

Efficient extraction of high-order force constants by machine learning using the hiphive package

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The efficient extraction of force constants (FCs) is crucial for the analysis of many thermodynamic materials properties. Approaches based on the systematic enumeration of finite differences scale poorly with system size and can rarely extend beyond third order when input data is obtained from first-principles calculations. Methods based on parameter fitting in the spirit of interatomic potentials, on the other hand, can extract FC parameters from semi-random configurations of high information density and advanced regularized regression methods can recover physical solutions from a limited amount of data. Here, we present the HIPHIVE Python package, that enables the construction of force constant models up to arbitrary order. HIPHIVE exploits crystal symmetries to reduce the number of free parameters and then employs advanced machine learning algorithms to extract the force constants. Depending on the problem at hand both over and underdetermined systems are handled efficiently. The FCs can be subsequently analyzed directly and or be used to carry out e.g., molecular dynamics simulations. The utility of this approach is demonstrated via several examples including ideal and defective monolayers of MoS₂ as well as bulk nickel.

I. INTRODUCTION

The vibrational properties of solids are pivotal for a large number of physical phenomena, including phase stability and thermal conduction. In crystalline solids the vibrational motion of the atoms is periodic and commonly described using phonons – quasi-particles that represent collective excitations of the lattice. At the first level of approximation, phonons can be obtained within the harmonic limit, which implies non-interacting quasi-particles with infinite lifetimes. This approach, along with its so-called quasi-harmonic extension, already provides a wealth of information. There are, however, countless examples where anharmonic effects are crucial and must be accounted for in order to capture the correct physical behavior of a system. Notable examples include the lattice contribution to the thermal conductivity or the vibrational stabilization of metastable phases, e.g., the body-centered cubic phase of the group IV elements (Ti, Zr, Hf) or the cubic phase of zirconia.¹ In more general terms, phonon-phonon coupling must be taken into account, which leads to finite phonon lifetimes and temperature-dependent frequencies.

Formally, the analysis of vibrational material properties requires a set of force constants (FCs), which allows the computation of atomic forces solely based on the displacements of atoms from their reference positions (see Eq. (1)). The harmonic approximation requires only knowledge of the second-order FCs, which can be readily extracted using software packages such as PHONOPY.² Third-order FCs, which are required e.g., for computing the thermal conductivity to the lowest permissible order of perturbation theory, can be constructed using, e.g., PHONO3PY,³ SHENGBTE,⁴ ALMABTE,⁵ and AAPLAFLOW.⁶ These packages employ finite differences and a systematic enumeration of atomic displacements, while reference forces are usually obtained using density functional theory (DFT) calculations.⁷

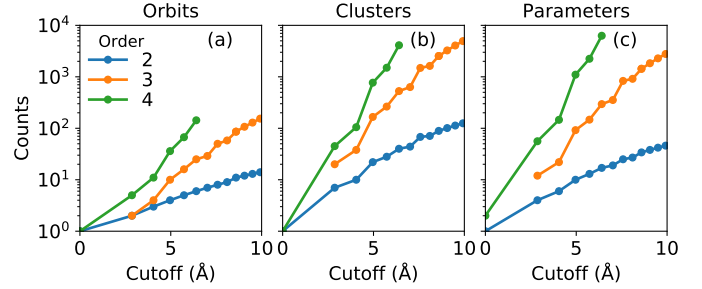


FIG. 1. (a) Number of unique types of clusters, (b) total number of clusters per primitive cell, and (c) number of unknown parameters in FCC aluminum as a function of the cutoff radius imposed during construction of the cluster space.

FCs beyond third-order are required to describe, e.g., metastable systems or the temperature dependence of phonon modes. The number of degrees of freedoms (DOFs) in higher-order FCs quickly increases (see Fig. 1 for an example) and they are hence increasingly difficult to extract by enumeration schemes. Alternatively, one can employ regression schemes,^{8,9} as implemented in the ALAMODE¹⁰ and TDEP codes.¹¹ They employ linear least-square fitting and thus require the number of input forces to exceed the number of parameters, i.e. they solve an *overdetermined* problem. More recently, techniques based on compressive sensing¹² have been proposed^{13–16} that can also efficiently solve *underdetermined* systems.

Here, we introduce the HIPHIVE Python package, which allows one to efficiently obtain high-order FCs both in large systems and systems with low-symmetry. HIPHIVE can take advantage of various powerful machine learning algorithms for FC extraction via SCIKIT-LEARN¹⁷ and it can be readily interfaced with a large number of electronic structure codes via the atomic simulation environment (ASE) package.¹⁸ This enables a flexible workflow with easy access to various advanced optimization

techniques some of which are designed to find sparse solutions^{13,19} that reflect the short-range nature of the FCs. If the input configurations are constructed sensibly this approach requires a *much* smaller number of input configurations and thus considerably reduces the computational effort, the overwhelming part of which is usually associated with DFT calculations. This approach becomes genuinely advantageous for obtaining second-order FCs in large and/or low symmetry systems (defects, interfaces, surfaces, large unit cells etc) and high order FCs, for which a strict enumeration scheme quickly leads to a dramatic increase in the number of force calculations.

FCs can be post-processed in a number of ways including analysis via PHONOPY and PHONO3PY as well as molecular dynamics (MD) simulations via ASE. An extensive user guide is available online,²⁰ which includes a basic tutorial as well as a number of advanced examples. The package is maintained under an open source license on GITLAB and can be installed from the Python Package Index (PYPI).

The remainder of this paper is organized as follows. The next section provides a concise summary of FC expansions, which sets up a description of algorithmic and methodological aspects in Sect. III as well as the HIPHIVE workflow in Sect. IV. Possible applications are finally illustrated by several examples in Sect. V.

II. FORCE CONSTANTS

This section provides a brief introduction to FC expansions. The similarities between a FC and a cluster expansion are described and the effect of crystal symmetries is demonstrated. Finally, the constraints due to translational and rotational symmetry are summarized.

A. Basics

The potential energy V of a solid can be represented by a Taylor expansion of the potential energy surface (PES) in ionic displacements $\mathbf{u} = \mathbf{R} - \mathbf{R}_0$ away from the equilibrium positions \mathbf{R}_0

$$V = V_0 + \Phi_i^\alpha u_i^\alpha + \frac{1}{2} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!} \Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \dots,$$

where the Einstein summation convention applies and

$$\Phi_i^\alpha = \frac{\partial V}{\partial u_i^\alpha}, \quad \Phi_{ij}^{\alpha\beta} = \frac{\partial^2 V}{\partial u_i^\alpha \partial u_j^\beta} \quad \text{etc.}$$

Φ_i , Φ_{ij} , ... are the FCs corresponding to increasing orders of the expansion. Latin indices i indicate the atomic labels, where the summation is over an infinite crystal lattice, while Greek indices α run over the Cartesian coordinates x, y, z . V_0 is a constant term, which is commonly ignored when dealing with lattice dynamics. The first order FC is also often dropped since the

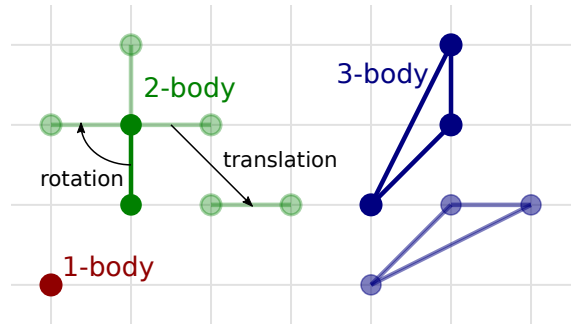


FIG. 2. Examples for one-body (singlet; red), two-body (pair; green), and three-body (triplet; blue) clusters. Dark colors indicate representative cluster whereas lighter colors represent symmetry equivalent clusters that belong to the associated orbit. While the two-body clusters shown here are related by a simple fourfold rotation, the three-body clusters can be mapped onto each by application of a fourfold rotation combined with a mirror operation.

expansion in displacements can be made around an equilibrium lattice configuration with vanishing forces. These two terms are important for some applications but here are considered zero. Truncating the potential after the second-order term results in the conventional harmonic phonon theory, which is analytically solvable and widely used.^{21,22}

The forces can be written in terms of the FCs as

$$F_i^\alpha = -\Phi_{ij}^{\alpha\beta} u_j^\beta - \frac{1}{2} \Phi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma - \dots \quad (1)$$

Crucially, this expression that takes the functional form of an interatomic many-body potential is linear in the FCs, which will become relevant in Sect. III.

The number of DOFs in the FC expansion scales exponentially with $\mathcal{O}(N^n)$, where N is the number of atomic sites of the supercell and n is the order after which the expansion is truncated. The number of *independent* parameters is, however, much smaller due to the symmetries of the underlying lattice as well as constraints due to the conservation of linear and angular momentum.⁸ The number of *numerically relevant* parameters is smaller still due to the decay of the FCs with interaction distance, order, and finite many-body interactions.

B. Clusters

To represent the FCs and their inherent symmetries it is convenient to consider clusters of sites ($ij\dots$), each of which can be assigned a size, taken for example as the largest distance between any two sites in the cluster. The FCs correspond to interactions between the sites forming a cluster; for example, the term Φ_{ijkk} describes a fourth-order interaction in the three-body cluster (ijk). Clusters can be categorized based on the number of sites they comprise and accordingly there are one-body (singlet), two-body (pair), and n -body (many-body) clusters

(Fig. 2). In general a cluster of order n is a multiset of order (or cardinality) n consisting of up to n different atoms. As a result of the locality of the interactions, one commonly truncates the FC expansion both in size, order, and cluster size. It is thus possible to create for example a non-central, short ranged, anharmonic pair potential or a long ranged harmonic pair potential with short ranged anharmonic many-body corrections.

C. Symmetries

The FCs obey a number of symmetries, the most fundamental of which stems from the requirement that the differentiation of the total energy and thus Φ must be invariant under a simultaneous permutation P of atomic and Cartesian indices

$$\Phi_{ij\dots}^{\alpha\beta\dots} = \Phi_{P(ij\dots)}^{P(\alpha\beta\dots)} \quad (2)$$

The FCs must further comply with the symmetry of the underlying lattice as expressed by the associated spacegroup. Each symmetry operation S consists of a (possibly improper) rotation R and a translation T . If application of S maps a cluster $(ij\dots)$ onto another cluster $(i'j'\dots)$ the FCs corresponding to these two clusters are related to each other according to

$$\Phi_{ij\dots}^{\alpha\beta\dots} = \Phi_{i'j'\dots}^{\alpha'\beta'\dots} R^{\alpha'\alpha} R^{\beta'\beta} \dots \quad (3)$$

Clusters, which can be transformed into each other as a result of the application of such a symmetry operation, are said to belong to the same *orbit* (Fig. 2) and the associated FC parameters are related by the respective symmetry operation. The lattice symmetry can thus be used to reduce the number of free parameters by grouping clusters in orbits.

Furthermore, a symmetry operation that maps a cluster onto itself implies a reduction in the number of internal DOFs in the FCs,

$$\Phi_{ij\dots}^{\alpha\beta\dots} = \Phi_{ij\dots}^{P^{-1}(\alpha'\beta'\dots)} R^{\alpha'\alpha} R^{\beta'\beta} \dots, \quad (4)$$

where P can be a permutation, e.g., a mapping of the indices (ij) onto (ji) . Sect. III addresses how these constraints are imposed in practice.

D. Constraints

The conservation of linear momentum constrains the FCs further leading to a set of translational (acoustic) sum rules.

$$\sum_i \Phi_{ij\dots}^{\alpha\beta\dots} = 0, \quad (5)$$

which apply for all Cartesian indices independently.²¹

Rotational invariance is general harder to enforce than translational invariance. This is partly due to subtle difficulties that arise when combining periodic boundary conditions with a rotationally invariant expansion around equilibrium.²³ Many authors have described and proposed rotational sum rules.^{22,24–27} In general it is recognized that the conservation of angular momentum leads to a set of rotational sum rules that relate force constants of order n and $n+1$ as^{8,22}

$$\Phi_{i_1\dots i_n}^{\alpha'\dots\alpha_n} \omega_\gamma^{\alpha'\alpha_1} + \dots \Phi_{i_1\dots i_n}^{\alpha_1\dots\alpha'} \omega_\gamma^{\alpha'\alpha_n} + \Phi_{i_1\dots i_{n+1}}^{\alpha_1\dots\alpha_{n+1}} \omega_\gamma^{\alpha_{n+1}\alpha'} r_{i_{n+1}}^{\alpha'} = 0, \quad (6)$$

where ω is a generator of infinitesimal rotations with the same representation as the Levi-Civita symbol and r_i^α denotes the position vector of atom i .

To simplify things, we only consider the two simplest sum rules derived by Born and Huang²¹ and apply them to second order FCs. The Born-Huang sum rule reads

$$\Phi_{ij}^{\alpha\beta} r_j^\gamma = \Phi_{ij}^{\alpha\gamma} r_j^\beta, \quad (7)$$

which is a truncation of Eq. (6), whereas the Huang invariance imposes

$$\sum_{ij} \Phi_{ij}^{\alpha\beta} r_{ij}^\gamma r_{ij}^\delta = \sum_{ij} \Phi_{ij}^{\gamma\delta} r_{ij}^\alpha r_{ij}^\beta, \quad (8)$$

where r_{ij} is the distance vector between the equilibrium positions of atoms i and j .

These two constraints do not suffice to render the expansion fully rotationally invariant and thus MD simulations can potentially behave unphysical. As shown below, they do, however, enforce the correct dispersion relation near the Γ -point, which is crucial for e.g., two-dimensional materials.²³

III. METHODOLOGY

This section will start with a concise overview of the computational methods used when implementing the framework described above. In the subsequent subsections each step is described in more detail.

The *cluster space* represents a fundamental element of the algorithm implemented in HIPHIVE. It comprises information concerning

- the clusters that an atom in the primitive cell can be part of given the cutoff,
- the organization of clusters into orbits,
- the FC for each orbit (relative to a representative cluster of that orbit),
- the free parameters allowed by symmetry in each FC, and
- the constraints imposed on the free parameters by translational and rotational invariance.

The cluster space thus contains all the information needed to construct the template FCs for any supercell of the same structure.

The information is generated by the following procedure, which requires user input in the form of a structure (defined by cell metric, basis, and chemical species) as well as a set of cutoff radii per order.

1. Find all applicable symmetry operations for the input structure using, e.g., SPGLIB.²⁸
2. Enumerate all possible sites in periodic images of the primitive cell located at the origin (zero-cell) that reside within the specified cutoff relative to any atom in the center cell
3. Construct all possible clusters, which contain at least one site in the zero-cell and are consistent with the cutoff.
4. Apply symmetry operations and establish the symmetry relations between clusters; group the clusters into orbits.
5. Use the symmetry operations that map the representative cluster of an orbit onto itself to reduce the FCs into reduced components that obey the symmetries.
6. Finally, construct the system of equations describing the sum rules and find the solution space satisfying the constraints.

The cluster space can then be used together with a supercell with displaced atoms to create the so called sensing matrix, which relates the free parameters to the resulting forces.

A. Clusters and orbits

Finding the possible clusters in a structure can be done in several ways. Keep in mind that even though a lower order cluster (e.g., 0-0-3-7) might be invariant under a symmetry, a higher-order cluster involving the same atoms (e.g. 0-3-3-7-7) need not be invariant under the same symmetry. One simple way to generate clusters is to generate all possible unique multisets of increasing cardinality with elements drawn from the atom enumeration of the periodic images. To decide if the cluster (multiset) should be kept all atoms must be within the cutoff distance from each other and it must contain at least one atom in the zero-cell.

The symmetry operations can now be used to categorize the clusters into orbits, each of which contains a representative cluster. All other clusters in the orbit are related to the representative (prototype) cluster by a symmetry operation together with a permutation. If during the categorization process a symmetry maps a cluster onto a permutation of itself it can be used to reduce the number of free components in the FC as described below.

B. Cluster symmetries and invariant bases

If a representative cluster is symmetric under a set of crystal symmetries $\{S_i\}$ the corresponding representative FC must obey the same symmetries. Using multi-index notation ${}^\Lambda = \{\cdot_{ij}^{\alpha\beta}, \cdot_{ijk}^{\alpha\beta\gamma}, \dots\}$, the problem of finding valid solutions can be transformed into an eigenvalue problem by flattening the tensors

$$\Phi^\Lambda = \Phi^{\Lambda'} \widetilde{R}^{P(\Lambda')\Lambda}. \quad (9)$$

The eigenvectors, after back-transformation, are then solutions φ to the original equation (4), which form an invariant basis with respect to the symmetries of the cluster. A FC associated with the respective cluster that fulfills the symmetry can then be constructed as a linear combination of these basis functions

$$\Phi = \sum_p a_p \varphi_p, \quad (10)$$

where a_p represents the parameters that must be found by optimization (see below) and cannot be determined by symmetry alone and the basis elements φ we denote as eigentensors. Equation (9) can in principle be solved by any suitable algorithm. It is, however, preferable to work in scaled coordinates since then the rotation matrices are integer matrices allowing one to use an optimized algorithm. This has some additional advantages including exact precision and conservation of sparsity, i.e., a 3×3 matrix with 9 unknowns can be decomposed into 9 dense 3×3 matrices or 9 sparse 3×3 matrices with only one element per matrix.

C. Translational sum rules

While the parametrization obtained after enforcing the crystal symmetries could in principle be used as the final parametrization of the model, the resulting FCs are not guaranteed to be translational or rotational invariant. The constraints due to sum rules can be enforced by projecting the parameters onto a subspace of the parameter space (i.e. the nullspace of Eq. (5)) that fulfills the sum rule. As noted below, this method is used in HIPHIVE to enforce the rotational sum rules.

Sum rules can also be applied via re-parametrization by only considering linear combinations of parameter vectors, which span the aforementioned nullspace of the sum rule. HIPHIVE adopts this approach to enforce the translational sum rules. The corresponding constraint matrix is constructed as described below.

Let Θ denote an orbit and $T_{\Theta c}$ the combined rotation and permutation operation that maps the representative cluster c_Θ onto a cluster c belonging to the same orbit. Then together with Eq. (10) the sum rule Eq. (5) can be

written as

$$\sum_i \sum_{\Theta} \sum_p a_{p\Theta} \varphi_{p\Theta}^{\alpha'\beta' \dots} T_{\Theta(ij \dots)}^{\alpha'\beta' \dots \alpha\beta \dots} = 0 \quad \forall j \dots \alpha\beta \dots$$

$$= \mathbf{C}^{\text{trans}} \mathbf{a} = \mathbf{0} \quad (11)$$

where $\mathbf{C}^{\text{trans}}$ is the translational constraint matrix. Interpreting $p\Theta$ as a multi-index the equation above represents a system of linear equations in the parameters $a_{p\Theta}$. The solutions to this system are referred to as constraint vectors $A_{p\Theta,i}$ and specify how the parameters $a_{p\Theta}$ must be related in order to fulfill the sum rules.

$$a_{p\Theta} = A_{p\Theta,i} \tilde{a}_i$$

where \tilde{a} is the new parameters guaranteed to fulfill the translational sum rules.

D. Sensing matrix

To extract the independent parameters the so called sensing (or fit) matrix \mathbf{M} must be constructed for each input structure. This matrix, which depends on the $3N_{\text{at}}$ -dimensional displacement vector \mathbf{u} , relates the $3N_{\text{at}}$ -dimensional vector of predicted forces \mathbf{f} to the N_{par} -dimensional parameter vector $\tilde{\mathbf{a}}$,

$$\mathbf{f}(\mathbf{u}, \tilde{\mathbf{a}}) = \mathbf{M}(\mathbf{u}) \tilde{\mathbf{a}}, \quad (12)$$

where N_{at} and N_{par} denote the number of atoms in the supercell and the number of parameters, respectively. This form is possible due to Eq. (1), which has the form of an interatomic potential with tunable parameters. The crucial step here is to recognize that the forces \mathbf{f} are linearly related to the FC parameters $\tilde{\mathbf{a}}$ for given displacements \mathbf{u} . The FCs in turn are linearly dependent on the FC parameters via the crystal symmetries and the FC parameters associated with the orbits, where the parameters are either the true expansion parameters associated with the orbits or the constrained parameters that include the translational sum rules.

E. Rotational sum rules

In principle the procedure used to enforce the translational sum rules can also be employed to apply the rotational sum rules. Since the rotational sum rules involve the positions of the lattice sites (which can assume any real value) the algorithm to extract the nullspace must, however, be numerically very robust. Alternatively, one can project a previously determined parametrization onto the correct subspace while maintaining lattice symmetries and translational invariance, which is the approach adopted here.

The sum rules, e.g.,

$$\Phi_{ij}^{\alpha\beta} r_j^\gamma - \Phi_{ij}^{\alpha\gamma} r_j^\beta = 0, \quad (13)$$

are constructed and flattened to a column in a new constraint matrix. This is repeated for all parameters $\tilde{\mathbf{a}}$ leading to a $N_{\text{prim}} \times \tilde{N}_{\text{par}}$ matrix where N_{prim} is the number of atoms in the primitive cell times 3^4 and \tilde{N}_{par} is equal to the number of independent parameters after the enforcement (re-parametrization) of the translational sum rules. The sum rules using this new constraint matrix \mathbf{C}^{rot} and the parameters $\tilde{\mathbf{a}}$ is written analogous to the translational sum rules as

$$\mathbf{C}^{\text{rot}} \tilde{\mathbf{a}} = \mathbf{0}. \quad (14)$$

Given a solution $\tilde{\mathbf{a}}$, the above is in general not fulfilled. Let us assume $\mathbf{C}^{\text{rot}} \tilde{\mathbf{a}} = \mathbf{d}$, where \mathbf{d} is a vector describing how well the sum rule is fulfilled. Now we want to find a correction $\Delta \tilde{\mathbf{a}}$ to $\tilde{\mathbf{a}}$, which is as small as possible and ensures the sum rules are fulfilled,

$$\mathbf{C}^{\text{rot}} (\tilde{\mathbf{a}} + \Delta \tilde{\mathbf{a}}) = \mathbf{0}. \quad (15)$$

Thus we have a new problem, i.e. to find $\Delta \tilde{\mathbf{a}}$ such that $\|\mathbf{C}^{\text{rot}} \Delta \tilde{\mathbf{a}} + \mathbf{d}\| < \varepsilon_1$ while $\|\Delta \tilde{\mathbf{a}}\| < \varepsilon_2$, where ε_i are numerical tolerance parameters. This problem can be solved efficiently by e.g., ridge regression using the ℓ_2 -norm.

IV. WORKFLOW

The approach outlined above has been implemented in the Python package HIPHIVE. The latter also provides functionality for performing related tasks such as fitting and validation, can be interfaced with other Python packages such as e.g., PHONOPY²⁹ and SCIKIT-LEARN.¹⁷ The following subsections described the key steps involved in creating a force constant potential (FCP) (Fig. 3).

A. Cluster space

To build a FCP, one must create a cluster space (CS) object based on a prototype structure and a set of cutoffs, which specify the maximum interaction range considered for each order. As described in Sect. III, the CS compiles the information needed to completely specify the clusters and eigentensors of any supercell based on a certain primitive cell. The CS is associated with a number of free parameters, which can be extracted by fitting to forces obtained by pseudo-random displacements for a number of supercell structures.

B. Structure container

In order to fit the parameters, one requires a set of reference forces and displacements for some structures. The reference structures should span the configuration space of interest and for computational reasons it is desirable to

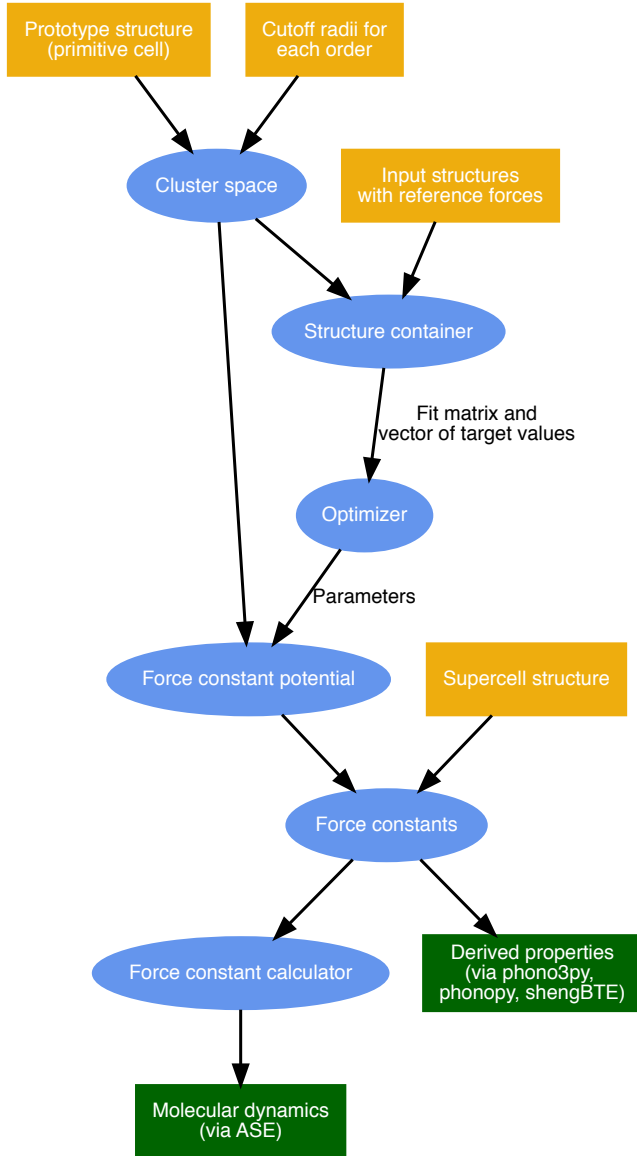


FIG. 3. Overview of HIPHIVE workflow. Square orange nodes represent data supplied by a user. Blue ellipses represent HIPHIVE objects. Green squares represent output data that can be used directly or processed further using other packages or programs.

use as few structures as possible. The simplest approach is to apply randomized atomic displacements, which can, however, lead to some very large forces due to close encounters between atoms. Physically more sound configurations can be obtained by superposing harmonic phonon modes^{30,31} using random phase factors. To this end, one does not require the exact second-order FCs but it suffices e.g., to generate an approximate FCP generated from one (or a few) configurations with small randomized displacements. In general, larger atomic displacements (or temperature) imply larger anharmonic contributions. There must thus be a correspondence between the extent of the

CS in range as well as order and the displacement magnitude.

HIPHIVE can handle any combination of supercell structures as long as they share the same equivalent primitive cell. For convenience, all configurations available for training and validation are compiled into a structure container (SC). Upon addition of a structure its corresponding sensing matrix is constructed as described in Sect. III. The SC then provides functionality for selecting subsets of structures in the form of sensing matrices and target forces suitable for training and validation.

C. Training and validation

Having constructed CS and SC one can train the associated parameters. This involves solving a set of linear equations, which can be readily achieved by a number of linear regression techniques. The equation system can be over or underdetermined and in both cases some form of regularization is useful since the solution is often sparse and/or the data contains noise originating from the input data or the truncation of the CS. The validity of the solution can be assessed by cross validation techniques including.

HIPHIVE supports a number of popular regularized training and validation techniques via the SCIKIT-LEARN machine learning library. This includes for example methods such as least absolute shrinkage and selection operator (LASSO), automatic relevance detection regression (ARDR), singular-value decomposition, elastic net, Bayesian-ridge regression, and recursive feature elimination. There is also functionality for generating ensembles of models. Further training/validation protocols can be readily implemented thanks to the modular structure of the approach.

D. Force Constant Potential

Once the free parameters have been obtained the CS can be transformed into a so-called FCP. During this step it is also possible to enforce rotational sum rules. The FCP enables calculating the FCs in any supercell compatible with the original primitive cell.

The final FCs can be analyzed using PHONOPY to obtain e.g., phonon dispersions or thermodynamic quantities in the (quasi-)harmonic approximation. It is also possible to compute transport properties using e.g., PHONO3PY or SHENGBTE or to carry out MD simulations via an ASE calculator.

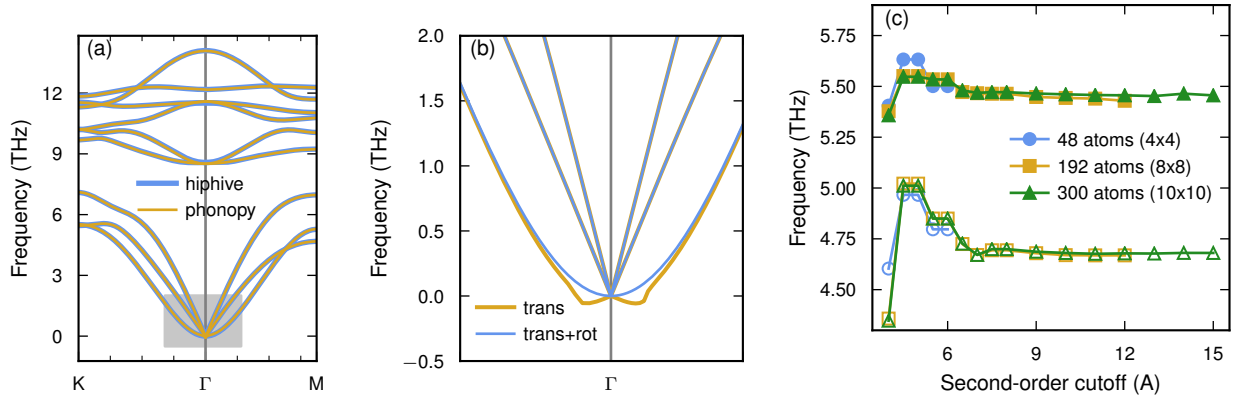


FIG. 4. Vibrational properties of an ideal monolayer of MoS_2 . (a) Phonon dispersions obtained using HIPHIVE and PHONOPY, respectively. (b) Effect of rotational invariance conditions on the dispersion in the gray shaded region in (a) near the Γ -point. (c) Convergence of the lowermost modes at K (filled symbols) and M (open symbols) with supercell size and the cutoff for second-order terms.

V. APPLICATIONS

A. Phonon dispersion of monolayer- MoS_2

Two-dimensional (2D) materials such as graphene are attracting a lot of interest due to their exceptional properties. As a result of their dimensionality they exhibit a quadratic dispersion of one of the transverse acoustic modes near the Γ -point.²³ This is in contrast to (three-dimensional) bulk materials, for which all acoustic branches exhibit a linear dispersion in the center of the Brillouin zone. It has been shown that in order for this behavior to be captured correctly the FCs must fulfill crystal symmetry, translational invariance, as well as *rotational* invariance conditions.²³ This provides an opportunity for demonstrating the impact of the rotational sum rules on the phonon dispersion.

Here, we consider a monolayer of the transition metal dichalcogenide (TMD) MoS_2 , which belongs to space group $P\bar{6}m2$ (International Tables of Crystallography number 187). Input configurations were generated by imposing random displacements on ideal supercells comprising up to 300 atoms (equivalent to $10 \times 10 \times 1$ unit cells). The average displacement amplitudes for these configurations were approximately 0.008 \AA leading to average forces of 170 meV/\AA and maximum forces of about 1.1 eV/\AA . Reference forces were obtained from DFT calculations using the projector augmented wave (PAW) method^{32,33} as implemented in Vienna ab-initio simulation package (VASP)³⁴ and the vdW-DF-cx method, which combines semi-local exchange with non-local correlation.^{35–38} The Brillouin zone was sampled using Monkhorst-Pack \mathbf{k} -point grids equivalent to a $16 \times 16 \times 1$ mesh relative to the primitive cell, except for the 300-atom cells, which were sampled using only the Γ -point. The plane-wave energy cutoff was set to 260 eV , a finer grid was employed for evaluating the forces, and

the reciprocal projection scheme was used throughout.

FCPs were constructed using second-order cutoffs of up to 15 \AA and including third-order terms up to a range of 3.0 \AA . The latter procedure was found to stabilize the convergence of the second-order terms. For the largest supercell (300 atoms) and cutoff radius 15 \AA one obtains 319 parameters. Parameters were optimized by conventional least-squares regression. For validation the phonon dispersion was also computed using PHONOPY.²

The phonon dispersion obtained using HIPHIVE with all invariance conditions imposed is virtually indistinguishable from the one generated by PHONOPY (Fig. 4a). Here, the lowermost transverse acoustic branch clearly exhibits a quadratic dispersion. If the rotational sum rules are deactivated the dispersion is almost unchanged save for the emergence of a small imaginary pocket in the immediate vicinity of the Brillouin center (Fig. 4b), and thus does *not* yield a quadratic dispersion. As noted in Ref. 23, this seemingly small error can have a pronounced effect whenever the acoustic modes contribute substantially to a property, as in the case of e.g., the thermal conductivity.

This example also enables us to illustrate the effect of supercell size on the phonon dispersion and thus effectively the range of the FCs (Fig. 4c). Convergence is achieved at a cutoff of just over 9 \AA equivalent to a supercell size of $6 \times 6 \times 1$ (108 atoms).

B. Sulfur vacancy in monolayer- MoS_2

Defects in general and sulfur vacancies in particular are present in comparably large numbers in monolayers of MoS_2 ³⁹ and they can have a very pronounced effect on the thermal conductivity.⁴⁰ To analyze this effect one requires the second-order FCs matrix of a defect supercell, which enables one to evaluate the perturbation matrix connecting the ideal and defective systems. Due to the

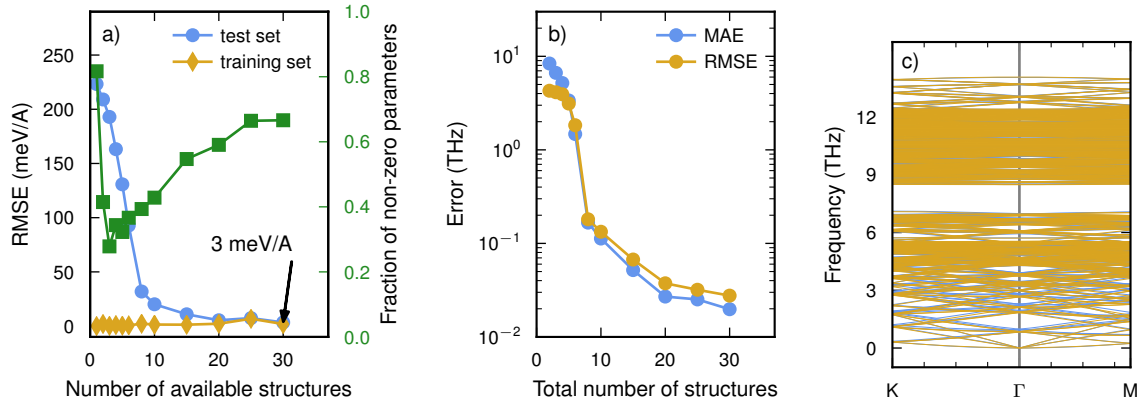


FIG. 5. Vibrational properties of a sulfur vacancy in a monolayer of MoS_2 . Convergence of the (a) RMSE and (b) the MAE and RMSE with the number of available structures. (c) Phonon dispersions obtained using HIPHIVE and PHONOPY, respectively.

size of a defect configuration and its low symmetry, computing the FCs using the enumeration approach alluded to above commonly requires a large number of individual displacement/force calculations. Here, we demonstrate that this number can be considerably reduced using HIPHIVE and advanced linear regression techniques.

The sulfur vacancy was described using a 192-atom supercell ($6 \times 6 \times 1$ unit cells), which has been found above to yield well-converged FCs in the case of the ideal monolayer. Reference DFT calculations were carried out using the same computational parameters as for the ideal monolayer. Structures for reference force calculations were generated by rattling using an average displacement of 0.016 \AA , with an average/maximum force of $330 \text{ meV/\AA}/1.02 \text{ eV/\AA}$. The CS was constructed using cutoffs of 9.0 and 3.0 \AA for second and third-order terms, respectively, yielding 1,670 orbits, 9,376 clusters, and 13,030 parameters. FCP parameters were determined using ARDR with a λ -threshold of 10^4 and without standardization. During training and validation the set of reference forces was split at ratio of 4 to 1 into training and test sets, whereas the final FCPs were obtained by fitting against all available data.

The RMSE converges rather quickly with the number of structures (Fig. 5a). Already for about 25 to 30 structures the RMSE for the force components in the test set relative to the DFT reference calculations is only about 3 meV/\AA , where the PHONOPY analysis required 215 individual DFT calculations. This convergence behavior also translates to the MAE and RMSE over the frequencies (Fig. 5) as well as the overall phonon dispersion (Fig. 5c).

The regression produces sparse models as evident from the fraction of non-zero parameters, which remains below 70% (green squares in Fig. 5a). This is in line with physical intuition, according to which FCs ought to decay rather quickly with interaction distance and order.

	1-body	2-body	3-body	4-body
2nd order	1 (1)	4 (12)	—	—
3rd order	0 (0)	2 (8)	2 (14)	—
4th order	1 (2)	4 (29)	3 (75)	3 (40)

TABLE I. Number of orbits and parameters (in brackets) by order and body.

C. Molecular dynamics simulations of nickel

Anharmonic FCPs can in principle be sampled using MD simulations, which provide access to dynamic properties including, e.g., dynamical structure factors, velocity auto-correlation functions, and free energies.⁴¹ As illustrated in the following, HIPHIVE enables such simulations by providing an ASE calculator class that merely requires a set of FCs as input.

A fourth order FCP was created for bulk Ni using cut-off radii of 5.0 , 4.0 , and 4.0 \AA for second, third, and fourth-order terms, respectively, corresponding to 171 clusters in the unit cell. The associated CS contained 20 unique orbits (5, 4, and 11 for second, third, and fourth-order, respectively) with interactions up to the fourth nearest neighbor for the pairs, leading to 119 free parameters.

Training data comprised five structures with 256 atoms ($4 \times 4 \times 4$ conventional unit cells) for a total of 3,840 force components. The structures were obtained by applying displacements randomly drawn from a normal distribution, modified to avoid interatomic distances shorter than 2.3 \AA . The resulting average atomic displacement were about 0.13 \AA . Reference forces were obtained using an effective medium theory model as implemented in ASE.¹⁸

The parameters of the model were trained by standard least-squares fitting as the system is heavily overdetermined.

The integration of the equations of motion was carried out using functionality provided by ASE while HIPHIVE

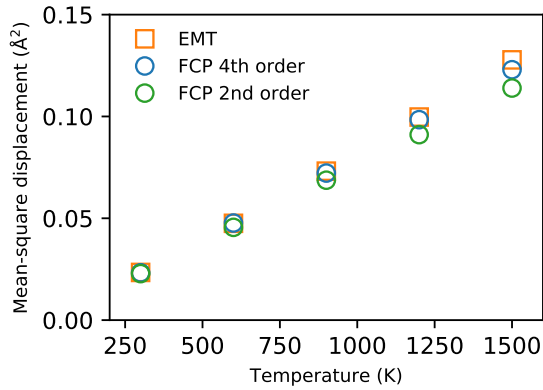


FIG. 6. Atomic mean-square displacement in FCC Ni as a function of temperature as obtained within the harmonic approximation as well as from MD simulations based on the original potential (EMT) and a fourth-order Hamiltonian.

was used to provide an interaction model in the form of an ASE calculator object. Simulations were carried out using a 864-atom supercell ($6 \times 6 \times 6$ conventional unit cells). The equations of motion were integrated for 50 ps using a time step of 5 fs at temperatures 300, 600, 900, 1200 and 1500 K using a Langevin thermostat.

The atomic mean-square displacements computed using the full fourth-order FCP as well as using only the second order FCs are practically identical to those obtained using the effective medium theory (EMT) model at low temperatures (Fig. 6). At higher temperatures where anharmonic effects are more important the second order model yields a systematic error whereas the fourth order model remains very accurate. Very close to the melting point even the fourth order model starts to deviate from the exact solution, which is due to even higher

order terms becoming relevant at these temperatures.

VI. CONCLUSIONS AND OUTLOOK

Second and higher-order FC are fundamental to the description of the thermodynamics of materials. Here, we have introduced the HIPHIVE package that enables their efficient extraction from first-principles calculations using regression techniques with regularization. The implementation take advantage of symmetry and sum rules in order to constrain the number of DOFs and is computationally efficient. Potential applications have been illustrated by several examples including ideal and defective systems, phonon analysis as well as dynamic simulations.

The package is designed for integration in various workflows including e.g., applications in high-throughput calculations, as it can be readily interfaced with a large number of electronic structure codes via ASE and machine learning techniques via SCIKIT-LEARN. The flexibility of the interface also enables one to systematically explore the efficacy of different optimization algorithms for the construction of FCPs and the compilation of databases of such models for future use.

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⁷ It is also possible to obtain FCs from density functional perturbation theory calculations as implemented, for example, in the ABINIT⁴² and QUANTUM-ESPRESSO packages.⁴³ The latter approach is, however, commonly limited to second and third-order FCs as the computation of higher-order terms, by power of the $2n + 1$ theorem (see e.g., Ref. 44), would require knowledge of second and

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