

Lattice Dynamics and Phonon

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2020/12/31

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

- 2 Density functional perturbation theory

$$\mathcal{H}(\{\mathbf{r}\}, \{\mathbf{R}\})$$

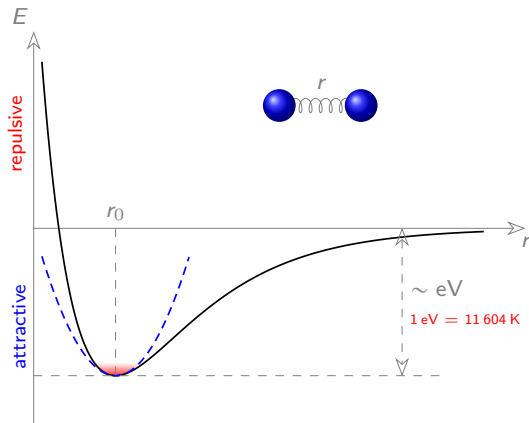
$$\parallel$$

$$\sum_i \frac{\hat{\mathbf{p}}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,l} \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|} + \sum_l \frac{\hat{\mathbf{P}}_l^2}{2M_l} + \frac{1}{2} \sum_{l,j} \frac{Z_l Z_j e^2}{|\mathbf{R}_l - \mathbf{R}_j|}$$

$$\Downarrow$$

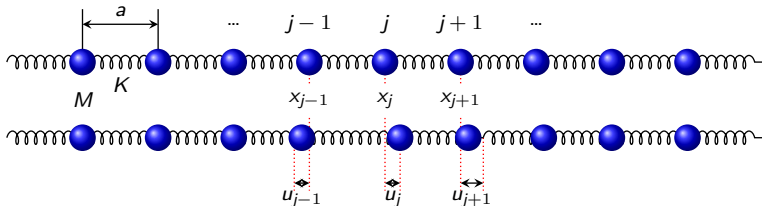
$$i\hbar \frac{\partial}{\partial t} \psi(\{\mathbf{r}\}, \{\mathbf{R}\}) = \mathcal{H}(\{\mathbf{r}\}, \{\mathbf{R}\}) \psi(\{\mathbf{r}\}, \{\mathbf{R}\})$$

Harmonic Approximation



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

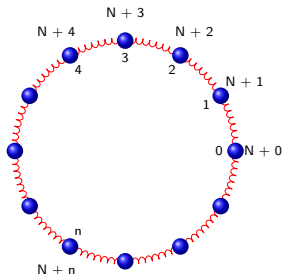
$$\begin{aligned} \omega^2 &= \frac{K}{M} (2 - e^{iqa} - e^{-iqa}) \\ &= \frac{2K}{M} (1 - \cos qa) \\ \Rightarrow \quad \omega &= \sqrt{\frac{4K}{M}} \left| \sin \frac{qa}{2} \right| \end{aligned}$$

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:

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

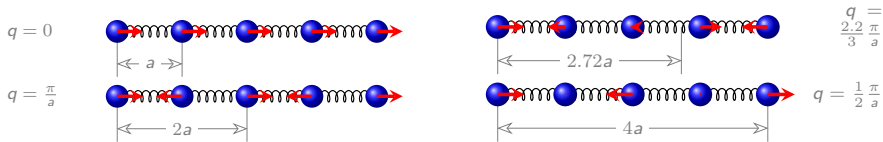
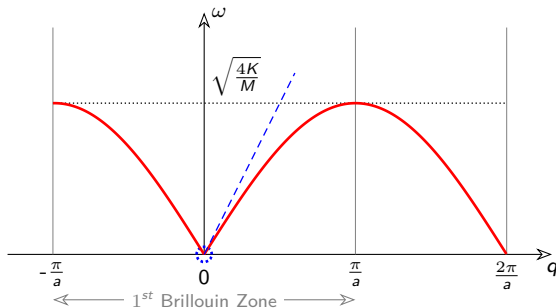
$$\Rightarrow q = \frac{2\pi}{a} \frac{l}{N}; \quad (l = 0, 1, \dots, N)$$



Usually, q is restricted within the first Brillouin Zone

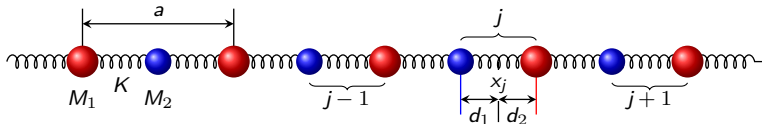
$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}$$

Dispersion and Vibration Pattern



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

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

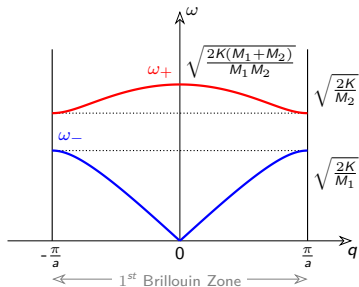
We then have

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

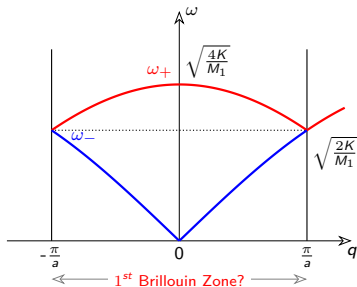
$$\Rightarrow \omega_{\pm}^2 = \frac{K}{M_1 M_2} \left((M_1 + M_2) \pm \sqrt{M_1^2 + M_2^2 + 2M_1 M_2 \cos qa} \right)$$

Dispersion and Vibration Pattern

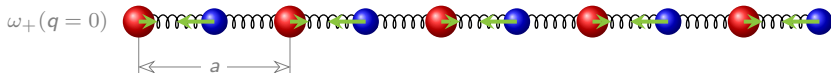
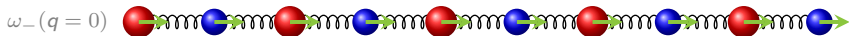
$$M_1 = 2M_2$$



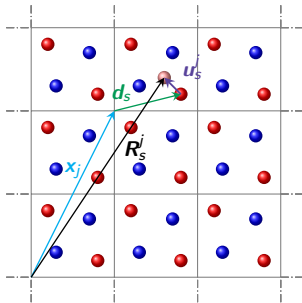
$$M_1 = M_2$$



$$\frac{A_q}{B_q} = \left[\frac{K(1 + e^{-iqa})}{\sqrt{M_1 M_2}} \right] / \left[\frac{2K}{M_1} - \omega^2 \right]$$



3D Lattice



- \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

$$\mathbf{R}_s^j(t) = \mathbf{x}_j + \mathbf{d}_s + \mathbf{u}_s^j(t)$$

$$= \mathbf{r}_s^j + \mathbf{u}_s^j(t)$$

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

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

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

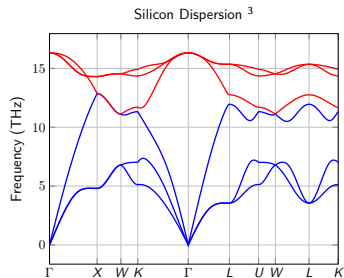
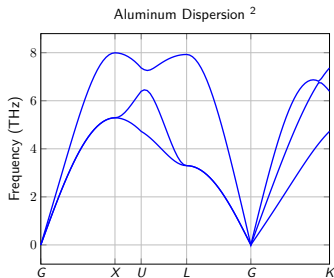
In matrix form

$$\begin{pmatrix} \ddots & & \\ & D_{s\alpha,t\beta}(\mathbf{q}) & \\ & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix} = \omega^2(\mathbf{q}) \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix}$$

$3N_a \times 3N_a$ $3N_a$ polarization vector

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

3D Dispersion



- If N_a atoms in the primitive cell, $3N_a$ modes for each \mathbf{q} .

- At each \mathbf{q} , 3 acoustic modes, $3N_a - 3$ optical modes.

²<https://wiki.fysik.dtu.dk/ase/ase/phonons.html>

³<https://github.com/phonopy/phonopy/tree/master/example/Si-CRYSTAL>

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

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

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*.

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

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

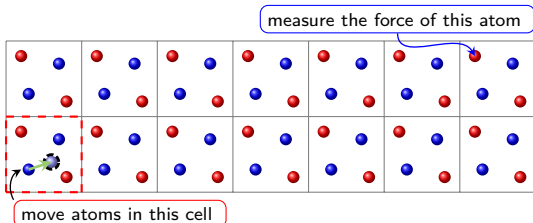
The definition of the dynamical matrix

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

1 Finite-difference and supercell approach — Frozen phonon method

IFC by finite-difference:

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

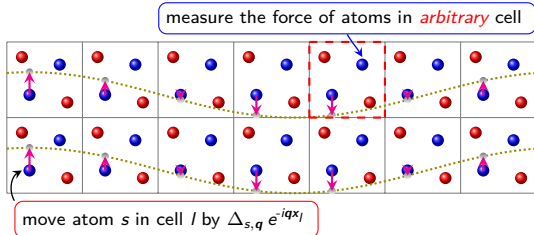


- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done *only* in one primitive cell.
- $3 \times N_a \times 2$ movements, i.e. move by $\pm\Delta$ in $x/y/z$ directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of movements.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

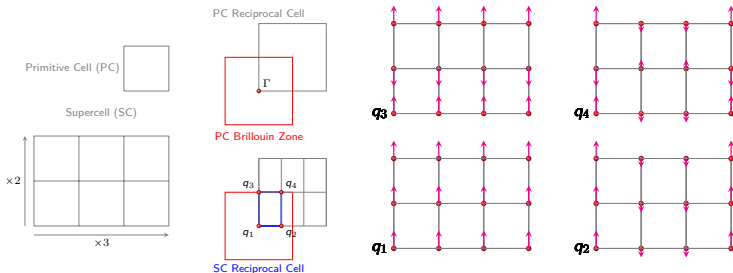
How to Calculate the Dynamical Matrix II

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} .

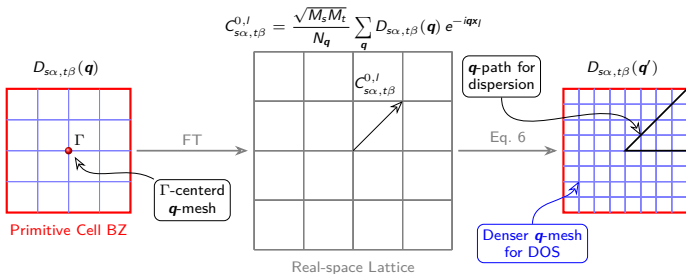


$$D_{s\alpha, t\beta}(\mathbf{q}) \xrightarrow{\text{FT}} C_{s\alpha, t\beta}^{0,l} \xrightarrow{\text{Eq. 6}} D_{s\alpha, t\beta}(\mathbf{k})$$

How to Calculate the Dynamical Matrix III

Linear response approach — density functional perturbation theory

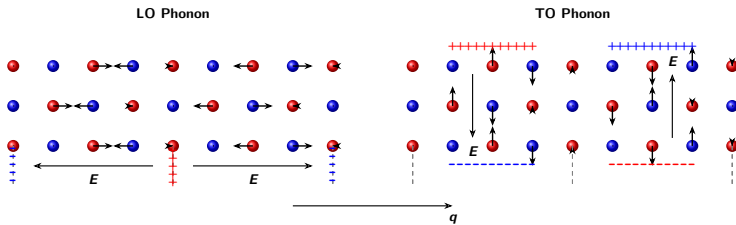
- Can calculate $D_{s\alpha,t\beta}(\mathbf{q})$ at **arbitrary** \mathbf{q} using a **primitive cell**.
- $D_{s\alpha,t\beta}(\mathbf{q})$ is periodic in reciprocal space: $D_{s\alpha,t\beta}(\mathbf{q} + \mathbf{G}) = D_{s\alpha,t\beta}(\mathbf{q})$



- 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 $\mathbf{q} \rightarrow 0$.

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 ⁴

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

where the nonanalytic part is written as

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

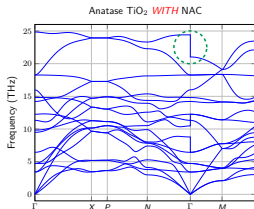
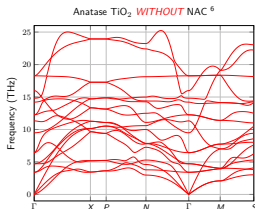
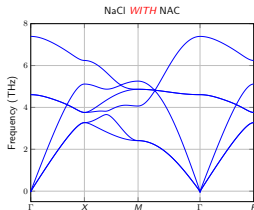
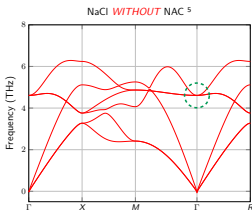
- Z_s^* is the Born effective charge tensor for atom s

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

- 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 Sum rules: $\sum_s Z_s^{*\alpha\beta} = 0$
 - ④ 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.

⁴X. Gonze and C. Lee, *Phys. Rev. B* 55, 10355(1997).

Phonon Band Structure with/without NAC

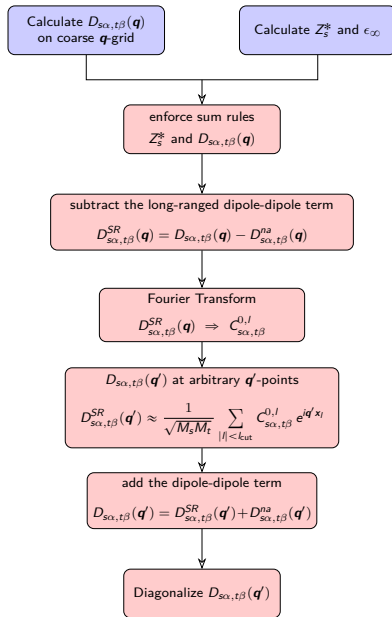


- The limiting value of Eq. 7 may be different for different $\mathbf{q} \rightarrow 0$ directions, as can be seen in the phonon dispersion of Anatase TiO₂.
- This strange behavior is physical and the frequency of the observed phonons depends on the polarizability in the different directions, with respect to the propagation of the incoming electric field.

⁵<https://github.com/phonopy/phonopy/tree/master/example/NaCl>

⁶<https://github.com/phonopy/phonopy/tree/master/example/TiO2-anatase>

DFPT Interpolation Scheme for Polar Material




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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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Electron density response to the perturbation

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_n^{\text{occ}} \left[\frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right] \quad (13)$$

$$\frac{\partial \psi_n(\mathbf{r})}{\partial \mu} = \sum_{m \neq n} \frac{\langle \psi_m | \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} | \psi_n \rangle}{\epsilon_n - \epsilon_m} \psi_m(\mathbf{r}) \quad (14)$$

Where n is the index for the occupied staets and m runs over all the states.

Define $P_v = \sum_n^{\text{occ}} |\psi_n\rangle \langle \psi_n|$ as the projector on the valence bands, then $P_c = \mathbb{1} - P_v$ is the projector on the conduction bands

$$\begin{aligned} \frac{\partial \rho(\mathbf{r})}{\partial \mu} &= \sum_n^{\text{occ}} \left[P_c \frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) P_c \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right] + \sum_n^{\text{occ}} \left[P_v \frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) P_v \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right] \\ &= \sum_n^{\text{occ}} \left[P_c \frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) P_c \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right] + \sum_{mn}^{\text{occ}} \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) \left(\langle \frac{\partial \psi_n}{\partial \mu} | \psi_m \rangle + \langle \psi_n | \frac{\partial \psi_m}{\partial \mu} \rangle \right) \end{aligned}$$

Due the orthonormality of $\psi_n(\mathbf{r})$, i.e. $\langle \psi_m | \psi_n \rangle = \delta_{mn}$

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_n^{\text{occ}} \left[P_c \frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) P_c \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right] \quad (15)$$

The electron density response depends only on the component of the perturbation that *couples the occupied states with the empty ones*.

Apply P_c on the left and right-hand side of Eq. 10

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r}) + \alpha P_v - \varepsilon_n \right] P_c \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} = -(\mathbb{1} - P_v) \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) \quad (16)$$

where the αP_v is added to make the left-hand-side nonsingular.

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} = \frac{\partial V_{ext}(\mathbf{r})}{\partial \mu} + \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d\mathbf{r}' + \int \frac{dV_{xc}}{d\rho(\mathbf{r}')} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d\mathbf{r}' \quad (17)$$

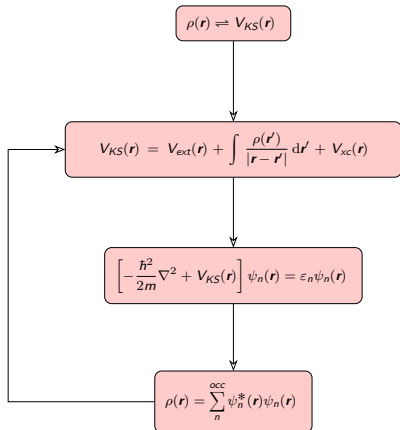
$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_n^{occ} \left[P_c \frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) P_c \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right]$$

Considering the time-reversal symmetry $\psi_{n,-\mathbf{k}}^*(\mathbf{r}) = \psi_{n,\mathbf{k}}(\mathbf{r})$

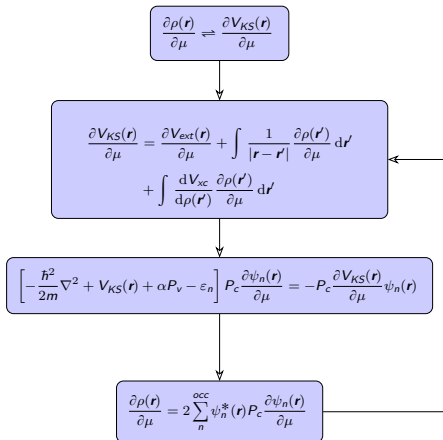
$$\begin{aligned} \frac{\partial \rho(\mathbf{r})}{\partial \mu} &= \sum_{n,-\mathbf{k}}^{occ} P_c \frac{\partial \psi_{n,-\mathbf{k}}^*(\mathbf{r})}{\partial \mu} \psi_{n,-\mathbf{k}}(\mathbf{r}) + \sum_{n,\mathbf{k}}^{occ} \psi_{n,\mathbf{k}}^*(\mathbf{r}) P_c \frac{\partial \psi_{n,\mathbf{k}}(\mathbf{r})}{\partial \mu} \\ &= 2 \sum_{n,\mathbf{k}}^{occ} \psi_{n,\mathbf{k}}^*(\mathbf{r}) P_c \frac{\partial \psi_{n,\mathbf{k}}(\mathbf{r})}{\partial \mu} \end{aligned} \quad (18)$$

Eq. 16, Eq. 17 and Eq. 18 form a set of self-consistent equations for the perturbed system.

DFT



DFPT



Add a monochromatic perturbation characterized by generic wavevector \mathbf{q} to the periodic potential

$$V_{\text{ext}}(\mathbf{r} + \mathbf{x}_j) = V_{\text{ext}}(\mathbf{r}); \quad \Delta V_{\text{ext}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = e^{i\mathbf{q} \cdot \mathbf{x}_j} \Delta V_{\text{ext}}^{\mathbf{q}}(\mathbf{r})$$

It can be shown that all the linear responses are also characterized by wavevector \mathbf{q}

$$\Delta V_{\text{KS}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = e^{i\mathbf{q} \cdot \mathbf{x}_j} \Delta V_{\text{KS}}^{\mathbf{q}}(\mathbf{r})$$

$$\Delta \rho^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = e^{i\mathbf{q} \cdot \mathbf{x}_j} \Delta \rho^{\mathbf{q}}(\mathbf{r})$$

$$\Delta \psi_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = e^{i\mathbf{q} \cdot \mathbf{x}_j} \Delta \psi_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r})$$

Let us define the related periodic quantities

$$\Delta V_{\text{ext}}^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{V}_{\text{ext}}^{\mathbf{q}}(\mathbf{r});$$

$$\tilde{V}_{\text{ext}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \tilde{V}_{\text{ext}}^{\mathbf{q}}(\mathbf{r});$$

$$\Delta V_{\text{KS}}^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{V}_{\text{KS}}^{\mathbf{q}}(\mathbf{r});$$

$$\tilde{V}_{\text{KS}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \tilde{V}_{\text{KS}}^{\mathbf{q}}(\mathbf{r});$$

$$\Delta \rho^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{\rho}^{\mathbf{q}}(\mathbf{r});$$

$$\tilde{\rho}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \tilde{\rho}^{\mathbf{q}}(\mathbf{r});$$

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r});$$

$$u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{x}_j) = u_{n,\mathbf{k}}(\mathbf{r});$$

$$\Delta \psi_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r}) = e^{i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r}} \Delta u_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r});$$

$$\Delta u_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \Delta u_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r});$$

Substitute into Eq. 16

$$\left[H_{KS}(\mathbf{r}) + \alpha P_v - \varepsilon_{n,k} \right] P_c e^{i(\mathbf{k}+\mathbf{q}) \cdot \mathbf{r}} \frac{\partial u_{n,k}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} = -P_c e^{i(\mathbf{k}+\mathbf{q}) \cdot \mathbf{r}} \frac{\partial \tilde{V}_{KS}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} u_{n,k}(\mathbf{r}) \quad (19)$$

Apply the phase $e^{-i(\mathbf{k}+\mathbf{q}) \cdot \mathbf{r}}$ to the both sides of Eq. 19

$$\left[H_{KS}^{\mathbf{k}+\mathbf{q}}(\mathbf{r}) + \alpha P_v^{\mathbf{k}+\mathbf{q}} - \varepsilon_{n,k} \right] P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial u_{n,k}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} = -P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{V}_{KS}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} u_{n,k}(\mathbf{r}) \quad (20)$$

where

$$\begin{aligned} \frac{\partial \tilde{V}_{KS}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} &= \frac{\partial \tilde{V}_{\text{ext}}(\mathbf{r})}{\partial \mu} + \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \tilde{\rho}^{\mathbf{q}}(\mathbf{r}')}{\partial \mu} d\mathbf{r}' + \int \frac{dV_{\text{xc}}}{d\rho(\mathbf{r}')} \frac{\partial \tilde{\rho}^{\mathbf{q}}(\mathbf{r}')}{\partial \mu} d\mathbf{r}' \\ \frac{\partial \tilde{\rho}^{\mathbf{q}}(\mathbf{r}')}{\partial \mu} &= 2 \sum_{n,k}^{\text{occ}} u_{n,k}^*(\mathbf{r}) P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial u_{n,k}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} \\ P_v^{\mathbf{k}+\mathbf{q}} &= \sum_n^{\text{occ}} |u_{n,\mathbf{k}+\mathbf{q}}\rangle \langle u_{n,\mathbf{k}+\mathbf{q}}|; \quad P_c^{\mathbf{k}+\mathbf{q}} = \mathbb{1} - P_v^{\mathbf{k}+\mathbf{q}} \end{aligned}$$

The treatment of perturbations incommensurate with the unperturbed system periodicity is mapped onto the *original periodic system*.

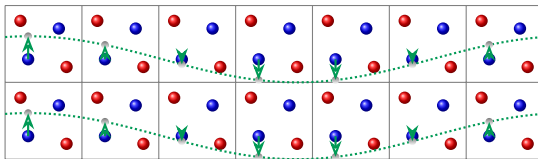
Periodic Displacement of Ions — Phonon Perturbation I

In a solid, the external potential can be expressed as the superposition of atomic potential $v_s(\mathbf{r})$

$$V_{\text{ext}}(\mathbf{r}) = \sum_j \sum_s^{N_a} v_s(\mathbf{r} - \mathbf{x}_j - \mathbf{d}_s - \mathbf{u}_s^j)$$

Consider the periodic displacement of the ions of the form

$$\mathbf{u}_{s\alpha}^j(\mathbf{q}) = \mu_{s\alpha} e^{i\mathbf{q} \cdot \mathbf{x}_j} + \mu_{s\alpha}^* e^{-i\mathbf{q} \cdot \mathbf{x}_j} \quad (\alpha = x, y, z) \quad (21)$$



$$\begin{aligned} \frac{\partial V_{\text{ext}}^{\mathbf{q}}(\mathbf{r})}{\partial \mu_{s\alpha}} &= - \sum_j e^{i\mathbf{q} \cdot \mathbf{x}_j} \left. \frac{\partial v_s(\mathbf{r} - \mathbf{x}_j - \mathbf{d}_s)}{\partial r_\alpha} \right|_{\mathbf{u}_s^j=0} \\ &= -e^{i\mathbf{q} \cdot \mathbf{r}} \sum_j e^{i\mathbf{q} \cdot (\mathbf{x}_j - \mathbf{r})} \left. \frac{\partial v_s(\mathbf{r} - \mathbf{x}_j - \mathbf{d}_s)}{\partial r_\alpha} \right|_{\mathbf{u}_s^j=0} \end{aligned}$$

The **colored quantity** has the periodicity of the lattice.

The dynamical matrix

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_k e^{-i\mathbf{q} \cdot \mathbf{x}_j} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} e^{i\mathbf{q} \cdot \mathbf{x}_k} = \frac{N}{\sqrt{M_s M_t}} \frac{\partial^2 E_{\text{tot}}^0}{\partial \mu_{s\alpha}^* \partial \mu_{t\beta}}$$

Inserting the equation for the second derivative Eq. 9

$$\begin{aligned} D_{s\alpha,t\beta}(\mathbf{q}) &= \frac{N}{\sqrt{M_s M_t}} \int_V \sum_k e^{-i\mathbf{q} \cdot \mathbf{x}_j} \frac{\partial^2 V_{\text{ext}}^{\mathbf{q}}(\mathbf{r})}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{x}_k} d\mathbf{r} \\ &+ \frac{1}{\sqrt{M_s M_t}} \int_V \sum_k e^{-i\mathbf{q} \cdot \mathbf{x}_j} \frac{\partial V_{\text{ext}}^{\mathbf{q}}(\mathbf{r})}{\partial u_{s\alpha}^j} \frac{\partial \rho(\mathbf{r})}{\partial u_{t\beta}^k} e^{i\mathbf{q} \cdot \mathbf{x}_k} d\mathbf{r} \end{aligned}$$

Thank you!