoccupied states, can be ,folded back' to only occupied states v using projection operator $P_c = 1 - \sum_v |\varphi_v\rangle\langle\varphi_v|$

- Implementations for normconserving, ultrasoft pseudopotentials and PAWs exist

- More details (with lots of math) can be found in Phys Rev Mod 73, 515 (2001)

- Convenient: - We can calculate perturbation of Kohn-Sham potential for any $\vec{q}$ simply using the primitive cell, no need for supercells

          - We can obtain phonon dispersion easily through interpolation:

Use DFPT to calculate $D(\vec{q})$ on regular q-grid	→	Fourier transform $D(\vec{q})$ to real space	→	Fourier transform $D(\vec{R})$ back to desired $\vec{q}$

- We now only need to calculate N_q $(= N_R)$ interatomic force constants instead of N_R^2

- Can also calculate higher order force constants (anharmonic effects) using the „(2n+1) theorem"

- Silicon phonon dispersion, DFPT vs. FD

- Time spent for FD run: 75 mins with 20 CPUs
- Time spent for DFPT run: 20 mins with 20 CPUs
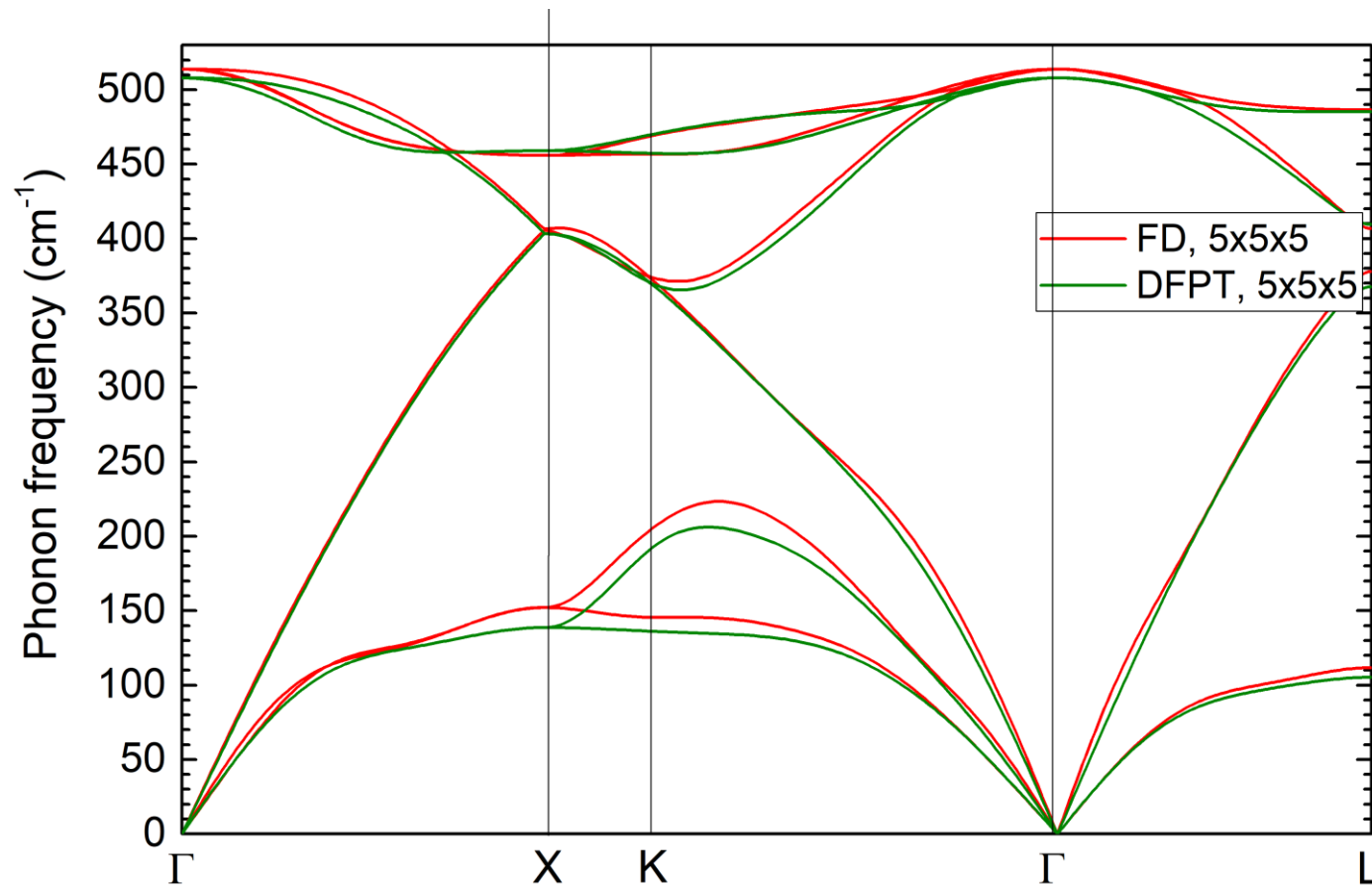
- Atomic motion causes polarization of non-metallic crystals

- The resulting long-range dipole-dipole interaction gives rise to a macroscopic electric field, which creates resistance for longitudinal-optical (LO) modes, but not for the TO modes

- This causes a frequency gap between (otherwise) degenerated LO-TO modes (LO-TO-splitting) for $\vec{q} \rightarrow 0$

- Inclusion through a (direction dependent) non-analytical contribution to dynamical matrix

$$\widetilde{D}_{\alpha,\beta}^{j,j'}(\vec{q} \rightarrow 0) = \frac{4\pi}{V\sqrt{m_j m_{j'}}} \frac{(\vec{q} \cdot Z_j^*) \cdot (\vec{q} \cdot Z_{j'}^*)}{\vec{q} \cdot \varepsilon_\infty \cdot \vec{q}}$$

- Born effective charge tensor $Z_{j,\alpha\beta}^* = \frac{\partial^2 E_{KS}}{\partial u_{0j,\alpha} \partial G_\beta}$ and dielectric permitivity $\varepsilon_\infty = \delta_{\alpha\beta} - \frac{\partial^2 E_{KS}}{\partial G_\alpha \partial G_\beta}$ can be calculated using DFPT

  External electric field component

- DFPT allows us also straight-forward ab initio access to Infrared and Raman *intensities*

- Infrared intensity of phonon mode *i*:
$$I_i^{IR} \propto \left| \sum_{k=1}^{3N} \frac{d\vec{\mu}}{dR_{k\alpha}} c_{ik\alpha} \right|^2$$

  Dipole moment

$$\propto \sum_\beta \left| \sum_\alpha \sum_{k=1}^{3N} \frac{\partial^2 E_{KS}}{\partial G_\beta \partial R_{k\alpha}} c_{ik\alpha} \right|^2$$

- 1st order Raman cross section of mode *i*:
$$\frac{d\sigma_i}{d\Omega} \propto \left| \vec{e}_S \cdot \left(\sum_\gamma \sum_{k=1}^{3N} \frac{d\vec{\alpha}}{dR_{k\gamma}} c_{ik\gamma} \right) \cdot \vec{e}_L \right|^2$$

  Polarizability tensor

  (nonresonant)
$$\propto \left| e_{S,\beta} \cdot \left(\underbrace{\sum_\gamma \sum_{k=1}^{3N} \frac{\partial^3 E_{KS}}{\partial G_\beta \partial G_\nu \partial R_{k\gamma}} c_{ik\gamma}}_{\text{Raman tensor } \tilde{R}} \right) \cdot e_{L,\nu} \right|^2$$
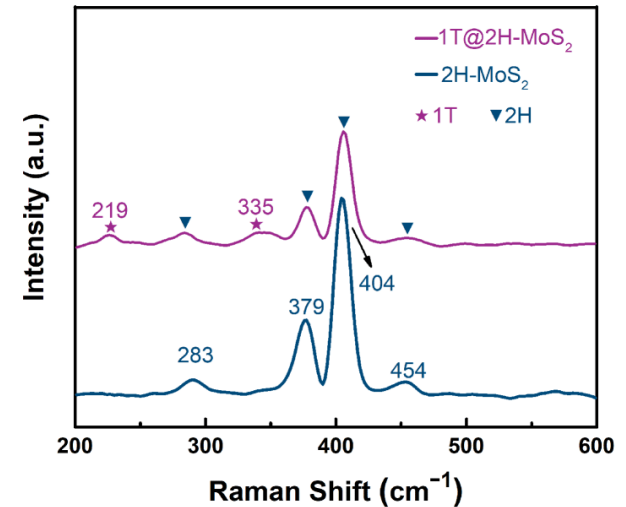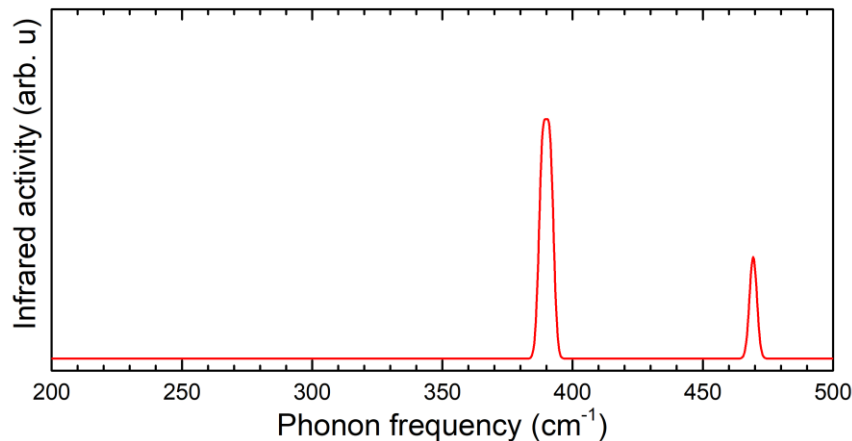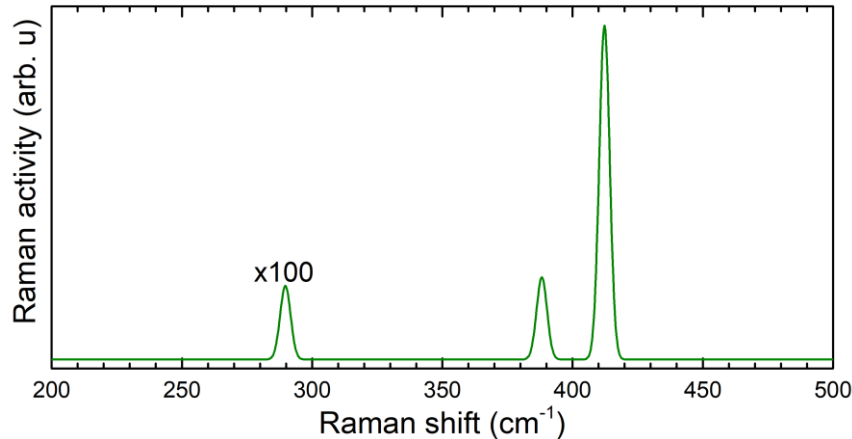
- Raman-scattering activity: $I^R = 45{\alpha'}^2 + 7{\beta'}^2$

  Averaged over all incident and scattering directions

  with $\alpha' = \frac{1}{3}(\tilde{R}_{xx} + \tilde{R}_{yy} + \tilde{R}_{zz})$, $\beta' = \frac{1}{2}\left[\sum_{\gamma,\nu>\gamma}(\tilde{R}_{\gamma\gamma} - \tilde{R}_{\nu\nu})^2 + 6(\tilde{R}_{xy}^2 + \tilde{R}_{xz}^2 + \tilde{R}_{yz}^2) \right]$

- Energy derivatives can be calculated using DFPT+"(2n+1)" theorem

Phys. Rev. B 54, 7830 (1996)

- Example: (bulk) 2H-MoS$_2$

Nanomaterials 9, 844 (2019)

- Relative intensities from DFPT often quite good, but subject to errors from „Placzek approximation" (i.e. that the Raman tensor is determined by polarizability change)

- Some degree of caution always has to be kept when comparing DFT phonon frequencies to experimental data

- Some error comes from neglecting anharmonic effects

$$U_{ion}(u) \approx U_{ion}(0) + \frac{1}{2}\frac{\partial^2 U_{ions}}{\partial u^2}u^2 + \frac{1}{6}\frac{\partial^3 U_{ions}}{\partial u^3}u^3 + \frac{1}{24}\frac{\partial^4 U_{,ions}}{\partial u^4}u^4 + \cdots$$

Third−order "force constants"

- Temperature-dependent phonon-phonon scattering in the 3rd and 4th order terms can renormalize phonon frequencies

- Anharmonic effects are responsible for lattice expansion, thermal conductivity etc.

- Can be treated as well within a DFPT framework (but expensive!!!!)