

Phonons and Electron-Phonon Couplings

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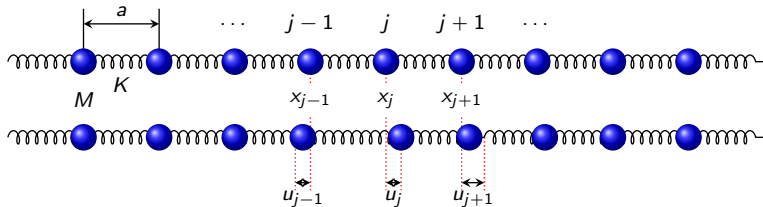
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1 Lattice Dynamics

- 1D Atomic Chain
- 3D Lattice
- How to calculate the dynamical matrix

1D Chain of Atoms — 1 Atom per Unit

A 1D chain of N equally spaced atoms at $R_j(t) = x_j + u_j(t)$



The Newton's Equation

$$M \frac{d^2 u_j}{dt^2} = K(u_{j+1} + u_{j-1} - 2u_j) \quad j = 1, \dots, N$$

Assume the solution has the form $u_j(t) = \frac{A_q}{\sqrt{M}} e^{i(qx_j - \omega t)}$, then ¹

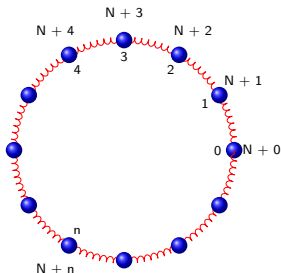
$$\begin{aligned} \omega^2 &= \frac{K}{M} (2 - e^{iqa} - e^{-iqa}) \\ &= \frac{2K}{M} (1 - \cos qa) \\ \Rightarrow \quad \omega &= \sqrt{\frac{4K}{M}} \left| \sin \frac{qa}{2} \right| \end{aligned}$$

¹ $u_j(t)$ here is complex. In practice, take the real part, i.e. $\text{Re}[u_j(t)]$.

The Born-von Karman Periodic Boundary Condition:

$$u_n = u_{N+n} \Rightarrow e^{iqx_j} = e^{iqx_{N+j}} \Rightarrow e^{iqNa} = 1$$

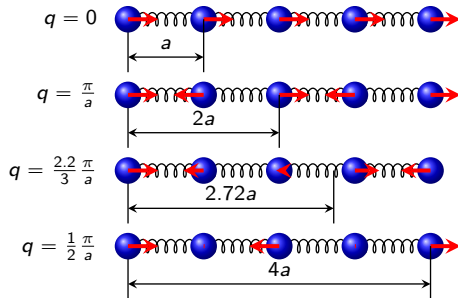
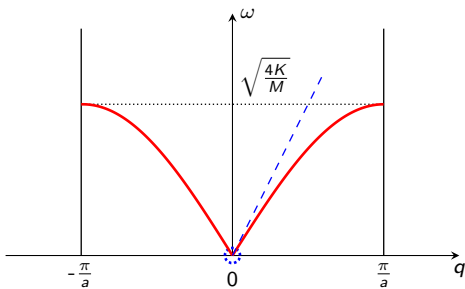
$$\Rightarrow q = \frac{2\pi}{a} \frac{l}{N}; \quad (l = 0, 1, \dots, N)$$



Usually, q is restricted within the first Brillouin Zone

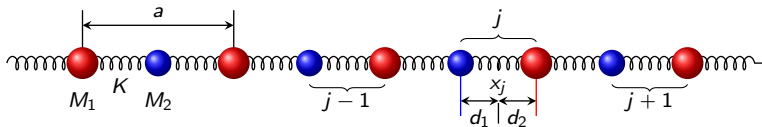
$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}$$

1D Chain of Atoms



1D Chain of Atoms — 2 Atoms per Unit

A 1D chain with 2 atoms in each unit: $R_s^j(t) = x_j + d_s + u_s^j(t)$; $s = 1, 2$



The Newton's Equation

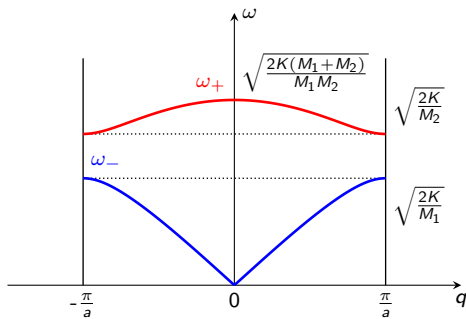
$$\begin{aligned} M_1 \frac{d^2 u_1^j}{dt^2} &= K(u_2^j + u_2^{j-1} - 2u_1^j) \\ M_2 \frac{d^2 u_2^j}{dt^2} &= K(u_1^j + u_1^{j+1} - 2u_2^j) \end{aligned} \quad \Rightarrow \quad \begin{cases} u_1^j(t) = \frac{A_q}{\sqrt{M_1}} e^{i(qx_j - \omega t)} \\ u_2^j(t) = \frac{B_q}{\sqrt{M_2}} e^{i(qx_j - \omega t)} \end{cases}$$

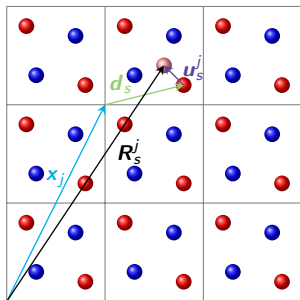
We then have

$$\begin{pmatrix} \frac{2K}{M_1} & \frac{-K}{\sqrt{M_1 M_2}} (1 + e^{-iqa}) \\ \frac{-K}{\sqrt{M_1 M_2}} (1 + e^{iqa}) & \frac{2K}{M_2} \end{pmatrix} \begin{pmatrix} A_q \\ B_q \end{pmatrix} = \omega^2 \begin{pmatrix} A_q \\ B_q \end{pmatrix}$$

$$\Rightarrow \quad \omega_{\pm}^2 = \frac{K}{M_1 M_2} \left((M_1 + M_2) \pm \sqrt{M_1^2 + M_2^2 + 2M_1 M_2 \cos qa} \right)$$

1D Chain of Atoms





- \mathbf{x}_j : the position of unit cell j
- \mathbf{d}_s : the equilibrium position of the atom s in the cell
- \mathbf{u}_s^j : displacement from the equilibrium position for the atom s in the cell j
- \mathbf{R}_s^j : the position of the atom s in the cell j

$$\begin{aligned}\mathbf{R}_s^j(t) &= \mathbf{x}_j + \mathbf{d}_s + \mathbf{u}_s^j(t) \\ &= \mathbf{r}_s^j + \mathbf{u}_s^j(t)\end{aligned}$$

$$R_{s\alpha}^j(t) = r_{s\alpha}^j + u_{s\alpha}^j(t) \quad (\alpha = x, y, z)$$

The total energy can be written as

$$E_{\text{tot}}(\{\mathbf{R}_s^j(t)\}) = E_{\text{tot}}^0(\{\mathbf{r}_s^j\}) + \sum_{js\alpha} \frac{\partial E_{\text{tot}}^0}{\partial u_{s\alpha}^j} u_{s\alpha}^j + \frac{1}{2} \sum_{js\alpha} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} u_{s\alpha}^j u_{t\beta}^k + \dots$$

- The expression is exact if we take all the orders in the expansion.
- All the derivatives are taken at the equilibrium positions $\{\mathbf{r}_s^j\}$, i.e. $\frac{\partial E_{\text{tot}}^0}{\partial u_{s\alpha}^j} = 0$.
- Harmonic approximation: truncated at *second* order.

Within the harmonic approximation, the Newton's equation for the atom s in cell j

$$M_s \frac{d^2 u_{s\alpha}^j(t)}{dt^2} = - \frac{\partial E_{\text{tot}}}{\partial u_{s\alpha}^j} = - \sum_{kt\beta} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} u_{t\beta}^k = - \sum_{kt\beta} C_{s\alpha,t\beta}^{j,k} u_{t\beta}^k \quad (1)$$

The ansatz of the solution

$$u_{s\alpha}^j(t) = \frac{\eta_{s\alpha}^\sigma(\mathbf{q})}{\sqrt{M_s}} e^{i\mathbf{q}\cdot\mathbf{x}_j} e^{-i\omega_\sigma t} \quad (2)$$

Substitute Eq. 2 into Eq. 1

$$\omega_\sigma^2(\mathbf{q}) \eta_{s\alpha}^\sigma = \sum_{t\beta} \left[\sum_k \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} e^{i\mathbf{q}\cdot(\mathbf{x}_k - \mathbf{x}_j)} \right] \eta_{t\beta}^\sigma = \sum_{t\beta} D_{s\alpha,t\beta}(\mathbf{q}) \eta_{t\beta}^\sigma$$

In matrix form

$$\begin{pmatrix} \ddots & & \\ & D_{s\alpha,t\beta}(\mathbf{q}) & \\ & & \ddots \end{pmatrix}_{3N_a \times 3N_a} \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix}_{3N_a} = \omega^2(\mathbf{q}) \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix}_{\text{polarization vector}}$$

where $\sigma = 1, \dots, 3N_a$ and N_a is the number of atoms in the *primitive cell*.

The Interatomic Force Constants (IFC)

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = C_{s\alpha,t\beta}^{j,k}$$

- Symmetric because partial differentiation is commutative

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{t\beta}^k \partial u_{s\alpha}^j} \Rightarrow C_{s\alpha,t\beta}^{j,k} = C_{t\beta,s\alpha}^{k,j} \quad (3)$$

- Translation invariance, only depend on the difference between j and k

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^{(k-j)}} \Rightarrow C_{s\alpha,t\beta}^{j,k} = C_{s\alpha,t\beta}^{0,k-j} \quad (4)$$

- Acoustic Sum Rule (ASR): if we displace the whole solid by an arbitrary uniform displacement, the forces acting on the atoms must be zero.

$$F_{s\alpha}^j = - \sum_{\beta} \left[\sum_{kt} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} \right] \delta_{\beta} = 0 \Rightarrow \sum_{kt} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = 0 \quad (5)$$

The Dynamical Matrix

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^l} e^{i\mathbf{q}\mathbf{x}_l} = \frac{1}{\sqrt{M_s M_t}} \sum_l C_{s\alpha,t\beta}^{0,l} e^{i\mathbf{q}\mathbf{x}_l}$$

- If we define the distortion pattern $\mathbf{u}_s^l(\mathbf{q}) = \mathbf{v}_s(\mathbf{q}) e^{i\mathbf{q}\mathbf{x}_l}$

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{N} \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E_{\text{tot}}^0}{\partial v_{s\alpha}^*(\mathbf{q}) \partial v_{t\beta}(\mathbf{q})}$$

- Dynamical matrix is Hermitian and admit real eigenvalues $\omega^2(\mathbf{q})$

$$D_{s\alpha,t\beta}(\mathbf{q}) = D_{t\beta,s\alpha}^*(\mathbf{q})$$

PROOF

$$\begin{aligned} D_{s\alpha,t\beta}(\mathbf{q}) &= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{s\alpha,t\beta}^{0,l} e^{i\mathbf{q}\mathbf{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{s\alpha,t\beta}^{-l,0} e^{i\mathbf{q}\mathbf{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{t\beta,s\alpha}^{0,-l} e^{i\mathbf{q}\mathbf{x}_l} \end{aligned} \quad \rightarrow \quad \begin{aligned} D_{s\alpha,t\beta}^*(\mathbf{q}) &= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{t\beta,s\alpha}^{0,-l} e^{-i\mathbf{q}\mathbf{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C_{t\beta,s\alpha}^{0,l} e^{i\mathbf{q}\mathbf{x}_l} \\ &= D_{t\beta,s\alpha}(\mathbf{q}) \end{aligned}$$

The eigenvectors $\boldsymbol{\eta}^\sigma(\mathbf{q})$ of the Hermitian matrix $D_{s\alpha,t\beta}(\mathbf{q})$ are called the phonon polarization vector.

- The polarization vector is *cell-periodic*.

$$u_{s\alpha}^j(t) = \frac{\eta_{s\alpha}^\sigma(\mathbf{q})}{\sqrt{M_s}} e^{i\mathbf{q}\cdot\mathbf{r}_j} e^{-i\omega_\sigma t}$$

So the solution is a cell-periodic part multiply by $e^{i\mathbf{q}\cdot\mathbf{x}}$ — Bloch's theorem.

- Orthogonalization relation:

$$\sum_{s\alpha} \eta_{s\alpha}^{\sigma'}(\mathbf{q}) \eta_{s\alpha}^\sigma(\mathbf{q}) = \delta_{\sigma\sigma'}; \quad \sum_{\sigma} \eta_{s\alpha}^{\sigma*}(\mathbf{q}) \eta_{t\beta}^\sigma(\mathbf{q}) = \delta_{st} \delta_{\alpha\beta}$$

- Relation to phonon displacement — direction and amplitude of the vibration.

$$\xi_{s\alpha}^\sigma = \frac{1}{\sqrt{M_s}} \eta_{s\alpha}^\sigma(\mathbf{q})$$

- At some high-symmetry \mathbf{q} -path

$$\begin{cases} \mathbf{q} \parallel \boldsymbol{\eta}(\mathbf{q}) & \text{Longitudinal Wave} \\ \mathbf{q} \perp \boldsymbol{\eta}(\mathbf{q}) & \text{Transverse Wave} \end{cases}$$

How to Calculate the Dynamical Matrix I

The definition of the dynamical matrix

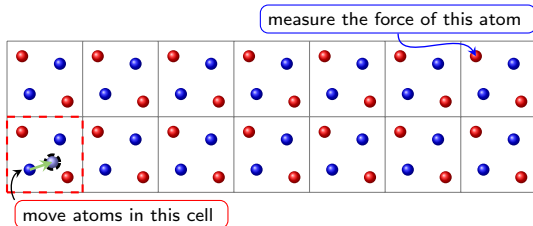
$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{l=-\infty}^{\infty} C_{s\alpha,t\beta}^{0,l} e^{i\mathbf{q}\cdot\mathbf{x}_l} \approx \frac{1}{\sqrt{M_s M_t}} \sum_{|l| < l_{\text{cut}}} C_{s\alpha,t\beta}^{0,l} e^{i\mathbf{q}\cdot\mathbf{x}_l} \quad (6)$$

① Finite-difference and supercell approach — Frozen phonon method

IFC by finite-difference:

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^l} = \frac{\partial F_{t\beta}^l}{\partial u_{s\alpha}^0}$$

$$\approx \frac{F_{t\beta}^l(\Delta_{s\alpha}) - F_{t\beta}^l(-\Delta_{s\alpha})}{2\Delta_{s\alpha}}$$

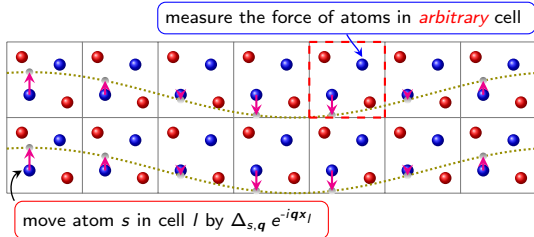


- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done **only** in one primitive cell.
- $3 \times N_a \times 2$ movements, i.e. move by $\pm \Delta$ in x/y/z directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of movements.
- The dynamical matrix can then be obtained at arbitrary \mathbf{q} by Eq. 6.

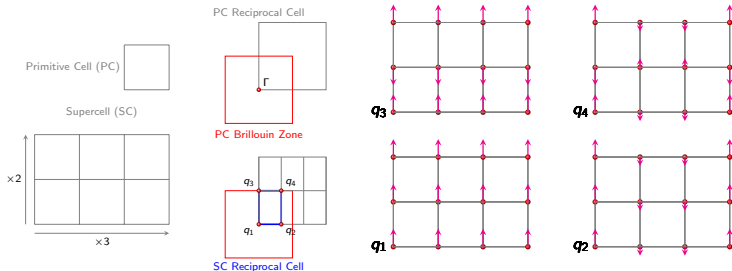
How to Calculate the Dynamical Matrix II

Dynamical matrix:

$$D_{s\alpha,t\beta}(\mathbf{q}) \approx \frac{1}{\sqrt{M_s M_t}} \times \frac{F_{t\beta}^I(\Delta_{s,\mathbf{q}}) - F_{t\beta}^I(-\Delta_{s,\mathbf{q}})}{2\Delta_{s,\mathbf{q}}}$$



- Can only obtain dynamical matrix at certain \mathbf{q} .

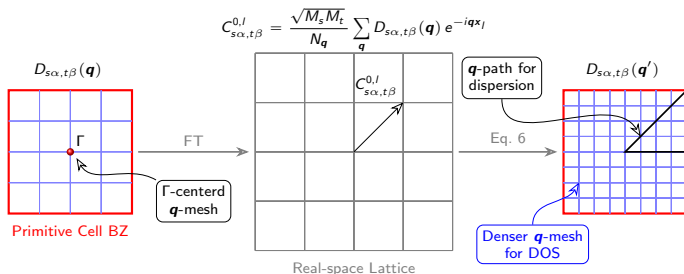


$$D_{s\alpha,t\beta}(\mathbf{q}) \xrightarrow{\text{FT}} C_{s\alpha,t\beta}^{0,l} \xrightarrow{\text{Eq. 6}} D_{s\alpha,t\beta}(\mathbf{k})$$

How to Calculate the Dynamical Matrix III

② Linear response approach — density functional perturbation theory

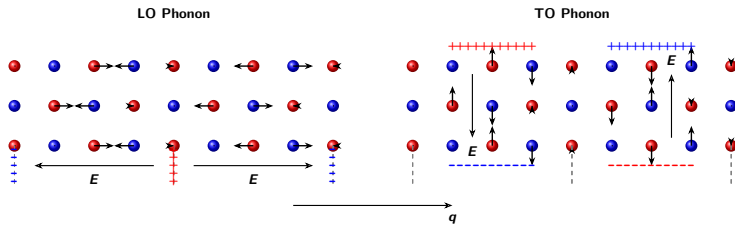
- Can calculate $D_{s\alpha,t\beta}(\mathbf{q})$ at **arbitrary** \mathbf{q} using a **primitive cell**.
- $D_{s\alpha,t\beta}(\mathbf{q})$ is periodic in reciprocal space: $D_{s\alpha,t\beta}(\mathbf{q} + \mathbf{G}) = D_{s\alpha,t\beta}(\mathbf{q})$



- In practice, first calculate $D_{s\alpha,t\beta}(\mathbf{q})$ with a small \mathbf{q} -mesh. Then, perform FT to get the IFC in real space. Finally, dynamical matrix at arbitrary \mathbf{q} can be obtained.
- Fails in metal with Kohn anomalies or in polar semiconductors where the dynamical matrix is non-analytic for $\mathbf{q} \rightarrow 0$.

③ Codes: Phonopy, PHON, YPHON, PhonTS, ShengBTE, ALM, ALAMODE, Quantum Espresso, Abinit, Siesta ...

LO-TO Splitting



The dynamical matrix in polar materials can be separated into two parts ²

$$D_{s\alpha,t\beta}(\mathbf{q} \rightarrow 0) = D_{s\alpha,t\beta}^{\text{an}}(\mathbf{q} = 0) + D_{s\alpha,t\beta}^{\text{na}}(\mathbf{q} \rightarrow 0)$$

where the nonanalytic part is written as

$$D_{s\alpha,t\beta}^{\text{na}}(\mathbf{q} \rightarrow 0) = \frac{1}{\sqrt{M_s M_t}} \frac{4\pi e^2}{\Omega} \frac{\left(\sum_{\gamma} q_{\gamma} Z_s^{*\gamma\alpha} \right) \left(\sum_{\mu} q_{\mu} Z_t^{*\mu\beta} \right)}{\sum_{\gamma\mu} q_{\gamma} \epsilon_{\infty}^{\gamma\mu} q_{\mu}} \quad (7)$$

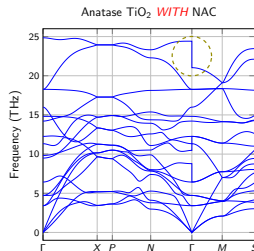
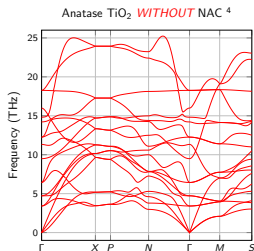
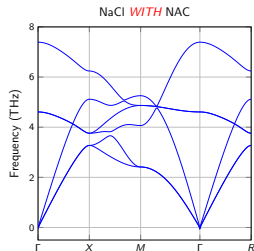
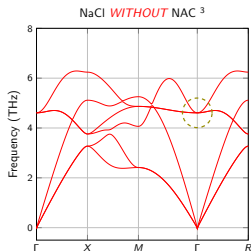
- Z_s^* is the Born effective charge tensor for atom s

$$Z_s^{*\alpha\beta} = \Omega_0 \frac{\partial \mathcal{P}_{\beta}}{\partial u_{s\alpha}} = \frac{\partial F_{s\alpha}}{\partial \mathcal{E}_{\beta}}$$

- 1 The response of the polarization per unit cell along the direction β induced by a displacement along the direction α of the atoms belonging to the sublattice s , under the condition of a zero electric field.
 - 2 The force on the atom s along α induced by the macroscopic field along β .
 - 3 The infrared absorption: $I_{\text{IR}}(\omega_{\sigma}) \propto \sum_{\alpha=1}^3 \left| \sum_{s\beta} Z_s^{*\alpha\beta} \eta_{s\beta}^{\sigma} \right|^2$
- ϵ_{∞} is the **electronic** dielectric tensor of the crystal, i.e. the static dielectric constant with clamped nuclei.

²X. Gonze and C. Lee, *Phys. Rev. B* 55, 10355(1997).

Phonon Band Structure with/without NAC




³<https://github.com/phonopy/phonopy/tree/master/example/NaCl>

⁴<https://github.com/phonopy/phonopy/tree/master/example/TiO2-anatase>

First and Second-order Derivatives of the Total Energy

Within DFT, the total energy is given by

$$E_{\text{tot}} = \sum_i^{\text{occ}} \langle \psi_i(\mathbf{r}) | -\frac{\hbar^2}{2m} \nabla^2 | \psi_i(\mathbf{r}) \rangle + \int_V V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_H[\rho] + E_{\text{xc}}[\rho] + U_{II}$$

over the entire space 

- $V_{\text{ext}}(\mathbf{r})$: electron-ion interaction
- U_{II} : ion-ion interaction
- $E_H[\rho]$: electron Hartree energy
- $E_{\text{xc}}[\rho]$: exchange-correlation energy

- $\rho(\mathbf{r})$: electron density

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} \langle \psi_i^*(\mathbf{r}) | \psi_i(\mathbf{r}) \rangle$$

The first and second order derivative with respect to external parameter λ, μ

$$\frac{\partial E_{\text{tot}}}{\partial \lambda} = \int_V \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d\mathbf{r} + \frac{\partial U_{II}}{\partial \lambda} \quad (8)$$

$$\begin{aligned} \frac{\partial^2 E_{\text{tot}}}{\partial \lambda \partial \mu} &= \int_V \frac{\partial^2 V_{\text{ext}}(\mathbf{r})}{\partial \lambda \partial \mu} \rho(\mathbf{r}) d\mathbf{r} + \frac{\partial^2 U_{II}}{\partial \lambda \partial \mu} \\ &+ \int_V \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \lambda} \frac{\partial \rho(\mathbf{r})}{\partial \mu} d\mathbf{r} \end{aligned} \quad (9)$$

2-nd derivative requires the extra calculation of the *linear response* of the charge density to the external perturbation!

The Kohn-Sham equation

With a small perturbation μ

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r}; \mu) \right] \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_n^{occ} |\psi_n(\mathbf{r})|^2$$

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$V_{KS}(\mathbf{r}; \mu) = V_{KS}(\mathbf{r}; \mu = 0) + \mu \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu}$$

$$\psi_n(\mathbf{r}; \mu) = \psi_n(\mathbf{r}; \mu = 0) + \mu \frac{\partial \psi_n(\mathbf{r})}{\partial \mu}$$

$$\varepsilon_n(\mu) = \varepsilon_n(\mu = 0) + \mu \frac{\partial \varepsilon_n}{\partial \mu}$$

Inserting these equations and keeps only the first-order terms

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_n \right] \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} = - \left[\frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} - \frac{\partial \varepsilon_n}{\partial \mu} \right] \psi_n(\mathbf{r}) \quad (10)$$

where

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} = \frac{\partial V_{ext}(\mathbf{r})}{\partial \mu} + \frac{\partial V_H(\mathbf{r})}{\partial \mu} + \frac{\partial V_{xc}(\mathbf{r})}{\partial \mu} \quad (11)$$

$$\frac{\partial V_H(\mathbf{r})}{\partial \mu} = \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d\mathbf{r}'; \quad \frac{\partial V_{xc}(\mathbf{r})}{\partial \mu} = \frac{dV_{xc}}{d\rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial \mu} \quad (12)$$

Thank you!