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Practical methods in *ab initio* lattice dynamics

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Abstract. A popular method of extracting phonon frequencies from *ab initio* calculations is to find the equilibrium structure of a material and then build up the matrix of force constants by calculating forces acting due to small displacements of the atoms. If the range of the force constants is assumed to be short, as it typically is in parametrized force-model calculations, the entire dispersion relation can be evaluated from data taken from small *ab initio* calculations. In this paper we highlight the practical difficulties introduced by low-symmetry structures with free internal parameters and present practical solutions to them. By way of example, we present a number of calculations where solution of these problems is essential. These include *ab initio* calculation of phonon dispersion in a non-centrosymmetric structure (silver gallium diselenide) and good agreement between calculations and neutron scattering data for a structure with free internal parameters (germanium sulphide).

1. Introduction

Ab initio methods have been very successful in calculating properties of materials to high accuracy [1]. The vibrational properties of a crystal determine a wide range of macroscopic behaviour: specific heat, sound velocity and infrared and Raman absorption. In addition, very low-frequency modes can be associated with phase transformations, while imaginary frequencies provide an indication that the calculated structure is not the most stable. Finally, the phonon spectrum enables a good approximation to free energies to be made via the quasi-harmonic approximation. In view of these properties, calculating phonons from *ab initio* calculation has become a very important topic.

Very early work involved calculating the energy of frozen phonons [2, 3]. Here the eigenvector of the phonon in question was assumed, and the appropriate atomic displacements frozen in. From a graph of cohesive energy against amplitude the phonon frequency could then be found without the need for force evaluation. It was demonstrated early on that using forces provided similar results. More recently, linear response methods with dielectric screening [4] incorporating iteration to self-consistency [5] have been applied to obtain phonons of arbitrary wavevector from plane wave electronic structure calculations.

Traditionally, phonon dispersion relations have been calculated by lattice dynamics. This involves proposing an analytic model for the interactions between atoms, evaluating the force constants between atoms, constructing the dynamical matrix at a given point in the Brillouin zone and diagonalizing it. In the *ab initio* method we seek to replace the analytic model by a full quantum mechanical electronic structure calculation of a supercell of N atoms.

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This can be done by making a series of small displacements of the atoms, and evaluating the forces exerted on the other atoms [6, 7]. Each such calculation provides $3N$ elements of the force constant matrix, and symmetry can be used to deduce further elements, thus reducing the number of electronic structure calculations required. It should be noted that the force constants calculated by this method are not the true atom–atom force constants but rather represent a sum over supercells of forces between one atom and all periodic images of another.

Elements of the force constant matrix [8], $\Phi_{i\alpha,j\beta}$ (where i and j label the atoms and α and β label Cartesian directions) can be found from the calculated forces on atom j , $F_{j\beta}$, due to a displacement $u_{i\alpha}$ of atom i in direction α :

$$\Phi_{i\alpha,j\beta} = \frac{\partial F_{j\beta}}{\partial u_{i\alpha}} = \frac{\partial^2 E}{\partial u_{i\alpha} \partial u_{j\beta}} \quad (1)$$

where the dynamical matrix, $D_{i\alpha,j\beta}(\mathbf{k})$, is the Fourier transform of $\Phi_{i\alpha,j\beta}$ at wavevector \mathbf{k} . In this paper we examine the problem of numerical inaccuracies which occur in *ab initio* methods and several ways to reduce their effects on lattice dynamics calculations. From this we also discuss a method for calculating complete dispersion relations based on a short-range approximation [6, 9, 10]. The majority of empirical models in use assume short-ranged interactions [11], and as a consequence the force constants between atoms beyond (typically) the second-neighbour shell are taken as zero. To obtain matrix elements up to a comparable range by *ab initio* methods thus requires only relatively small calculations.

We illustrate the various points raised in the paper with three examples, based on density functional theory in the local density approximation (LDA) using the pseudopotential plane wave method. These are chosen to illustrate the importance of three distinct aspects of the method, but are also of significant interest in themselves. The effect of force constant matrix range is examined for the familiar example of silicon; the importance of correcting for errors is demonstrated for a non-centrosymmetric structure, chalcopyrite GaAgSe₂; finally the importance of cutoff in the range of the force constants is illustrated for GeS, a material with free internal parameters for which neutron diffraction data are available.

2. Sum rules in the matrix of force constants

We will be concerned with satisfying two properties of the matrix of force constants [8], $\Phi_{i\alpha,j\beta}$ (where i and j label the atoms and α and β label Cartesian directions) which are difficult to impose simultaneously in *ab initio* lattice dynamics. Firstly, it should be symmetric because partial differentiation is commutative:

$$\Phi_{i\alpha,j\beta} = \Phi_{j\beta,i\alpha} \quad (2)$$

although from equation (1) we see that this explicit symmetry is missing when the element is calculated from the force. Secondly, it should obey the following sum rule which follows from Newton's third law:

$$\Phi_{i\alpha,i\beta} = - \sum_{j \neq i} \Phi_{i\alpha,j\beta} \quad (3)$$

It follows from these two rules that:

$$\sum_{j \neq i} \Phi_{i\alpha,j\beta} = \sum_{j \neq i} \Phi_{i\beta,j\alpha} \quad (4)$$

These three rules are true regardless of the actual symmetry of the system under consideration. If the force calculation is exact, then the rules above are automatically

satisfied. A difficulty for an *ab initio* calculation is that whereas force constants can be easily evaluated to arbitrary precision from analytic force models, electronic structure calculation is a time consuming iterative process and a practical calculation can only be converged to a finite accuracy.

3. Treatment of errors in *ab initio* forces

There are several sources of error in the *ab initio* force constants. Since our calculations are based on the plane-wave pseudopotential DFT method, we discuss this in particular, but we also make reference to other *ab initio* techniques where appropriate. There are errors in the pseudopotential plane-wave method itself, due to treatment of exchange, correlation and the pseudopotential approximation. These errors do not lead to violation of the sum rules, and will not be considered here.

Since equation (3) arises from translational invariance, it will be satisfied if all the force constants can be evaluated from the same calculation, regardless of how well converged they are. Only the error due to discretization will apply.

However, a single displacement gives only one row of the matrix of force constants. One column can be deduced from (2) and further elements may be generated by symmetry, but in general the method of small displacements requires more than one calculation to evaluate all the force constants. This means in turn that some elements will be calculated more than once, and that if there are errors, (3) cannot be satisfied for all rows and columns simultaneously. For example if each row is taken from a single calculation, and hence satisfies (3), each column must contain elements from different calculations.

Errors which can lead to violation of the sum rules are as follows.

(i) *Errors associated with evaluating forces using a finite basis set and a finite k-point set.* Typically these are converged to 10^{-3} eV \AA^{-1} .

Errors of this type are present in any *ab initio* calculation. The Hellmann–Feynman theorem demonstrates that errors in the wavefunctions which cause only second-order errors in the energy lead to first-order errors in the forces, so more stringent convergence is required.

(ii) *Errors in the finite convergence of the structural parameters.* If the structure contains free parameters then the relaxation is performed until the forces on the atoms reach a suitably small value [12].

(iii) *Forces arising from anharmonicity since forces are calculated using finite displacements.* The minimum possible displacement for which the force can be reliably calculated is governed by the errors in the force calculation. The degree of anharmonicity is strongly dependent on structure.

(iv) *Computational rounding errors and interpolation errors due to the discrete grid on which the wavefunction is represented [13] since the total energy is not conserved under a rigid shift of the entire crystal.* The theoretical limit on this is set by the interpolation between FFT grid points, typically of order 10^{-5} eV \AA^{-1} .

In a practical calculation the minimum number of displacements required to build up the matrix of force constants is determined by crystal symmetry. The cutoff in the range of the force constants determines the size of the supercell required. To minimize anharmonic effects, displacements of different sign and magnitude are made. If an element and one or more of its symmetric equivalents, (i.e. any elements $\Phi_{i\alpha,i\beta}$ which must be equal by symmetry) are calculated directly, equation (2) is satisfied by taking average values.

Equation (3) can then be satisfied by ignoring the calculated values of $\Phi_{i\alpha,i\beta}$ and simply setting $\Phi_{i\alpha,i\beta} = -\sum_{j\neq i} \Phi_{i\alpha,j\beta}$. This is equivalent to disregarding the calculated restoring force on the atom which has been moved. If equation (4) does not hold, this procedure has the unfortunate effect for $\alpha \neq \beta$ that it will introduce a violation of equation (2).

Equation (4) is trivially satisfied for $\alpha = \beta$, so it is thus only necessary to consider the case $\alpha \neq \beta$. Since this constraint requires that two sums of elements be equal, there is no unique way of imposing it. Problems arising from violations of equation (4) have not previously been discussed because if an atom is sited at a centre of inversion symmetry, equal and opposite pairs in the sum cancel out exactly regardless of errors and $\sum_{j\neq i} \Phi_{i\alpha,j\beta} = 0$ for $\alpha \neq \beta$. In these cases all sum rules are automatically satisfied.

We compare two options for dealing with the violation of equation (4) in the case of non-centrosymmetric crystals. The first is to symmetrize each term between the same atoms in the off-diagonal sums $\Phi_{i\alpha,j\beta} = \Phi_{i\beta,j\alpha}$. This is equivalent to using a central-force model. The second option is to evaluate the amount of the violation, and to adjust each non-zero term in the sum by an identical amount so as to satisfy equation (4). This procedure will violate the symmetry of the matrix (2), but this violation will be small, a manifestation of the error in the forces, so a loop to self-consistency of adjustment and symmetrization is performed before diagonalization. Neither approach requires prior determination of the full symmetry of the system for each application, unlike the method used in [6].

In what follows we shall examine the different approaches to satisfying the sum rules, and show that the major effect of errors in the forces is on the acoustic modes.

4. Complete dispersion relations

It is possible to calculate the complete dispersion relation from the *ab initio* force calculation by making the approximation that the force constants are short ranged. When using periodic boundary conditions the calculated force constants are actually sums over all repeats of the simulation supercell

$$\Phi_{i\alpha,j\beta}^{\Gamma} = \sum_l \Phi_{l,i\alpha,j\beta}$$

where l runs over all repeat cells.

The short-range approximation assumes zero force constants for interactions between atoms separated by a large enough distance, which in practice is determined by the size of the simulation.

For most materials, all atoms can be categorized into shells of progressively distant neighbours with respect to each other. In the particular case of covalently bonded materials we will demonstrate that it is important to include or exclude an entire *shell* of neighbours, defined by the number of bonds required to link atoms, even if some of the interatomic distances are longer than others.

It will often occur that a calculated matrix element is the sum of two or more elements from the same shell of similar magnitude and remaining elements which are small. If the shortest separations are equivalent, half the supercell dimension, then we assume $\Phi_{i\alpha,j\beta}^{\Gamma}$ to be a sum over equal elements from each of the equivalent atoms in the shell. The individual elements are then simply fractions of the whole.

The approximate short-ranged force constants are thus

$$\begin{array}{ll} \text{at short range} & \Phi_{l,i\alpha,j\beta} = N^{-1} \Phi_{i\alpha,j\beta}^{\Gamma} \\ \text{at long range} & \Phi_{l,i\alpha,j\beta} = 0 \end{array}$$

where N is the number of periodic repeats of the atom j which are in the same shell relative to i .

We notice that this particular short-range approximation does not lead to a violation of (3), since all force constants are folded into the approximated short-ranged constants. For purposes of lattice dynamics, the long-range terms are added with phase factors to give exactly correct Γ point phonons.

If the separations are not exactly equal, then a number of schemes can be applied, ranging from assuming that the force constants fall off as a power law or exponential, to setting all but the shortest-ranged to zero.

To illustrate the method, we have chosen three examples which highlight the important aspects of this work—the range of the force constants, the importance of including complete shells of neighbours and the importance of enforcing the sum rules. In each case force constants have been calculated by the LDA plane wave pseudopotential method. The internal and lattice parameters are first relaxed until the residual forces and stresses on the unit cell are less than $0.001 \text{ eV \AA}^{-1}$; the finite displacements are then made and the total electronic energy again iterated toward its self-consistent energy minimum without moving ions until the forces are converged to $0.001 \text{ eV \AA}^{-1}$.

5. Application to silicon

Calculation of phonons in the diamond structure provides a good test of the approximations used in the method: the LDA pseudopotential method works very well for silicon; since it has very high symmetry, a single calculation is required to evaluate the force constants for a given range. Because of translational invariance within this single calculation, all the sum rules are satisfied automatically. Calculations were performed using a 64-atom supercell, generating force constants for nine shells of neighbours.

This LDA [14] calculation used a non-local pseudopotential generated by the Kerker [15] method in Kleinman–Bylander [16] form to describe the ion–valence electron interactions. The basis set had a kinetic energy cutoff of 150 eV, which converges total energy differences to better than 0.001 eV/atom. Four special k -points for Brillouin zone integration were used, which we find converges the total energy to 0.001 eV/atom.

In figure 1(a)–(d) we show complete dispersion relations calculated from the assumption of various ranges of interatomic force constants. These ranges were obtained by setting all elements beyond a certain shell of neighbours to zero, and adjusting the on-diagonal terms to satisfy equation (3). Failing to make this adjustment leads to major shifts in the acoustic modes around Γ while the optic branches are virtually unaffected. This is easily understood since violation of equation (3) describes the energy erroneously associated with a rigid shift of the crystal: the corresponding eigenstates are the acoustic modes at Γ . Figure 1(e) shows a comparison between the calculated result and neutron scattering data [17].

The case of near neighbours only (figure 1(a)) is equivalent to a simple network of near-neighbour springs, and it is interesting that there is no sign of the mechanical instabilities of this system in the phonon spectrum, because all the unstable modes couple to finite strains. Incorporating second-neighbour interactions (figure 1(b)) captures most of the essential features, but when incorporating further shells, convergence is slow and non-monotonic. Interestingly, including third neighbours in the model makes the spectrum worse. The most demanding feature is the flat band at TA(X), which requires interactions to eighth neighbours (fifth-neighbour interactions give a flat band [18], but this becomes peaked when seventh neighbours are included).

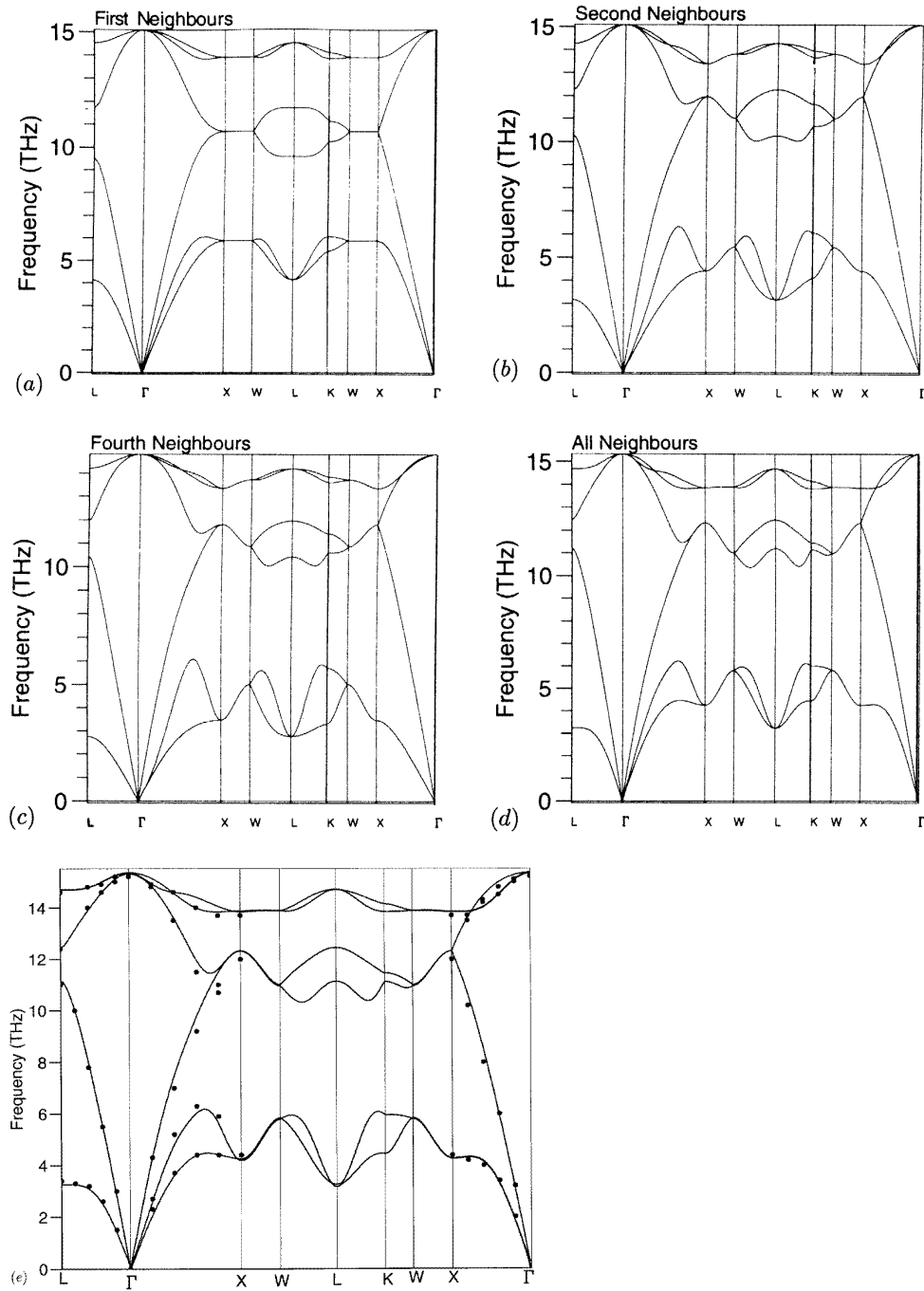


Figure 1. Calculated phonon dispersion relations for silicon, with elements calculated from a large (64-atom) supercell to minimize the effects of periodic boundary conditions. The effect of truncating the range of the force constants at (a) first, (b) second and (c) fourth neighbours are shown, while the result of including all calculated neighbours is shown in (d). (e) A comparison of calculated silicon dispersion relation (d) (lines) with neutron scattering data [17] (dots).

The density of phonon states can also be calculated by this method. Using a grid of 10^6 k -points a good Brillouin zone integration is obtained. Since it is an integrated quantity, one might expect that the shape of the density-of-states (DOS) would converge rapidly. As shown in figure 2 this is not the case: the shape of the DOS varies significantly with the cutoff of the force constants.

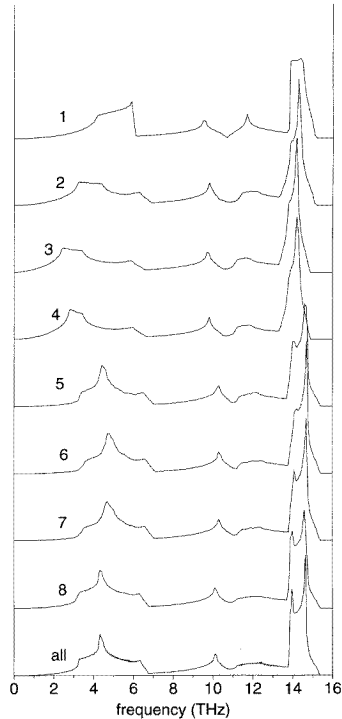


Figure 2. Phonon DOSs for silicon, showing the slow convergence of the shape of the DOS with the range of the interactions.

A further integrated quantity, the quasiharmonic vibrational free energy, can also be calculated from the phonon DOS. In contrast to the DOS, this quantity converges very rapidly as the range of the force constants is increased.

We thus conclude that, while the major features of the dispersion spectrum can be captured with a second-neighbour model, some subtler features converge very slowly with the range of the force constants. Moreover, while it is possible to fit subtle features of the density of states with a fairly short-ranged model, the actual physical cause of these features is the inherently long-ranged interactions.

6. Application to chalcopyrite

Silver gallium diselenide AgGaSe_2 is one of numerous tetrahedral semiconductors which crystallize in the chalcopyrite structure, the ternary analogue of diamond. The wide variety of materials which adopt this structure have found applications in LEDs, solar cells and various nonlinear optic devices.

Calculation of the phonon frequencies in the chalcopyrite structure is complicated, since it has a non-centrosymmetric structure with free internal parameters. The elements required to build up the force constant matrix have been taken from the calculation by Karki *et al* [19] using Q_c tuned pseudopotential and the LDA for the exchange and correlation. In

this calculation the plane wave basis set was cut off at 400 eV with the stress corrected for finite basis set size [20]. The Brillouin zone was sampled at six special k -points from a $3 \times 3 \times 3$ mesh [21] and the structural parameters were relaxed until the forces were below $0.001 \text{ eV \AA}^{-1}$; the forces for subsequent displacements were converged to 1% of the maximum force [12].

We use a supercell for this calculation which includes eight atoms, and hence the short-range approximation includes non-central interactions up to second neighbours. The symmetry of the system is such that seven separate displacement calculations were required to calculate all the $\Phi_{i\alpha,j\beta}^{\Gamma}$. To minimize anharmonic effects the force constants were calculated as an average of the forces found for displacements in both positive and negative directions. Some force constants were also calculated more than once within the seven displacement calculations, and in these cases the average value was taken.

In figure 3(a) we show the dispersion relations calculated in the short-range approximation with the raw data, which were first symmetrized by taking averages of $\Phi_{i\alpha,j\beta}$ and $\Phi_{j\beta,i\alpha}$ where possible within the minimal set of seven displacements for this symmetry group. It can be seen that since Newton's third law is not obeyed the Γ acoustic modes are significantly non-zero.

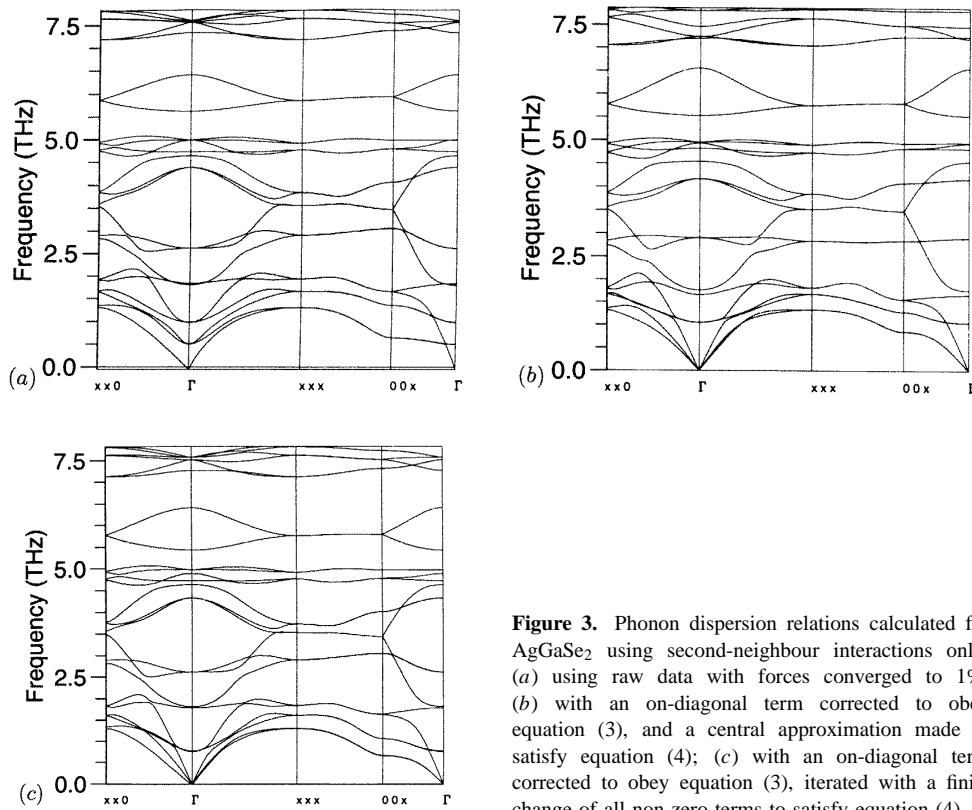


Figure 3. Phonon dispersion relations calculated for AgGaSe_2 using second-neighbour interactions only: (a) using raw data with forces converged to 1%; (b) with an on-diagonal term corrected to obey equation (3), and a central approximation made to satisfy equation (4); (c) with an on-diagonal term corrected to obey equation (3), iterated with a finite change of all non-zero terms to satisfy equation (4).

If the on-diagonal terms are adjusted to obey Newton's third law, by setting $\Phi_{i\alpha,i\beta} = -\sum_{j \neq i} \Phi_{i\alpha,j\beta}$, then the dispersion relation in figure 3(c) is obtained (note that this procedure violates equation (4)). The Γ -point acoustic modes now have zero frequency, but only small changes occur in the remainder of the dispersion relation. This suggests that the

optic frequencies converge more rapidly than the acoustic ones. If we satisfy equation (4) using the approximation following from central interactions, $\Phi_{i\alpha,j\beta} = \Phi_{i\beta,j\alpha}$, the spectrum is altered (figure 3(b)) with some bands becoming almost non-dispersive.

If, however, we satisfy equation (4) by adding a constant to each term, the phonon spectrum is indistinguishable from figure 3(c). This procedure leads to better agreement with Raman data than the central-force approximation. We conclude that the central-force approximation is an inappropriate way to enforce equation (4) in chalcopyrite.

Previous workers have characterized the phonons of AgGaSe₂ in terms of a three-band picture [22, 23]. Our results show that this picture, derived from Raman and infrared data [22, 23], breaks down, although the upper band remains distinct and relatively dispersionless. The reason for this is that our method probes the whole of the Brillouin zone, while the experimental probes are restricted to modes at the Γ point.

Analysis of the eigenvectors of the dynamical matrix allow us to obtain some insight into the type of oscillation represented by each band. The upper band consists of modes primarily involving vibration of one gallium atom, and their quasi-localized nature results in the small dispersion. Likewise, a low dispersion band comprising primarily of vibrations of one silver atom is found just below 5 THz. The short-ranged coupling between these cations and the rest of the lattice illustrates why doping with alternate isoelectronic species can be attained without significant distortion to the lattice structure, while anion doping is more difficult.

7. Application to germanium sulphide

Germanium sulphide is an interesting material, which has a layered structure useful for applications in intercalation compounds. It is a challenge to model since it exhibits both strong covalent intralayer bonding and weaker interlayer electrostatic interactions. This leads to a distinct gap in the phonon spectrum between interlayer and intralayer modes.

We have selected GeS because it provides an excellent test of the short-range approximation, having numerous different neighbour spacings, yet these neighbours can be categorized by the number of covalent bonds of interlayer crossings between them.

It also requires careful treatment of sum rule violations because it has an inversion centre (which allows characterization of the modes into Raman and infrared active), but this centre is not situated at one of the atomic sites (which means that the sum rules are not enforced by symmetry). Finally, there also exist neutron scattering data for the low-frequency modes which enable us to compare our results with experiment. The data $\Phi_{i\alpha,j\beta}^{\Gamma}$ for GeS are taken from the work of Hsueh *et al* [7] on an eight-atom unit cell for which all three unit-cell parameters and all internal parameters were optimized.

The calculations used the LDA approximation to exchange and correlation in the parametrization of Perdew and Zunger [14]. The plane wave basis set had an energy cut off at 300 eV, giving approximately 2500 basis functions per wavefunction. Non-local ionic pseudopotentials were implemented in the Kleinmann–Bylander [16] form generated by the Q_c tuning method [26, 27]. For these pseudopotentials, the 300 eV cutoff converged the total energy to 10^{-4} eV/atom.

The Brillouin zone was sampled at eight special k -points corresponding to a $4 \times 4 \times 4$ grid [21]: at this sampling density the total energies were converged to 10^{-4} eV/atom. The forces and charge density were symmetrized to reflect the symmetry of the distorted structure for each of the six separate calculations required to obtain all the (non-central) force constant components.

Figure 4(a) shows the difficulties that can occur from incorrect choice of cutoff of the

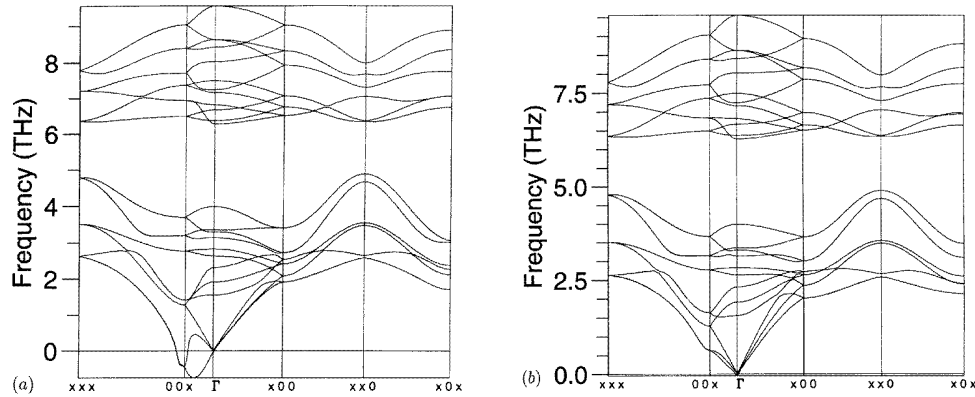


Figure 4. Phonon dispersion relations calculated for GeS: (a) interactions truncated at half the unit-cell distance, including only the closer second neighbours; (b) interactions extending to all the second shell of neighbours.

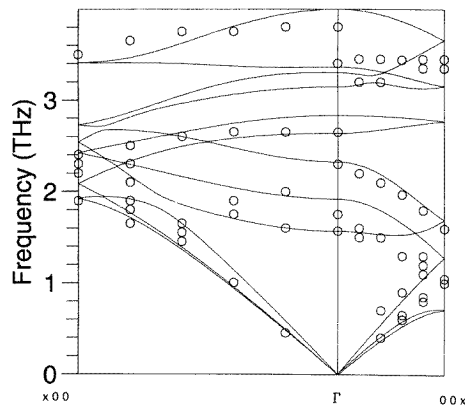


Figure 5. A comparison of calculated dispersion curves for GeS with neutron [28] (non- Γ), infrared and Raman [24,25] (Γ) measurements at room temperature. Our calculations are at 0 K, and are therefore at slightly higher frequencies than experiment.

force constants. Here we have truncated the interactions at a distance of half the unit cell rather than including all second covalent neighbours, thus some second-neighbour matrix elements are zero. The unphysical effect is to produce apparent instabilities in the acoustic branch, while once again the optic modes are relatively unaffected. A similar effect occurs in chalcopyrite.

Figure 4(b) shows the calculated dispersion relation, with *all* covalently bonded second-neighbour interactions (defined by atoms two covalent bonds apart) included. Good agreement of this *ab initio* data set with available Raman, neutron [28] and infrared data can be seen (figure 5). Figure 4 shows the anticipated distinctive divide between the low-frequency interlayer and the high-frequency intralayer modes.

8. Conclusions

We have investigated common numerical inaccuracies in *ab initio* force constants and the ways in which they manifest themselves in calculated phonon dispersion relations. We find that the errors introduced into calculation of phonon dispersion relations from noise in *ab initio* forces mainly affect the acoustic phonons if the sum rules are not satisfied. A number of strategies for enforcing these sum rules were used; we found that the most satisfactory were to set $\Phi_{i\alpha,i\beta} = -\sum_{j\neq i} \Phi_{i\alpha,j\beta}$ (equation (3)) and to add (subtract) a constant term to (from) each element to satisfy the sum rule of equation 4.

We have also shown that for covalent materials that reasonable phonon dispersion relations can be obtained from small *ab initio* calculations (provided complete shells of neighbours are either included or excluded), and that the force constants must be fairly short ranged. For fine detail, longer-range interactions may be necessary.

Three systems have been evaluated to show the importance of treating the sum rules correctly. The standard example of silicon illustrates what can be expected from a model of finite range. The chalcopyrite calculations show the importance of enforcing the sum rules to the low-frequency states. The calculation is of intrinsic interest in that it disproves the ‘three-band’ model of the density of states proposed on the basis of Γ -point phonons only. It also illustrates from the dispersionless nature of some of the bands that the anions behave as though rattling in a confined space, with little coupling of their vibrations to the rest of the lattice.

The GeS calculation illustrates the importance of defining complete shells of neighbours by topology rather than purely by distance, and shows good agreement with experimental data [29]. In this case the two-band picture of the dispersion relation is confirmed, and calculations to observe the breakdown of this with pressure are anticipated.

We have demonstrated the method using the plane wave pseudopotential method, but calculating phonon dispersion relations by this method, can be done using other existing *ab initio* codes or commercial packages, introducing no new approximations beyond those of conventional lattice dynamics.

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