



# Convergence and pitfalls of density functional perturbation theory phonons calculations from a high-throughput perspective

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## ABSTRACT

The diffusion of large databases collecting different kind of material properties from high-throughput density functional theory calculations has opened new paths in the study of materials science thanks to data mining and machine learning techniques. Phonon calculations have already been employed successfully to predict materials properties and interpret experimental data, e.g. phase stability, ferroelectricity and Raman spectra, so their availability for a large set of materials will further increase the analytical and predictive power at hand. Moving to a larger scale with density functional perturbation calculations, however, requires the presence of a robust framework to handle this challenging task. In light of this, we automatized the phonon calculation and applied the result to the analysis of the convergence trends for several materials. This allowed to identify and tackle some common problems emerging in this kind of simulations and to lay out the basis to obtain reliable phonon band structures from high-throughput calculations, as well as optimizing the approach to standard phonon simulations.

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## 1. Introduction

In the latest years, the development of efficient density functional theory (DFT) software packages and the constant increase of the computational capabilities of modern supercomputers have opened new possibilities in the field of material science, including the discovery of new materials based on the high-throughput screening of large number of compounds [1]. Following this trend, several open databases have been created containing a number of properties obtained from DFT calculations [2–6] thanks to *ad hoc* frameworks developed to help the automation of the whole process [7–11]. High-throughput techniques have not only allowed to search for materials candidates for a specific application but also to use data mining and machine learning techniques to understand trends and limitations in materials science [12–17].

Building on the experience gained so far and on the tools made available, it is now possible to address the calculation of more and more involved quantities for a vast number of materials, with efforts that are ongoing to analyze properties obtained with calculations beyond the ground state [18–23]. Vibrational properties in solids are essential to many applications as they govern several materials properties (e.g. vibrational entropy [24,25], thermal con-

ductivity [26–28], ferroelectric and ferroelastic transitions [29,30]). Phonon computations can be performed very efficiently using the Density functional perturbation theory (DFPT) [31] providing a computational access to these important properties.

Before moving to large scale calculations it is mandatory to implement a robust procedure to handle the whole process and provide a reliable set of input parameters that suits most of the possible cases that will be considered. In this regard, it has been shown how the validation of the results is an element of great relevance when approaching the high-throughput regime [20,32].

In this paper we present the outcome of a study concerning the convergence rate of phonon related quantities with respect to the sampling of the Brillouin zone alongside a validation of the results generated within an automated process. In addition, since performing a considerable amount of simulations provides a stress test for the DFT and DFPT code, we have been able to identify some subtleties and pitfalls, that tend to show up under certain conditions and that may go unnoticed in a standard approach. Given the substantial difference in terms of requirements between metals and semiconductors and the difficulty of expressing a general recipe that would allow to capture peculiar phenomena as the Kohn anomalies, we have limited our analysis to the case of semiconducting materials.

In the following, after the definition of the theoretical framework (Section 2), we will first discuss the evolution of the phonon frequencies with respect to the density of  $k$ -points and  $q$ -points in

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Sections 3 and 4, respectively, highlighting the problems related with the sampling. In the second part we proceed to demonstrate the reliability of our results through a validation process, involving also a comparison with experimental data (Section 5).

## 2. Formalism and methodologies

In this study we considered a set of 48 semiconducting materials. These were chosen to cover a variety of elements of the periodic table and all the crystal systems, with different system sizes and band gaps. Detailed information about the properties of each material can be found in the [Supplemental Material \(SM\)](#).

All the simulations were performed with the ABINIT software package [33–35], which relies on the DFPT formalism to carry on calculations related to phononic and electric field perturbations [31,36,37]. The Perdew-Burke-Ernzerhof (PBE) [38] was used as exchange–correlation (xc) functional. While this standard approximation has been demonstrated to underperform for phonon frequencies compared to other exchange–correlation functionals, it still produces results in reasonable agreement with experimental data [39] and we assume that our conclusions will still hold for other local and semilocal xc functional approximations (e.g., LDA and PBEsol).

Optimized norm-conserving pseudopotentials (ONCV) [40] were used for all the elements treating semi-core states as valence electrons for transition metals (as available from the pseudopotentials table Pseudo-dojo version 0.2 [41]). The cutoff was chosen independently for each material according to the values suggested in the Pseudo-dojo (see SM). These pseudopotentials and the cutoff values have been carefully tested with respect to all electron codes [42] and with respect to the fulfillment of the acoustic sum rule (ASR). Checks on the ASR and the charge neutrality [37], that are sensitive to the cutoff, were also performed on each material and the convergence with respect to the cutoff was further verified for problematic cases.

The splitting between longitudinal and transverse optical mode (LO-TO) was taken into account through the calculation of the non-analytic term containing the Born effective charges  $Z^*$  (BECs) [37]. Phonon frequencies at generic  $q$ -points were obtained through Fourier interpolation and, in that case, the ASR and the charge neutrality at the  $\Gamma$  point were enforced explicitly.

For all the materials, the unit cells were standardized according to Ref. [43] and each was relaxed until all the forces on the atoms were below  $10^{-6}$  Ha/Bohr and the stresses were below  $10^{-4}$  Ha/Bohr<sup>3</sup>.

All the calculations were carried out using Fireworks as a workflow manager [7] integrated with the different libraries: pymatgen [8], abipy [44] and abiflows [45].

The Monkhorst-Pack grids used to sample the Brillouin zone were distinguished considering the number of the points per reciprocal atom for both the electron wavefunctions (referred to as  $k$ -points) and for the phonon wavefunctions (referred to as  $q$ -points), respectively. These quantities, the number of points in the full Brillouin zone times the number of atoms, are labelled  $kpra$  and  $qpra$ , respectively.

For the statistical analysis, we identified, for each material, a reference grid (leading to converged phonon frequencies, see below). For each other sampling density the errors were defined as the absolute value of the difference between the phonon frequencies  $\omega$  calculated with that grid and those obtained with the reference grid. In this context, when analyzing the  $k$ -point convergence we considered the frequencies at the high symmetry points of the Brillouin zone [43], while when varying the  $q$ -points grid the convergence was checked for the interpolated values on very dense regular grids of  $q$ -points (100,000  $qpra$ ). In the latter case,  $q$ -points belonging to the dense grids explicitly obtained from the DFPT

calculation were excluded from the statistical analysis, as their error would be zero by definition.

For each specific grid we considered mainly the mean absolute error (MAE) and the mean absolute relative error (MARE) over all the frequencies. The choice of focusing on averaged errors stems from the fact that many quantities derived from phonon calculations that can be compared to experimental results are obtained integrating over the whole Brillouin zone (e.g. DOS and thermodynamic properties [46]). In addition, in order to get a better insight on the presence of possible problematic regions, the maximum absolute error (MxAE) and the maximum absolute relative error (MxARE) were also considered.

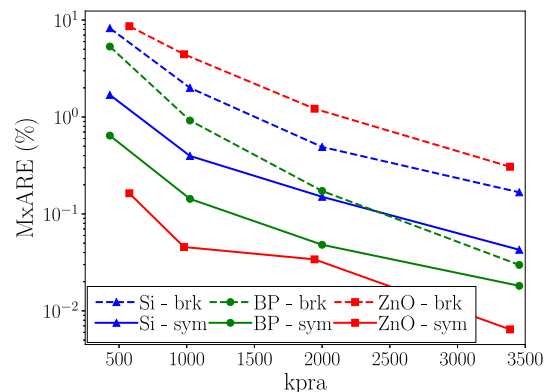
The reference configuration was selected independently for each material and for the  $k$  and  $q$  grids, by considering progressively increasing densities in the reciprocal space, until a convergence was reached based on the MAE and MARE.

## 3. Electron wavevector grid convergence

Before any statistical analysis, we would like to highlight the importance of the choice of the  $k$ -point grid itself. For a subset of the materials considered (Si, BP and ZnO) the  $k$ -point dependence of the phonon frequencies was investigated for a list of  $\Gamma$  centered grids, thus satisfying the same symmetries of the crystal, and for the same grids with a shift that breaks the symmetry. The values of the MxAE with respect to a reference grid of approximately 5500  $kpra$  are reported in Fig. 1, showing that the symmetric set of grids can reduce the error by up to two orders of magnitude compared to the non-symmetric one. This demonstrates the importance of choosing a  $k$ -point grid that respects the symmetries of the system to improve the rate of convergence. In the following, the  $k$ -point grids were thus chosen with appropriate shifts satisfying this criterion.

The relative and absolute errors for the  $k$ -point grids were calculated as described in Section 2 for each different grid available. Considering a threshold  $\varepsilon$  for the maximum error tolerated and given a specific value  $\overline{kpra}$  of the  $k$ -points per reciprocal atom, we analyzed the fraction  $F$  of materials for which the results are converged within the limits  $\varepsilon$  and  $\overline{kpra}$ . More precisely, we define  $F$  as:

$$F(\overline{kpra}, \varepsilon) = \frac{\sum_{i=1}^{48} [|\text{Err}_i(\kappa_i)| < \varepsilon]}{48}, \quad (1)$$



**Fig. 1.** Evolution of the maximum relative error for different  $k$ -point samplings for Si (blue triangle), BP (green circle) and ZnO (red square). The reference grids have approximately 5500  $kpra$ . Solid lines represent the error for a  $\Gamma$  centered grid, while dashed lines are for shifted grids, preserving and breaking the symmetries (sym and brk) of the crystals, respectively. The lines are a guide to the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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