Effect of Parameter Choice in Density Functional Perturbation Theory Calculations of Phonons and Related Properties

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Abstract

In atomic matter, phonon modes and frequencies determine material properties such as thermal and electrical conductivity. Allowed vibrational frequencies are found by solving a characteristic equation for the dynamical matrix constructed through the second derivatives of energy with respect to displacements of the atoms. One method for effecting quantum mechanical solutions in this context is density functional perturbation theory (DFPT). In this method, the electron density is calculated by solving a mean-field Hamiltonian self-consistently for the its energy and wave functions, keeping the atoms at their relaxed positions. Then, the perturbation in energy with respect to perturbations of the atoms is calculated for every unique atomic displacement combination. DFPT has multiple parameters to control for to produce realistic simulations. We investigate the effects of varying these parameters on the resulting phonon frequencies in terms of the relative and absolute error from a highly convergent phonon frequency using several electronically distinctive solid-state systems. We take the same approach to compare calculated with experimentally determined phonon frequencies, aiming to provide advice in choosing parameters for accurate DFPT calculations.

Model

Density functional theory (DFT) [3] replaces explicit many-electron interactions with fictitious particles ("orbitals") interacting with a background potential (exchange-correlation) through the electron density [4]; this transformation is exact when the exchange-correlation potential is exact; practical potentials are based on perturbing model systems such as a uniform electron gas and work well when realistic systems are close to the model ones. The self-consistent field (SCF) method produces the orbitals (or potential perturbations) using the variational principle:
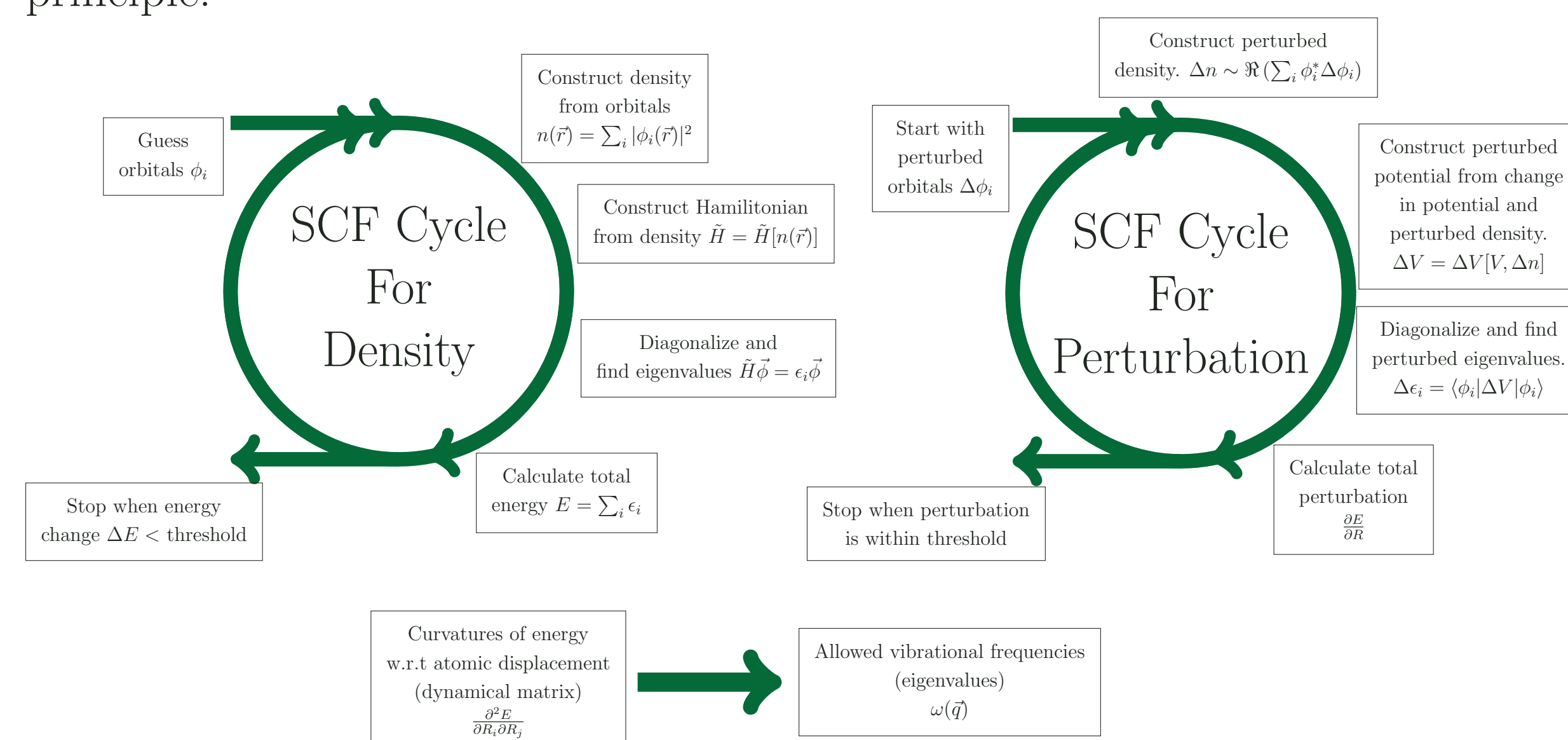
Workflow

AiiDA [7] creates an organization in Python to control the DFPT workflow inside Quantum ESPRESSO [2] (QE) code execution as follows:

Results

For a given parameter, we vary its value until all of the calculated phonon frequencies no longer vary within some threshold. Then, we analyze the resulting frequencies according to the average and absolute average relative difference from the converged frequencies:

$$\Delta_r = \frac{1}{N}\sum_j \frac{\omega_j - \omega_{j,\text{conv}}}{\omega_{j,\text{conv}}} \qquad |\Delta_r| = \frac{1}{N}\sum_j \frac{|\omega_j - \omega_{j,\text{conv}}|}{|\omega_{j,\text{conv}}|}$$

where $\omega_{j,\text{conv}}$ is the presumed converged corresponding phonon frequency to ω_j.
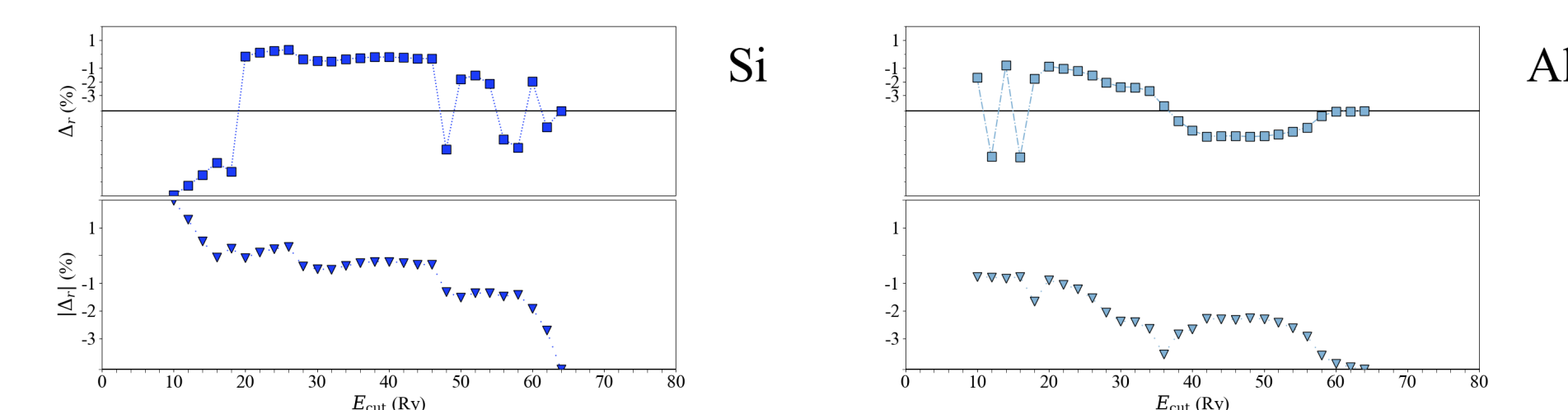

Fig. 1: Average and absolute average relative difference of phonon frequencies with varying **plane-wave basis set cutoff** $|\vec{G}_i|^2/2 \leq E_{\text{cut}}$ in the orbitals for diamond Si (left) & fcc Al (right)
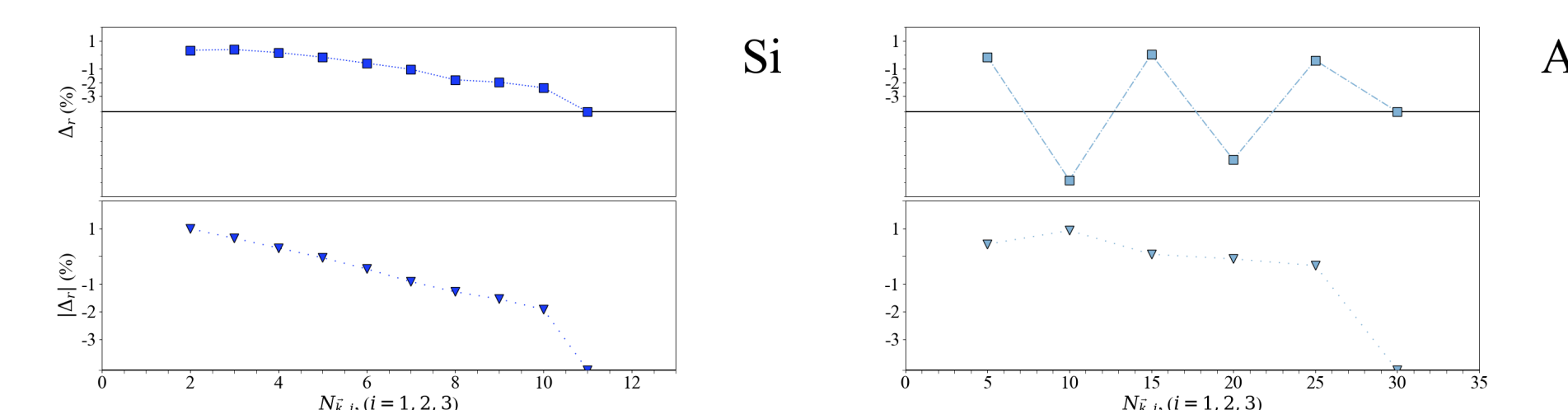

Fig. 2: Average and absolute average relative difference of frequencies with varying **electronic reciprocal-space sampling** ($\vec{k}$-point) per direction for diamond Si (left) & fcc Al (right)
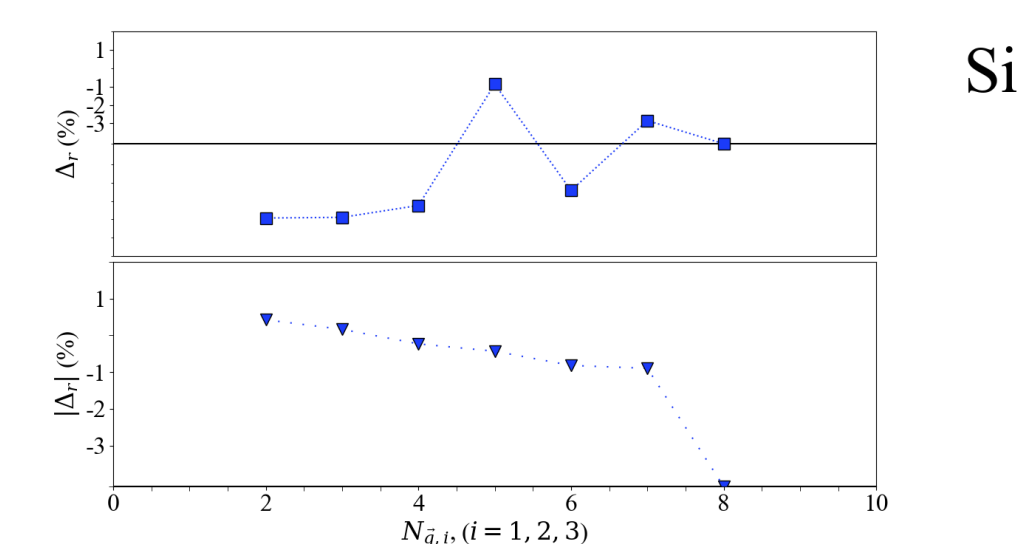

Fig. 3: Average and absolute average relative difference of phonon frequencies with varying **vibrational reciprocal-space sampling** ($\vec{q}$-point) per direction for diamond Si
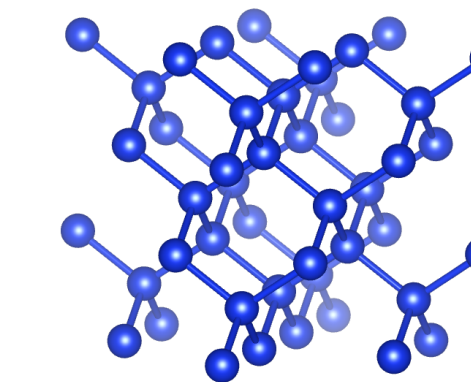
Test Systems

Fig. 4: Diamond Si (symmetry: $Fd\bar{3}m$)

Fig. 5: fcc Al (symmetry: $Fm\bar{3}m$)

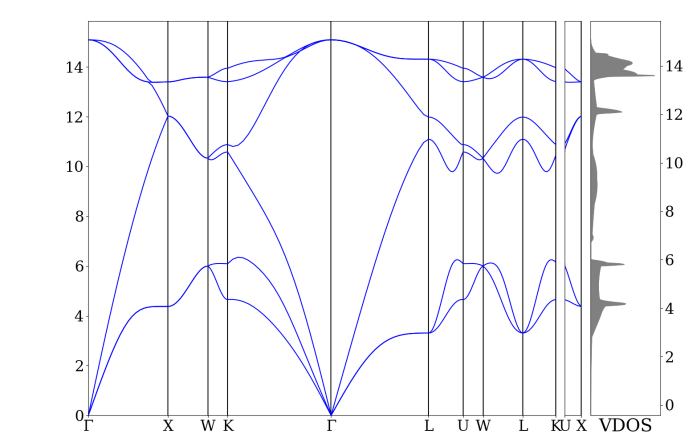

Fig. 6: Phonon bands and vibrational density of states for diamond Si calculated in DFPT using the GGA-PBE exchange-correlation functional
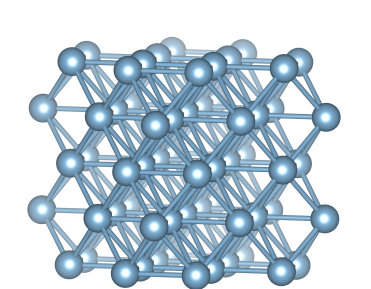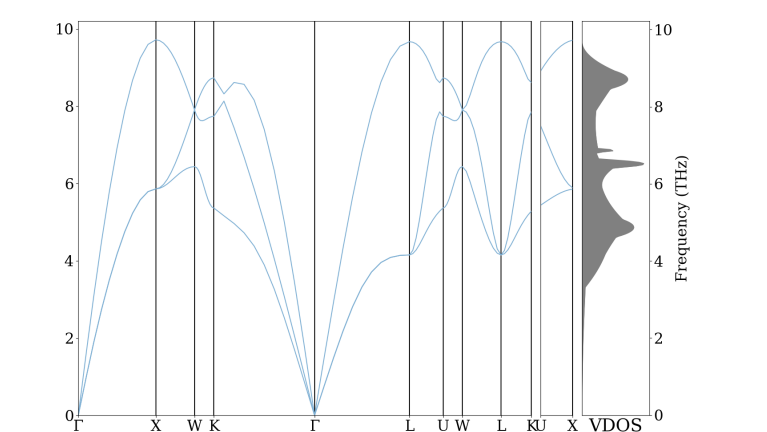

Fig. 7: Phonon bands and vibrational density of states for fcc Al using the GGA-PBE exchange-correlation functional

Conclusions

The integration of a more automated workflow using AiiDA to control Quantum ESPRESSO DFPT calculation allowed us to confirm efficiently that phonons exhibit greater sensitivity to convergence parameters than the total energy (unsurprising given phonon frequencies' dependence on the Hessian of the energy with respect to atomic displacements). We hope that clear detailing of these convergences will provide guidance on parameter choice. Future work includes:

- Extending the scope and range of parameter testing on Si and Al and include comparison to experiment;
- Expanding test systems to include rock-salt NaCl as a prototypical insulator.

Reference

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