SSCHA School 2023

Lecture 2: Non-perturbative anharmonicity and the SSCHA

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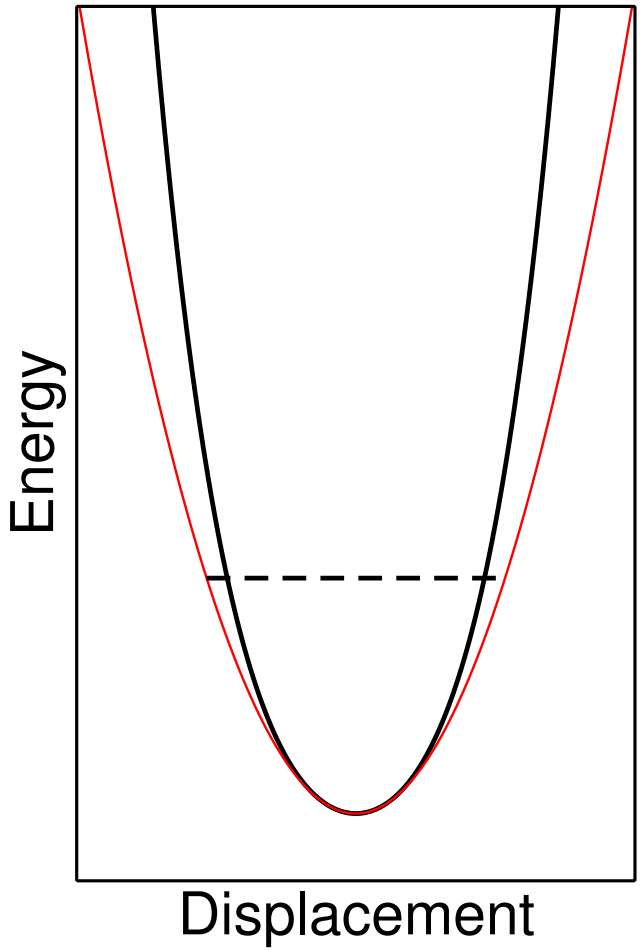
Outline

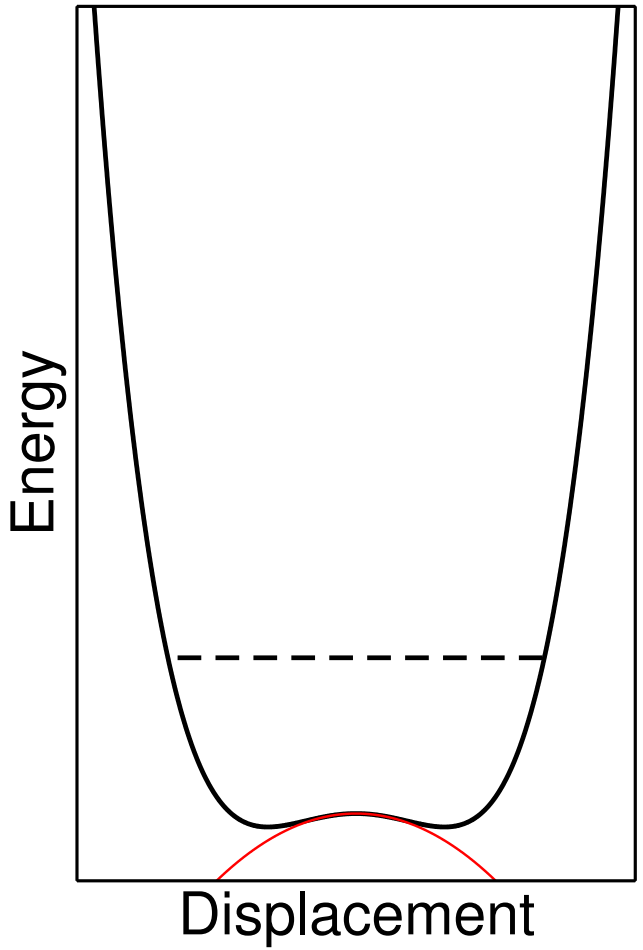
Two different regimes for anharmonicity

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

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



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



Self-energy and the Dyson equation

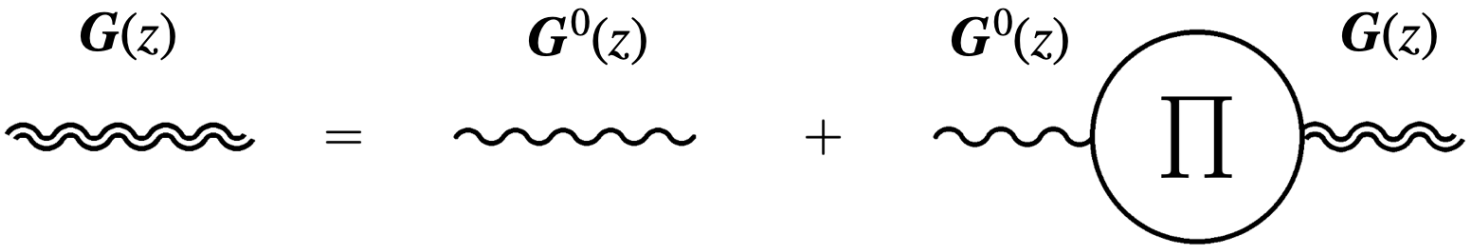
- The effect of anharmonicity (and any other interaction) can be included within many-body perturbation theory in the displacement correlation function or Green's function

$$G_{ab}(z) = -\sqrt{M_a M_b}\,\langle T_z u_a(z) u_b(0)\rangle_{\rho_H}$$

  where now H includes anharmonic interactions
- All the interactions affecting the phonons define the phonon self energy $\mathbf{\Pi}$
- The interacting Green function can be calculated through Dyson's equation

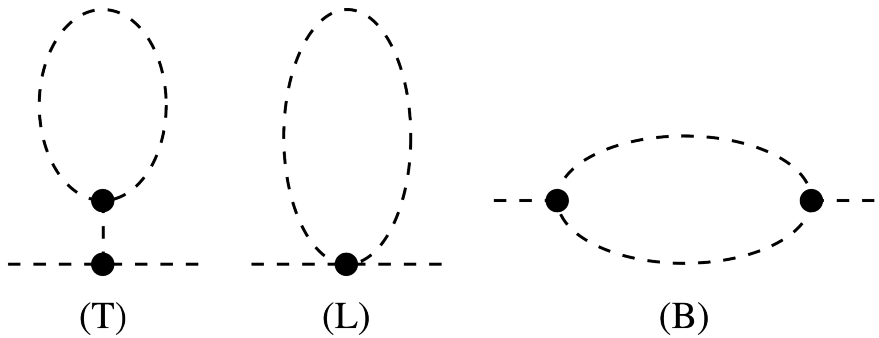
$$\boldsymbol{G}(z) = \boldsymbol{G}^0(z) + \boldsymbol{G}^0(z)\mathbf{\Pi}(z)\boldsymbol{G}(z)$$

- The non-interacting Green's function is calculated with the harmonic H_0



The anharmonic self-energy in the perturbative limit

- At the perturbative lowest order there are 3 diagrams that contribute to the phonon self-energy: tadpole (T), loop (L), and bubble (B)
- The self-energy diagrams need to be constructed with Feyman diagram rules and have to be calculated with Matsubara summation techniques (see Mahan book)
  - These are the self-energy terms



$$\overset{(T)}{\Pi}_{\mu}(\boldsymbol{q}) = \frac{-2\omega_{\mu}(\boldsymbol{q})}{N}\sum_{\nu\nu'\boldsymbol{q}'}\overset{(3)}{\phi}_{\nu\nu\nu'}(-\boldsymbol{q}',\boldsymbol{q},0)\overset{(3)}{\phi}_{\nu'\mu\mu}(0,\boldsymbol{q},-\boldsymbol{q})\frac{2n_B(\omega_{\nu}(\boldsymbol{q}'))+1}{\omega_{\nu'}(0)}$$

$$\overset{(L)}{\Pi}_{\mu}(\boldsymbol{q}) = \frac{\omega_{\mu}(\boldsymbol{q})}{N}\sum_{\nu\boldsymbol{q}'}\overset{(4)}{\phi}_{\mu\mu\nu\nu}(\boldsymbol{q},-\boldsymbol{q},\boldsymbol{q}',-\boldsymbol{q}')(2n_B(\omega_{\nu}(\boldsymbol{q}'))+1)$$

$$\overset{(B)}{\Pi}_{\mu}(\boldsymbol{q},\omega+i\eta) = \frac{-\omega_{\mu}(\boldsymbol{q})}{N}\sum_{\nu\nu'\boldsymbol{q}'}|\overset{(3)}{\phi}_{\mu\nu\nu'}(\boldsymbol{q},\boldsymbol{q}',-\boldsymbol{q}-\boldsymbol{q}')|^2 F(\omega+i\eta,\omega_{\nu}(\boldsymbol{q}'),\omega_{\nu'}(-\boldsymbol{q}-\boldsymbol{q}'))$$

The anharmonic self-energy in the perturbative limit

- In the equation above

$$\overset{(n)}{\phi}_{\mu_1\cdots\mu_n}(\boldsymbol{q}_1,\cdots,\boldsymbol{q}_n) = \sum_{a_1\cdots a_n} \frac{\overset{(n)}{\phi}_{a_1\cdots a_n}(\boldsymbol{q},\cdots,\boldsymbol{q}_n)}{\sqrt{M_{a_1}\cdots M_{a_n}}} \frac{e^{a_1}_{\mu_1}(-\boldsymbol{q}_1)\cdots e^{a_n}_{\mu_n}(-\boldsymbol{q}_n)}{\sqrt{2^n\omega_{\mu_1}(\boldsymbol{q}_1)\cdots\omega_{\mu_n}(\boldsymbol{q}_n)}}$$

$$F(\omega+i\eta,\omega_1,\omega_2) = \frac{2(\omega_1+\omega_2)(1+n_B(\omega_1)+n_B(\omega_2))}{(\omega_1+\omega_2)^2-(\omega+i\eta)^2} + \frac{2(\omega_1-\omega_2)(n_B(\omega_2)-n_B(\omega_1))}{(\omega_1-\omega_2)^2-(\omega+i\eta)^2}$$

  and the phonon frequencies and polarization vectors are the eigenvalues and eigenvectors of the harmonic dynamical matrix:

$$\sum_b \frac{\overset{(2)}{\phi}_{ab}(\boldsymbol{q})}{\sqrt{M_a M_b}} e^b_\mu(\boldsymbol{q}) = \omega^2_\mu(q) e^q_\mu(\boldsymbol{q})$$

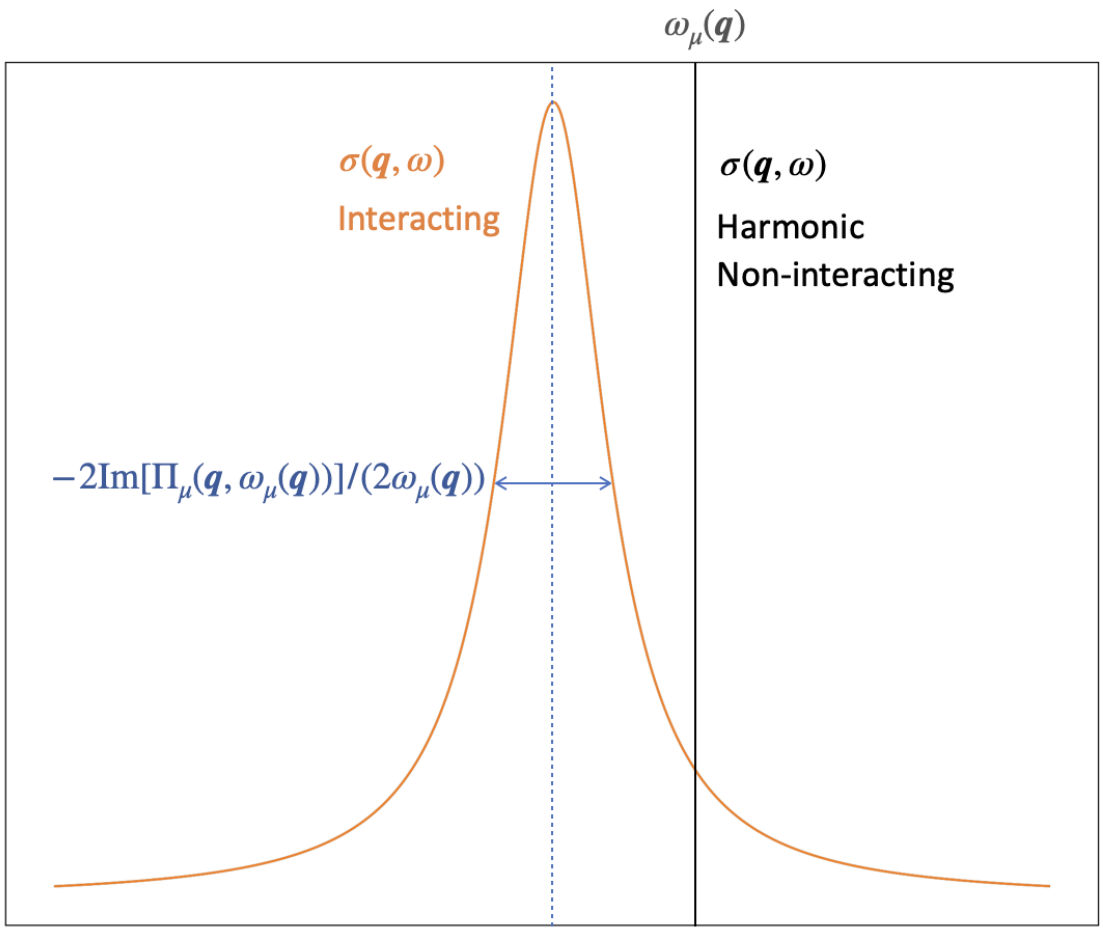
- These force constansts are derivatives of the Born-Oppenheimer potential calculated at the $\boldsymbol{R}_0$ positions that minimize it:

$$\overset{(n)}{\phi}_{a_1\cdots a_n} = \left[\frac{\partial^n V(\boldsymbol{R})}{\partial R_{a_1}\cdots\partial R_{a_n}}\right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

The spectral function in the perturbative limit

- Experimental signals are proportional to the spectral function

$$\sigma(\boldsymbol{q},\omega) = -\frac{\omega}{\pi}\sum_{a}\mathrm{Im}\left[G_{aa}(\boldsymbol{q},\omega+i\eta)\right]$$



Obtaining 3rd and 4th order force-constants is complex

$$\overset{(n)}{\phi}_{a_1 \cdots a_n} = \left[\frac{\partial^n V(\boldsymbol{R})}{\partial R_{a_1} \cdots \partial R_{a_n}} \right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

- Density Functional Perturbation Theory and the $2n+1$ theorem to obtain 3rd order force-constants

  Paulatto *et al.*, PRB (2013)

- Finite difference approaches (very tedious)

  Errea *et al.*, PRL (2011)

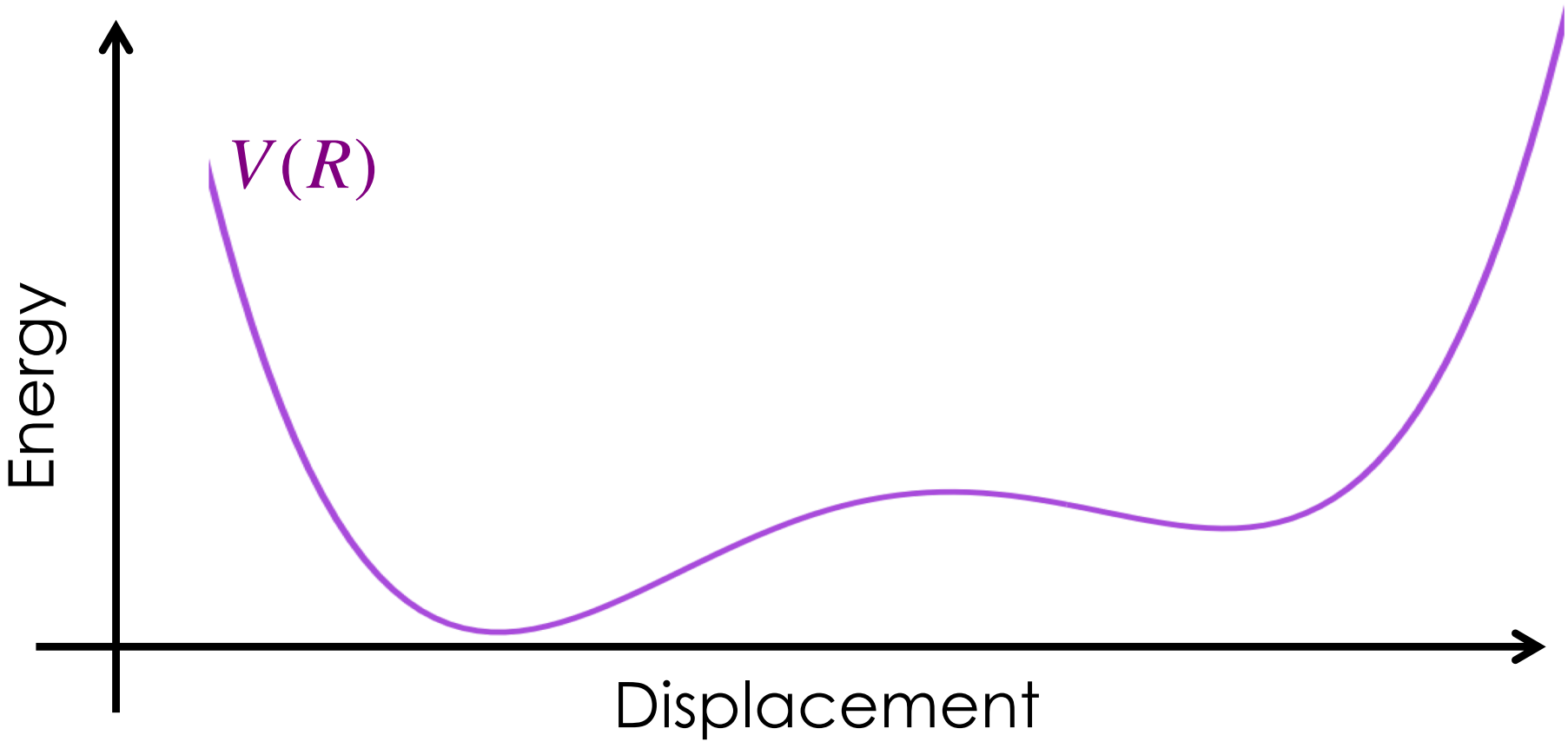
- Empirical potentials

  Chen *et al.*, PRL (2014)

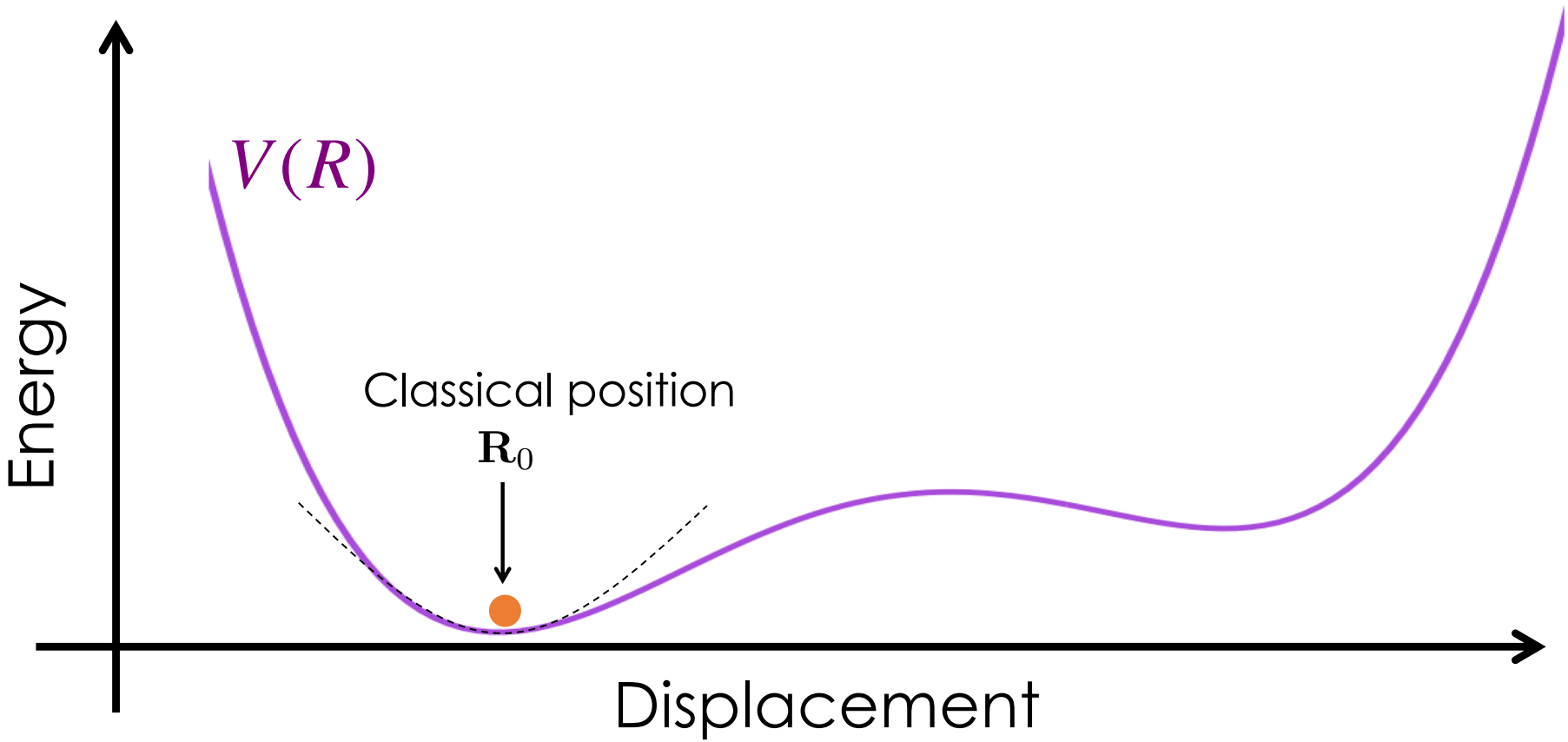
- Compressive sensing lattice dynamics

  Zhou *et al.*, PRL (2014)

Quantum and non-perturbative anharmonic effects



Quantum and non-perturbative anharmonic effects



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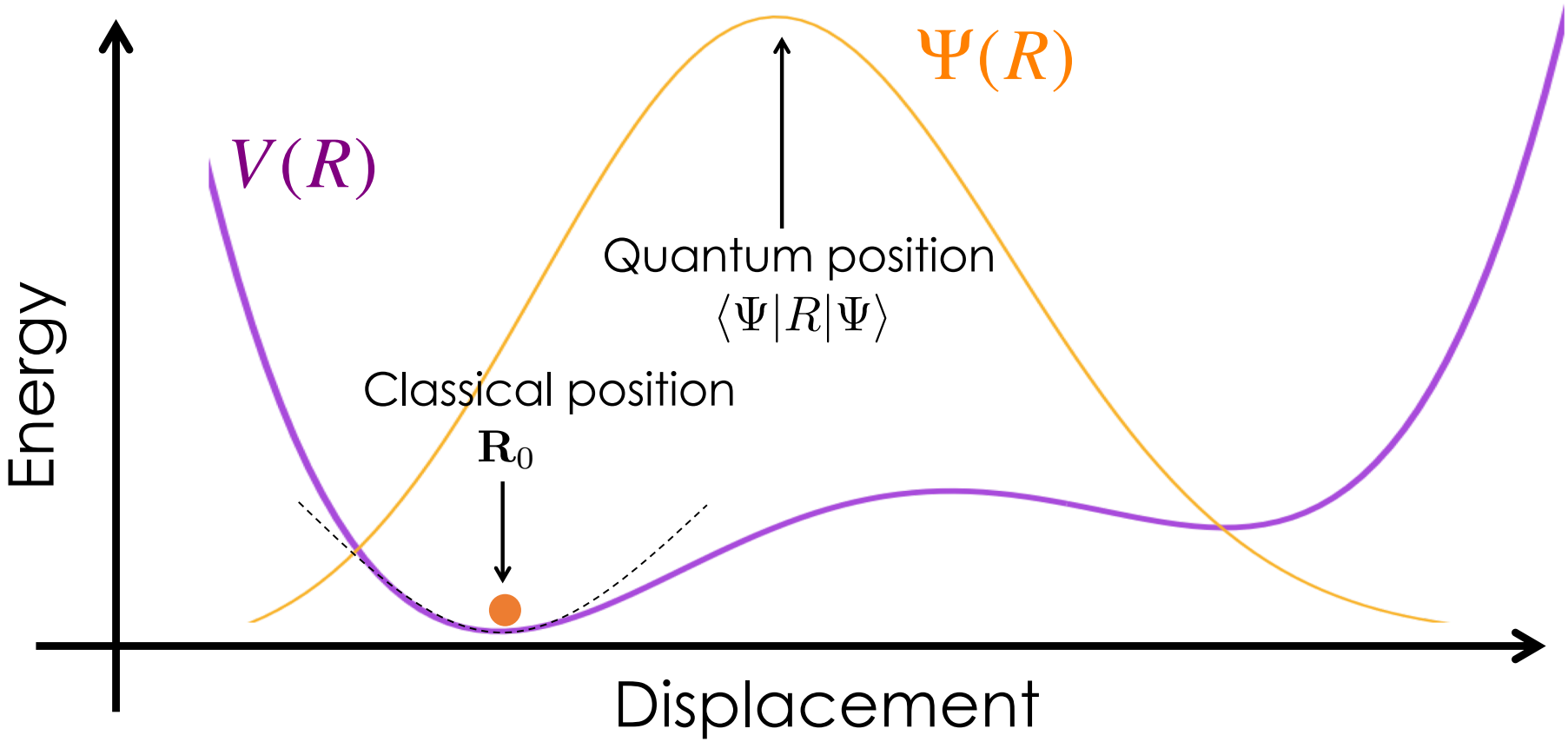
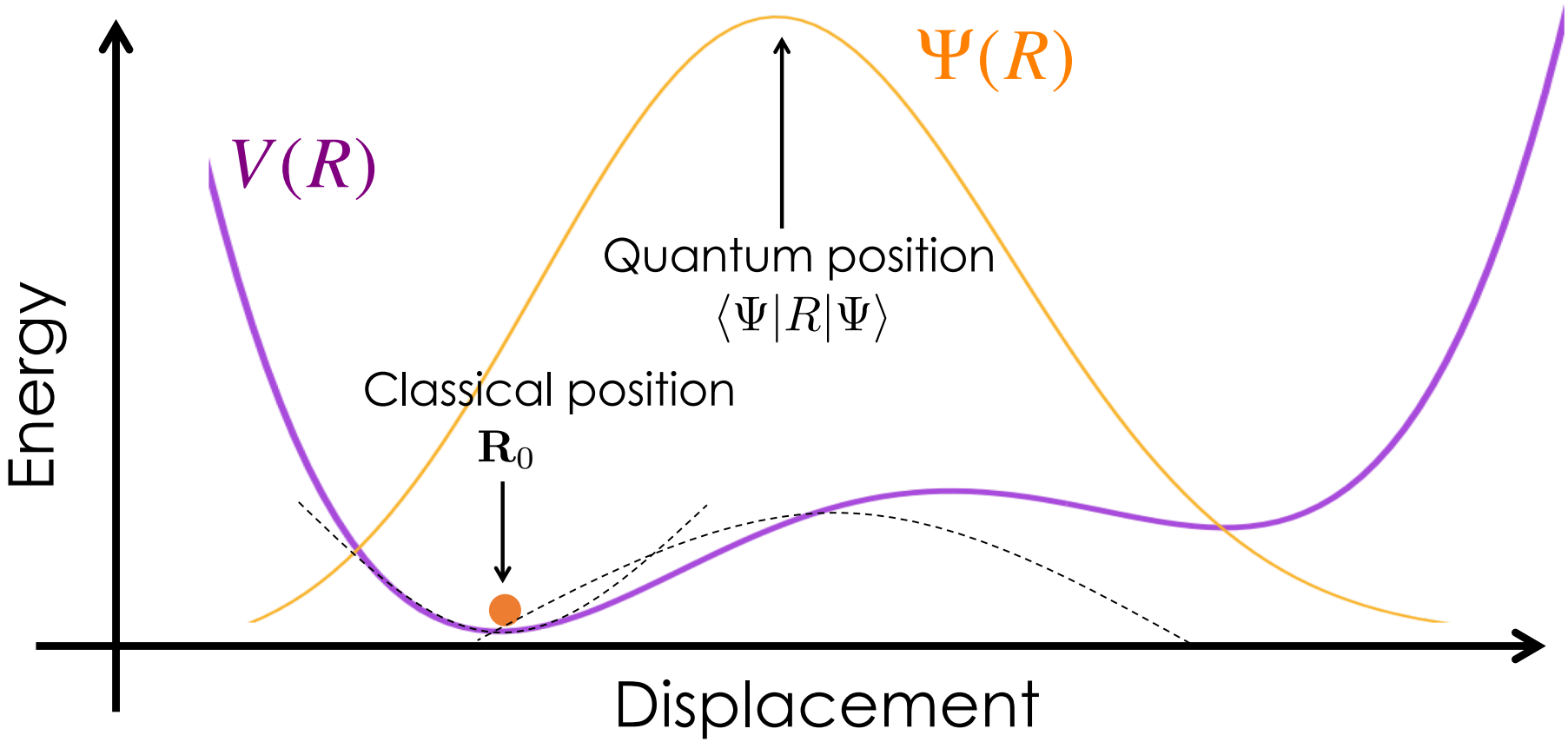


Quantum and non-perturbative anharmonic effects



Non-perturbative anharmonic regime occurs in many systems

Compounds with light atoms

- Hydrogen storage materials
- Hydrogen-based superconductors
- Hydrogen at high pressures
- ...

At very high temperatures

- Close to melting
- ...

Second-order structural displacive phase transitions in

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

How to deal with non-perturbative anharmonicity from first-principles

- *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)

How to deal with non-perturbative anharmonicity from first-principles

- *Ab initio* molecular dynamics (AIMD): Newtonian mechanics with DFT forces
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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`

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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 $\boldsymbol{\Phi}$
- It is like a Hartree-Fock theory but for the phonons

$$\begin{aligned} \Psi_{\alpha_1 \ldots \alpha_n}(\boldsymbol{r}) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(\boldsymbol{r}_1) & \ldots & \psi_{\alpha_1}(\boldsymbol{r}_N) \\ \vdots & \vdots & \vdots \\ \psi_{\alpha_N}(\boldsymbol{r}_1) & \ldots & \psi_{\alpha_N}(\boldsymbol{r}_N) \end{vmatrix} \\ E &= \langle \Psi_{\alpha_1 \ldots \alpha_n} | \left(T_e + V_{ee} \right) | \Psi_{\alpha_1 \ldots \alpha_n} \rangle \end{aligned}$$

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

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

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

Variational principle

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

The SSCHA trial Hamiltonian

- 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

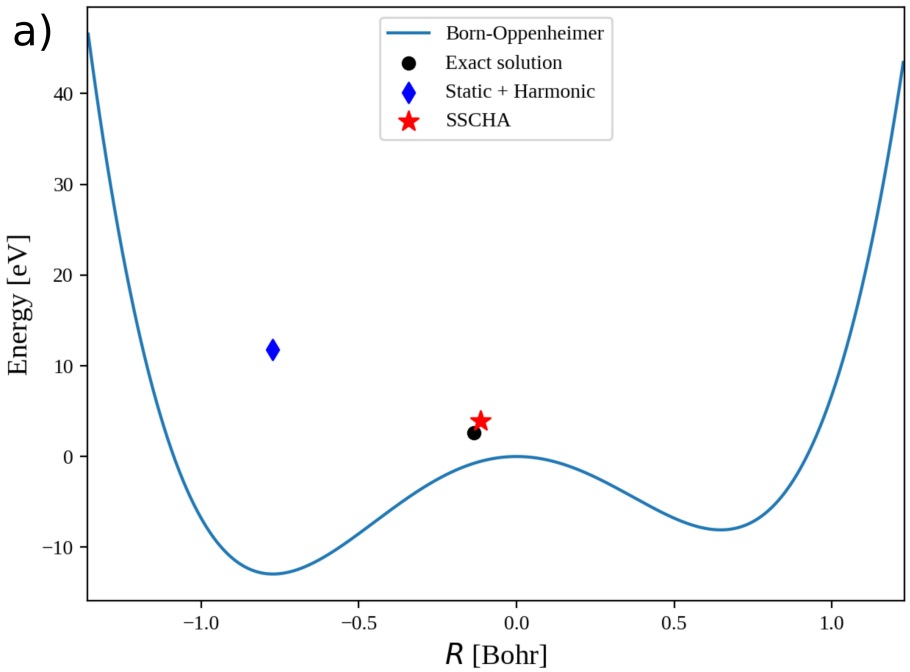
$$V_2(\boldsymbol{R}) = \frac{1}{2} \sum_{ab} \overset{(2)}{\phi}_{ab} (R_a - R_{0a})(R_b - R_{0b})$$

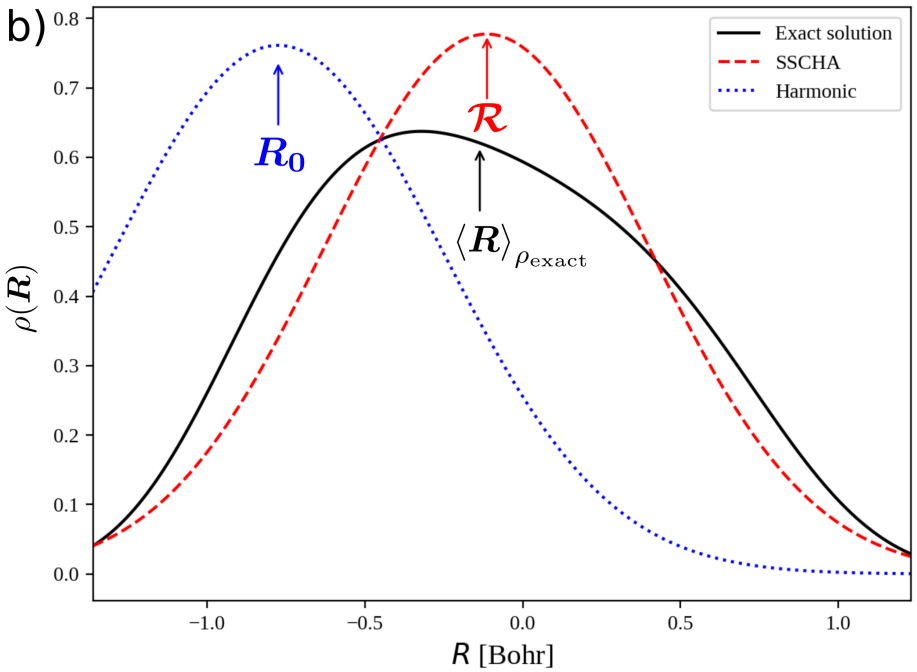
- The variational free energy will depend only on $\boldsymbol{\mathcal{R}}$ and $\boldsymbol{\Phi}$ so we will write $\tilde{\rho}_{\mathcal{H}} \rightarrow \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}$ and $\mathcal{F}[\mathcal{H}] \rightarrow \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$
- 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 solution in a 1D example





The SSCHA probability distribution function

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

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

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

- At $T = 0$ K it equals the ground state ionic wave function
- In the equations above the frequencies and the polarization vectors are not the eigenvalues and eigenfunctions of the harmonic force-constants,

$$\sum_b \frac{\overset{(2)}{\phi}_{ab}}{\sqrt{M_a M_b}} \mathrm{e}_\mu^b = \omega_\mu^2 \mathrm{e}_\mu^a,$$

but of the auxiliary force-constants

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

The SSCHA probability distribution function

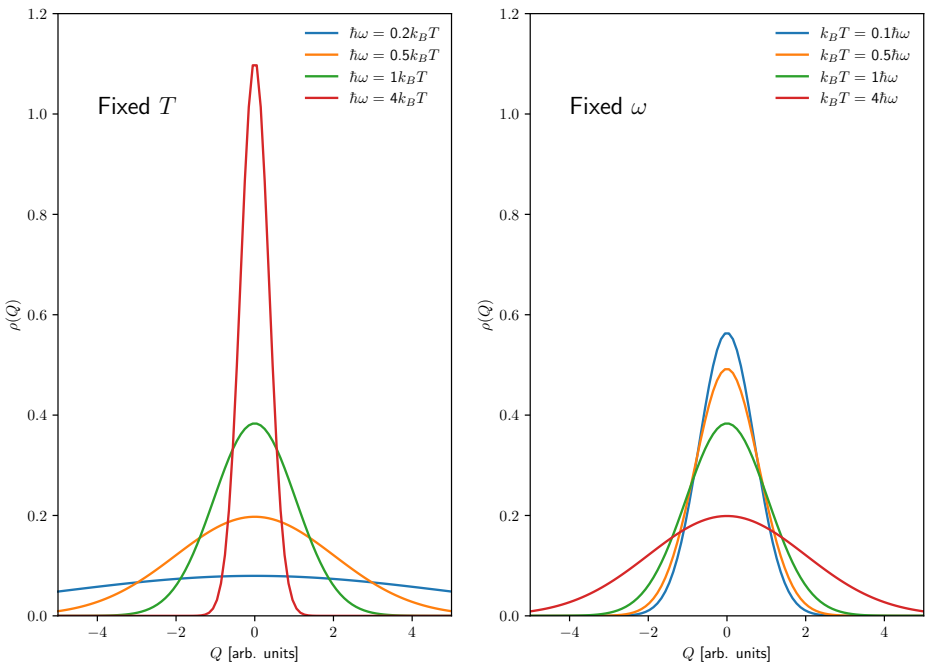
- The auxiliary frequencies $\mathtt{w}_\mu$ are just parameters that describe the SSCHA probability distribution function, not physical quantities, and are positive definite by construction
- The expectation value of the position operator are the centroids since

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

- In normal mode basis ($Q_\mu = \sum_a (R_a - \mathcal{R}_a) \frac{\mathtt{e}^a_\mu}{\sqrt{M_a}}$) the probability distribution function is

$$\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{Q}) = \prod_\mu \frac{1}{\sqrt{2\pi \mathtt{a}^2_\mu}} e^{-\frac{Q^2_\mu}{2\mathtt{a}^2_\mu}}$$

- The width of the Gaussian probability is proportional to a
- The higher the frequency the more peaked the distribution, the higher the temperature the wider



Quantum statistical averages

- Given the density matrix, the quantum statistical average of any operator that just depends on the ionic positions $O(\boldsymbol{R})$ can be calculated as

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

- An example:
  The mean square displacement of an ion

$$\begin{aligned}
\left\langle (R_a - \mathcal{R}_a)^2 \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} &= \int d\boldsymbol{R} (R_a - \mathcal{R}_a)^2 \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{R}) \\
&= \sum_{\mu\nu} \frac{e^a_\mu e^a_\nu}{M_a} \int d\boldsymbol{Q} Q_\mu Q_\nu \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{Q}) \\
&= \sum_{\mu} \frac{e^a_\mu e^a_\mu}{M_a} \frac{\hbar}{2\mathtt{w}_\mu} [1 + 2n_B(\mathtt{w}_\mu)]
\end{aligned}$$

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
  - $\boldsymbol{\mathcal{R}}$ 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

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

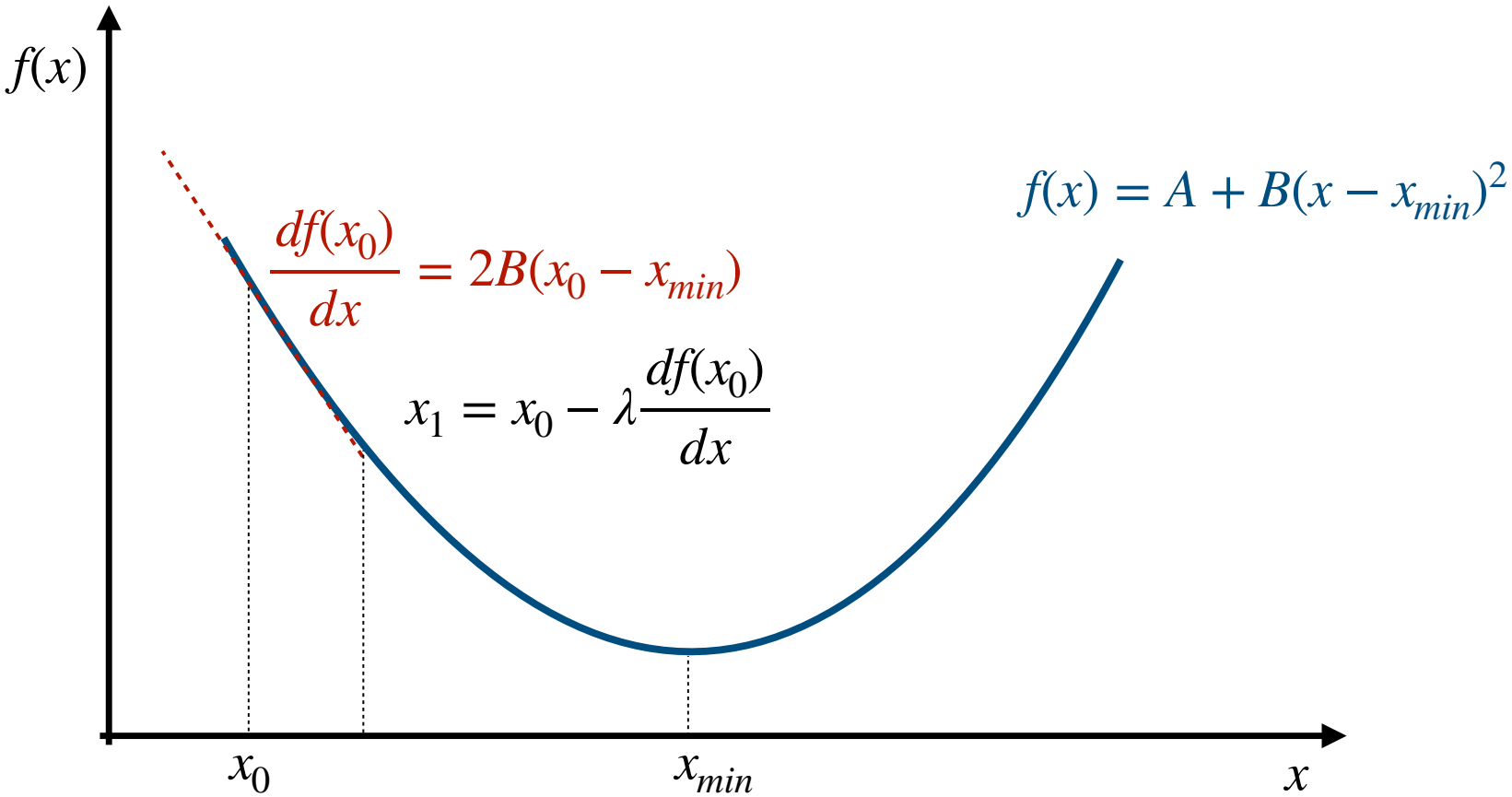
$$\frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \Phi_{cd}} = \sum_{ab} \frac{\Lambda[0]^{abcd}}{\sqrt{M_a M_b M_c M_d}} \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right) \sum_e \Psi^{-1}_{ae} (R_e - \mathcal{R}_e) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},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

- 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

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

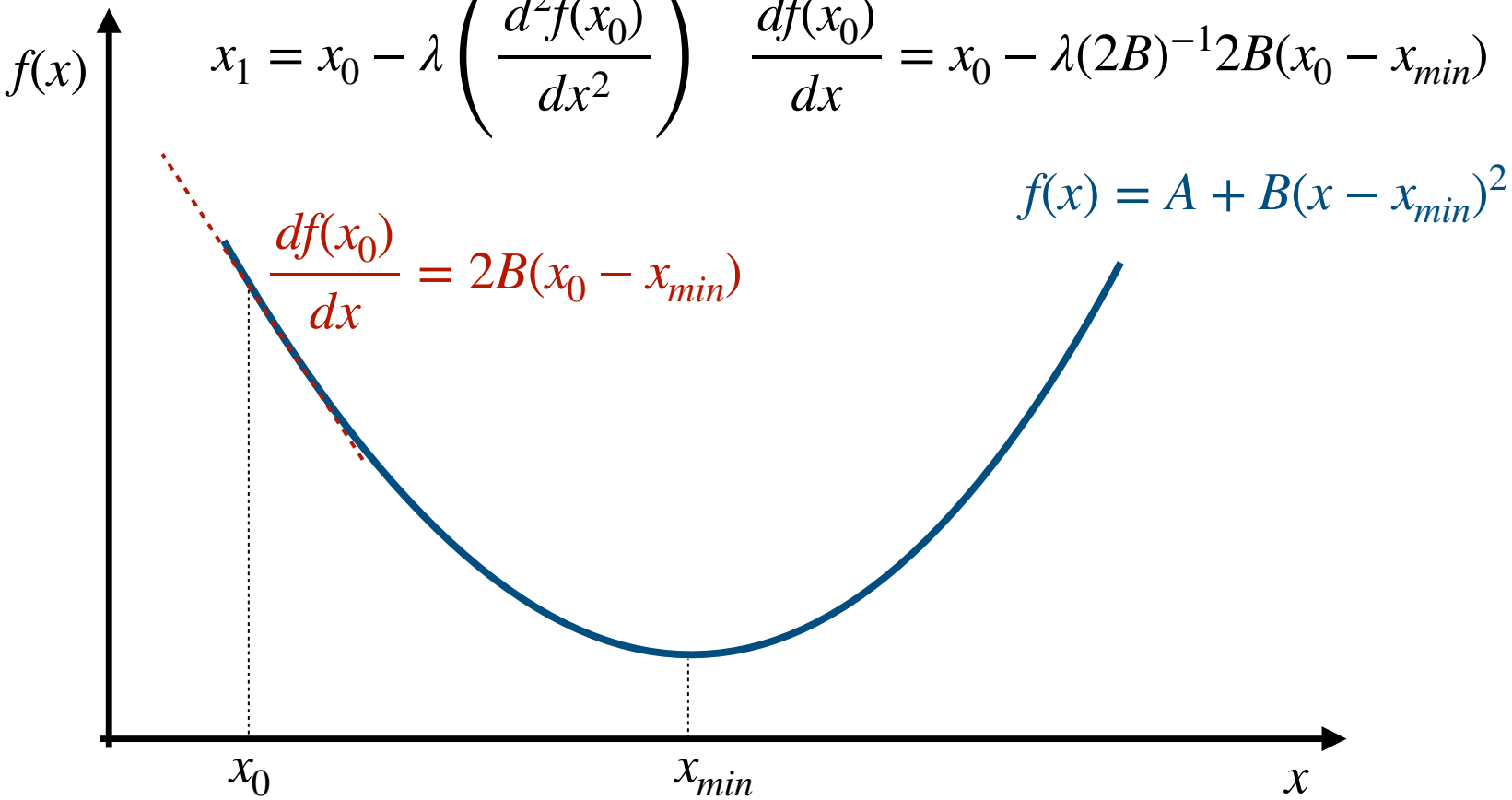
- With the gradients a gradient-descent minimization can be performed
- The gradient is symmetrized at every step, so the minimization is performed respecting the symmetries

A preconditioned gradient descent



A preconditioned gradient descent

$$x_1 = x_0 - \lambda \left(\frac{d^2 f(x_0)}{dx^2} \right)^{-1} \frac{df(x_0)}{dx} = x_0 - \lambda (2B)^{-1} 2B(x_0 - x_{min})$$



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: $\langle O\rangle_{\rho_{\mathcal{H}_0}} \simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O(\mathbf{R}_I)$

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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

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

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

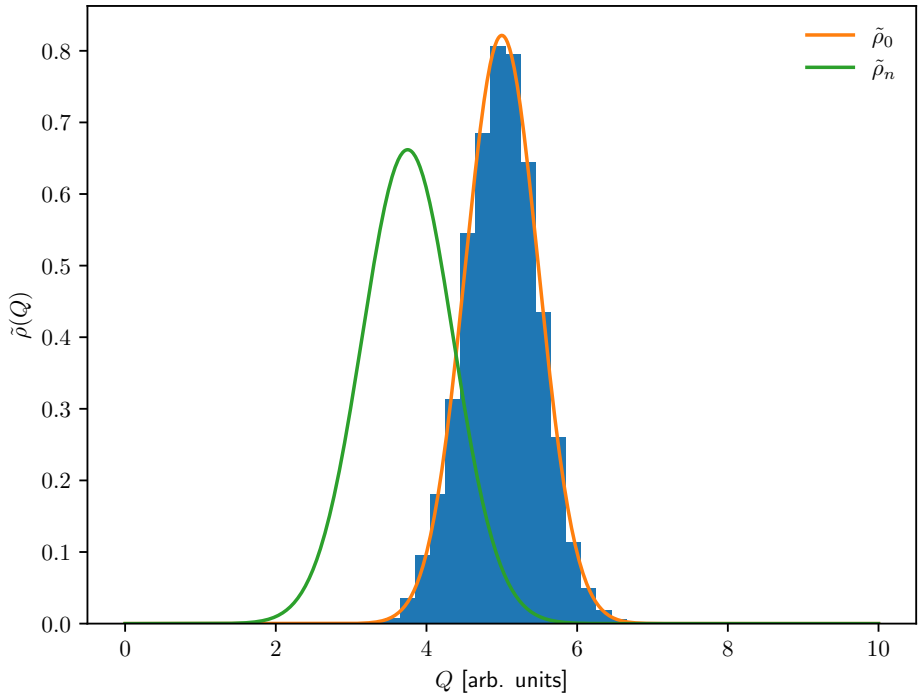
The SSCHA coming out of statistical range

- 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

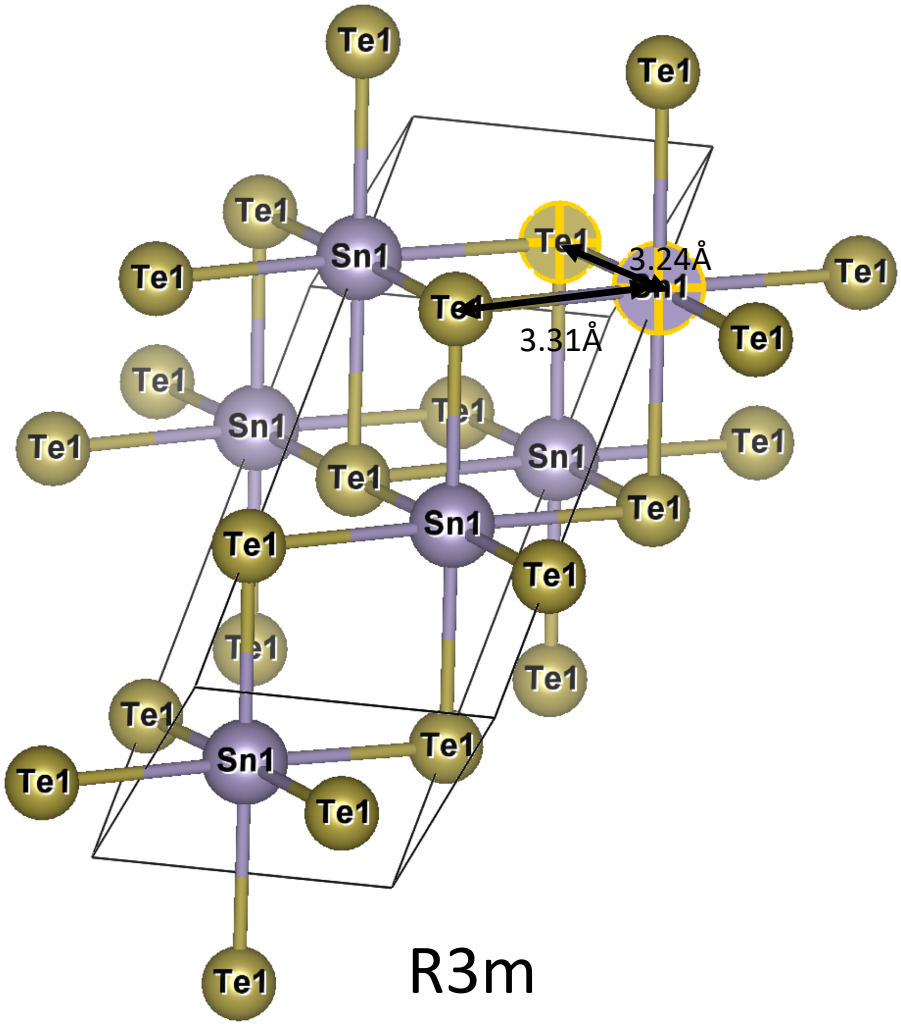
- The SSCHA calculation is stopped when the values of the gradients become smaller than a ratio (δ) of its estimated error

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

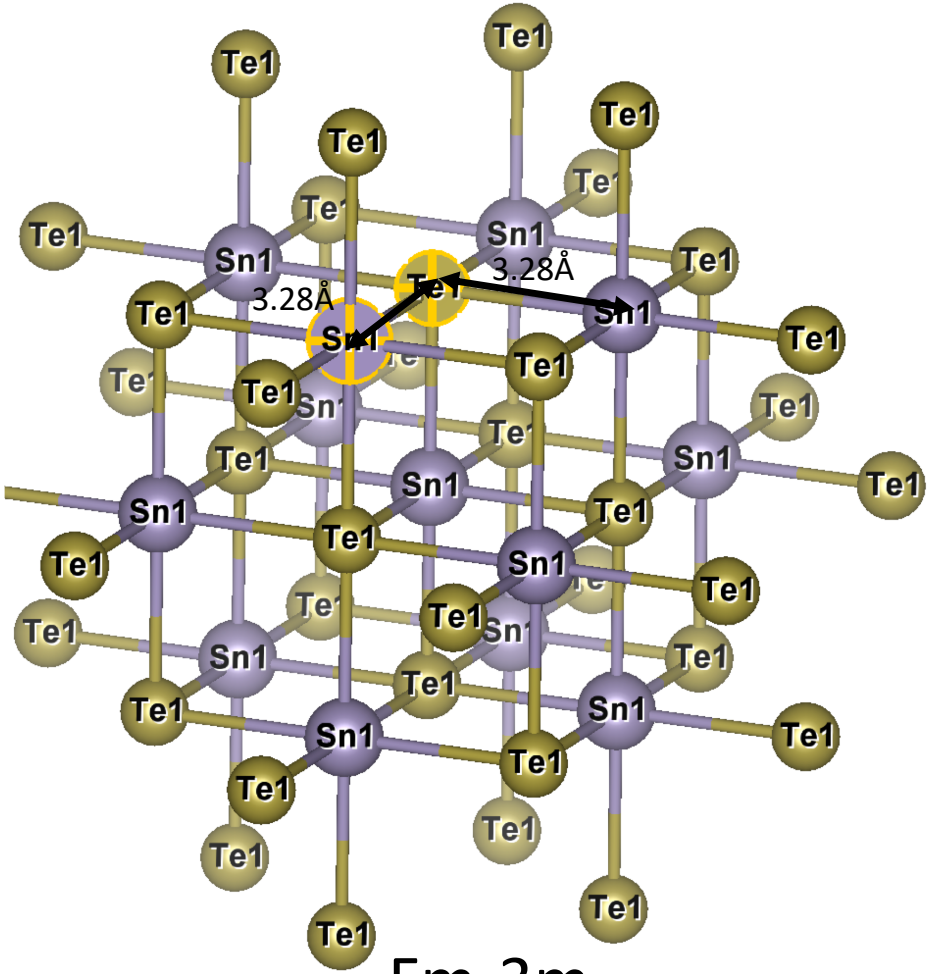
$$\left| \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\mathcal{R}}} \right| < \delta \left| \Delta \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\mathcal{R}}} \right|$$

- 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 reach 0 gradients

SSCHA calculation example



R3m

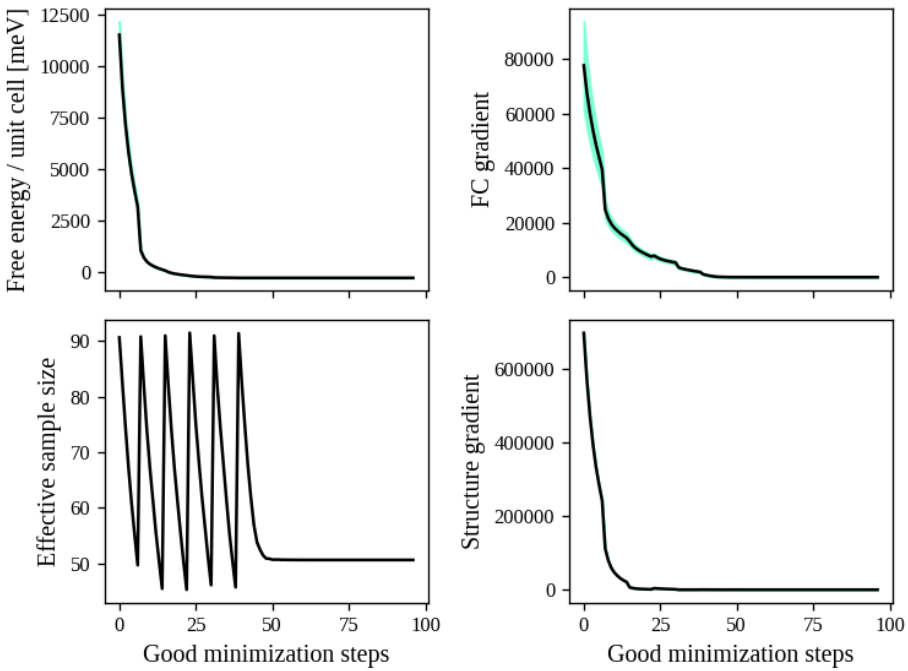


Fm-3m

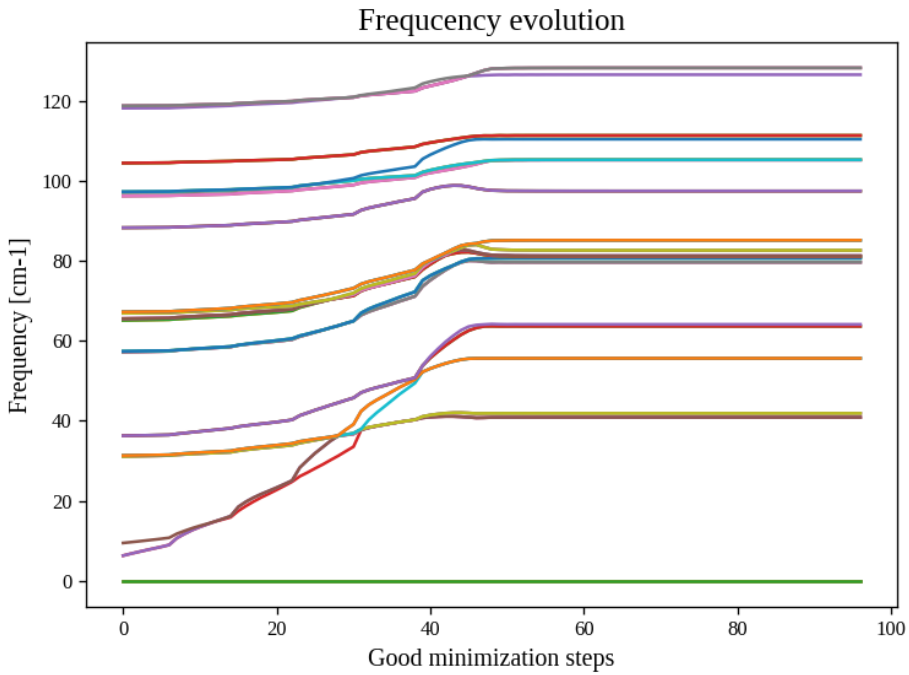
SSCHA calculation example

- First populations with 100 configurations each
- 6 populations to reach convergence

Evolution of the free energy, gradients, and Kong-Liu ratio



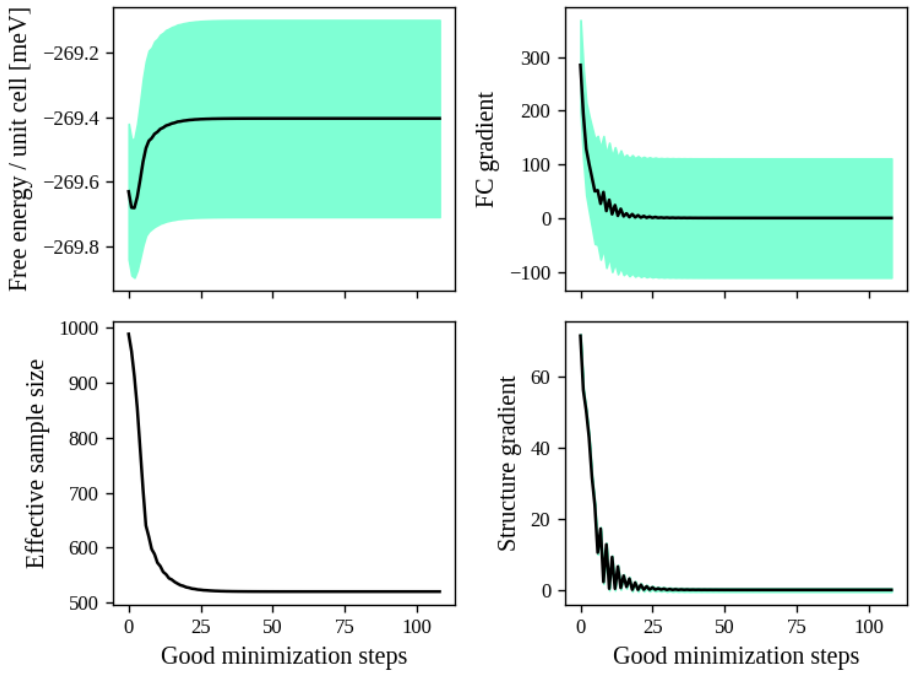
Evolution of the auxiliary frequencies



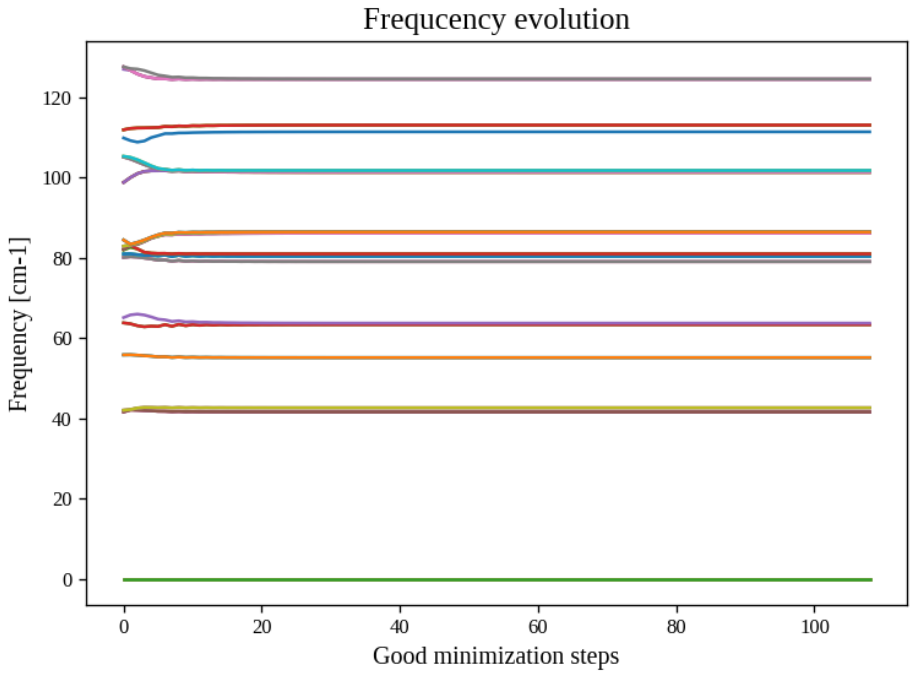
SSCHA calculation example

- Add more configurations for a final run

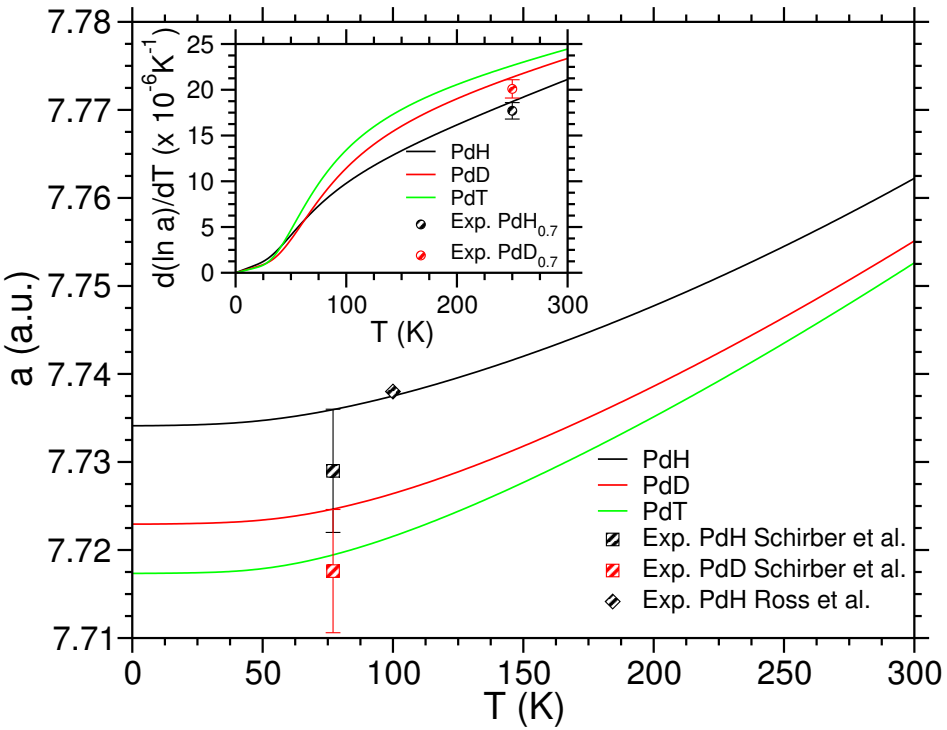
Evolution of the free energy, gradients, and Kong-Liu ratio

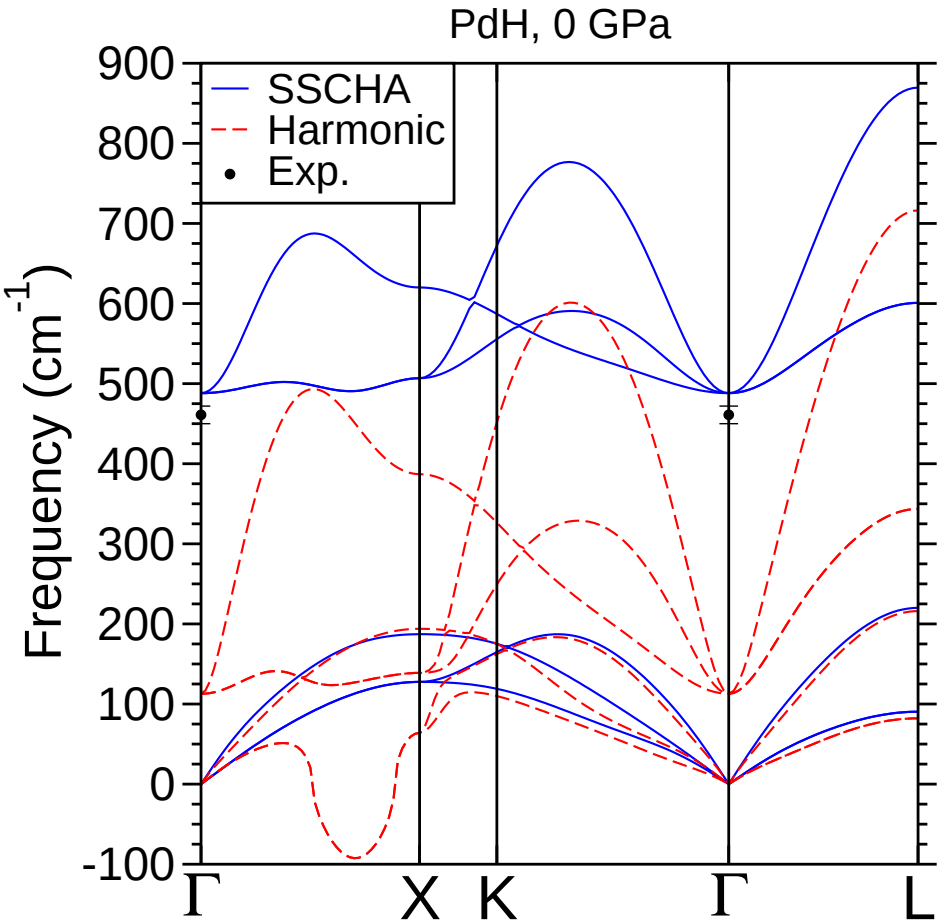


Evolution of the auxiliary frequencies



Thermodynamic properties of PdH





Errea, Calandra, Mauri PRL (2013)

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 including 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

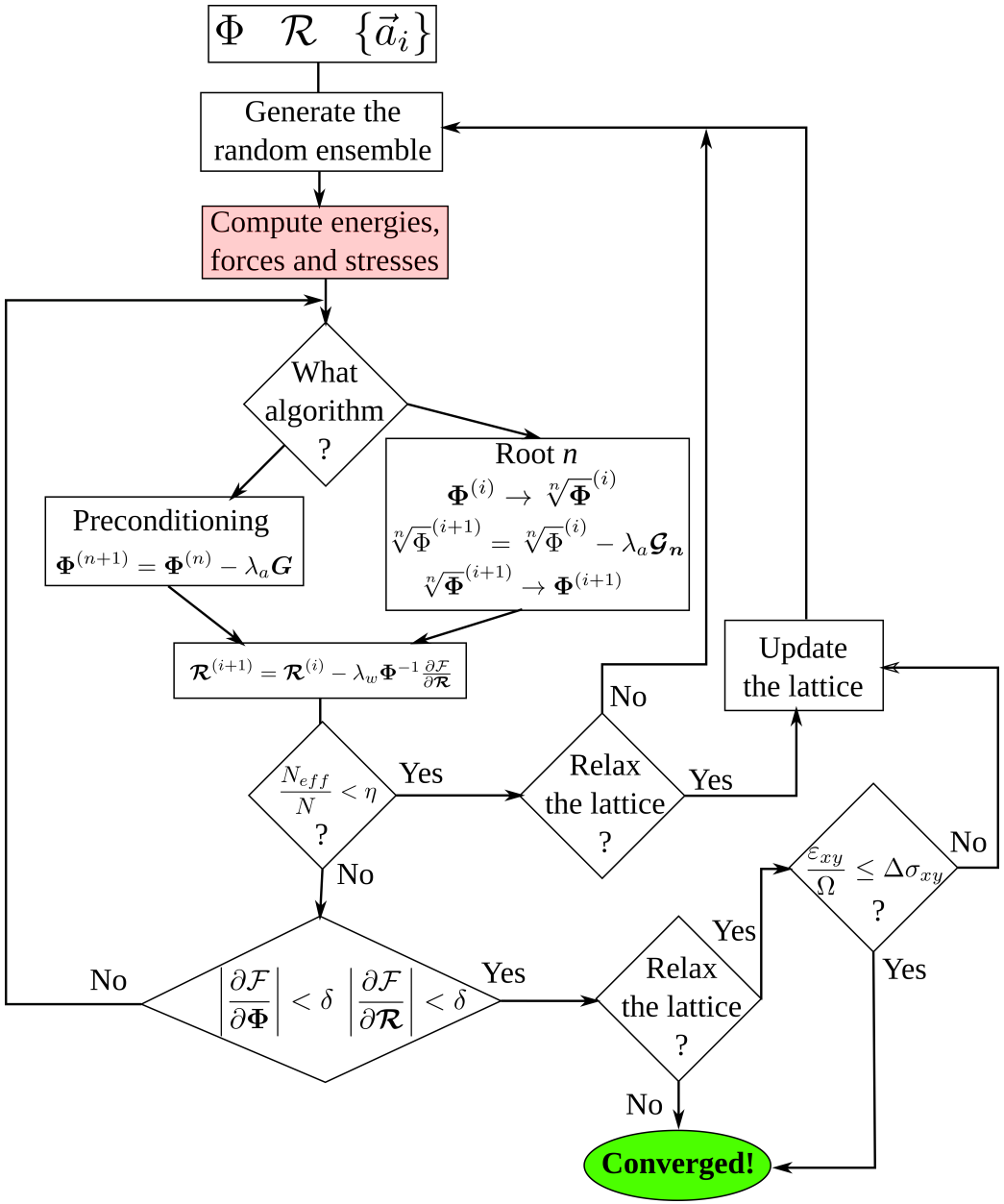
$$\varepsilon_{\alpha\beta} = \frac{\Omega}{N} \left(P_{\alpha\beta} - P^* \delta_{\alpha\beta} \right)$$

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

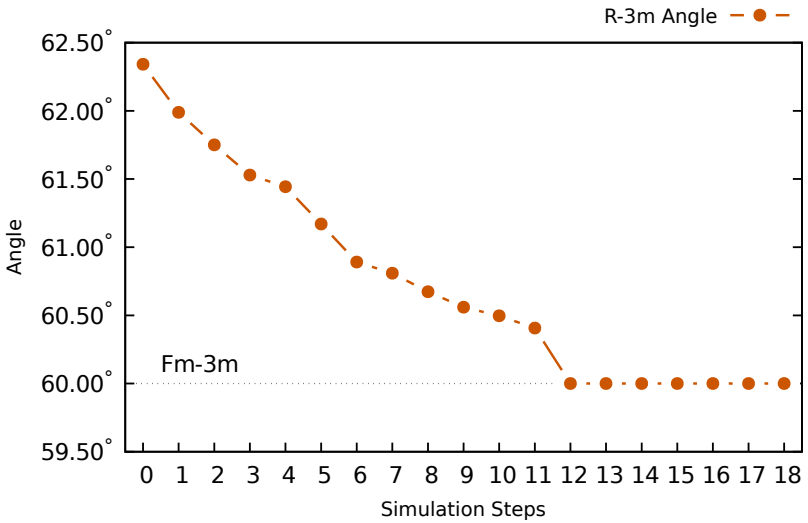
$$\lambda_{\{\boldsymbol{a}_i\}} = \frac{1}{3\Omega B_0}$$

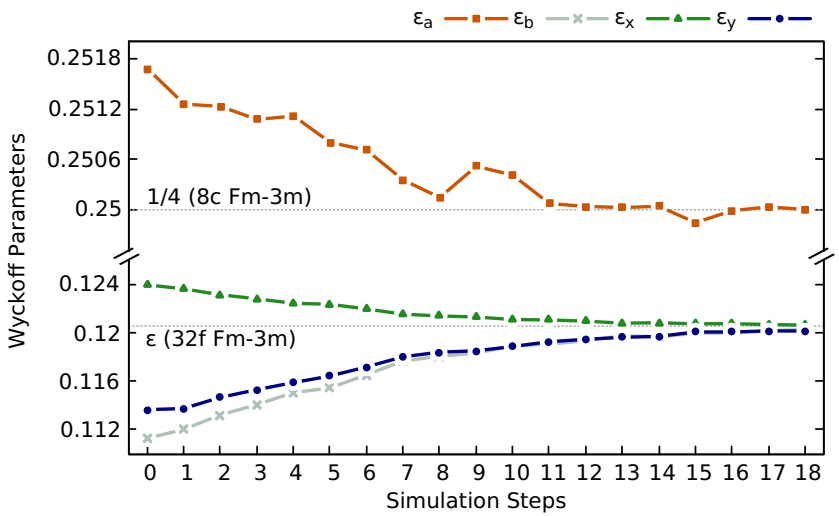
with B_0 the bulk modulus

SSCHA calculation flowchart with cell relaxation



Structural relaxation with the SSCHA in LaH_{10}





Errea et al. Nature (2020)

Take-home message

1. The SSCHA is a variational method based on the thermodynamic free energy
2. The SSCHA can deal with strong anharmonicity in the non-perturbative regime
3. The SSCHA can relax structures, both internal and cell parameters, in the quantum anharmonic energy landscape
4. SSCHA auxiliary frequencies are related to the width of the ionic wave function (probability distribution) and are not in principle physically relevant quantities
5. So far the SSCHA does not describe anharmonic phonon linewidths
6. Lectures 3 and 4 will clarify a lot these issues