Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation

Lecture 7: Anharmonicity Beyond Perturbation Theory: the SSCHA method

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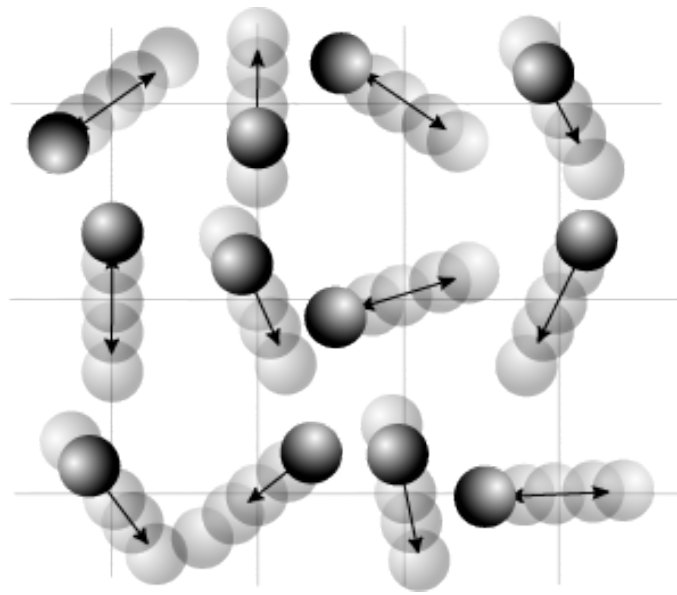
March and April 2022



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Universidad del País Vasco

Euskal Herriko Unibertsitatea

CFM Materials Physics Center

Centro de Física de Materiales

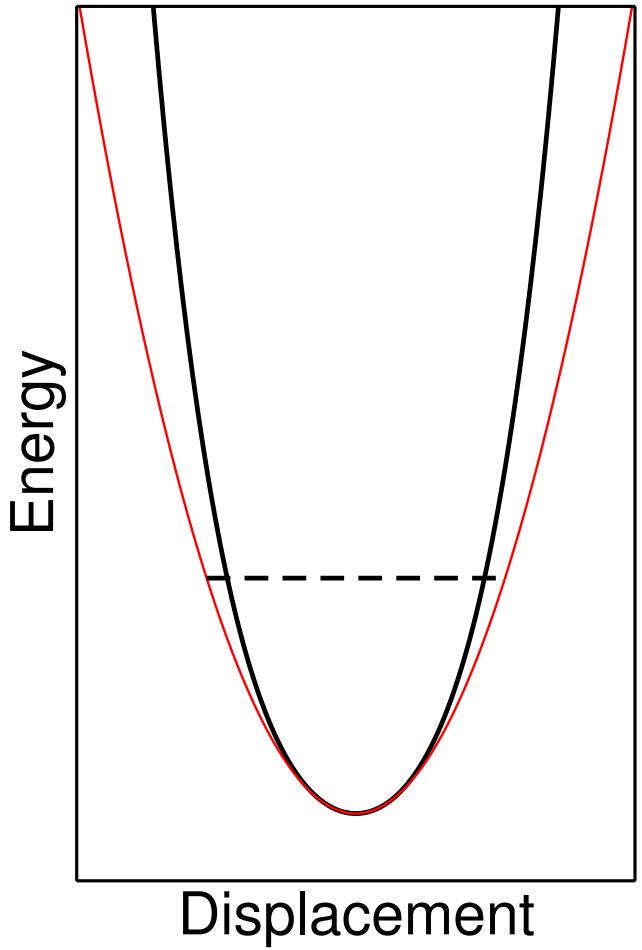
DIPC Donostia International Physics Center

Outline

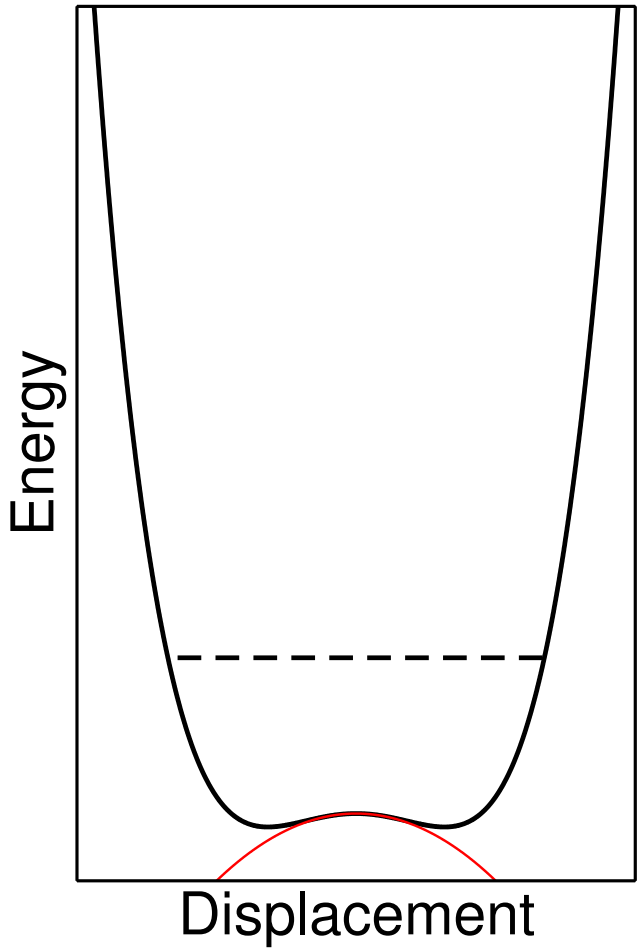
Two different regimes for anharmonicity

$$V(\mathbf{R}) = V_0 + V_2(\mathbf{R}) + V_3(\mathbf{R}) + V_4(\mathbf{R}) + \dots$$

- Perturbative regime:
  $V_3(\mathbf{R}) + V_4(\mathbf{R}) + \cdots \ll V_2(\mathbf{R})$

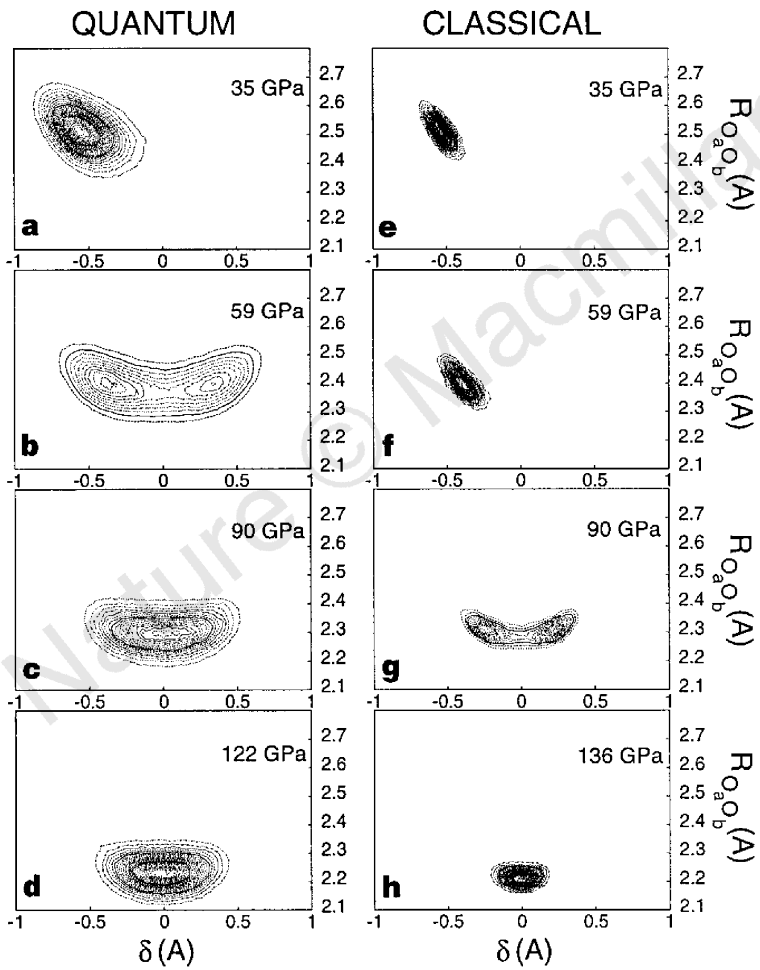


- Non-perturbative regime:
  $V_3(\mathbf{R}) + V_4(\mathbf{R}) + \cdots \sim V_2(\mathbf{R})$

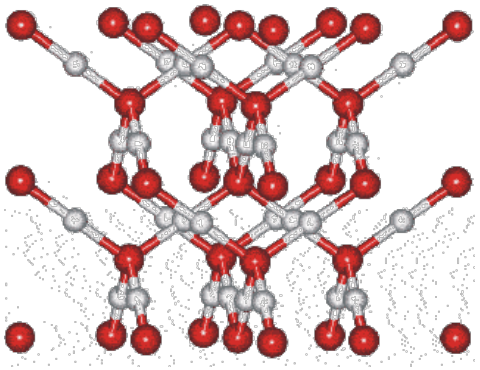


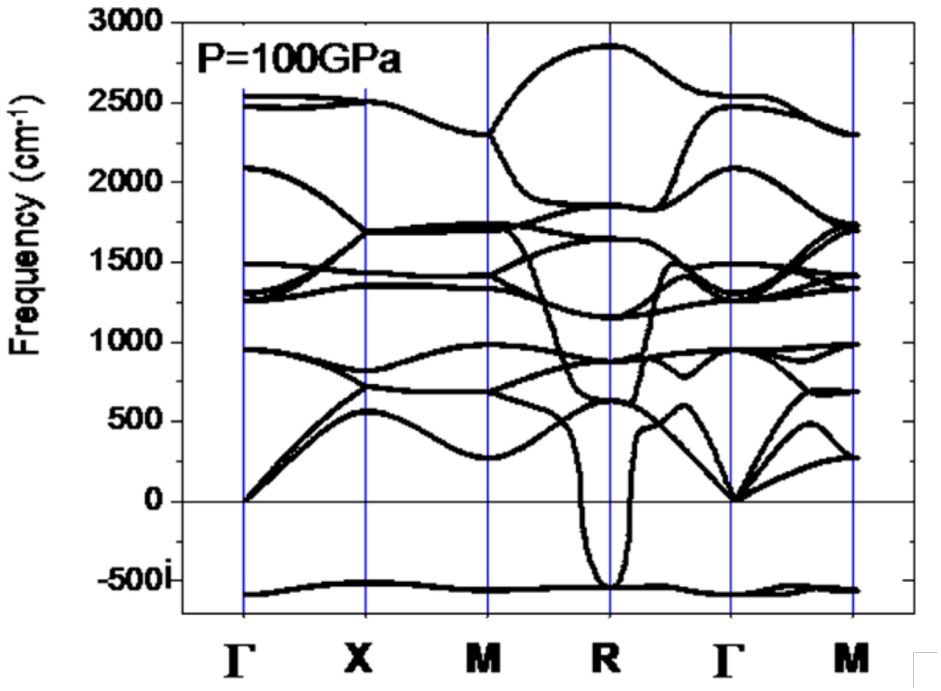
Non-perturbative regime in hydrides

Ice X



Benoit *et al.*, Nature (1998)





Caracas, PRL (2008)

Non-perturbative regime close to a structural instability

Second-order structural phase transitions in

- Charge-density wave (CDW) materials
- Thermoelectrics
- Ferroelectrics

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- Charge-density wave (CDW) materials
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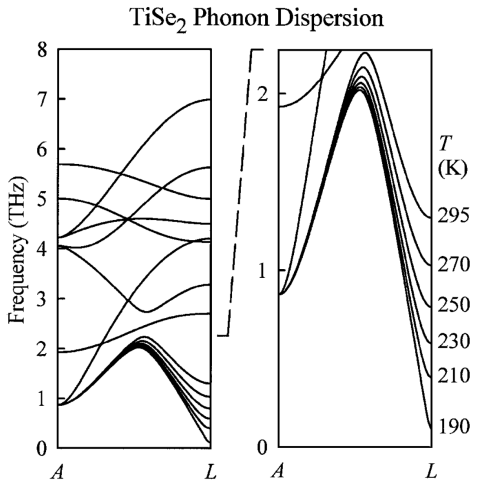
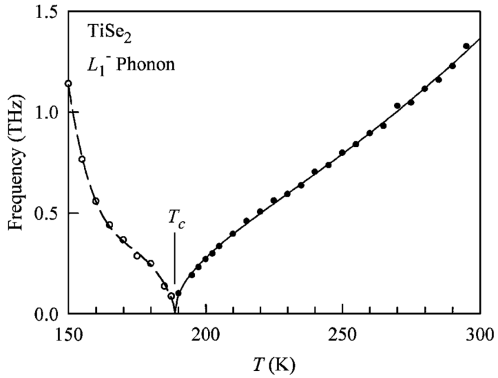
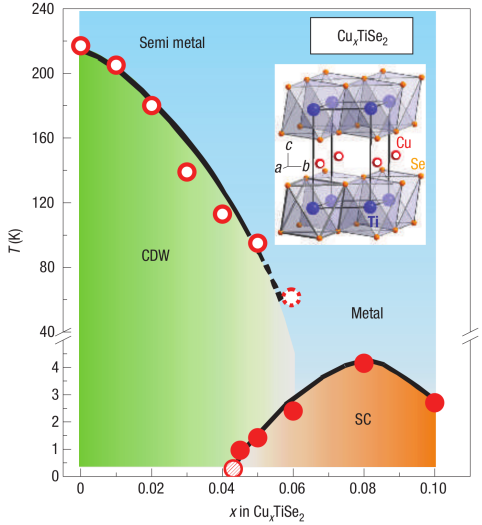
CDW in $TiSe_2$

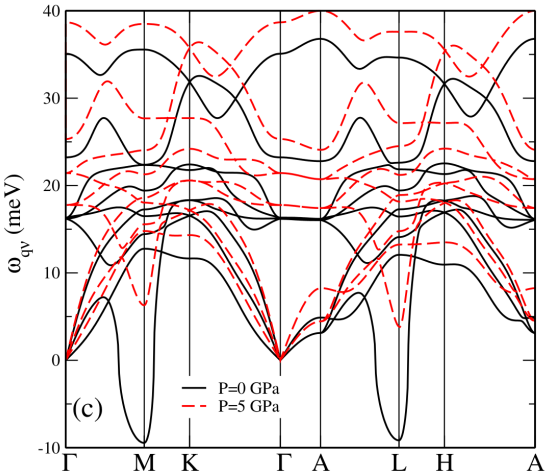




Holt *et al.*, PRL (2001)



Morosan *et al.*, Nat. Phys. (2006)



Calandra *et al.*, PRL (2011)

Dealing with anharmonicity from first-principles is complex

$$V(\boldsymbol{R}) = V_0 + V_2(\boldsymbol{R}) + V_3(\boldsymbol{R}) + V_4(\boldsymbol{R}) + \dots$$
$$V_n(\boldsymbol{R}) = \frac{1}{n!} \sum_{a_1 \cdots a_n} \overset{(n)}{\phi}_{a_1 \cdots a_n} (R_{a_1} - R_{0a_1}) \cdots (R_{a_n} - R_{0a_n})$$

Impossible to obtain $\overset{(n)}{\phi}_{a_1 \cdots a_n}$

- Limit to 3rd and 4th order force-constants (very tedious)

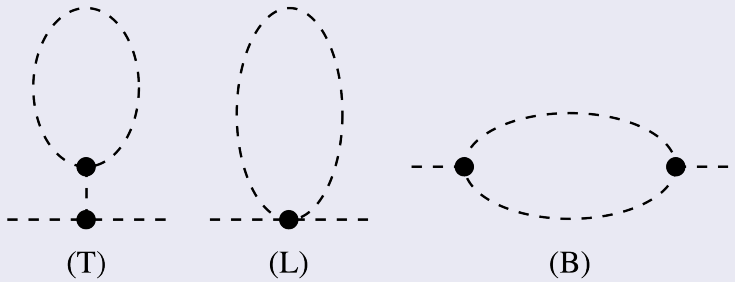
  Errea *et al.*, PRL (2011)
- Empirical potentials

  Chen *et al.*, PRL (2014)
- Compressive sensing lattice dynamics

  Zhou *et al.*, PRL (2014)

Perturbation theory

- Requires 3rd and 4th order force-constants



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Beyond perturbation theory

- *Ab initio* molecular dynamics (AIMD): Newtonian mechanics with DFT forces
  - Phonons from velocity autocorrelation functions

    Zhang *et al.*, PRL (2014)
  - TDEP: effective temperature dependent V_2 and V_3 from AIMD

    Hellman *et al.*, PRB (2011)
- Path integral molecular dynamics (PIMD): quantum dynamics with DFT forces
- Variational methods:
  - VSCF: Variational self-consistent field equations

    Bowman, J. Chem. Phys. (1978); Monserrat *et al.*, PRB (2013)
  - SCHA: Minimization of the free energy with a trial harmonic density matrix

    Hooton, Philos. Mag. Ser. (1955)

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  - SCHA: Minimization of the free energy with a trial harmonic density matrix

    Hooton, Philos. Mag. Ser. (1955)
  - SSCHA: Stochastic implementation of the SCHA

Outline

SSCHA

Stochastic Self-Consistent
Harmonic Approximation

`sscha.eu`

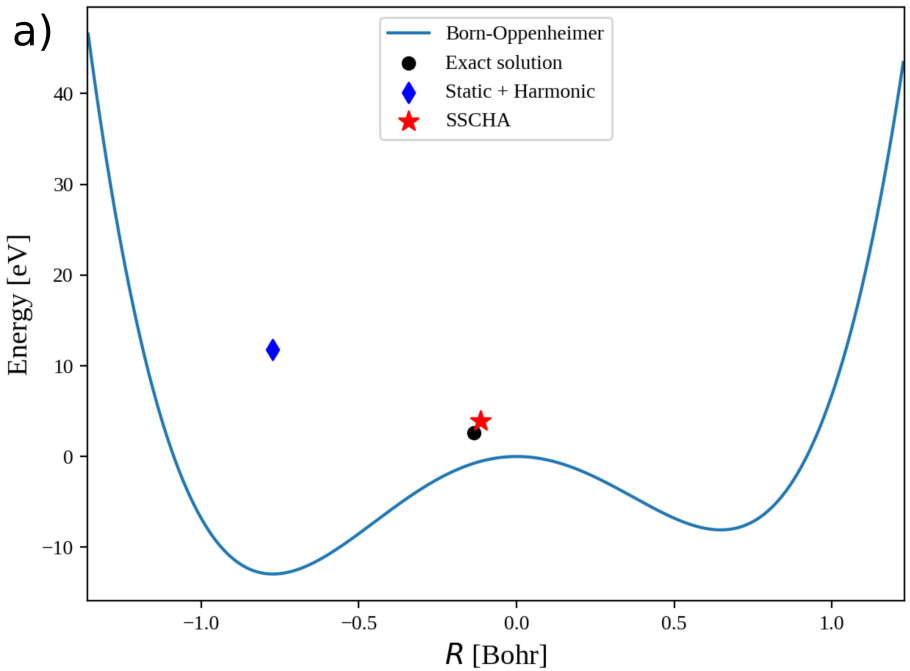
Journal of Physics: Condensed Matter 33, 363001 (2021)

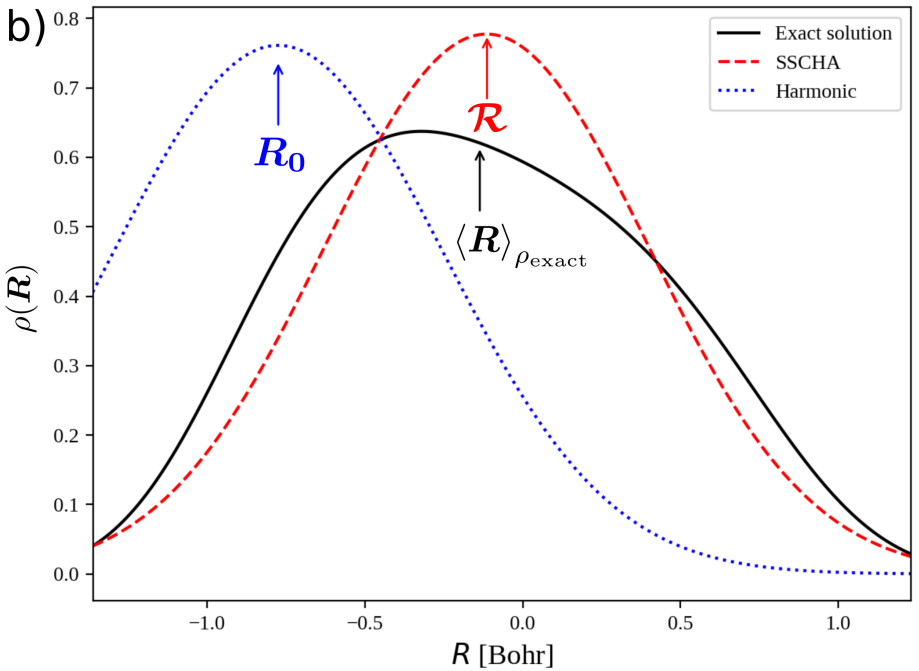
The stochastic self-consistent harmonic approximation (SSCHA)

- The idea of the SSCHA is to obtain the *harmonic* density matrix $\tilde{\rho}$ that minimizes the total free energy

$$\mathcal{F}[\tilde{\rho}] = \langle T_i + V \rangle_{\tilde{\rho}} + \frac{1}{\beta} \langle \ln \tilde{\rho} \rangle_{\tilde{\rho}}$$

- The probability distribution function that $\tilde{\rho}$ defines, $\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{R})$, is a Gaussian and can be parametrized by *centroid* positions $\boldsymbol{\mathcal{R}}$ and *auxiliary* second-order force constants $\boldsymbol{\Phi}$





The SSCHA is a quantum variational method

The exact problem

- The exact density matrix

$$H = T_i + V(\boldsymbol{R}) \quad \rho_H = e^{-\beta H} / Z_H$$

- The exact free energy

$$F = \langle T_i + V \rangle_{\rho_H} + \frac{1}{\beta} \langle \ln \rho_H \rangle_{\rho_H}$$

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The variational problem

- Trial density matrix $\tilde{\rho}_{\mathcal{H}}$ from a trial Hamiltonian

$$\mathcal{H} = T_{ion} + \mathcal{V}(\boldsymbol{R}) \quad \tilde{\rho}_{\mathcal{H}} = e^{-\beta \mathcal{H}}/Z_{\mathcal{H}}$$

- The variational free energy

$$\mathcal{F}[\mathcal{H}] = \langle T_i + V \rangle_{\tilde{\rho}_{\mathcal{H}}} + \frac{1}{\beta} \langle \ln \tilde{\rho}_{\mathcal{H}} \rangle_{\tilde{\rho}_{\mathcal{H}}}$$

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Variational principle

$$\mathcal{F}[\mathcal{H}] \geq F$$

The SSCHA is a quantum variational method

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Variational principle

$$\mathcal{F}[\mathcal{H}] \geq F$$

The SSCHA trial Hamiltonian

- In the trial Hamiltonian is harmonic and is parametrized with the *centroid* positions $\boldsymbol{\mathcal{R}}$ and *auxiliary* second-order force constants $\boldsymbol{\Phi}$

$$\mathcal{V}(\boldsymbol{R}) = \frac{1}{2}\sum_{ab} \Phi_{ab}(R_a - \mathcal{R}_a)(R_b - \mathcal{R}_b)$$

- Note that this potential is different from the harmonic potential

$$V_2(\boldsymbol{R}) = \frac{1}{2}\sum_{ab} \overset{(2)}{\phi}_{ab}(R_a - R_{0a})(R_b - R_{0b})$$

- The variational free energy will depend only on $\boldsymbol{\mathcal{R}}$ and $\boldsymbol{\Phi}$ so we will write $\tilde{\rho}_{\mathcal{H}} \rightarrow \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}$ and $\mathcal{F}[\mathcal{H}] \rightarrow \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$
- The goal of the SSCHA is to minimize $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ with respect to $\boldsymbol{\mathcal{R}}$ and $\boldsymbol{\Phi}$
- It is easy to show that the SSCHA free energy can be written as

$$\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}] = F_{\mathcal{H}} + \langle V - \mathcal{V} \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

where $F_{\mathcal{H}}$ is the harmonic free energy given by the trial harmonic Hamiltonian

The SSCHA probability distribution function

- The SSCHA probability distribution function is a product of Gaussians, exactly as the harmonic probability distribution function

$$\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{R}) = \langle \boldsymbol{R} | \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}} | \boldsymbol{R} \rangle = \sqrt{\det[\boldsymbol{\Psi}^{-1}/(2\pi)]} e^{-\frac{1}{2}\sum_{ab}(R_a - \mathcal{R}_a)\Psi^{-1}_{ab}(R_b - \mathcal{R}_b)}$$

  where

$$\Psi^{-1}_{ab} = \sqrt{M_a M_b} \sum_\mu \frac{\mathrm{e}^a_\mu \mathrm{e}^b_\mu}{\mathrm{a}^2_\mu} \qquad \mathrm{a}_\mu = \frac{\hbar}{2\mathtt{w}_\mu}\left[1 + 2n_B(\mathtt{w}_\mu)\right]$$

- In the equations above the frequencies and the polarization vectors are not the eigenvalues and eigenfunctions of the harmonic force-constants (ω_μ and e^a_μ), but of the auxiliary force-constants

$$\sum_b \frac{\Phi_{ab}}{\sqrt{M_a M_b}} \mathrm{e}^b_\mu = \mathtt{w}^2_\mu \mathrm{e}^a_\mu$$

- Defining the displacement from the centroid as $u_a = R_a - \mathcal{R}_a = \sum_\mu \frac{\mathrm{e}^a_\mu}{\sqrt{M_a}} Q_\mu$, we can write the distribution in the normal mode basis
- The average ionic positions are the centroids since

$$\langle \boldsymbol{R} \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = \boldsymbol{\mathcal{R}}$$

The SSCHA minimization

Conjugate-gradient (CG) minimization of $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$

- Minimization trajectory in the parameter space $(\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})$

$$\begin{array}{ccccccccc} \mathcal{H}_0 & \rightarrow & \mathcal{H}_1 & \rightarrow & \mathcal{H}_2 & \rightarrow & \dots & \rightarrow & \mathcal{H}_n \\ (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_0 & \rightarrow & (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_1 & \rightarrow & (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_2 & \rightarrow & \dots & \rightarrow & (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_n \end{array}$$

- At the minimum
  - The eigenvalues $\mathtt{w}_\mu^2$ and the eigenvectors $\mathtt{e}_\mu^a$ of $\boldsymbol{\Phi}$ define the renormalized probability distribution function, not the experimental phonon frequencies and polarization vectors. They are auxiliary phonons
  - $\boldsymbol{\mathcal{R}}$ are the renormalized positions at which the ionic wave function are centered (the centroids)
  - $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ is a good variational approximation of the exact free energy

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  - $\boldsymbol{\mathcal{R}}$ are the renormalized positions at which the ionic wave function are centered (the centroids)
  - $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ is a good variational approximation of the exact free energy
- Need the gradient of the functional $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$

The SSCHA gradients

- The gradients of $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ are

$$\frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \mathcal{R}_a} = -\left\langle f_a(\boldsymbol{R}) - f_a^{\mathcal{V}}(\boldsymbol{R}) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}}}$$

$$\frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \Phi_{cd}} = \sum_{ab} \frac{\Lambda[0]^{abcd}}{\sqrt{M_a M_b M_c M_d}} \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right) \sum_e \Psi^{-1}_{ae} (R_e - \mathcal{R}_e) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}}}$$

- We have quantum statistical averages of BO forces f_a and BO forces times displacements. $f_a^{\mathcal{V}}(\boldsymbol{R}) = -\sum_b \Phi_{ab}(R_b - \mathcal{R}_b)$ is the force derived from the trial potential
- The $\boldsymbol{\Lambda}[0]$ tensor is

$$\Lambda[0]^{abcd} = \sum_{\mu\nu} \frac{\hbar}{4 \mathtt{w}_\nu \mathtt{w}_\mu} \mathtt{e}^a_\nu \mathtt{e}^b_\mu \mathtt{e}^c_\nu \mathtt{e}^d_\mu \begin{cases} \frac{d n_B(\mathtt{w}_\mu)}{d \mathtt{w}_\mu} - \frac{2 n_B(\mathtt{w}_\mu)+1}{2 \mathtt{w}_\mu} & , \mathtt{w}_\nu = \mathtt{w}_\mu \\ \frac{n_B(\mathtt{w}_\mu) - n_B(\mathtt{w}_\nu)}{\mathtt{w}_\mu - \mathtt{w}_\nu} - \frac{1 + n_B(\mathtt{w}_\mu) + n_B(\mathtt{w}_\nu)}{\mathtt{w}_\mu + \mathtt{w}_\nu} & , \mathtt{w}_\nu \neq \mathtt{w}_\mu \end{cases}$$

- With the gradients a gradient-descent minimization can be performed
- The gradient is symmetrized at every step, so the minimization is performed respecting the symmetries

A preconditioned gradient descent

- The gradient-descent is much more efficient if the descent is preconditioned and the update of the centroids and auxiliary force constants is performed as

$$\boldsymbol{\Phi}^{(n+1)} = \boldsymbol{\Phi}^{(n)} - \lambda_{\boldsymbol{\Phi}} \sum_{ab} \left(\frac{\partial^2 \mathcal{F}}{\partial \boldsymbol{\Phi} \partial \Phi_{ab}} \right)^{-1} \frac{\partial \mathcal{F}}{\partial \Phi_{ab}}$$

$$\boldsymbol{\mathcal{R}}^{(n+1)} = \boldsymbol{\mathcal{R}}^{(n)} - \lambda_{\boldsymbol{\mathcal{R}}} \sum_{a} \left(\frac{\partial^2 \mathcal{F}}{\partial \boldsymbol{\mathcal{R}} \partial \mathcal{R}_a} \right)^{-1} \frac{\partial \mathcal{F}}{\partial \mathcal{R}_a}.$$

- The steps $\lambda_{\boldsymbol{\mathcal{R}}}$ and $\lambda_{\boldsymbol{\Phi}}$ are adimensional
- It can be shown that in this case

$$\Phi_{ab}^{(n+1)} = \Phi_{ab}^{(n)} - \lambda_{\boldsymbol{\Phi}} \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right) \sum_c \Psi^{-1}{}_{ac} \left(R_c - \mathcal{R}_c \right) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

$$\mathcal{R}_a^{(n+1)} = \mathcal{R}_a^{(n)} + \lambda_{\boldsymbol{\mathcal{R}}} \sum_b \Phi_{ab}^{-1} \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

The SSCHA self-consistent equation

- The SSCHA minimization can be performed fixing $\boldsymbol{\mathcal{R}}$ and only optimizing the auxiliary force constants
- In that case the SSCHA solution will obey the following self-consistent equation

$$\Phi_{ab}(\boldsymbol{\mathcal{R}}) = \left\langle \frac{\partial^2 V}{\partial R_a \partial R_b} \right\rangle_{\tilde{\rho}_{\boldsymbol{\Phi}(\boldsymbol{\mathcal{R}})}}$$

- This self-consistent equation opens a way to implement the SSCHA without using the gradient-descent approach

Stochastic calculation of the free energy and its gradient

- The calculation of the free energy and the gradient need

$$\langle V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R})\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right)(R_c - \mathcal{R}_c)\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

Importance sampling for the quantum statistical averages

- Quantum statistical averages involve observables that depend on the position

$$\langle O\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = \mathrm{tr}[\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}} O] = \int \mathrm{d}\mathbf{R} O(\mathbf{R})\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\mathbf{R})$$

- Create N_c ionic configurations in a supercell according to $\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R})$: $\{\mathbf{R}_I\}_{I=1,\ldots,N_c}$
- Stochastic evaluation of the integral: $\langle O\rangle_{\rho_{\mathcal{H}_0}} \simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O(\mathbf{R}_I)$

Stochastic calculation of the free energy and its gradient

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- Stochastic evaluation of the integral: $\langle O\rangle_{\rho_{\mathcal{H}_0}} \simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O(\mathbf{R}_I)$
- Requires to evaluate forces and energies in supercells: $\mathbf{f}(\mathbf{R}_I), V(\mathbf{R}_I)$

Stochastic calculation of the free energy and its gradient

- The calculation of the free energy and the gradient need

$$\langle V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R})\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right)(R_c - \mathcal{R}_c)\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

Reweighting for the quantum statistical averages for CG step $n > 0$

- The calculated forces and energies can be recycled throughout the CG minimization

$$\int \mathrm{d}\mathbf{R} O(\mathbf{R}) \tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}) = \int \mathrm{d}\mathbf{R} O(\mathbf{R}) \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R})}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R})} \tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}) \simeq$$
$$\frac{1}{N_c} \sum_{I=1}^{N_c} O(\mathbf{R}_I) \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)}$$

- The reweighting procedure is valid as long as

$$\frac{1}{N_c} \sum_{I=1}^{N_c} \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)} \sim 1$$

Stochastic calculation of the free energy and its gradient

- The calculation of the free energy and the gradient need

$$\langle V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R}) \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right) (R_c - \mathcal{R}_c) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

Reweighting for the quantum statistical averages for CG step $n > 0$

- The calculated forces and energies can be recycled throughout the CG minimization

$$\int \mathrm{d}\mathbf{R} O(\mathbf{R}) \tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}) = \int \mathrm{d}\mathbf{R} O(\mathbf{R}) \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R})}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R})} \tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}) \simeq$$
$$\frac{1}{N_c} \sum_{I=1}^{N_c} O(\mathbf{R}_I) \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)}$$

- The reweighting procedure is valid as long as

$$\frac{1}{N_c} \sum_{I=1}^{N_c} \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)} \sim 1$$

- The SSCHA can be applied at any degree of theory
  - empirical potentials
  - DFT *ab initio*
  - Beyond DFT (Monte Carlo, GW, ...)

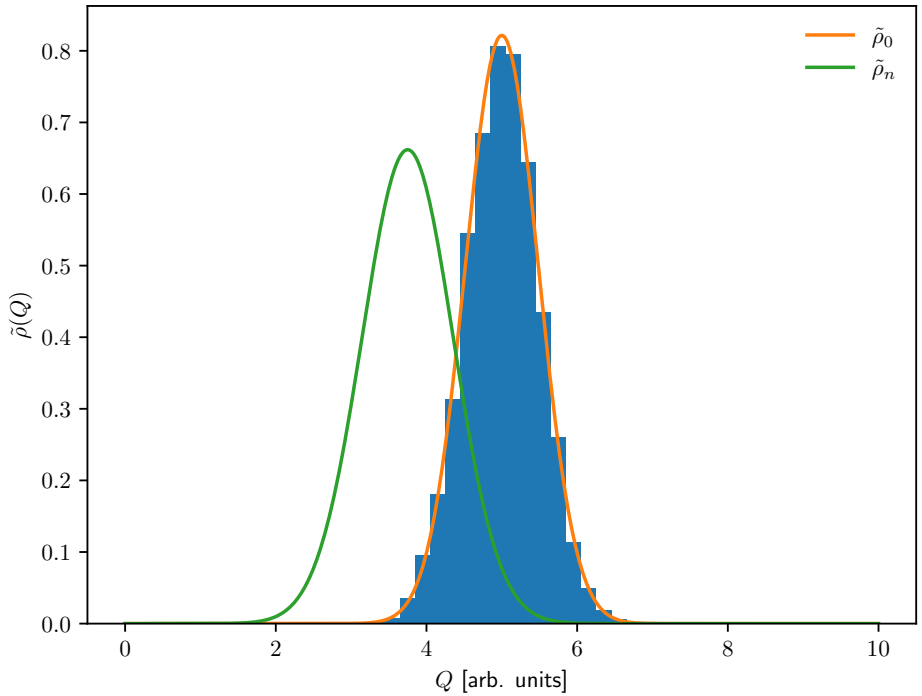
The SSCHA coming out of statistical range

- The SSCHA stops the minimization if the created set of configurations no longer resembles $\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}$
- This is detected according to the Kong-liu criteria that sets the number of effective configurations at step n

$$N_n^{eff} = \frac{\sum_{I=1}^{N_c} \rho_n^2(I)}{\left(\sum_{I=1}^{N_c} \rho_n(I)\right)^2}$$

where the weights are

$$\rho_n(I) = \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)}$$



- If at step n $N_n^{eff}/N_c < \eta$, where η is a number around 0.5, the SSCHA minimization stops and one should create new configurations with the updated $\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}$

The SSCHA convergence threshold

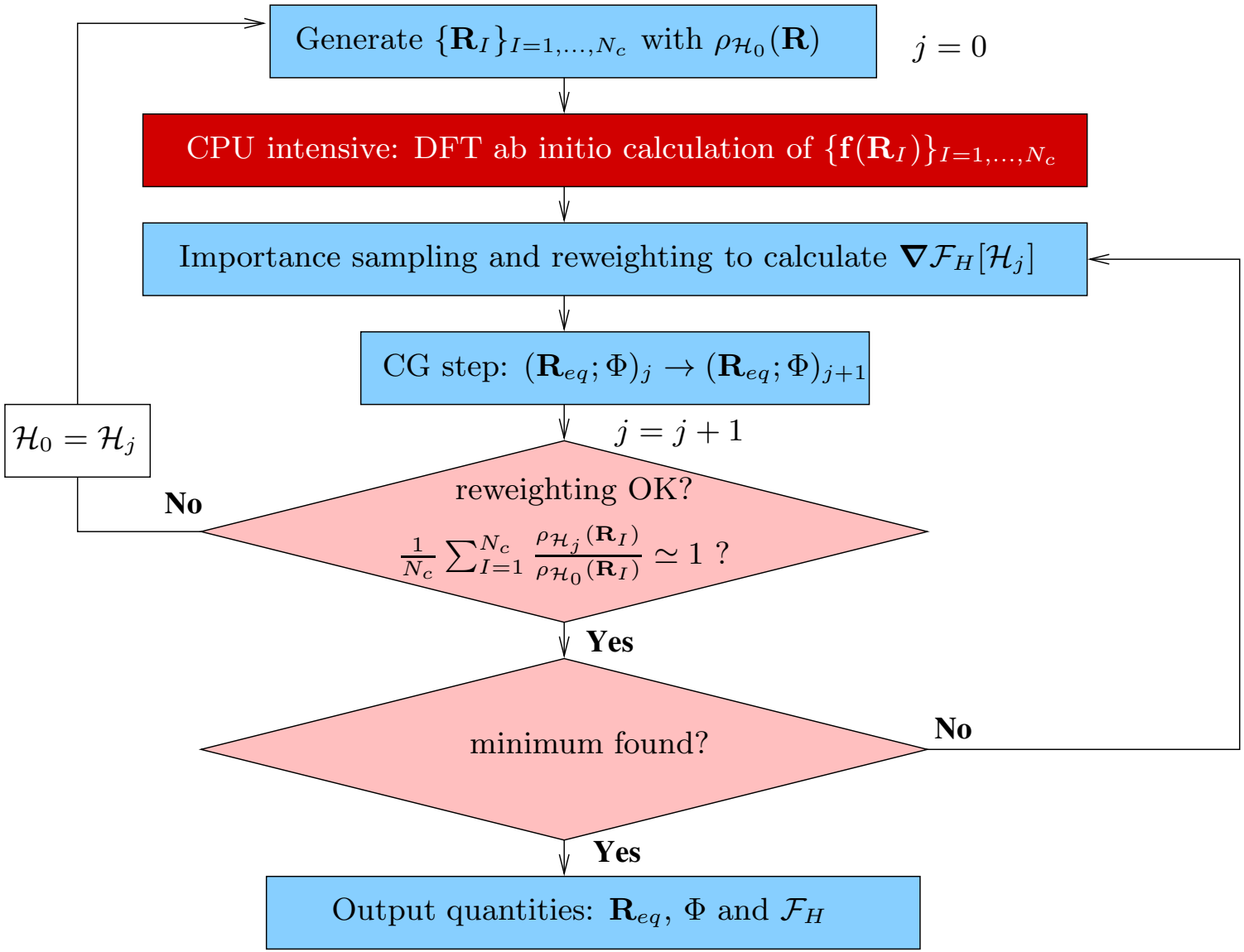
- The SSCHA calculation is stopped when the values of the gradients become smaller than a ratio (δ) of its estimated error

$$\left| \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\Phi}} \right| < \delta \left| \Delta \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\Phi}} \right|$$

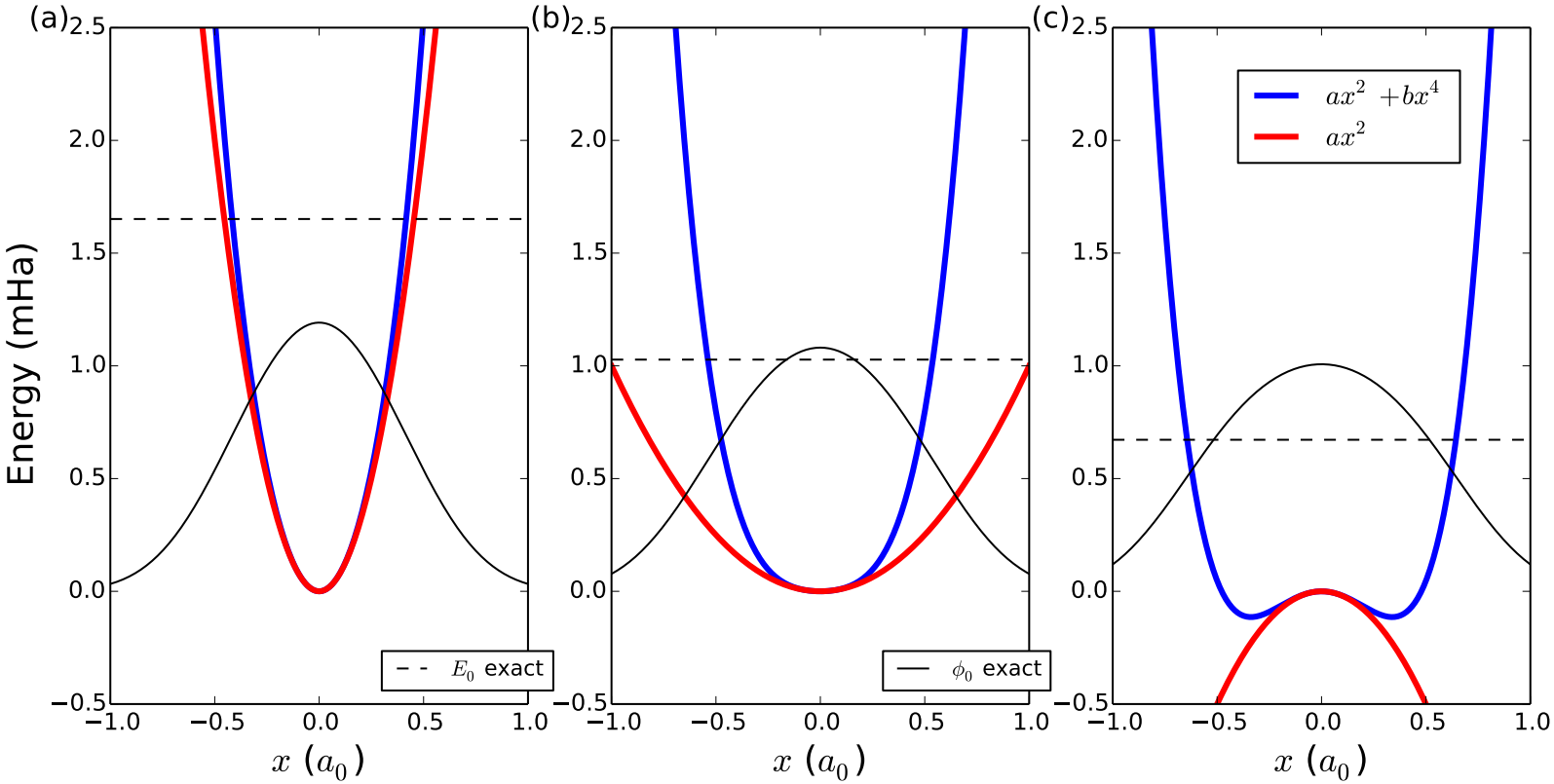
$$\left| \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\mathcal{R}}} \right| < \delta \left| \Delta \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\mathcal{R}}} \right|$$

- When this criteria is reached in both gradients the calculation is assumed to be converged
- The ideal thing is to use a very small δ and try to read 0 gradients

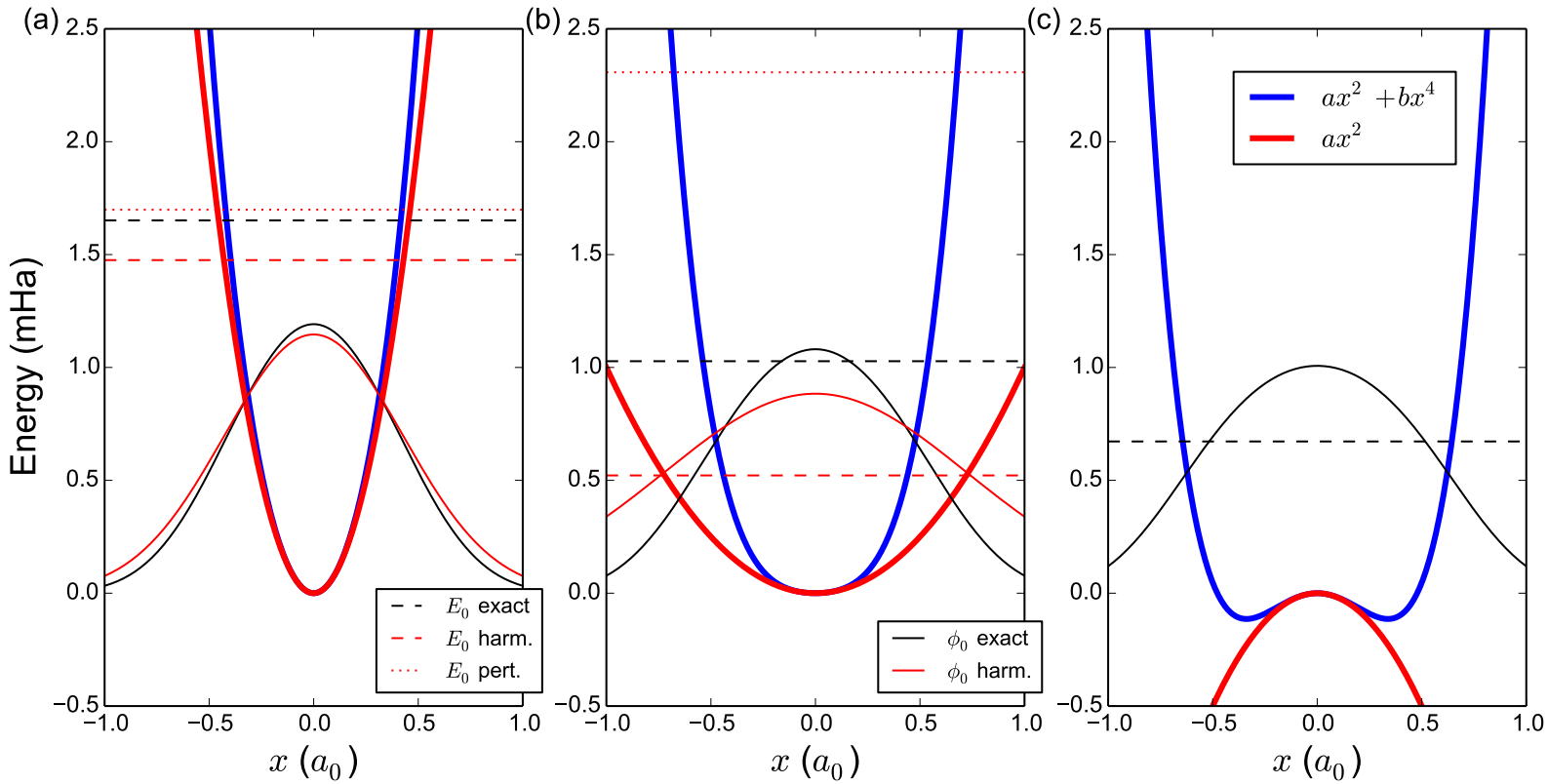
SSCHA calculation flowchart



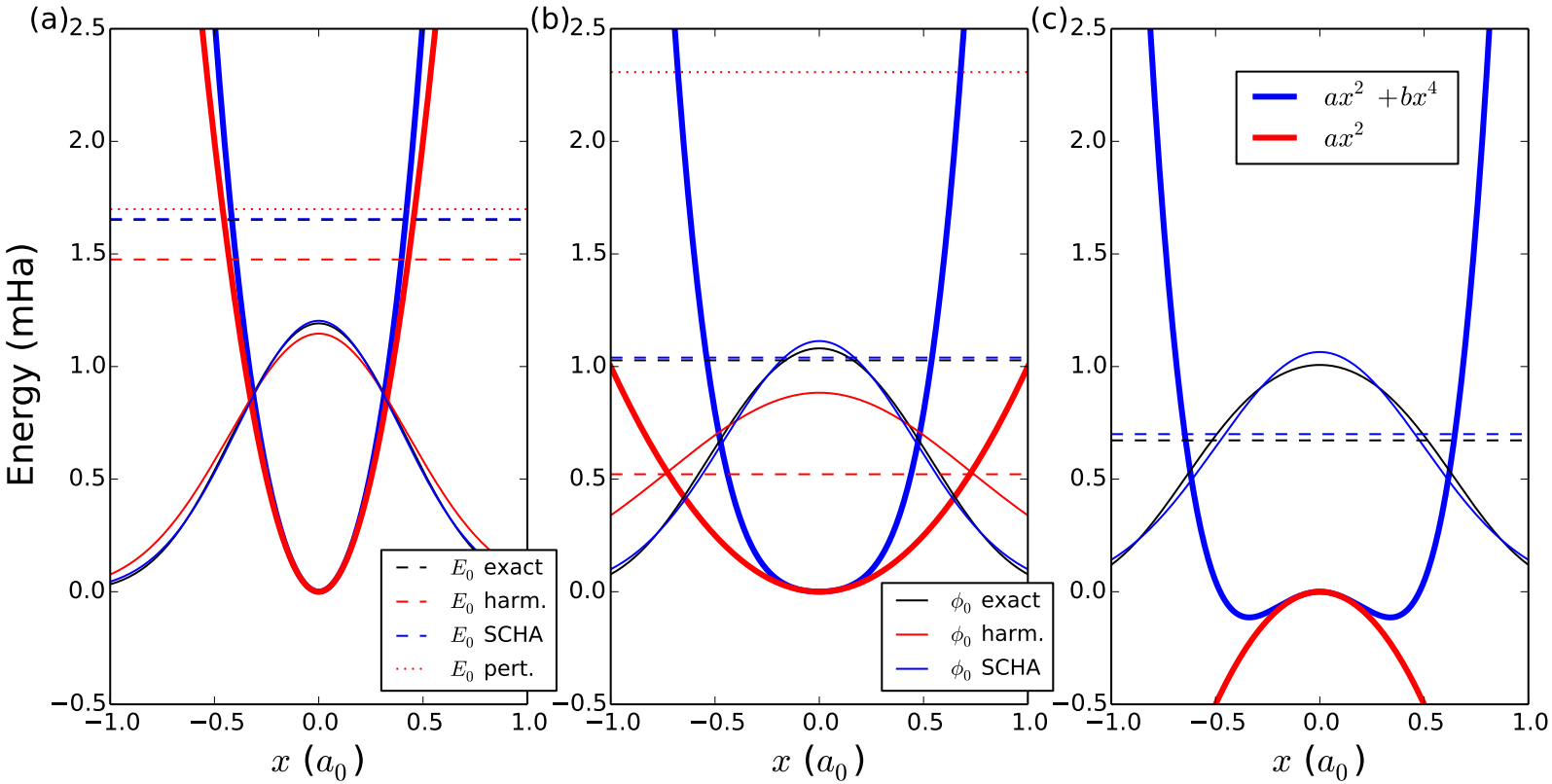
SSCHA example in 1D



SSCHA example in 1D

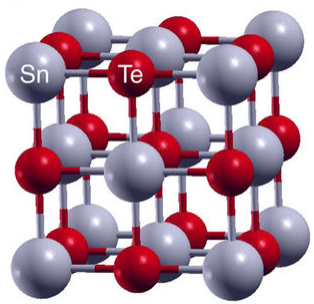


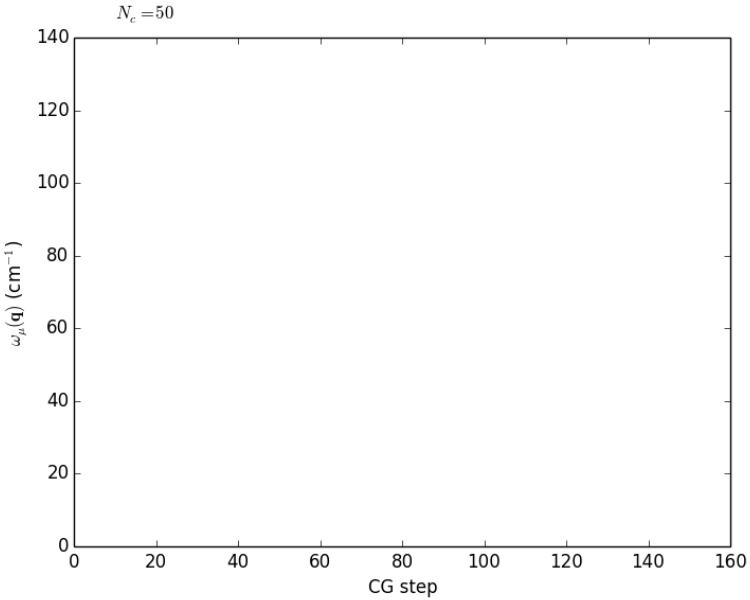
SSCHA example in 1D

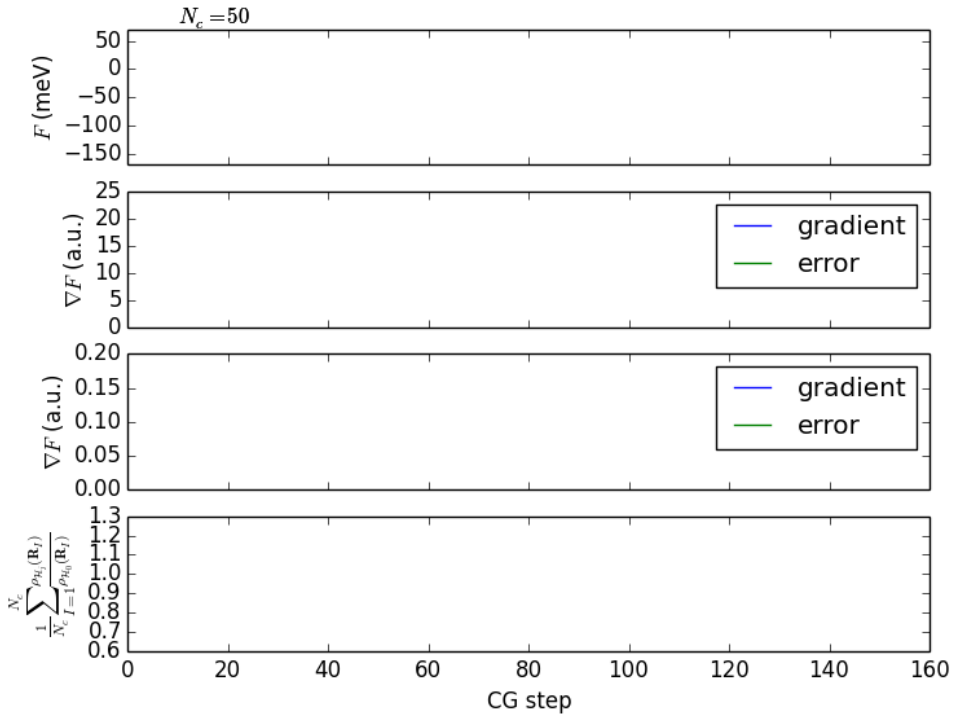


SSCHA calculation example

Model calculation with empirical potentials for SnTe with a 2×2×2 supercell







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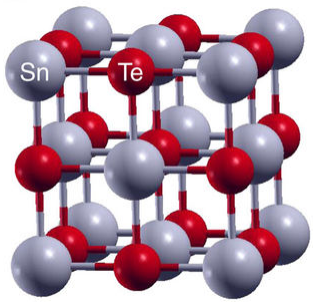

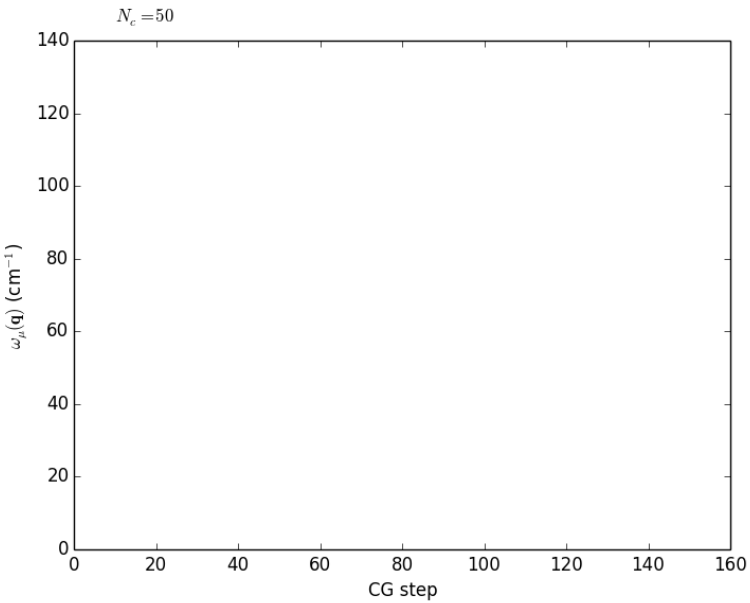

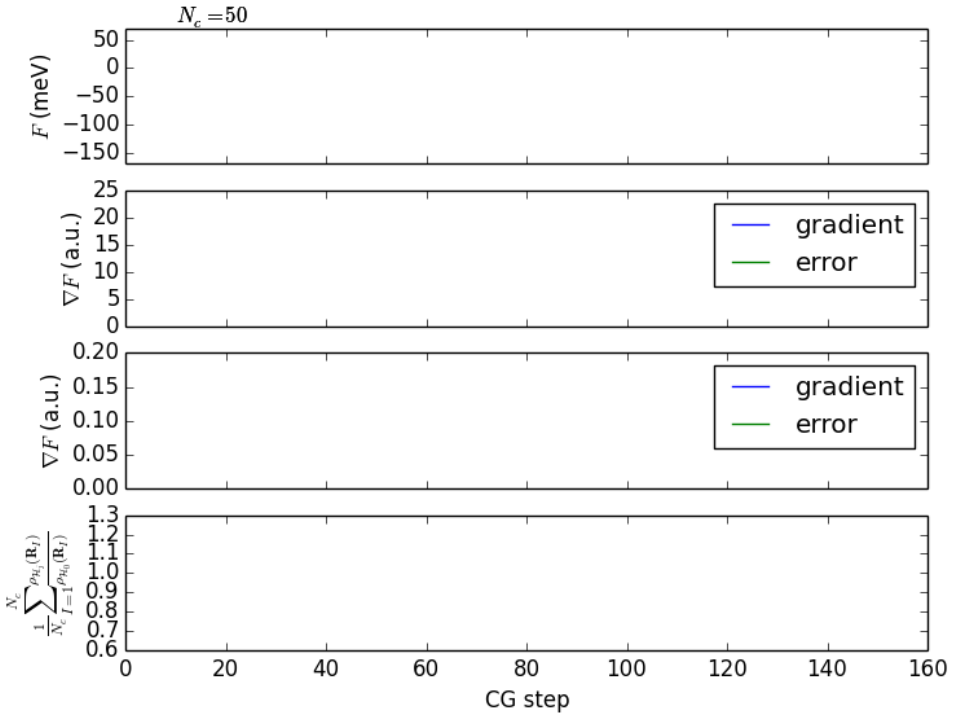

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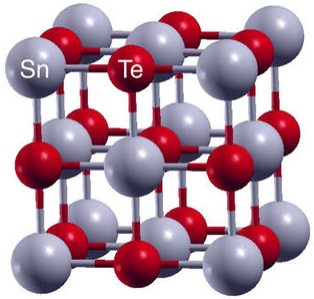

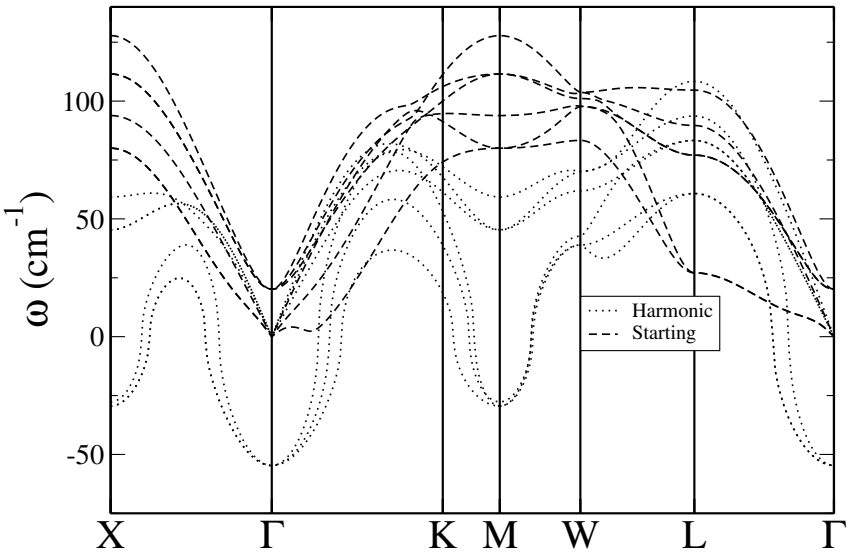

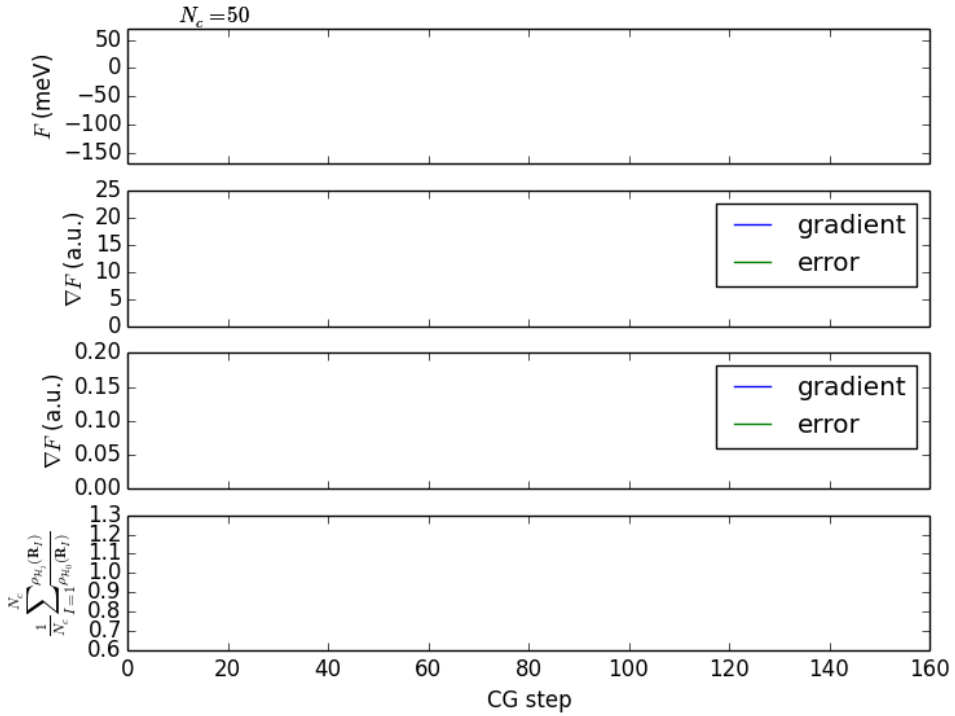

SSCHA calculation example

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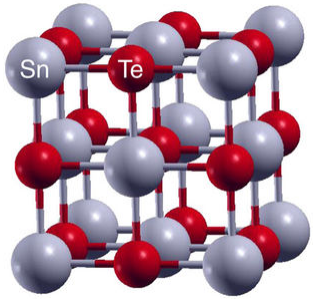

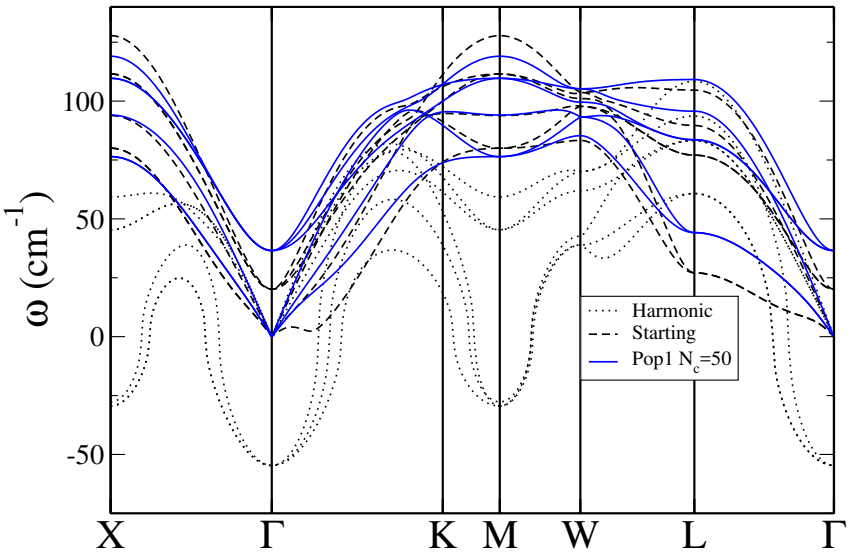

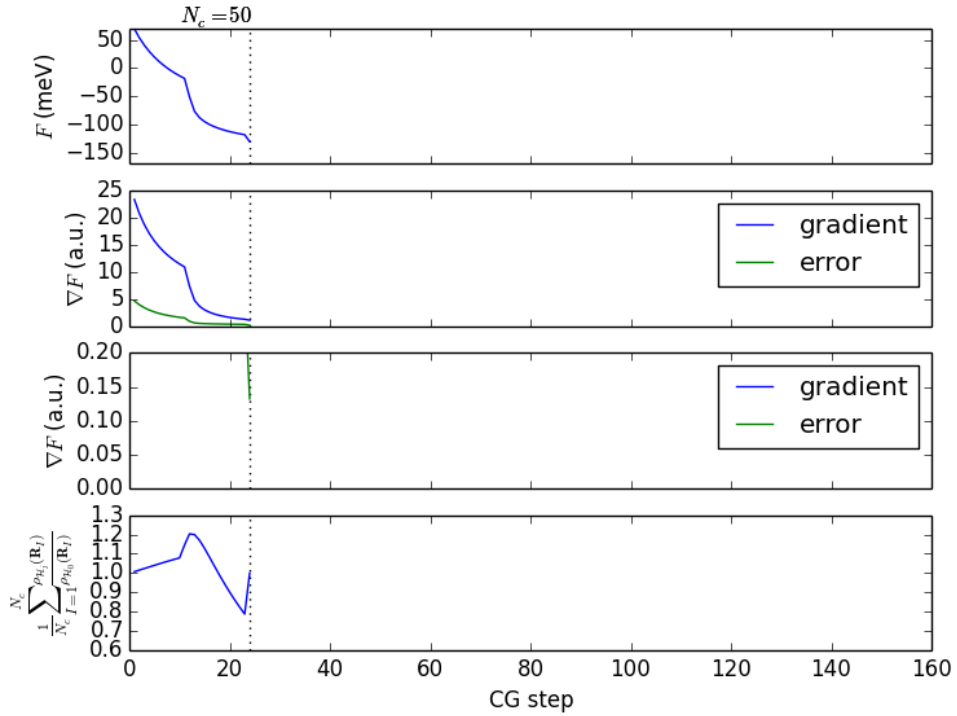

SSCHA calculation example

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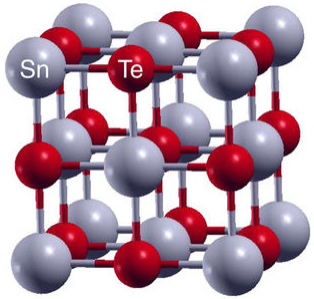

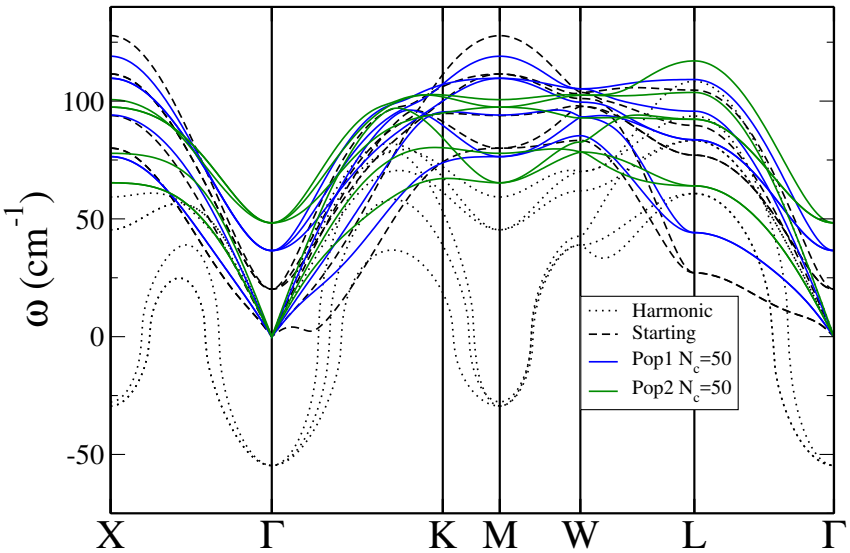

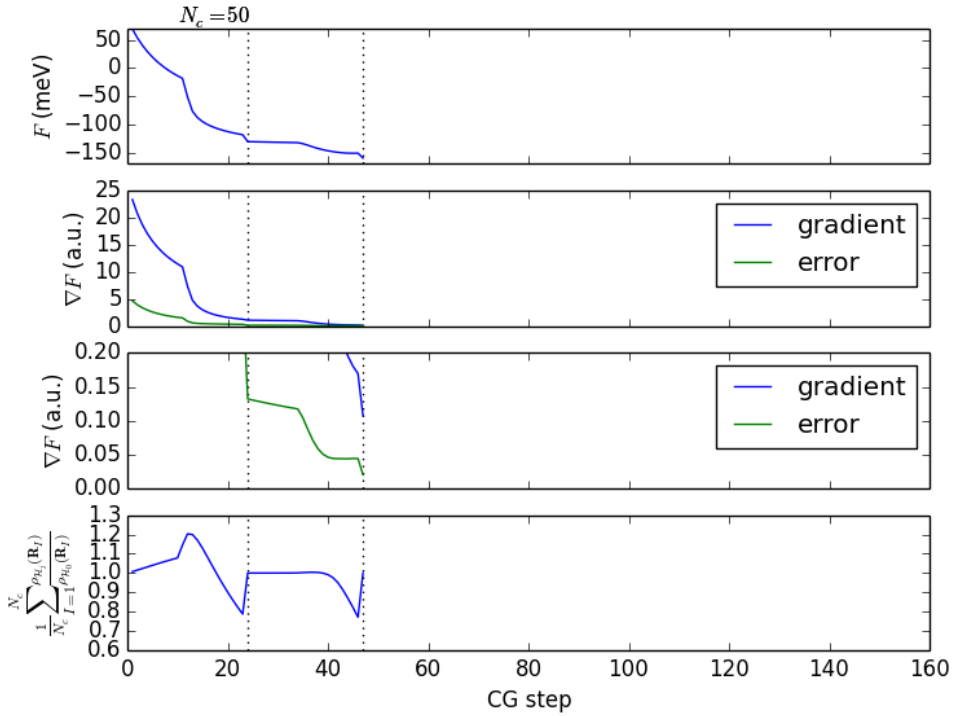

SSCHA calculation example

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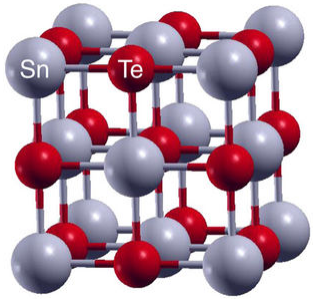
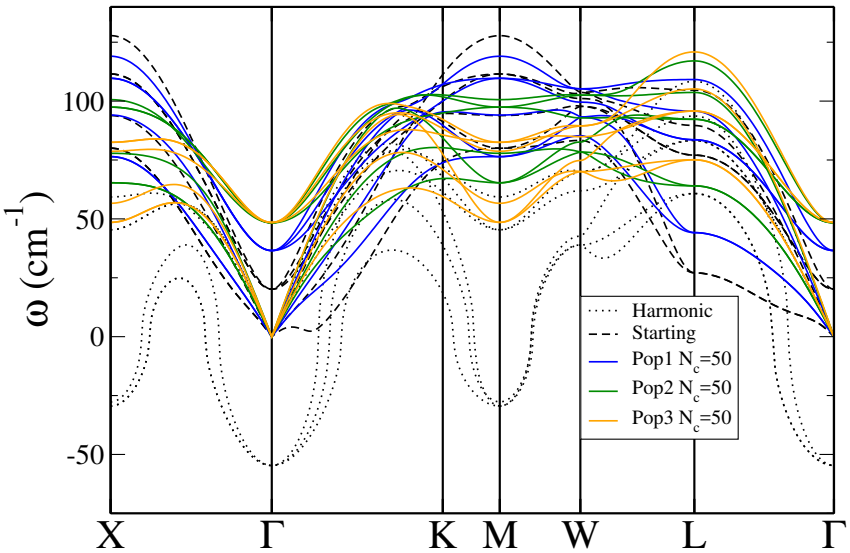
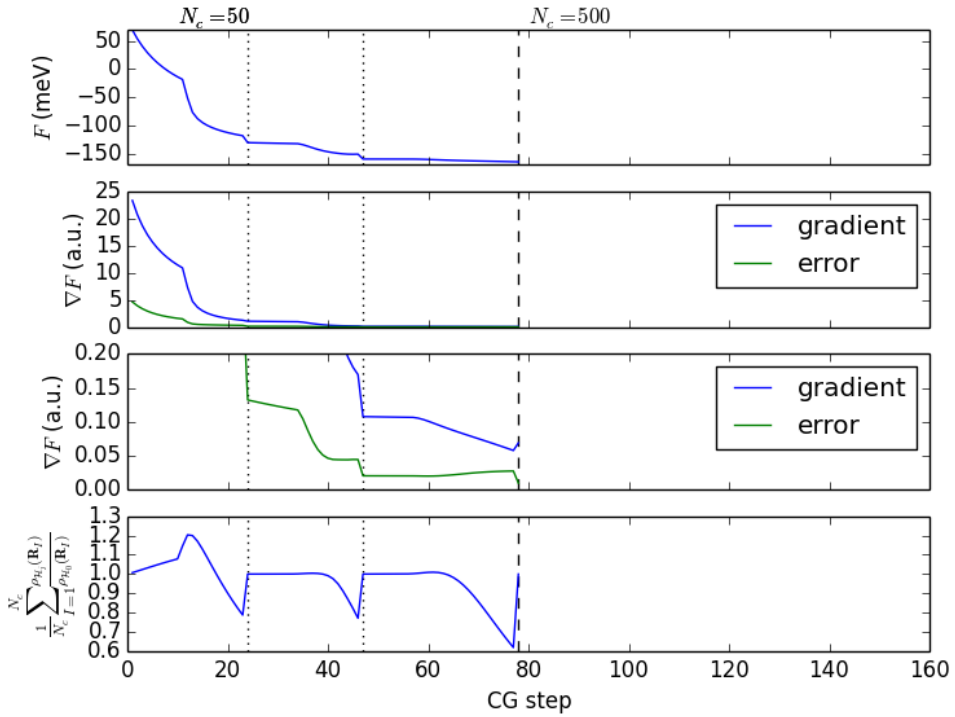
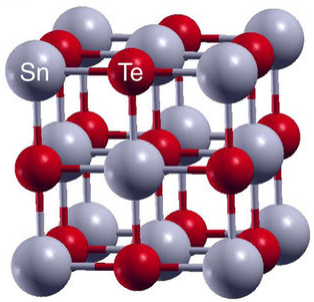


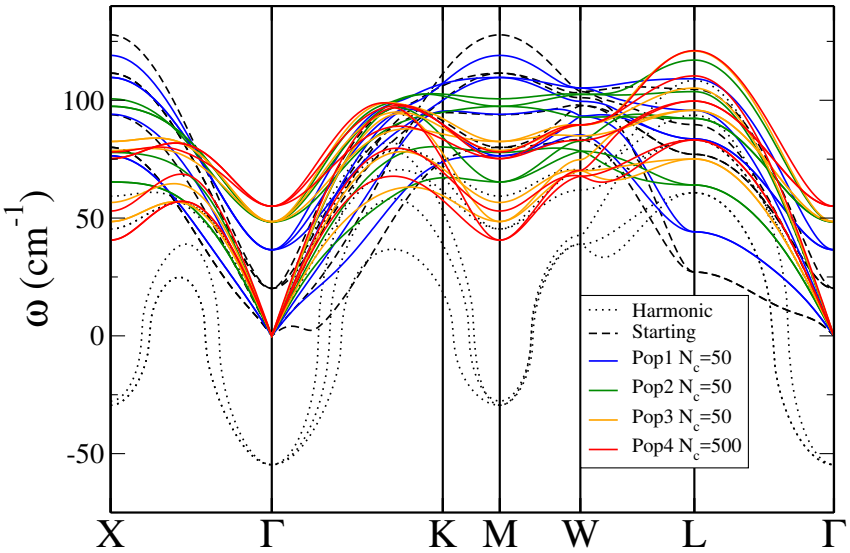


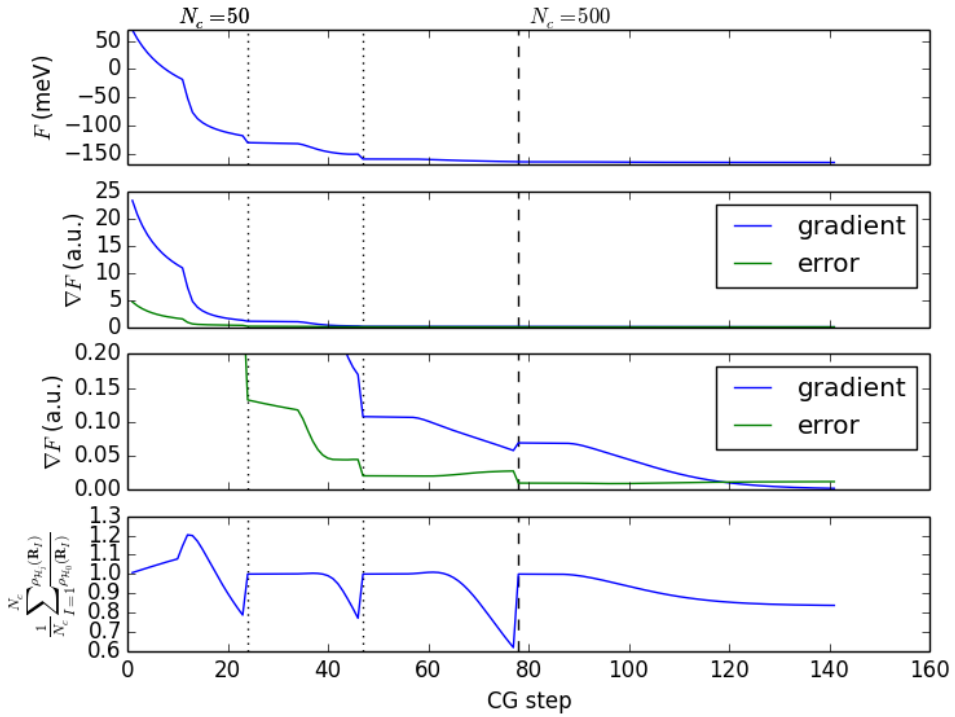


SSCHA calculation example

Model calculation with empirical potentials for SnTe with a 2×2×2 supercell

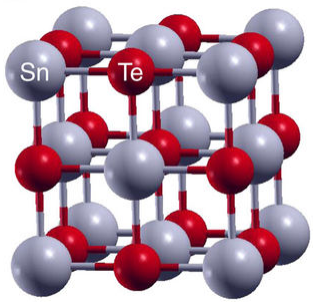


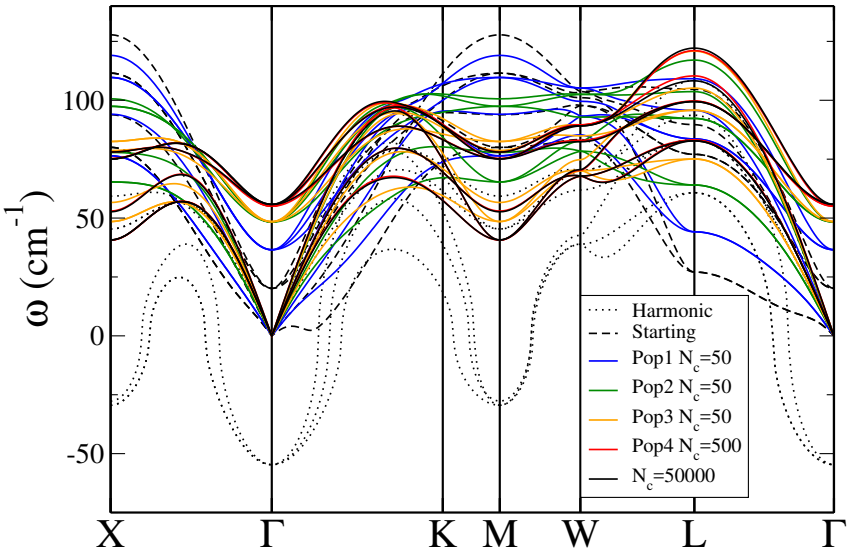


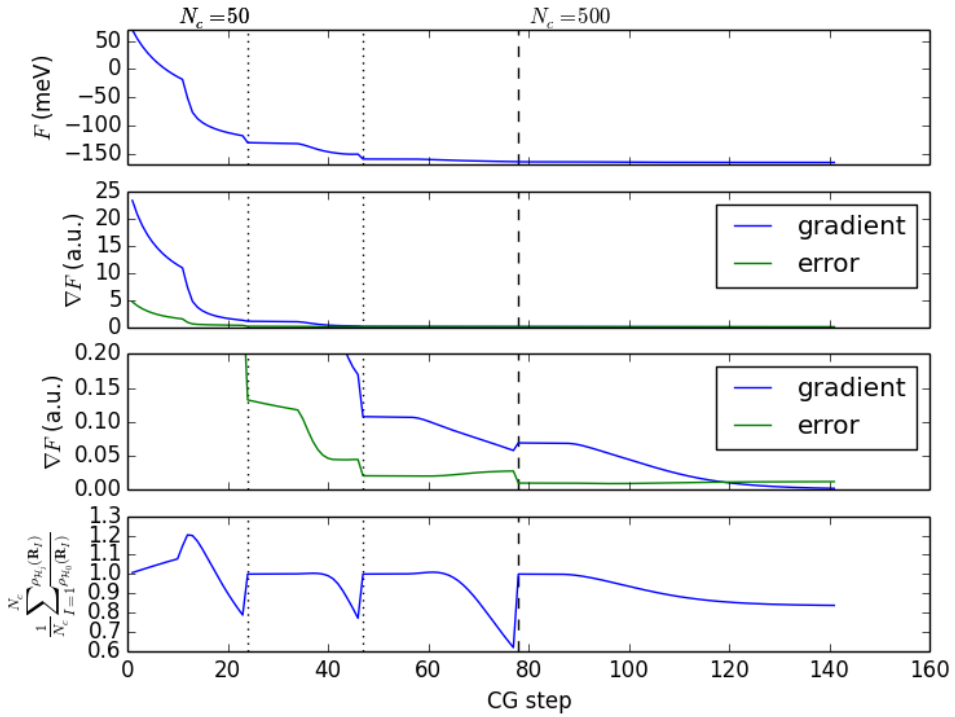


SSCHA calculation example

Model calculation with empirical potentials for SnTe with a 2×2×2 supercell







The optimization of the lattice in the SSCHA

- The SSCHA can be used to relax the lattice parameters of a structure considering quantum and thermal effects, and full anharmonicity
- When a lattice is relaxed in standard methods the contribution of the ions to the energy is neglected as the stress tensor is calculated from $V(\boldsymbol{R})$

$$P^{BO}_{\alpha\beta} = -\frac{N}{\Omega}\left[\frac{\partial V(\boldsymbol{R})}{\partial \varepsilon_{\alpha\beta}}\right]_{\boldsymbol{\varepsilon}=0}$$

- In the SSCHA we can calculate the stress tensor includes ionic quantum and thermal effects in the lattice parameters

$$P_{\alpha\beta} = -\frac{N}{\Omega}\left[\frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \varepsilon_{\alpha\beta}}\right]_{\boldsymbol{\varepsilon}=0} = \left\langle P^{BO}_{\alpha\beta}(\boldsymbol{R})\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} - \frac{N}{2\Omega}\sum_s \left\langle u_s^\alpha f_s^\beta + u_s^\beta f_s^\alpha \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

- For that, apart from forces, the classical $P^{BO}_{\alpha\beta}$ stresses need to be calculated for each of the structures in the ensemble

The optimization of the lattice in the SSCHA

- The ensemble is created with constant lattice and the lattice vectors $\{\boldsymbol{a}_i\}$ are updated when creating the next ensemble as

$$a'_{i\,\alpha} = a_{i\,\alpha} + \lambda_{\{\boldsymbol{a}_i\}} \sum_{\beta} \varepsilon_{\alpha\beta} a_{i\,\beta},$$

with

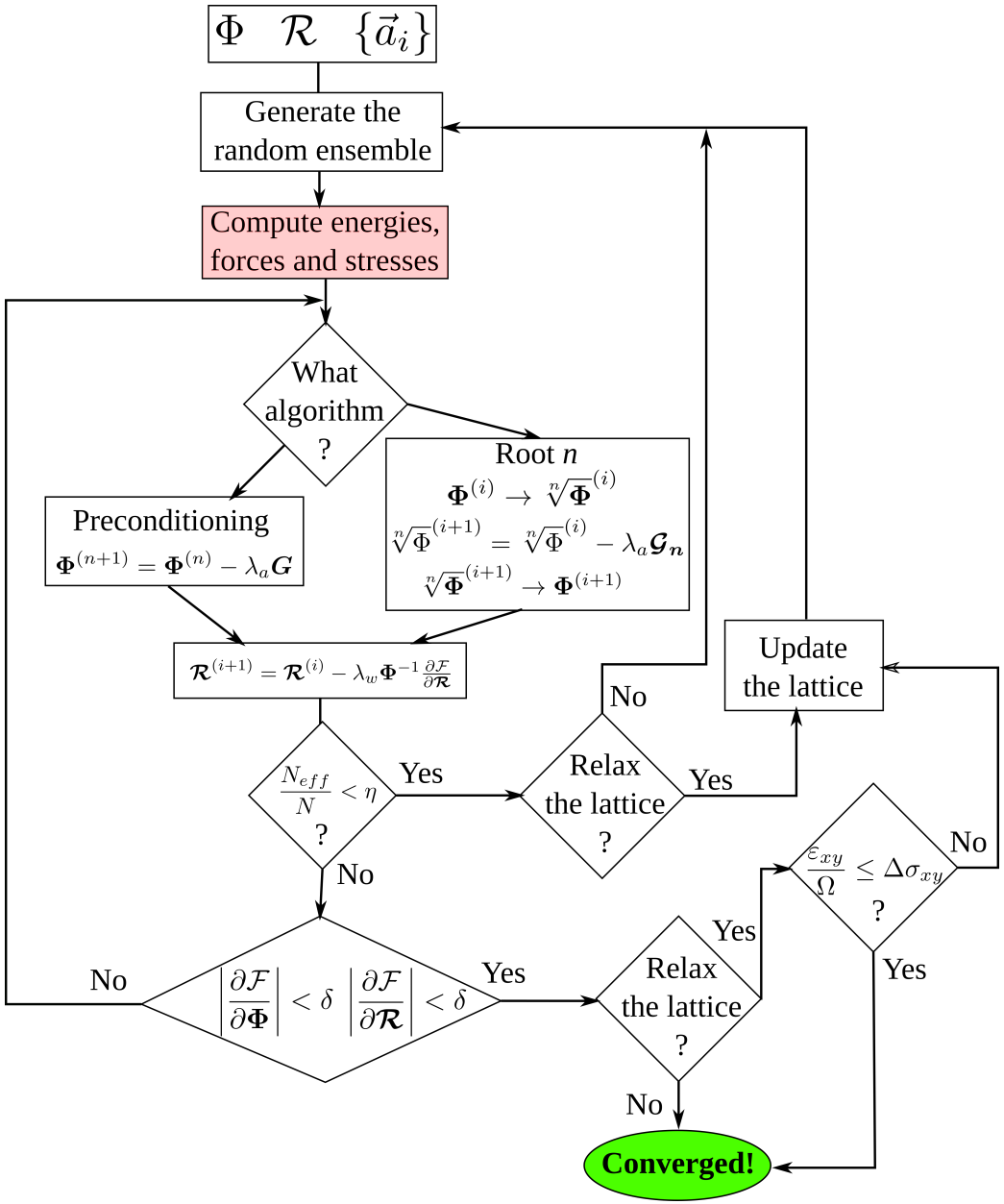
$$\varepsilon_{\alpha\beta} = \frac{\Omega}{N} \left(P_{\alpha\beta} - P^* \delta_{\alpha\beta} \right)$$

- P^* is the target pressure
- The best $\lambda_{\{\boldsymbol{a}_i\}}$ step is obtained with

$$\lambda_{\{\boldsymbol{a}_i\}} = \frac{1}{3\Omega B_0}$$

with B_0 the bulk modulus

SSCHA calculation flowchart with cell relaxation



Second-order displacive phase transition within the SSCHA

- Let's take $\boldsymbol{\mathcal{R}}$ fixed and calculate the SSCHA free energy for them:

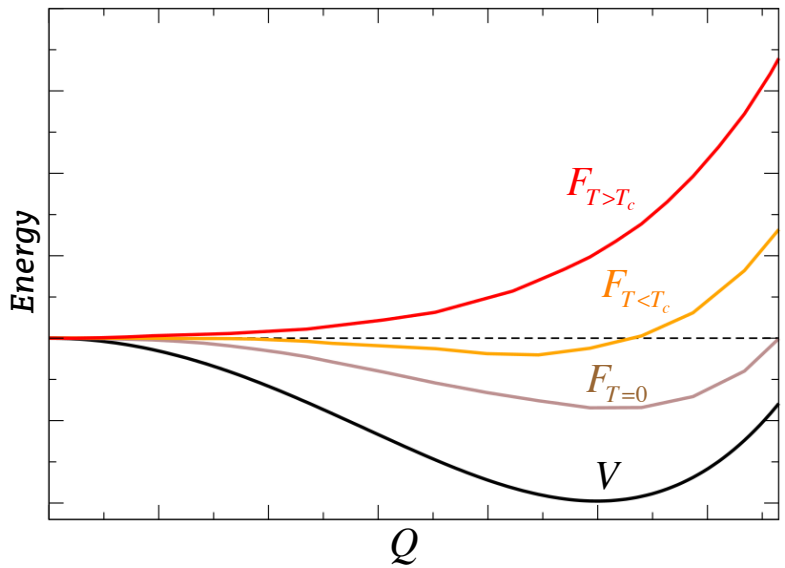
$$\left.\begin{array}{l}\mathcal{H} = T_i + \frac{1}{2}\sum_{ab}\Phi_{ab}(R_a - \mathcal{R}_a)(R_b - \mathcal{R}_b) \\ \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]\end{array}\right\} \rightarrow \mathcal{F}(\boldsymbol{\mathcal{R}})$$

- The SCHA free energy curvature

$$\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b}$$

- The second derivative with respect to the order parameter

$$\frac{d^2\mathcal{F}(Q)}{dQ^2} = \sum_{ab} \frac{d\mathcal{R}_a}{dQ} \frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} \frac{d\mathcal{R}_b}{dQ}$$



The free energy Hessian is analytic in the SSCHA

$$\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} = \Phi_{ab} + \sum_{cdefgh} \overset{(3)}{\Phi}_{acd} \Lambda_{cdef}[0] [\mathbf{1} + \overset{(4)}{\boldsymbol{\Phi}}\boldsymbol{\Lambda}[0]]^{-1}_{efgh} \overset{(3)}{\Phi}_{ghb}$$

- The SCHA auxiliary force-constants: $\boldsymbol{\Phi}$

- A contribution that depends on the 3rd derivatives of the BOES when $\overset{(4)}{\boldsymbol{\Phi}}\boldsymbol{\Lambda}[0] << 1$: $\overset{(3)}{\boldsymbol{\Phi}}\boldsymbol{\Lambda}[0]\overset{(3)}{\boldsymbol{\Phi}}$

$$\overset{(3)}{\Phi}_{abc} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

- If $\overset{(4)}{\boldsymbol{\Phi}}\boldsymbol{\Lambda}[0]$ is considered we also need to calculate

$$\overset{(4)}{\Phi}_{abcd} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c \partial R_d} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

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- The SCHA auxiliary force-constants: $\boldsymbol{\Phi}$
  It is positive definite
- A contribution that depends on the 3rd derivatives of the BOES when $\overset{(4)}{\boldsymbol{\Phi}} \boldsymbol{\Lambda}[0] << 1$: $\overset{(3)}{\boldsymbol{\Phi}} \boldsymbol{\Lambda}[0] \overset{(3)}{\boldsymbol{\Phi}}$

$$\overset{(3)}{\Phi}_{abc} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}}}$$

  It is negative definite
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$$\overset{(4)}{\Phi}_{abcd} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c \partial R_d} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}}}$$

The SCHA can only describe second-order phase transitions if $\overset{(3)}{\Phi} \neq 0$

The free energy curvature allows to define dynamical matrices that can describe inginary phonon frequencies

Different dynamical matrices:

- Harmonic dynamical matrix:

$$D_{ab}^{har} = \frac{1}{\sqrt{M_a M_b}} \left[\frac{\partial^2 V(\mathbf{R})}{\partial R_a \partial R_b} \right]_{\mathbf{R}=\mathbf{R}_0} = \frac{1}{\sqrt{M_a M_b}} \phi_{ab}$$

- SCHA dynamical matrix calculated at $\boldsymbol{\mathcal{R}}_0$:

$$D_{ab}^{S} = \frac{1}{\sqrt{M_a M_b}} \Phi_{ab}$$

- Dynamical matrix based on SCHA free energy curvature:

$$D_{ab}^{F} = \frac{1}{\sqrt{M_a M_b}} \left[\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} \right]_{\boldsymbol{\mathcal{R}}=\boldsymbol{\mathcal{R}}_0}$$

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  All the problems of the harmonic approximation

- SCHA dynamical matrix calculated at $\boldsymbol{\mathcal{R}}_0$:

$$D_{ab}^{S} = \frac{1}{\sqrt{M_a M_b}} \Phi_{ab}$$

  Includes non-perturbative anharmonic effects, temperature dependence . . . but positive eigenvalues by definition

- Dynamical matrix based on SCHA free energy curvature:

$$D_{ab}^{F} = \frac{1}{\sqrt{M_a M_b}} \left[\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} \right]_{\boldsymbol{\mathcal{R}}=\boldsymbol{\mathcal{R}}_0}$$

  Correction to D_{ab}^{S} including 3rd and 4th order derivatives of the BOES that may have negative eigenvalues and describe second-order phase transitions

The free energy curvature can be obtained stochastically by calculating forces on supercells

$$\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} = \Phi_{ab} + \sum_{cdefgh} \overset{(3)}{\Phi}_{acd} \Lambda_{cdef}[0][\mathbf{1} + \overset{(4)}{\boldsymbol{\Phi}}\boldsymbol{\Lambda}[0]]^{-1}_{efgh} \overset{(3)}{\Phi}_{ghb}$$

Requires

- Quantum stochastic average of 3rd derivatives of the BOES

$$\overset{(3)}{\Phi}_{abc} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = -\sum_{pq} \Psi^{-1}_{ap} \Psi^{-1}_{bq} \langle u^p u^q \tilde{f}_c \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

- Quantum stochastic average of 4th derivatives of the BOES

$$\overset{(4)}{\Phi}_{abcd} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c \partial R_d} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = -\sum_{pqr} \Psi^{-1}_{ap} \Psi^{-1}_{bq} \Psi^{-1}_{cr} \langle u^p u^q u^r \tilde{f}_d \rangle_{\rho_{\mathcal{H}}}$$

$u_a = R_a - \mathcal{R}_a$ and $\tilde{f}_a = f_a + \sum_b \Phi_{ab} u_b$

The free energy curvature can be obtained stochastically by calculating forces on supercells

$$\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} = \Phi_{ab} + \sum_{cdefgh} \overset{(3)}{\Phi}_{acd} \Lambda_{cdef}[0] [\mathbf{1} + \overset{(4)}{\boldsymbol{\Phi}} \boldsymbol{\Lambda}[0]]^{-1}_{efgh} \overset{(3)}{\Phi}_{ghb}$$

Requires

- Quantum stochastic average of 3rd derivatives of the BOES

$$\overset{(3)}{\Phi}_{abc} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = -\sum_{pq} \Psi^{-1}_{ap} \Psi^{-1}_{bq} \langle u^p u^q \tilde{f}_c \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

- Quantum stochastic average of 4th derivatives of the BOES

$$\overset{(4)}{\Phi}_{abcd} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c \partial R_d} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = -\sum_{pqr} \Psi^{-1}_{ap} \Psi^{-1}_{bq} \Psi^{-1}_{cr} \langle u^p u^q u^r \tilde{f}_d \rangle_{\rho_{\mathcal{H}}}$$

$u_a = R_a - \mathcal{R}_a$ and $\tilde{f}_a = f_a + \sum_b \Phi_{ab} u_b$

The free energy curvature can be calculated stochastically as a post-processing by using importance sampling after the SSCHA minimization

TAn important remark on the force constants

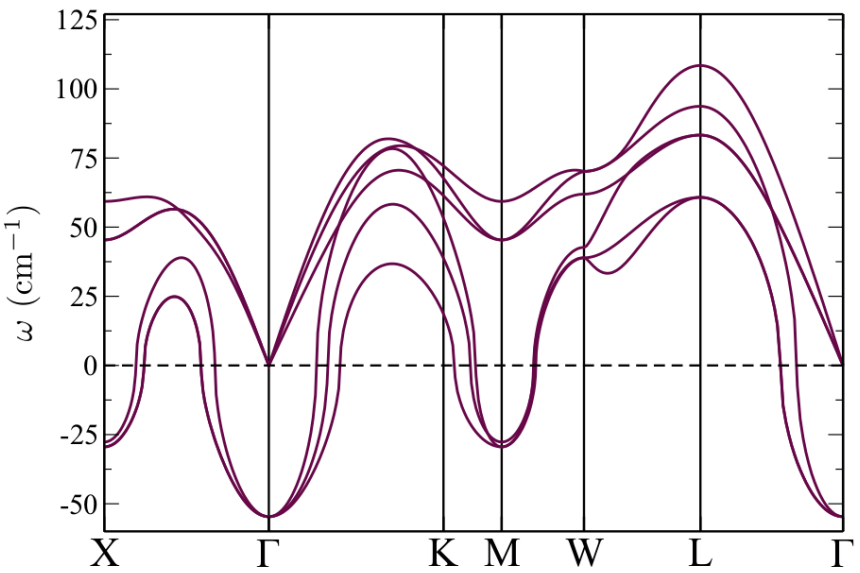
$$\overset{(3)}{\Phi}_{abc} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} \neq \overset{(3)}{\phi}_{abc} = \left[\frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c} \right]_{\boldsymbol{R}_0}$$

$$\overset{(4)}{\Phi}_{abcd} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c \partial R_d} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} \neq \overset{(4)}{\phi}_{abcd} = \left[\frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c \partial R_d} \right]_{\boldsymbol{R}_0}$$

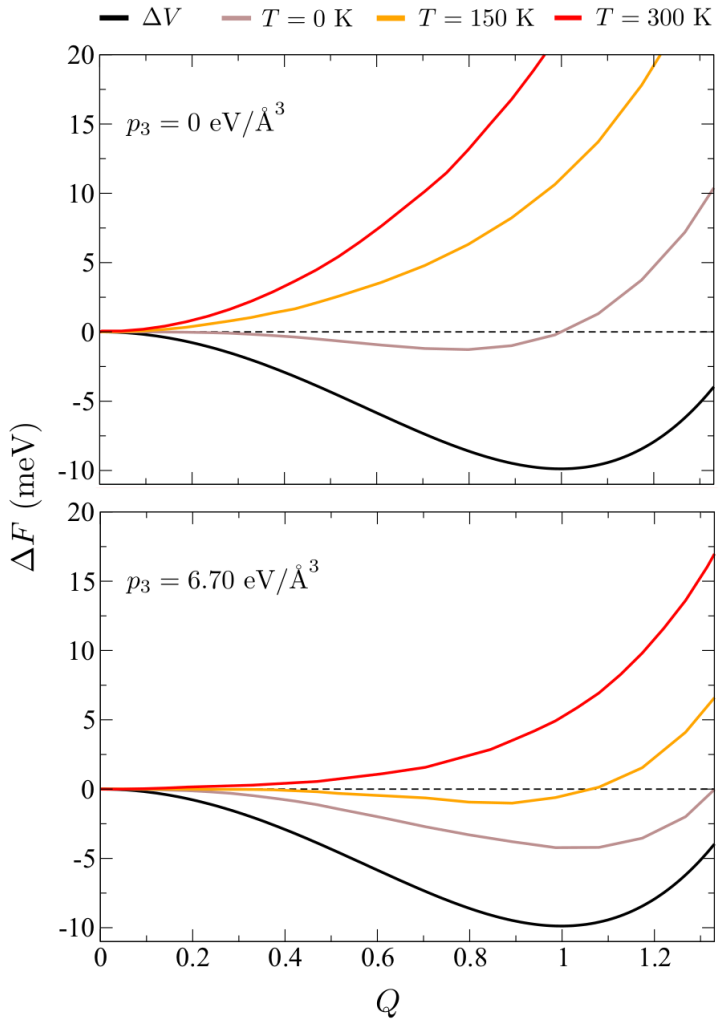
- Quantum stochastic averaged of 3rd and 4th order force constants consider higher order terms, are non-perturbative
- Quantum stochastic averaged of 3rd and 4th order force constants are taken at the centroid positions that minimize the free energy, not the $\boldsymbol{R}_0$ positions that minimize the potential

An example that models a ferroelectric phase transition shows the validity of the procedure

- An anharmonic model potential that describes the ferroelectric transition in SnTe ($Fm\bar{3}m \rightarrow R3m$)
- The transition is driven by the optical mode at Γ

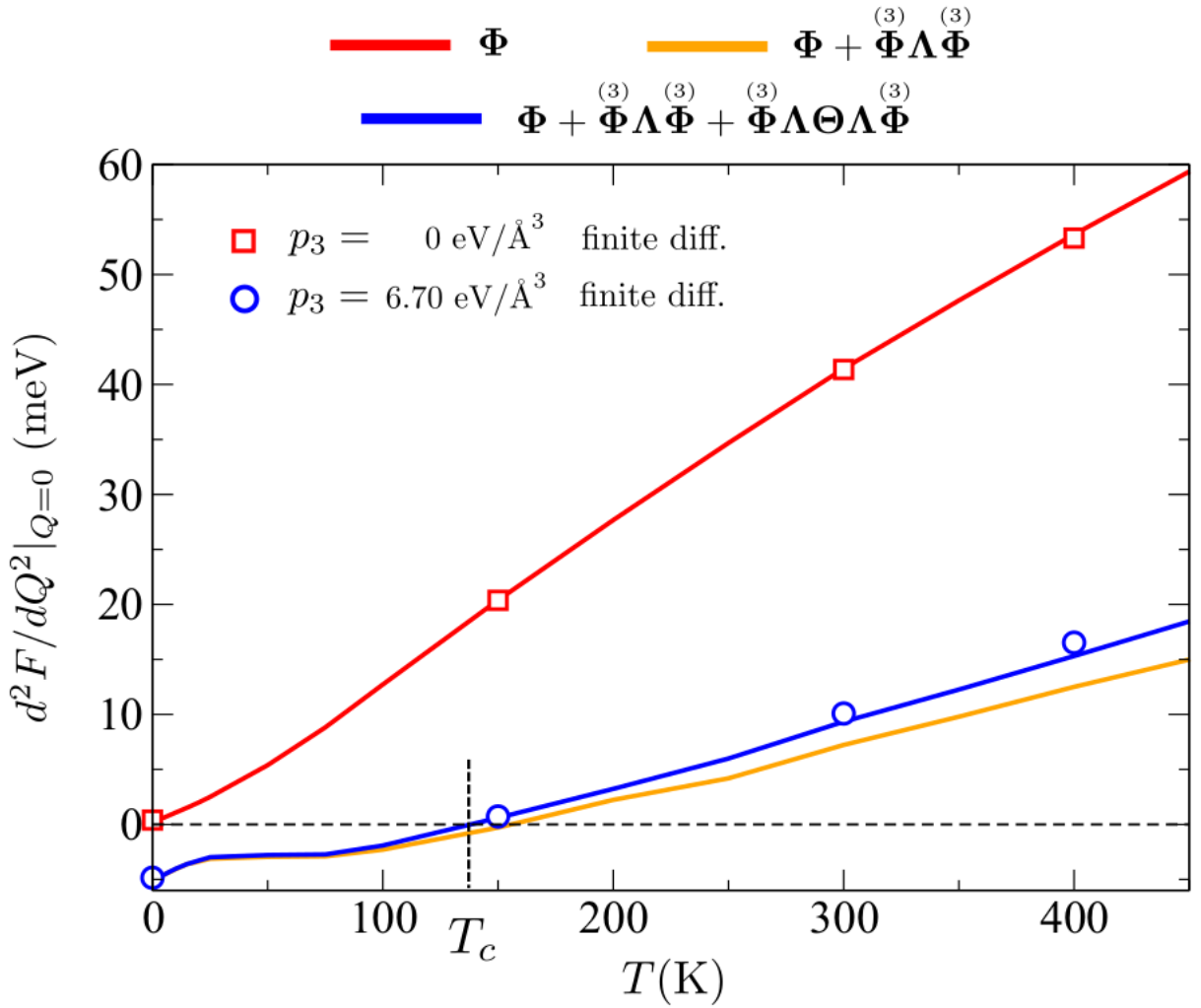


Harmonic phonons

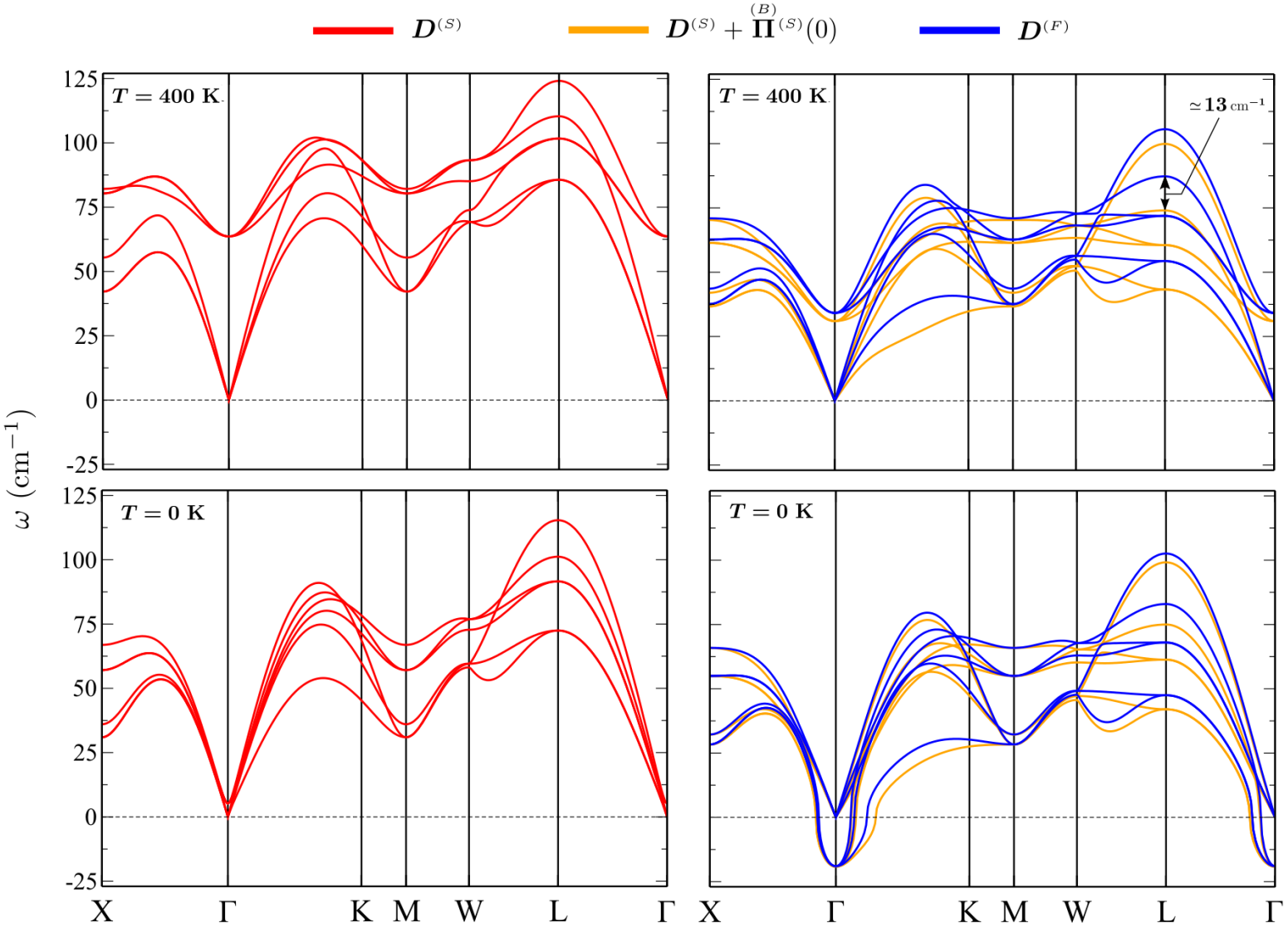


SSCHA free energy with/without 3rd order in the potential

The free energy curvature calculated matches finite difference calculations



The phonons obtained from the free energy curvature have strong corrections beyond the SCHA phonons



Physical phonons need to come from a dynamical theory

- The SSCHA auxiliary solution defines non-interacting Green's functions which are exactly like the harmonic
- The SSCHA solution can be used to build a fully dynamical theory based on a Dyson equation

$$G^{-1}_{ab}(\boldsymbol{q}, i\omega_n) = [G^S_{ab}]^{-1}(\boldsymbol{q}, i\omega_n) - \Pi_{ab}(\boldsymbol{q}, i\omega_n) = (i\omega_n)^2\delta_{ab} - \frac{\Phi_{ab}(\boldsymbol{q})}{\sqrt{M_a M_b}} - \Pi_{ab}(\boldsymbol{q}, i\omega_n)$$

where $\boldsymbol{G}^S$ is the non-interacting Green's function based on the SSCHA auxiliary force-constants

- The SSCHA self-energy is

$$\Pi_{ab}(\boldsymbol{q}, i\omega_n) = \frac{1}{\sqrt{M_a M_b}} \sum_{cdefgh} \overset{(3)}{\Phi}_{acd} \Lambda_{cdef}[i\omega_n][\mathbf{1} + \overset{(4)}{\boldsymbol{\Phi}}\boldsymbol{\Lambda}[i\omega_n]]^{-1}_{efgh} \overset{(3)}{\Phi}_{ghb}$$

with

$$\begin{aligned}\Lambda_{abcd}[i\omega_n] &= \sum_{\mu\nu} \frac{\hbar}{4\mathtt{w}_\nu \mathtt{w}_\mu} \mathtt{e}^a_\nu \mathtt{e}^b_\mu \mathtt{e}^c_\nu \mathtt{e}^d_\mu \\ &\times \left[\frac{(\mathtt{w}_\mu - \mathtt{w}_\nu)(n_B(\mathtt{w}_\mu) - n_B(\mathtt{w}_\nu))}{(\mathtt{w}_\mu - \mathtt{w}_\nu)^2 - (i\omega_n)^2} - \frac{(\mathtt{w}_\mu + \mathtt{w}_\nu)(1 + n_B(\mathtt{w}_\mu) + n_B(\mathtt{w}_\nu))}{(\mathtt{w}_\mu + \mathtt{w}_\nu)^2 - (i\omega_n)^2} \right]\end{aligned}$$

Physical phonons need to come from a dynamical theory

Two interesting limits of the theory

- If anharmonicity is small, the theory recovers the perturbative limit where the self-energy is given by the tadpole, loop, and bubble self-energies
- The static limit of the theory has Dirac-delta like peaks at the eigenvalues of the dynamical matrix derived from the Hessian of the free energy

$$G_{ab}^{-1}(\boldsymbol{q}, i\omega_n) = -D_{ab}^{F}$$

And a remark

- This theory allows to calculate the spectral function and phonon lifetimes in systems with very stron anharmonicity in which the harmonic and perturbative approaches collapse. It makes possible the calculation of the thermal conductivity possible in these cases

The spectral function

- All we said about the spectral function will be valid here, with the difference that the non-interacting frequencies are the SSCHA auxiliary frequencies
- In the no-mode-mixing approximation the spectral function can be written as

$$\begin{aligned}\sigma(\boldsymbol{q},\omega) &= \frac{1}{2\pi}\sum_{\mu}\left[\frac{-\mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)]}{(\omega-\mathrm{Re}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)])^2+\mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)]^2}\right.\\ &+ \left.\frac{\mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)]}{(\omega+\mathrm{Re}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)])^2+\mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)]^2}\right]\end{aligned}$$

where

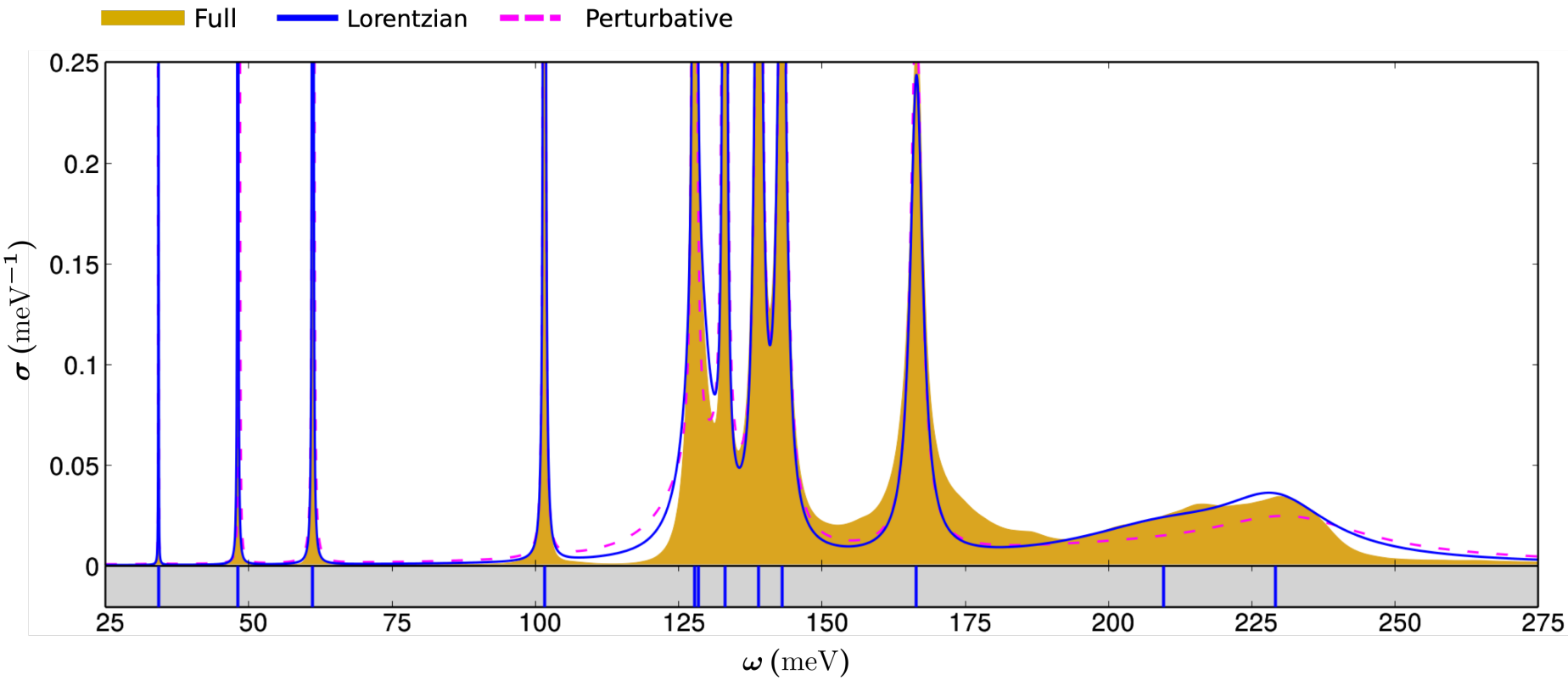
$$\mathcal{Z}_\mu(\boldsymbol{q},\omega)=\sqrt{\mathtt{w}_\mu^2(\boldsymbol{q})+\Pi_\mu(\boldsymbol{q},\omega+i\eta)}$$

- In the perturbative limit the spectral function will be a sum of Lorentzians with peaks at $\mathrm{Re}[\mathcal{Z}_\mu(\boldsymbol{q},\omega_\mu(\boldsymbol{q})+i\eta)]$ and the half-width at half maximum (HWHM) $-\mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\omega_\mu(\boldsymbol{q})+i\eta)]$ with

$$\begin{aligned}\mathrm{Re}[\mathcal{Z}_\mu(\boldsymbol{q},\mathtt{w}_\mu(\boldsymbol{q})+i\eta)] &\sim \mathtt{w}_\mu(\boldsymbol{q})+\frac{\mathrm{Re}[\Pi_\mu(\boldsymbol{q},\mathtt{w}_\mu(\boldsymbol{q})+i\eta)]}{2\mathtt{w}_\mu(\boldsymbol{q})}\\ \mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\mathtt{w}_\mu(\boldsymbol{q})+i\eta)] &\sim \frac{\mathrm{Im}[\Pi_\mu(\boldsymbol{q},\mathtt{w}_\mu(\boldsymbol{q})+i\eta)]}{2\mathtt{w}_\mu(\boldsymbol{q})}\end{aligned}$$

The spectral function

H_3S



Bianco *et al.*, PRB (2018)

Exercises

1. Show that
$$\langle \boldsymbol{R} \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = \boldsymbol{\mathcal{R}}$$
2. Inspired from the gradient equation with respect to the force constants and the relation $\langle \partial O/\partial R_a \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = \sum_b \Psi^{-1}_{ab} \langle O u_b \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$ show that
$$\Phi_{ab}(\boldsymbol{\mathcal{R}}) = \left\langle \frac{\partial^2 V}{\partial R_a \partial R_b} \right\rangle_{\tilde{\rho}_{\boldsymbol{\Phi}(\boldsymbol{\mathcal{R}})}}$$