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Method to extract anharmonic force constants from first principles calculations

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A method for extracting force constants (FCs) from first principles is introduced. In principle, provided that forces are accurate enough, it can extract harmonic as well as anharmonic FCs up to any neighbor shell. Symmetries of the FCs as well as those of the lattice are used to reduce the number of parameters to be calculated. The results are illustrated for the case of the Lennard-Jones potential, wherein forces are exact and FCs can be analytically calculated, and Si in the diamond structure. The latter are compared to the previously calculated harmonic FCs.

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I. INTRODUCTION

Two methodologies have been developed so far to calculate the force constants (FCs) of bulk crystals. One relies on perturbation theory and linear response formalism,[1] in which the infinitesimally small displacements of atoms are taken as the perturbing potential, and the required properties, namely, the FCs, are calculated as a function of the ground state eigenvalues and eigenstates of the crystal by using the perturbation theory. The other more traditional method, which is called the direct method,[2–4] requires a small Cartesian displacement of an atom placed in a supercell (preferably twice larger than the cutoff range of the FCs). Forces applied to other atoms divided by the small displacement produce the required FCs. This method, however, also needs the calculation of Born charges[5] in the case of polar semiconductors so that FCs due to long-range Coulombic forces can be analytically added to the obtained values. Anharmonic FCs of third or higher order can also be calculated in the same fashion. In the direct method, in principle, two small displacements along a given direction are needed in order to fit the produced force with a second order polynomial and extract the harmonic and cubic coefficients. However, we are not aware of any calculation based on the direct method involving three-body (or higher) interactions. A similar calculation, in spirit, to the direct method is the frozen phonon method, which was used to calculate cubic FCs of Si.[6,7]

The density functional perturbation theory (DFPT), on the other hand, uses the so-called $2n+1$ formula[8] to get FCs up to order $2n+1$ from an nth order perturbation expansion of the electronic wave functions. One can see that the direct method, not being a very systematic one, soon becomes prohibitive if FCs of third or fourth order are needed, given their very large number. The calculation of fourth order, or the so-called quartic,, terms also becomes quite involved by using the perturbation theory method because now wave functions need to be expanded up to second order.

In order to find phonon lifetimes, calculations of the cubic FCs for Si by using DFPT were performed in the past by several groups.[7,9] While Debernardi *et al.*[7] used the DFPT and frozen phonon methods to compute the cubic FCs, Lang *et al.*[9] used DFPT for the harmonic force constants but deduced the needed cubic and quartic coefficients from finite differentiation of the harmonic FCs evaluated at a few bond lengths around the equilibrium value. This method, however, would not give them all the FCs.

In this paper, we propose a methodology to extract the harmonic as well as cubic and quartic anharmonic FCs from first principles calculations in a systematic way. While harmonic FCs are used for the calculation of phonon spectra, vibrational modes, and elastic properties, cubic anharmonic FCs give the phonon lifetimes and scattering rates, and quartic ones correct the shift in the phonon frequencies. These quantities are the main ingredients in phonon transport theories, which calculate thermal conductivity. They can also be used for constructing a classical molecular dynamics (MD) potential of *ab initio* accuracy. From such molecular dynamics simulations, thermal conductivity, which can be written as the heat current autocorrelation function,[10] and other thermodynamic properties of bulk or nanostructured materials can be calculated. Phase transformations can also be investigated by using anharmonic potentials.

II. METHODOLOGY

The force constants are defined as derivatives of the potential energy with respect to atomic displacements about their equilibrium position. We write the potential energy in the following form:

$$V = V_0 + \sum_i \Pi_i u_i + \frac{1}{2!}\sum_{ij} \Phi_{ij} u_i u_j + \frac{1}{3!}\sum_{ijk} \Psi_{ijk} u_i u_j u_k + \frac{1}{4!}\sum_{ijkl} \chi_{ijkl} u_i u_j u_k u_l, \tag{1}$$

where the Roman index i labels the triplet (R,τ,α), with R as a translation vector of the primitive lattice, τ as an atom within the primitive unit cell, and α as the Cartesian coordinate of the atomic displacement u. In other words, u_i is the displacement of the atom (R,τ) in the direction α from its equilibrium or any reference position. Φ, Ψ, and χ are the harmonic, cubic, and quartic FCs, respectively, whereas Π is the negative of the residual force on atom i and is zero if the potential energy V is expanded around its minimum or equilibrium configuration. In clusters or molecules, the formalism is the same, and only the translation vector R needs to be dropped.

The resulting force on atom i would then be

$$\begin{aligned} F_i &= -\frac{\partial V}{\partial u_i} \\ &= -\Pi_i - \sum_j \Phi_{ij} u_j - \frac{1}{2} \sum_{jk} \Psi_{ijk} u_j u_k - \frac{1}{3!} \sum_{jkl} \chi_{ijkl} u_j u_k u_l. \end{aligned} \tag{2}$$

If one considers a simple FCC Bravais lattice in three dimensions, one can discover by inspection that there are 123 harmonic, 4867 cubic, and 95 663 quartic anharmonic FCs only within the first neighbor shell. Of course, they are related by different symmetry properties, which will be used here to reduce their number to 4, 12, and 56, respectively.

A. General symmetries of the problem

The symmetries of the FCs are deduced from rotational and translational invariance of the system, in addition to the symmetries of the crystal itself. These symmetries are as follows.

(a) Invariance under the permutation of indices:

$$\begin{gathered} \Phi_{ij} = \Phi_{ji}, \\ \Psi_{ijk} = \Psi_{ikj} = \Psi_{jik} = \Psi_{kji} = \cdots, \\ \chi_{ijkl} = \chi_{ikjl} = \chi_{ijlk} = \chi_{jikl} = \cdots, \end{gathered} \tag{3}$$

where i, j, k, and l refer to the neighboring atoms. This comes about because the force constants are derivatives of the potential energy, and one can change the order of differentiation for such analytic function.

(b) Invariance under an arbitrary translation of the system: Translational invariance of the whole system (even if not an ordered crystal) also implies $V(u)=V(u+c)$ and $F(u)=F(u+c)$ (which is easier to use), where $u(t)$ are the dynamical variables, and c is a constant arbitrary shift vector (may be incommensurate with R). This implies the well-known "acoustic sum rule" generalized to higher order FCs:

$$\begin{gathered} 0 = \sum_{\tau} \Pi^{\alpha}_{0\tau}, \quad \forall\,(\alpha)(\text{total force on unit cell} = 0), \\ 0 = \sum_{R_1,\tau_1} \Phi^{\alpha\beta}_{0\tau,R_1\tau_1}, \quad \forall\,(\alpha\beta,\tau), \\ 0 = \sum_{R_2,\tau_2} \Psi^{\alpha\beta\gamma}_{0\tau,R_1\tau_1,R_2\tau_2}, \quad \forall\,(\alpha\beta\gamma,R_1,\tau_1), \\ 0 = \sum_{R_3,\tau_3} \chi^{\alpha\beta\gamma\delta}_{0\tau,R_1\tau_1,R_2\tau_2,R_3\tau_3}, \quad \forall\,(\alpha\beta\gamma\delta,R_1R_2,\tau_1\tau_2), \end{gathered} \tag{4}$$

so that diagonal terms in these tensors can be defined in terms of their off-diagonal elements for arbitrary Cartesian components. For more details about the proof of these relations and the ones following on rotational invariances, we refer the reader to Ref. 11.

(c) Invariance under an arbitrary rotation of the system: Likewise, if the system is arbitrarily rotated, the total energy and forces should not change. This leads to the following relations:[11]

$$\begin{aligned} 0 &= \sum_{\tau} \Pi^{\alpha}_{0\tau} \tau^{\beta} \epsilon^{\alpha\beta\nu}, \quad \forall\,(\nu)(\text{torque on unit cell} = 0), \\ 0 &= \sum_{R_1,\tau_1} \Phi^{\alpha\beta}_{0\tau,R_1\tau_1} (R_1\tau_1)^{\gamma} \epsilon^{\beta\gamma\nu} + \Pi^{\beta}_{0\tau} \epsilon^{\beta\alpha\nu} \quad \forall\,(\alpha\nu,\tau), \\ 0 &= \sum_{R_2,\tau_2} \Psi^{\alpha\beta\gamma}_{0\tau,R_1\tau_1,R_2\tau_2} (R_2\tau_2)^{\delta} \epsilon^{\gamma\delta\nu} + \Phi^{\gamma\beta}_{0\tau,R_1\tau_1} \epsilon^{\gamma\alpha\nu} \\ &\quad + \Phi_{0\tau,R_1\tau_1} \alpha\gamma \epsilon^{\gamma\beta\nu}, \quad \forall\,(\alpha\nu,R_1,\tau\tau_1), \\ 0 &= \sum_{R_3\tau_3} \chi^{\alpha\beta\gamma\delta}_{0\tau,R_1\tau_1,R_2\tau_2,R_3\tau_3} (R_3\tau_3)^{\mu} \epsilon^{\delta\mu\nu} + \Psi^{\delta\beta\gamma}_{0\tau,R_1\tau_1,R_2\tau_2} \epsilon^{\delta\alpha\nu} \\ &\quad + \Psi^{\alpha\delta\gamma}_{0\tau,R_1\tau_1,R_2\tau_2} \epsilon^{\delta\beta\nu} + \Psi^{\alpha\beta\delta}_{0\tau,R_1\tau_1,R_2\tau_2} \epsilon^{\delta\gamma\nu}, \\ &\qquad \forall\,(\alpha\nu,R_1R_2,\tau\tau_1\tau_2). \end{aligned} \tag{5}$$

Here, $\epsilon^{\alpha\beta\gamma}$ is the antisymmetric Levy–Civita symbol, and $(R\tau)^{\alpha}$ refers to the Cartesian component α of the reference position vector of the atom τ in the unit cell defined by R. Moreover, an implicit summation over repeated Cartesian indices is implied.

As we see, rotational invariance relates the second to the third order terms, and the third to the fourth order terms, implying that if the expansion of the potential energy is truncated after the fourth order terms, we need to start with the fourth order terms, and application of rotational invariance rules will give us constraints on third and second order FCs, respectively.

B. Point and/or space group symmetries

The other constraints come from symmetry operations, such as lattice translation, rotation, mirror, or any symmetry operation of the space, and/or point group of the crystal and/or molecule which leaves the latter invariant. Invariance under a translation of the system by any translation lattice vector R implies the following relations:

$$\begin{gathered} \Pi^{\alpha}_{R\tau} = \Pi^{\alpha}_{0\tau} \quad \forall\,(R\tau\alpha), \\ \Phi^{\alpha\beta}_{R\tau,R_1\tau_1} = \Phi^{\alpha\beta}_{0\tau,R_1-R\tau_1}, \\ \Psi^{\alpha\beta\gamma}_{R\tau,R_1\tau_1,R_2\tau_2} = \Psi^{\alpha\beta\gamma}_{0\tau,R_1-R\tau_1,R_2-R\tau_2}, \\ \chi^{\alpha\beta\gamma\delta}_{R\tau,R_1\tau_1,R_2\tau_2,R_3\tau_3} = \chi^{\alpha\beta\gamma\delta}_{0\tau,R_1-R\tau_1,R_2-R\tau_2,R_3-R\tau_3}. \end{gathered} \tag{6}$$

So in an ideal crystal, this considerably reduces the number of force constants (by the number of unit cells, to be exact), meaning that, for the atoms in all the other cells, we will use the same FCs as those we have kept for the atoms in the "central" cell.

If a rotation or mirror symmetry operation is denoted by S, we must have

$$\Pi_{S\tau}^{\alpha} = \sum_{\alpha'} \Pi_{\tau}^{\alpha'} \mathcal{S}_{\alpha,\alpha'},$$

$$\Phi_{S\tau,S\tau_1}^{\alpha\beta} = \sum_{\alpha'\beta'} \Phi_{\tau,\tau_1}^{\alpha'\beta'} \mathcal{S}_{\alpha,\alpha'} \mathcal{S}_{\beta,\beta'},$$

$$\Psi_{S\tau,S\tau_1,S\tau_2}^{\alpha\beta\gamma} = \sum_{\alpha'\beta'\gamma'} \Psi_{\tau,\tau_1\tau_2}^{\alpha'\beta'\gamma'} \mathcal{S}_{\alpha,\alpha'} \mathcal{S}_{\beta,\beta'} \mathcal{S}_{\gamma,\gamma'},$$

$$\chi_{S\tau,S\tau_1,S\tau_2,S\tau_3}^{\alpha\beta\gamma\delta} = \sum_{\alpha'\beta'\gamma'\delta'} \chi_{\tau,\tau_1,\tau_2,\tau_3}^{\alpha'\beta'\gamma'\delta'} \mathcal{S}_{\alpha,\alpha'} \mathcal{S}_{\beta,\beta'} \mathcal{S}_{\gamma,\gamma'} \mathcal{S}_{\delta,\delta'}, \quad (7)$$

where $\mathcal{S}_{\alpha,\alpha'}$ are the 3×3 matrix elements of the symmetry operation S. These symmetry relations impose a linear set of constraints on the force constants.

We should note that in addition to these symmetries, there is a set of constraints on elastic constants, requiring the latter to be symmetric under the exchange of Voigt indices. These invariances are discussed by Huang (see Refs. 12 and also 4), and imply extra constraint equations for low symmetry crystals with internal degrees of freedom within the primitive cell (more than one atom per unit cell at off-symmetry positions). Since we are using the diamond structure in this study, Huang invariances will not give any extra constraints.

Any physically correct model of force constants must satisfy the invariance relations. On the other hand, we do approximations by truncating the range of FCs and their order in the Taylor expansion of the potential. Therefore, imposing the constraints will move their value away from the true value but has the advantage that they are physically correct and will, for instance, reproduce the linear dispersion of acoustic phonons near $k=0$. So, one should keep in mind that an unrealistic truncation to a too short of a range will produce results in disagreement with experiments.

III. IMPLEMENTATION

Given a crystal with its unit cell and atoms, we first identify its symmetry properties and construct the matrices $\mathcal{S}$. By using the latter and Eqs. (3) and (7), independent FCs of each rank are identified. Then, a set of force-displacement data calculated from first principles is constructed. Next, since the data set is (better be) larger than the number of unknown FCs, the linear set of Eqs. (2), (4), and (5) is fitted with this data set by using a singular value decomposition (SVD) algorithm. To our knowledge, this method was first used in this context by Sluiter *et al.*[4] In SVD, the unknown force constants will be calculated in a least squares sense, and furthermore, linear dependencies among the equations will not be a problem because the result is projected out of the "zero eigenvalue space."[13] One also has the option to use relations (4) and (5) to eliminate some of the FCs in Eq. (2) and solve for the remaining FCs. Here, one needs to make a judicious choice of FCs to be eliminated. We prefer not to eliminate the FCs and keep the option of checking the violation of the translational and rotational invariances if only relation (2) is used.

The data set can be obtained in several ways: a molecular dynamics run with small initial displacements, randomly moving all atoms by small displacements a few time steps and calculating the forces on all atoms, and finally, symmetrically displacing one atom at a time about its equilibrium position by a small displacement along the $x,-x,y,$ $-y,z$ and $-z$ directions and calculating the forces on all other atoms. Experience has shown that the latter works better for the computation of harmonic force constants and two-body force constants in general. For three- and four-body FCs, one needs to displace at least two and three atoms at a time, respectively.

We must add that the data set is obtained not from a unit cell but from displacements performed in a supercell, whose size should exceed the range of FCs, otherwise the contribution of images from neighboring supercells will also be included in a considered FC. In some cases, this could lead to errors in the evaluation of FCs. Notice that the exact outcome of this procedure includes, strictly speaking, the contribution of images as well. For instance, in the case of harmonic FCs, instead of $\Phi_{\tau,\tau'}$, actually the sum $\widetilde{\Phi}_{\tau,\tau'} = \Sigma_L \Phi_{\tau,L+\tau'}$, where L is a translation vector of the supercell, will be extracted. Therefore, supercells with low symmetry are preferable in order to avoid encountering FCs that cannot be determined. For example, in a cubic supercell, the force constants between the corners of the cube can never be calculated this way since the distance between adjacent corners never changes. It must, furthermore, be emphasized that the size of the data set and its accuracy are crucial in determining the correct set of force constants.

IV. RESULTS

To check the feasibility and accuracy of the method, we first used the Lennard-Jones (LJ) pair force, for which derivatives can be analytically calculated and compared to our results. Furthermore, the LJ forces are accurate within the printed number of digits by the computer and do not suffer from any convergence or round-off error problems. First, we considered an fcc-Bravais crystal of LJ particles with integer Cartesian coordinates. Particles were confined to interact only with their first neighbor. It was found that choosing a very small set of displacements (of the order of 0.001) produced the best results. Since in both the MD data and the fitting procedure the cutoff was set so that only first neighbors interact, the SVD procedure reproduced the exact FCs remarkably well: the error in the harmonic, cubic, and quartic FCs was in the seventh, fifth, and fourth digits, respectively.

As a more stringent test and in order to get confidence on the accuracy of the fitting method for a real material such as Si, we also considered a diamond structure of LJ particles with interactions up to the tenth nearest neighbor but limited them in our fitting up to the eighth neighbor only (i.e., we forced the ninth and tenth neighbor FCs to be zero when fitting). The energy unit was taken to be 1 and the length unit σ was taken to be equal to the first neighbor distance ($\sqrt{3}/4$). No MD was performed; instead, we only displaced the first atom by 0.0005 and 0.001 along the x direction and recorded the forces on all other atoms in a $3\times3\times3$ cubic supercell with 216 atoms. This was enough because all atoms and the three displacements along x,y,z are equivalent. The results are summarized in Table I. Three-body forces are found to be, respectively, 5 and 3 orders of magnitude smaller than the largest two-body values in cubic and quartic FCs. It is worth noticing that the fitted values obtained by imposing the invariance relations are slightly worse than those when invariances are not imposed. This is because some of the longer range FCs (ninth and tenth neighbors) were neglected in the fitting procedure, and as a result, the values of the included FCs are slightly affected when invariance relations are imposed. In a real material case, however, it is more important to have physically correct FCs, even though their values might not be exact. In any case, this can be checked by comparing the results with and without imposing invariance constraints. Imposing the constraint conditions in the SVD procedure results in the violation of the latter by typically 10^{-8}, whereas the force-displacement data could be violated, giving relative errors as large as a few percent if the chosen cutoff is too short, or first principles forces are not very accurate, or displacements are too large.

The same procedure was followed to extract FCs for a real material case: silicon (diamond). In this case, the range of FCs is unknown and probably longer ranged than we can exactly handle. The range of harmonic FCs was limited to 14 neighbors, that of the cubic coefficients was limited to 3, and quartic FCs were limited to the nearest-neighbor interactions. First, we used a data set that is similar to that in a previous LJ calculation, wherein atoms were displaced by 0.008 and 0.016 Å along all the three directions in order to minimize systematic and round-off errors, which occur in first principles calculations. Local density approximation (LDA) based ultrasoft pseudopotentials were used within the VASP density-functional simulation package.[14] A cutoff energy of 500 eV and 14 K points were used in the $3\times3\times3$ cubic supercell with 216 atoms.

This was the largest system we could handle. Perhaps more accurate determination of forces by using more K points and a higher cutoff energy would give better results. In the fitting, the number of shells for each rank of the FCs as well as the number of constraints and independent FCs is summarized in Table II.

Of course, phonon dispersion of diamond silicon has been calculated from first principles in the past by many groups,[15–19] but our purpose here is to illustrate how well the method performs in comparison to experiments and other calculations. In Table III, harmonic FCs are compared to two recent calculations[18,19] based on density-functional perturbation theory.[1,8]

The phonon spectrum that is obtained by including harmonic force constants up to 13th neighbors is plotted in Fig. 1 versus experimental data points[20] and a calculation that includes only eight neighbor shells. A slight difference between the two calculations is noticeable. In this case, three neighbor shells were included in the fitting of cubic and one

TABLE I. Comparison between analytical and numerically extracted (SVD) values of the LJ force constants in the diamond structure when invariance relations (4) and (5) were not imposed and only eight neighbor shells were included in the fitting. Real interactions were included up to ten neighbors ($R_{\text{cut}}=1.6$). The subscripts in the first column refer to the first or second atom in the primitive cell (τ index for Φ and $R\tau$ index for Ψ and χ), while the superscripts refer to the Cartesian coordinates (α index).

FCs	Nb Shell	Exact	SVD
$\Phi_{1,1}^{xx}$	0 (0,0,0)	711.01623	711.016
$\Phi_{1,2}^{xx}$	$1(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	−181.33329	−181.333
$\Phi_{1,2}^{xy}$	1	−213.33328	−213.333
$\Phi_{1,1}^{xx}$	$2(\frac{1}{2},\frac{1}{2},0)$	1.497986	1.49799
$\Phi_{1,1}^{yy}$	2	−0.5660705	−0.56607
$\Phi_{1,1}^{xy}$	2	2.064056	2.06406
$\Phi_{1,1}^{xz}$	2	0	2×10^{-15}
$\Phi_{1,2}^{xx}$	$3(-\frac{1}{4},-\frac{1}{4},-\frac{3}{4})$	−0.0502417	−0.050242
$\Phi_{1,2}^{zz}$	3	0.9066605	0.906668
$\Phi_{1,2}^{xy}$	3	0.1196113	0.119612
$\Phi_{1,2}^{xz}$	3	0.3588383	0.358840
$\Phi_{1,1}^{xx}$	$4(1,0,0)$	0.2700770	0.270080
$\Phi_{1,1}^{zz}$	4	−0.0390294	−0.039029
$\Phi_{1,2}^{xx}$	$5(-\frac{3}{4},-\frac{3}{4},-\frac{1}{4})$	0.05459899	0.0545990
$\Phi_{1,2}^{zz}$	5	−0.0114737	−0.0114737
$\Phi_{1,2}^{xy}$	5	0.07433175	0.0743320
$\Phi_{1,2}^{xz}$	5	0.02477725	0.0247773
$\Phi_{1,1}^{xx}$	$6(\frac{1}{2},\frac{1}{2},1)$	0.0025635	0.0025635
$\Phi_{1,1}^{zz}$	6	0.0335998	0.0336000
$\Phi_{1,1}^{xy}$	6	0.0103455	0.0103454
$\Phi_{1,1}^{xz}$	6	0.0206909	0.0206909
$\Phi_{1,1}^{yz}$	6	0.0206909	0.0206909
$\Phi_{1,2}^{xx}$	$7(\frac{1}{4},\frac{1}{4},\frac{5}{4})$	−0.00342573	−0.0034258
$\Phi_{1,2}^{zz}$	7	0.03109080	0.0310910
$\Phi_{1,2}^{xy}$	7	0.00143819	0.0014382
$\Phi_{1,2}^{xz}$	7	0.00719095	0.0071910
$\Phi_{1,2}^{xx}$	$7(-\frac{3}{4},-\frac{3}{4},-\frac{3}{4})$	0.00807978	0.0080798
$\Phi_{1,2}^{xy}$	7	0.01294370	0.0129437
$\Phi_{1,1}^{xx}$	8(1,1,0)	0.00739133	0.0073913
$\Phi_{1,1}^{zz}$	8	−0.00246785	−0.0024678
$\Phi_{1,1}^{xy}$	8	0.00985918	0.0098592
$\Phi_{1,1}^{xz}$	8	0	2×10^{-13}
$\Psi_{01,01,02}^{xxx}$		2673.7772	2673.793
$\Psi_{01,01,02}^{xxy}$		4380.4434	4380.590
$\Psi_{01,01,02}^{xyz}$		5233.7765	5234.127
$\Psi_{01,01,11}^{xyx}$		4.128112	4.1267
$\Psi_{01,01,11}^{yyy}$		−5.453064	−5.4645
$\Psi_{01,01,11}^{yzy}$		−13.70929	−13.705
$\chi_{01,01,02,02}^{xxxx}$		−19342.22	19401.9
$\chi_{01,01,02,02}^{xyxy}$		−96255.98	−96202.6
$\chi_{01,01,02,02}^{xxxy}$		−71907.54	−71896.1
$\chi_{01,01,02,02}^{xyxz}$		−113777.75	−113727.9

TABLE II. Statistics about the potential parameters for Si. The second column shows the number of included neighbor shells in the fitting. The third column shows the number of resulting independent FCs, the fourth represents the total number of FCs or terms present in the Taylor expansion of the total energy within that rank, and the last is the total number of invariance+symmetry constraints for that rank.

Rank	Shells	Independent	Total	Constraints
2	14	67	8412	2868
3	3	95	58062	16820
4	1	14	7980	3750

neighbor in that of quartic force constants. The spectrum was calculated at a lattice constant of 5.389 Å (minimum energy of the LDA calculation) compared to the experimental value of 5.43 Å. The major difference between our SVD results and Refs. 18 and 19 is in the inclusion of the neighbors along (1,1,0). While we include only up to 13 neighbors, they included 25. This is presumably the main reason for the discrepancy in the value of α_0 and the optical frequency at the Γ point. In Table IV, we only show those that were larger than 1/500 of the largest one in two units (last two columns).

Quartic FCs were included in the fit up to the first neighbor only. This means that we have only included the two-body contributions in the fit of quartic terms. There are 7980 such terms, which are related by symmetry, making up only 14 independent constants, as reported in Table V. Many of the 14 independent quartic terms turn out to be equal to each other presumably due to the fact that they are two-body terms. Had we included more shells in the fitting, the degeneracy would have been lifted because, in principle, the reported terms are not related by any symmetry.

TABLE III. Comparison between harmonic force constants of Si. Invariance relations (4) and (5) were imposed in the fitting. Up to 14 neighbor shells were included in the fitting of quadratic force constants. The notations in the first column follow those of Refs. 19 and 18. For brevity, we report the results on the first five shells. Units are in mhartree/bohr^2.

FCs	Nb Shell	Ref. 19	Ref. 18	SVD
α_0	(0,0,0)	138.36	139.04	136.21
α_1	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	−33.75	−33.85	−33.14
β_1		−23.54	−23.48	−23.17
μ_2	$(\frac{1}{2},\frac{1}{2},0)$	−1.88	−1.82	−1.90
ν_2		−1.82	−1.78	−1.84
δ_2		1.11	1.11	1.10
λ_2		4.30	4.33	4.22
μ_3	$(-\frac{1}{4},-\frac{1}{4},-\frac{3}{4})$	0.33	0.32	0.37
ν_3		−0.35	−0.35	−0.37
δ_3		0.28	0.29	0.29
λ_3		0.07	0.06	0.09
μ_4	(1,0,0)	−0.20	−0.20	−0.22
λ_4		−0.06	−0.05	−0.05
μ_5	$(\frac{3}{4},\frac{3}{4},\frac{1}{4})$	−0.18	−0.20	−0.17
ν_5		−0.28	−0.26	−0.26
δ_5		0.57	0.58	0.56
λ_5		−1.80	−1.83	−1.79

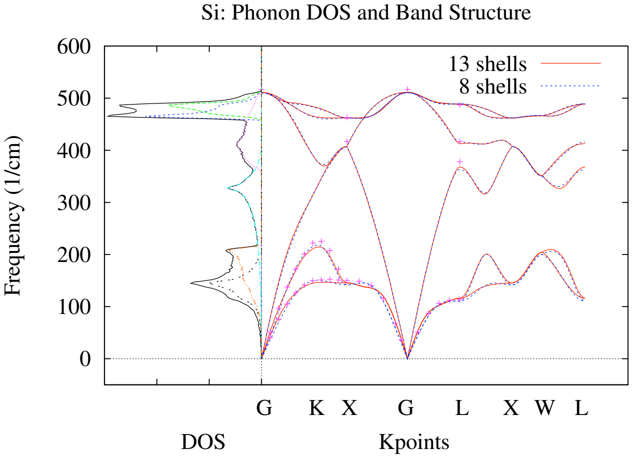

FIG. 1. (Color online) Projected phonon DOS band structure of Si by using up to eight (dashed blue line) and 13 (solid red line) neighbor shell FCs. Experimental data (Ref. 20) are represented with+sign.

TABLE IV. Nonequivalent cubic force constants for Si. Only the ones that are larger than 1/500 of the first one are displayed although in the fitting, up to four neighbor shells were included. The pairs in columns 3, 4, and 5 are the atom number and x,y,z coordinate $(\tau\alpha)$ [atoms τ=1,2,11,13 corresponding, respectively, to (0,0,0), (1/4,1/4,1/4), $(0,-1/2,-1/2)$, and $(1/2,0,-1/2)$]. Invariance relations (4) and (5) were imposed in the fitting. Units are in eV/Å^3 and mhartree/bohr^3 in the last two columns.

No. of FCs	Label	$\tau_1\alpha_1$	$\tau_2\alpha_2$	$\tau_3\alpha_3$	eV/Å^3	mhartree/bohr^3
1	1	1 1	1 2	1 3	32.26	175.7
13	2	1 1	1 1	2 1	−2.74	−14.9
139	3	1 1	1 2	2 1	−6.29	−34.3
643	4	1 2	1 2	2 1	−6.29	−34.3
895	5	1 2	1 3	2 1	−8.06	−43.9
1435	7	1 1	1 2	6 1	0.07	0.36
5971	21	1 1	1 1	11 1	0.14	0.74
6691	23	1 2	1 2	11 1	−0.07	−0.38
7267	25	1 1	1 1	11 2	−0.11	−0.61
7555	26	1 1	1 2	11 2	−0.07	−0.39
8707	28	1 2	1 2	11 2	0.21	1.16
8995	29	1 2	1 3	11 2	0.24	1.30
9571	30	1 3	1 3	11 2	0.16	0.87
31459	61	1 1	2 1	13 2	0.11	0.59
33835	64	1 1	2 2	13 2	−0.12	−0.63
36211	67	1 1	2 3	13 2	−0.16	−0.86
44131	77	1 2	2 3	13 3	−0.12	−0.66

TABLE V. Nonequivalent quartic force constants for Si. Only the first neighbor shell was included in the fitting. Similar to Table IV, the pairs in columns 3, 4, 5, and 6 are the atom number and x,y,z coordinate $(\tau\alpha)$ [atoms $\tau=1,2$ corresponding, respectively, to (0,0,0) and (1/4,1/4,1/4)]. Invariance relations (4) and (5) were imposed in the fitting. Units are in eV/Å^3 in the last column.

No. of FC	Label	$\tau_1\alpha_1$	$\tau_2\alpha_2$	$\tau_3\alpha_3$	$\tau_4\alpha_4$	FC4
1	1	1 1	1 1	1 1	1 1	−110.4
7	2	1 1	2 1	1 2	1 2	−25.2
43	3	1 1	1 1	1 1	2 1	27.6
211	4	1 1	1 1	1 2	2 1	13.6
1219	5	1 1	1 2	1 2	2 1	6.3
2227	6	1 1	2 3	1 3	2 1	1.6
3235	7	1 2	1 2	1 2	2 1	13.6
3571	8	1 2	1 2	1 3	2 1	1.6
4579	9	1 1	1 1	2 1	2 1	−27.6
4705	10	1 1	1 2	2 1	2 1	−13.6
5713	11	1 2	1 2	2 1	2 1	−6.3
5965	12	1 2	1 3	2 1	2 1	−1.6
6469	13	1 1	1 2	2 1	2 2	−6.3
6973	14	1 1	1 3	2 1	2 2	−1.6

V. DISCUSSIONS

The test example of Lennard-Jones potential shows that provided the actual calculation of force displacements is extremely accurate; it is possible to extract harmonic, cubic, and quartic force constants with very good precision by using the above method. Choosing low-symmetry supercells may be advantageous and avoids heavy calculations in big supercells. Our experience on Si has shown that it is possible to extract FCs of silicon up to the fifth neighbor by using a small 12 atom $(1\times 2\times 3)$ supercell. However, longer-range FCs would require larger cells because the fitting would fail in this case. In fact, large supercells are really needed for the extraction of longer-range harmonic FCs. Once the latter are known, it is possible to freeze them and extract higher-order FCs from a smaller size supercell but more accurate calculation. In this case, the force-displacement data can come from a molecular dynamics run with a small amplitude because more than one particle is needed to move in order to extract three- and four-body terms.

In case the so-developed potential is going to be used in performing large-scale molecular dynamics (MD) simulations, one does not even need to include harmonic (and anharmonic) FCs beyond a few, say, four or five, neighbor shells. In fact, most classical force fields have a shorter range. Although MD runs might be more time consuming with this method, it has the advantage of higher accuracy. Lattice distortions and defects can also be treated using this potential because the new force constants of a distorted atomic configuration can be obtained from the already developed Taylor expansion,

TABLE VI. Comparison between the first nearest neighbor force constant Grüneisen parameters of Si from Eq. (9) and direct finite differentiation (Ref. 18).

FCs	Nb shell	γ [a]	γ [Eq. (9)]
α_0	(0,0,0)	1.10	1.08
α_1	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	1.03	1.02
β_1		1.98	2.23

[a] Reference 18.

$$\Phi_{\text{new}} = \Phi + u_0\Psi + u_0u_0\chi/2,$$

$$\Psi_{\text{new}} = \Psi + u_0\chi,$$

$$\chi_{\text{new}} = \chi, \tag{8}$$

in which the static displacement u_0 is due to external forces and would be obtained by solving $F(u_0)=0$, where the force F is calculated from Eq. (2).

An additional complication arises when one is dealing with polar or ionic materials. In such cases, Born effective charges need to be calculated and their long-range effect on the FCs separately calculated by using the Ewald summation[5] or multipole expansion methods. Care must be taken since its short-range part is already included in the extracted FCs. So, it needs to be properly subtracted from the Ewald sum contribution. Needless to say, this problem is present in all polar materials and cannot be bypassed.

By using the extracted cubic force constants, one can calculate phonon lifetimes and frequency shifts. Details of such calculations will be published elsewhere. Below, we will only give the obtained values for the force constant Grüneisen parameters that are obtained from cubic FCs.

A uniform volume expansion can be parametrized as $R \to R(1+\epsilon)=R+u$, where ϵ is the linear expansion parameter. Due to this change in bond lengths, the harmonic force constants will change to leading order by $\Phi \to \Phi + u\Psi$. For a force constant Φ, we define the Grüneisen parameter by

$$\gamma = -\frac{1}{2}\frac{d\ln\Phi}{d\ln V} = -\frac{1}{6}\frac{d\Phi}{\Phi d\epsilon} = -\frac{1}{6}\frac{\Psi R}{\Phi}. \tag{9}$$

To assess the accuracy of the cubic FCs, in Table VI, we compare the force Grüneisen parameters that are obtained from Eq. (9) above to those obtained from DFPT by changing the volume and calculating γ by finite difference.[18] The agreement is reasonable. For further neighbors, one needs to include more neighbors in the fitting of the cubic FCs. Further neighbors with much smaller FCs would only slightly affect the mode Grüneisen parameters because the latter are essentially weighted sums of the force Grüneisen parameters.

VI. CONCLUSIONS

To summarize, we have developed a method to extract harmonic, cubic, and quartic force constants of any crystal from first principles force-displacement data. The methodology uses symmetries of the crystal to reduce the number of independent FCs and can include up to any number of neighbor shells, in principle. It requires, however, very accurate first principles data in order to produce reliable FCs. This method paves the way for the development of a new generation of interatomic potentials of *ab initio* accuracy.

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