Pheasy: a calculator for high-order anharmonicity and phonon quasiparticles

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1 Introduction

Lattice anharmonicity plays a vital role in a wealth of physical phenomena, including thermodynamics, phase transitions, superconductivity, and transport properties of materials. Conventional methods, such as finite differences, to derive the interatomic force constants (IFCs) of lattice potential become challenging and sometimes infeasible when going beyond third-order anharmonicity. Here, we present a user-friendly program, Pheasy, that allows for the efficient extraction of high-order IFCs, which can be further used to reconstruct accurately the potential energy surface up to the sixth-order. The obtained IFCs have been successfully applied to study thermal transport properties, inelastic scattering spectroscopies, and temperature renormalization of phonon quasiparticles.

2 Representation of potential surface

A. Cluster expansion

$$V = \frac{1}{\alpha!}\Phi_I(\alpha)u_I^\alpha$$

$$F_{\boldsymbol{a}} = -\frac{1}{\alpha!}\Phi_I(\alpha)\partial_{\boldsymbol{a}} u_I^\alpha$$

$\boldsymbol{a} \equiv \{a, i\}$, lattice site a and Cartesian direction i

Cluster $\alpha \equiv \{a_1 \dots a_n\}$ Cartesian $I \equiv \{i_1 \dots i_n\}$

$\alpha! \equiv \prod_n |\alpha_{a_n}|!$ $u_I^\alpha \equiv \prod_n u_{a_n i_n}$

B. Symmetry reduction of IFCs

$$\mathbb{B} \cdot \mathbf{\Phi} = \mathbf{0}$$

- Isotropy group: $\Phi_I(\alpha) = \Gamma_{IJ}(\hat{s})\Phi_J(\alpha)$
- Improper permutation: $\Phi_I(\alpha) = R_{IJ}\Phi_J(\alpha)$
- Translational invariance: $\sum_{\alpha\in A/S}\sum_{\hat{s}\alpha\in S\alpha}\Gamma_{IJ}(\hat{s})\Phi_J(\alpha) = 0$

C. Linear model solver

$$\mathbf{F} = \mathbb{A}' \cdot \mathbf{\Phi} = \mathbb{A}' \cdot \mathbb{C} \cdot \boldsymbol{\phi} = \mathbb{A} \cdot \boldsymbol{\phi}$$

$$\mathbb{A}'(\mathbf{a}, I) = -\sum_{\alpha\in A/S}\frac{1}{\alpha!}\sum_{\hat{s}\alpha\in S\alpha}\Gamma_{JI}(\hat{s})\partial_{\mathbf{a}} u_J^{\hat{s}\alpha}$$

Displacement matrix $\mathbb{A}'$
Sensing matrix $\mathbb{A}$
Null space $\mathbb{C}$
Force vector $\mathbf{F}$
IFC vector $\mathbf{\Phi}$
Reduced IFC vector $\boldsymbol{\phi}$

- Least square: $\boldsymbol{\phi}^{\mathrm{LS}} = \arg\min_{\boldsymbol{\phi}} \frac{1}{2}\|\mathbf{F} - \mathbb{A}\boldsymbol{\phi}\|_2^2$
- Compressive sensing: $\boldsymbol{\phi}^{\mathrm{CS}} = \arg\min_{\boldsymbol{\phi}} \|\boldsymbol{\phi}\|_1 + \frac{\mu}{2}\|\mathbf{F} - \mathbb{A}\cdot\boldsymbol{\phi}\|_2^2$

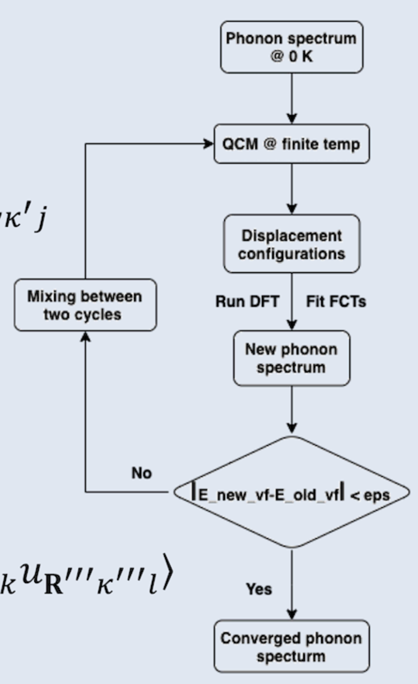
3 Temperature renormalization

A. Self-consistent *ab initio* lattice dynamics (SCAILD)

Quantum covariance

$$\Sigma_{\mathbf{R}\kappa i,\mathbf{R}'\kappa' j} = \sum_{\mathbf{q}\nu}\frac{\hbar(1/2 + n_{\mathbf{q}\nu}^0)}{N_{\mathbf{q}}\sqrt{m_\kappa m_{\kappa'}}\omega_{\mathbf{q}\nu}}\exp[i\mathbf{q}\cdot(\mathbf{R} + \boldsymbol{\tau}_\kappa - \mathbf{R}' - \boldsymbol{\tau}_{\kappa'})]e_{\mathbf{q}\nu\kappa i}e^*_{\mathbf{q}\nu\kappa' j}$$

Probability distribution $\rho(\{u_{\mathbf{R}\kappa i}\}) \propto \exp\left(-\frac{1}{2}\mathbf{u}^T\cdot\mathbf{\Sigma}^{-1}\cdot\mathbf{u}\right)$



B. Statistical perturbation-operator renormalization (SPOR)

$$\Phi^{\mathrm{SPOR}}_{\mathbf{R}\kappa i,\mathbf{R}'\kappa' j} = \Phi_{\mathbf{R}\kappa i,\mathbf{R}'\kappa' j} + \frac{1}{2}\sum_{\mathbf{R}''\kappa'' k}\sum_{\mathbf{R}'''\kappa''' l}\Phi_{\mathbf{R}\kappa i,\mathbf{R}'\kappa' j,\mathbf{R}''\kappa'' k,\mathbf{R}'''\kappa''' l}\langle u_{\mathbf{R}''\kappa'' k}u_{\mathbf{R}'''\kappa''' l}\rangle$$

4 Inelastic neutron and X-ray scattering spectroscopies

Coherent one-phonon scattering cross section

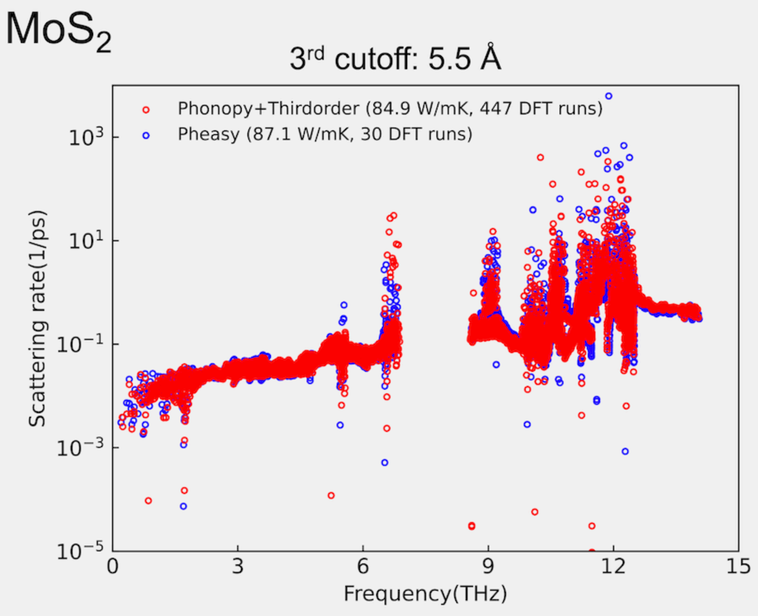
$$S(\mathbf{Q}, E) = \frac{k'}{k}\frac{(2\pi)^3}{\Omega_0}\sum_{\mathbf{q},\nu,\kappa}\left|\frac{\overline{b_\kappa}}{\sqrt{m_\kappa}}\exp(-W_\kappa + \mathrm{i}\mathbf{Q}\cdot\mathbf{d}_\kappa)(\mathbf{Q}\cdot\mathbf{e}_{\mathbf{q}\nu\kappa})\right|^2\frac{n_{\mathbf{q}\nu} + \frac{1}{2} \pm \frac{1}{2}}{\omega_{\mathbf{q}\nu}}\delta(E \pm \hbar\omega_{\mathbf{q}\nu})\delta(\mathbf{Q} \pm \mathbf{q} - \boldsymbol{\tau})$$

$$I(\mathbf{Q}, E) = \int_{\Delta\mathbf{Q}=-\infty}^{+\infty}\int_{\Delta E=-\infty}^{+\infty} S(\mathbf{Q}, E) \times R(\Delta\mathbf{Q}, \Delta E)\mathrm{d}\Delta\mathbf{Q}\mathrm{d}\Delta E.$$

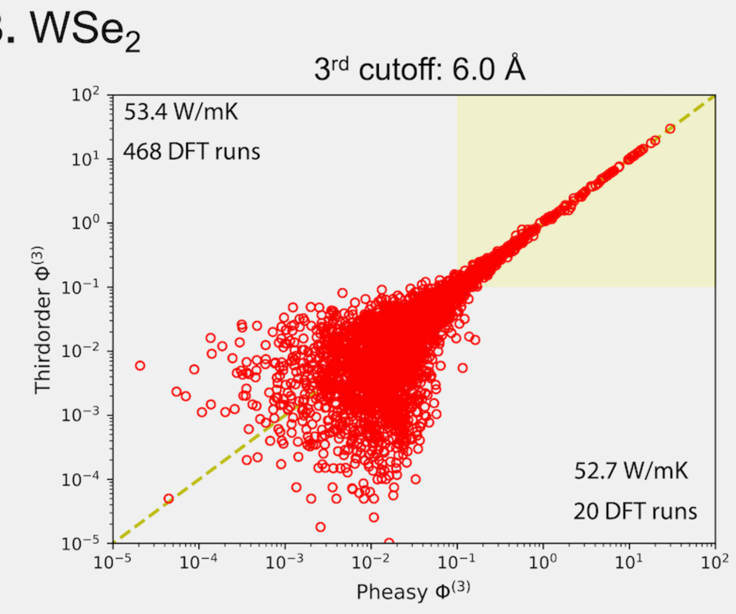
Atomic form factor $f(\mathbf{Q}) = \sum_i^5 a_i\exp(-b_i|\mathbf{Q}|^2) + c$ Debye-Waller factor $W_\kappa = \frac{1}{2}(\mathbf{Q}\cdot\mathbf{u}_\kappa)^2$

5 Benchmark: heat transport in bulk MoS_2 and WSe_2

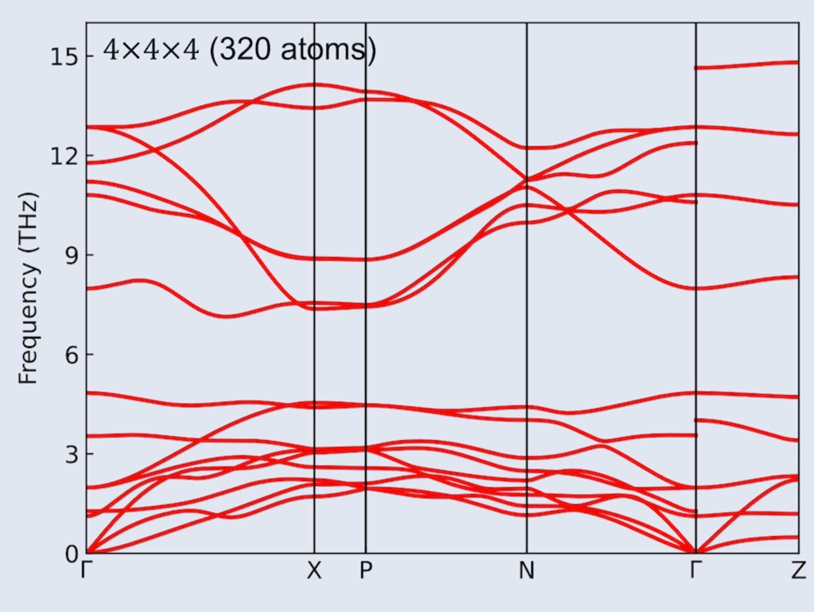
A. MoS_2

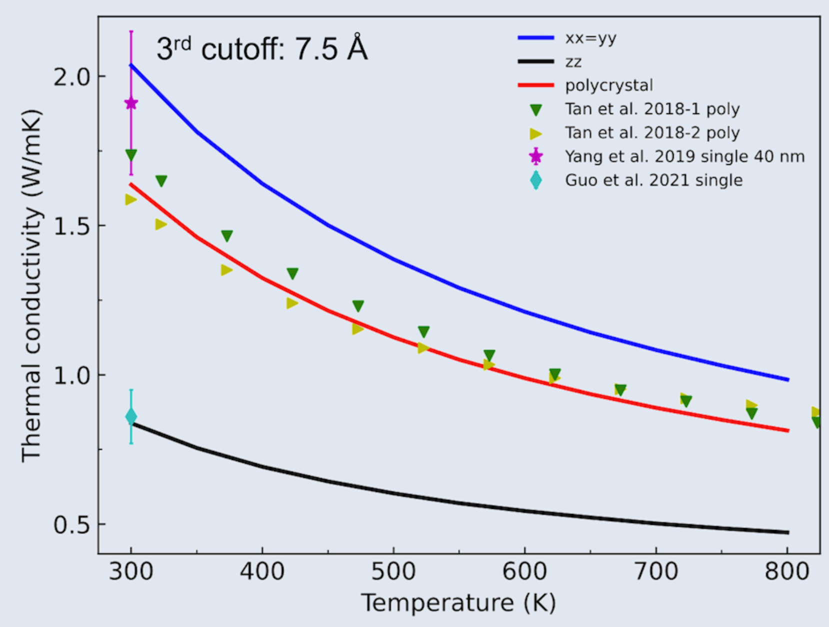


B. WSe_2



6 Application: heat transport in Bi_2O_2Se

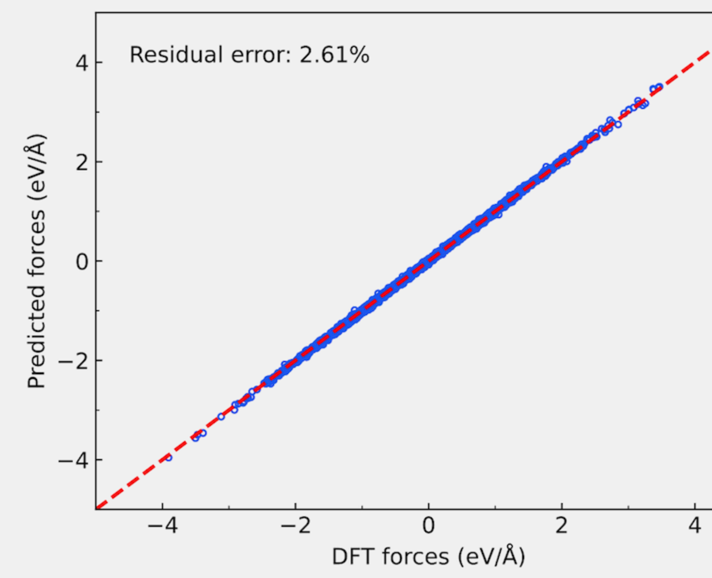




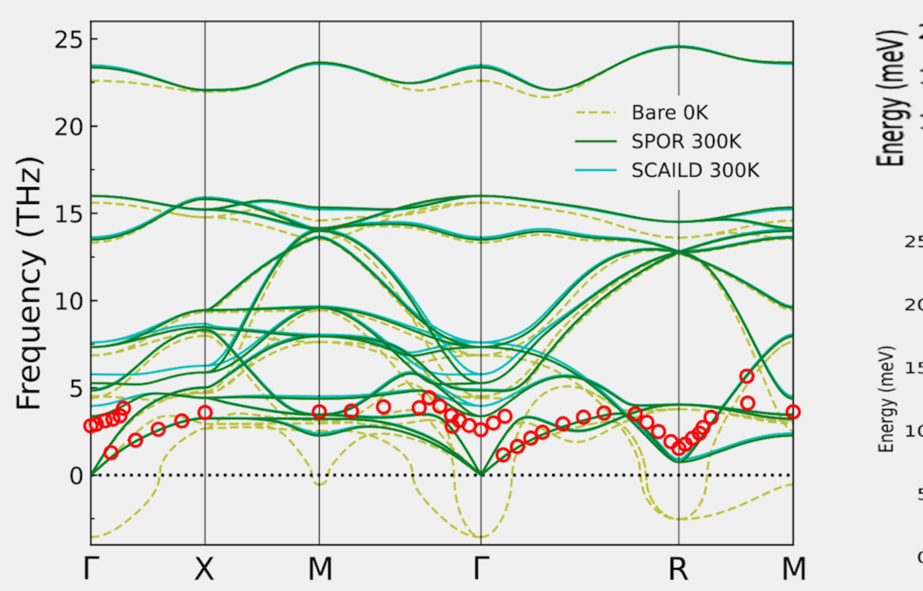
7 Application: phonon anharmonicity in cubic $SrTiO_3$

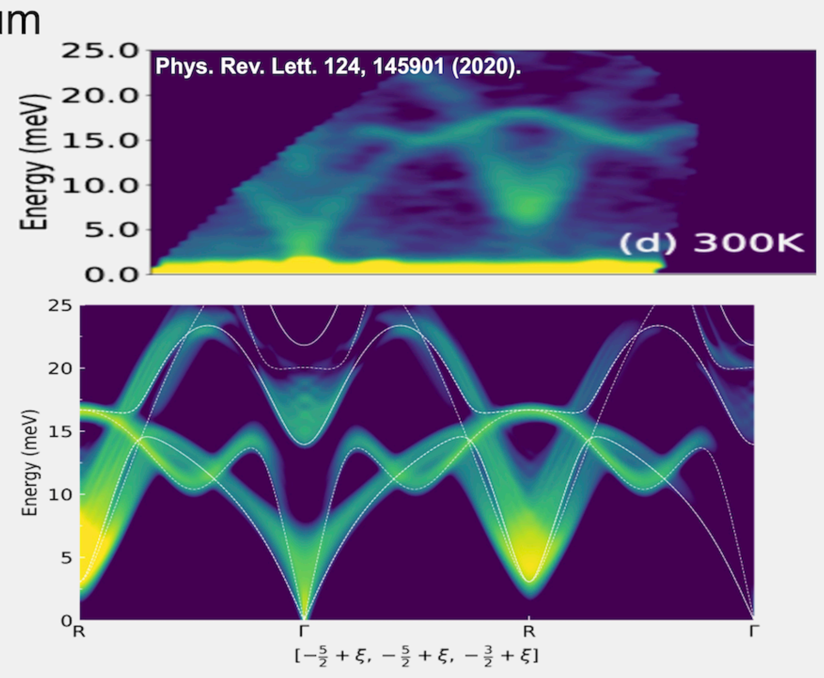
A. Interatomic force constants

2×2×2	2nd	3rd	4th	5th	6th
Cutoff (Å)	INF	INF	6.0	6.0	6.0
n-body	2	3	3	2	2
# of clusters	22	117	221	47	63
# of IFCs	198	3159	17901	11421	45927
# of free IFCs	45	698	2215	43	125
Total free IFCs	3126 (1965 non-zero IFCs)				



B. Temperature-dependent phonon spectrum





8 Summary of current features

- Efficient extraction of interatomic force constants up to sixth-order with the separate treatment of long-range Coulomb interactions for infrared-active solids;
- Anharmonic renormalization of phonon quasiparticles;
- Inelastic neutron and X-ray scattering spectroscopies;
- General invariance and equilibrium conditions for lattice dynamics;
- Calculation of elastic and mechanical properties from Born perturbation expansion;
- Interfaced to VASP and Quantum ESPRESSO as force and total energy calculators.

References

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