A new and efficient scheme for first-principles calculations of phonon spectra

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Abstract. We present a new method for performing first-principles frozen phonon calculations within the framework of density-functional theory and the adiabatic approximation. In our approach the super-cell Kohn–Sham Hamiltonian is diagonalised with sufficient accuracy to compute phonon properties in the harmonic approximation in a time which is independent of the super-cell size. This method dramatically improves the efficiency of the super-cell phonon technique and can be implemented rapidly by modifying an existing total energy program. We have applied this scheme to compute the properties of long-wavelength phonons in silicon in a plane-wave pseudopotential calculation. Results for phonon frequencies and the internal strain parameter are in good agreement with previously calculated and experimental values.

1. Introduction

In recent years first-principles plane-wave pseudopotential techniques have been used to compute a wide range of the dynamical properties of crystalline materials [1–5]. The method has been applied to compute both harmonic and anharmonic properties in a variety of different types of materials including insulators, non-polar and polar semiconductors and metals. In general excellent agreement is found between experimental data and the results of first-principles calculations; for example calculated phonon frequencies often agree with experimental values to within 1–3%. Dynamical properties have also been successfully obtained using other first-principles techniques, including the mixed-basis pseudopotential approach [6] and the linear muffin tin orbital (LMTO) method [7].

　　To date the most popular technique for computing the phonon properties of a crystal within the framework of total-energy calculations is the so-called 'direct' approach. In the simplest realisation of this method one takes a super-cell of the solid, subject to periodic boundary conditions, and freezes in the phonon mode of interest by slightly displacing each atom away from its perfect crystalline lattice site. Phonon frequencies are then computed within the adiabatic approximation either by computing the Hellmann–Feynman forces on the atoms or the differences in total energies between the perfect and distorted structures. The periodic boundary conditions impose a restriction on the range of phonon modes which can be addressed with any given super-cell. In particular

if we let L and g denote general real-space and reciprocal-space Bravais lattice vectors of the super-cell then only phonons whose wavevector q obeys

$$L \cdot q = 2\pi n_L \tag{1.1}$$

where n_L is integer for all L, can be accommodated within the cell. Equation (1.1) also implies that the phonon wavevector q must be a member of the set of super-cell reciprocal-space lattice vectors g. For q away from high symmetry points of the primitive zone of the solid the number of atoms in the super-cell demanded by condition (1.1) quickly becomes rather large, even if one uses the optimal choice of cell. The computational effort to solve for the charge density, total-energy and Hellmann–Feynman forces of a super-cell using conventional total-energy techniques scales as N_p^3 where N_p is the number of primitive cells contained within the super-cell. This consideration severely constrains the size of super-cells which can be studied using the conventional total-energy approach, which in turn limits the number of points in the Brillouin zone where phonon properties are computationally accessible. However, there is a large class of experimentally measurable quantities, which includes heat capacities, thermal expansion coefficients and temperature dependences of band gaps, which must be computed by integrating phonon properties over the whole zone. Under these circumstances it is highly desirable to have a computational technique which allows the calculation of phonon properties at arbitrary points in the zone.

In this paper we present a new and efficient method for performing first-principles frozen phonon calculations. We show that the dynamical properties of a crystalline solid, in the harmonic approximation, can be obtained from a super-cell calculation without recourse to a complete solution of the Kohn–Sham Hamiltonian. A scheme is described in which electronic eigenvectors are computed with sufficient accuracy to construct the dynamical matrix in a time which is independent of N_p. In our method the numerical work to obtain the charge density and the Hellmann–Feynman force on each atom is also independent of N_p. Our approach thus overcomes the limitations imposed by the N_p^3 scaling behaviour, found in the traditional frozen phonon method, for the computational effort to diagonalise the Kohn–Sham Hamiltonian and compute the Hellmann–Feynman forces.

The basis of our approach is similar to the method for computing the linear response functions of solids developed by Baroni *et al* [8]. Their method is rather flexible and enables them to compute the response of the solid at completely arbitrary wavevectors in the zone, including the infinite wavelength limit. The work of Baroni *et al* is formulated in terms of the Green's functions of the solid and provides similar speed improvements to the approach presented here. The advantage of the present formulation is that it is couched in the conventional language of total-energy calculations, and as a consequence, our scheme can be rapidly implemented by adapting an existing total-energy program.

2. The dynamical matrix

The primary purpose of this section is to establish some of the notation we shall use in this paper, and to briefly review the structure the dynamical matrix takes on within the framework of a first-principles total-energy calculation. We shall develop the formulation for a crystalline solid containing s atoms in the primitive unit cell and adopt the convention of labelling each atom of the solid by a primitive real-space Bravais lattice vector l specifying its unit cell and an index k, which runs from 1 to s, and which labels

the position of the atom in the primitive basis. It will be convenient to write the general position vector R of atom lk as

$$R_l^k = l + m^k + u_l^k \qquad (2.1)$$

where m^k is the position vector of atom lk measured from the origin of the cell l when there are no phonon displacements in the crystal and u_l^k is a vector giving the displacement of atom lk away from equilibrium. We shall use the symbol G to stand for a general element of the set of primitive reciprocal-space lattice vectors.

The theory of lattice dynamics in the harmonic and adiabatic approximations is formulated in terms of the dynamical matrix [9], which in direct space is given by

$$D_{\alpha\beta}^{kk'}(l - l') = (1/\sqrt{\mu^k \mu^{k'}})\varphi_{\alpha\beta}^{kk'}(l - l') \qquad (2.2)$$

where μ^k is the mass of the kth atom of the atomic basis and where

$$\varphi_{\alpha\beta}^{kk'}(l - l') = (\partial^2 E_{tot}/\partial u_{l\alpha}^k \partial u_{l'\beta}^{k'})_0 \qquad (2.2a)$$

where E_{tot} is the total-energy, α and β are Cartesian directions and $(\ )_0$ indicates that the derivative is to be evaluated with the atoms in their perfect crystal positions. Phonon frequencies and polarisations can be calculated directly from the eigenvalues and eigenvectors of the Fourier transform of the direct space dynamical matrix defined by [9]

$$D_{\alpha\beta}^{kk'}(q) = \sum_l D_{\alpha\beta}^{kk'}(l) \exp[-iq \cdot (l + m^k - m^{k'})]. \qquad (2.3)$$

In what follows we shall develop our formulation for the lattice dynamics in the general case where the ionic potential has both local and non-local components. Under these circumstances, within the framework of total-energy density-functional calculations the energies, Hellmann–Feynman forces and the dynamical matrix can be expressed as a sum of electrostatic terms, which depend only on the positions of the ions, and terms which in general depend on both the Kohn–Sham wavefunctions and the ionic coordinates [10, 11, 12]. In this communication we shall be concerned with computing those parts of the dynamical matrix which depend on the electron wavefunctions. The direct ion–ion electrostatic contributions to the dynamical matrix are readily evaluated at arbitrary wavevector using standard Ewald transformation methods [9] and therefore need not be considered further here. We shall find it convenient to define a matrix γ through

$$\gamma_{\alpha\beta}^{kk'}(l - l') = (\partial^2(E_{tot} - E_{II})/\partial u_{l\alpha}^k \partial u_{L'\beta}^{k'})_0 \qquad (2.4)$$

where E_{II} is the ion–ion contribution to the total-energy and to introduce the electron–ion component to the force on atom lk which is given by [12]

$$F_{l\alpha}^k = -\partial(E_{tot} - E_{II})/\partial u_{l\alpha}^k. \qquad (2.5)$$

3. Frozen phonon super-cell approach for the dynamical matrix

To date most first-principles calculations have concentrated on computing phonon properties at high symmetry points in the Brillouin zone, or along high symmetry directions. Under these circumstances it is often the case that symmetry considerations constrain many components of the dynamical matrix to be zero, allowing phonon

eigenvectors to be obtained by inspection. In this section we consider what information is necessary to calculate the dynamical matrix in the general case using the Hellmann–Feynman forces. We establish the result that a knowledge of the variation in the density matrix to first order in the atomic displacements is sufficient to compute phonon properties in the harmonic approximation. For completeness we also outline the connection between the force approach for the dynamical matrix, and the well known expressions for this quantity written in terms of the density response function of the solid.

In the direct frozen phonon approach the dynamical matrix at wavevector q is computed by freezing in a series of distortions of the form

$$u_{l\alpha}^{k} = (\lambda/2)\zeta_{\alpha}^{k} \exp[\mathrm{i}q \cdot (l + m^{k})] + \mathrm{CC} \tag{3.1}$$

where CC stands for the complex conjugate, ζ is a complex length vector and λ is a small parameter, chosen to ensure that anharmonic effects are small. Hellmann–Feynman forces, $F_{l\alpha}^{k}$, are then computed for the distorted structure. Using the definitions of γ (2.4) and $F_{l\alpha}^{k}$ (2.5) together with the Fourier transform convention (2.3) we find that the forces are related to γ through

$$F_{l\alpha}^{k} = -\frac{\lambda}{2} \sum_{k'\beta} \exp[\mathrm{i}q \cdot (l + m^{k})] \gamma_{\alpha\beta}^{kk'}(q) \zeta_{\beta}^{k'} + \mathrm{CC} + \mathrm{O}(\lambda^2). \tag{3.2}$$

Let us define the vector τ as

$$\tau_{\alpha}^{k} = \sum_{k'\beta} \gamma_{\alpha\beta}^{kk'}(q) \zeta_{\beta}^{k'} \tag{3.3}$$

We make two general observations about (3.2) and (3.3). Firstly it is clear from (3.3), that the entire dynamical matrix can be constructed provided we are able to compute the vector τ for $3s$ independent choices for the vector ζ. Secondly we see that in order to construct the vector τ from the forces in equation (3.2) it is not necessary to compute the variation in the forces beyond first order in the parameter λ. Finally we note in passing, that in principle, it is not necessary to compute the forces on all sN_{p} atoms in the super-cell to obtain the vector τ through (3.2) and (3.3); a particular element τ_{α}^{k} can be derived from forces on two atoms of type k in direction α, and thus the forces on $2s$ atoms suffice to determine completely the complex vector τ for each choice of the vector ζ.

The Hellmann–Feynman theorem allows us to express $F_{l\alpha}^{k}$ in terms of the density matrix of the Kohn–Sham eigenvectors through

$$F_{l\alpha}^{k} = \int\int \rho(r, r') \hat{F}_{l\alpha}^{k}(r', r) \, \mathrm{d}r \, \mathrm{d}r' \tag{3.4}$$

where

$$\hat{F}_{l\alpha}^{k}(r, r') = \frac{\partial V_{\mathrm{NL}}^{k}(r - R_{l}^{k}, r' - R_{l}^{k})}{\partial r_{\alpha}} + \frac{\partial V_{\mathrm{NL}}^{k}(r - R_{l}^{k}, r' - R_{l}^{k})}{\partial r'_{\alpha}}$$

$$+ \delta(r - r') \frac{\partial V_{\mathrm{L}}^{k}(r - R_{l}^{k})}{\partial r_{\alpha}} \tag{3.4a}$$

$V_{\mathrm{L}}^{k}(r)$ and $V_{\mathrm{NL}}^{k}(r, r')$ being the local and non-local potentials for the atom k. For small displacements of the nuclei away from equilibrium we may formally expand the density matrix as a power series in the parameter λ as

$$\rho(r, r') = \rho^0(r, r') + \lambda\rho^1(r, r') + O(\lambda^2) \tag{3.5}$$

$\rho^0(r, r')$ being the density matrix of the crystal without any displacements. Substituting this expansion into (3.4) we find that

$$F^k_{l\alpha} = \int\int (\rho^0(r, r') + \lambda\rho^1(r, r'))\, \hat{F}^k_{l\alpha}(r', r)\, dr\, dr' + O(\lambda^2). \tag{3.6}$$

We see, therefore, that in order to compute the forces in the distorted structure correct to first order in λ, and hence the dynamical matrix through (3.2), it is not necessary to compute the change in the density matrix beyond the first-order variation in the displacement parameter.

We note in passing that it is straightforward to transform (3.6) into a more familiar expression for the dynamical matrix in terms of the static density response function $\chi(r, r')$ in the case when the ionic potential is local. Under these conditions (3.6) simplifies to

$$F^k_{l\alpha} = \int (\rho^0(r) + \lambda\rho^1(r))\hat{F}^k_{l\alpha}(r)\, dr + O(\lambda^2) \tag{3.7}$$

where

$$\hat{F}^k_{l\alpha}(r) = \partial V^k_L(r - l - m^k - u^k)/\partial r_\alpha \tag{3.8}$$

and where $\rho^0(r)$ and $\rho^1(r)$ are the ground state and first-order changes in the charge density respectively. Formally the first-order variation in the charge density can be written in terms of the density response function of the system, $\chi(r, r')$, as

$$\lambda\rho^1(r) = \int \chi(r, r')\lambda V^1_{\text{ext}}(r')\, dr' \tag{3.9}$$

where λV^1_{ext} is the first order change in the external potential given by

$$\lambda V^1_{\text{ext}}(r) = -\sum_{lk\alpha} \frac{\partial V^k_L(r - l - m^k)}{\partial r'_\alpha} u^k_{l\alpha} \tag{3.9a}$$

Substituting (3.8), (3.9) and (3.9a) into (3.7) and expanding to first order in $u^k_{l\alpha}$ one readily finds

$$\gamma^{kk'}_{\alpha\beta}(l - l') = \delta_{l,l'}\delta^{k,k'} \int \rho^0(r) \frac{\partial^2 V^k_L(r - l - m^k)}{\partial r_\alpha \partial r_\beta}\, dr$$

$$+ \int\int \frac{\partial V^k_L(r - l - m^k)}{\partial r_\alpha} \chi(r, r') \frac{\partial V^k_L(r' - l' - m^{k'})}{\partial r'_\beta}\, dr\, dr' \tag{3.10}$$

which is in agreement with the expression for the dynamical matrix obtained by Sham [10] and Pick *et al* [11].

4. Kohn–Sham equations and solution for the first-order density matrix

In this section we state the Kohn–Sham equations and consider the form of the Kohn–Sham potential induced by a phonon distortion of the form (3.1). We also develop an approach for computing the expectation value of any operator for a given first-order

change in the potential, generated by a phonon distortion, using eigenvectors generated by a partial diagonalisation of the Kohn–Sham Hamiltonian.

The Kohn–Sham equations for the solid can be written as [12]

$$(-\tfrac{1}{2}\nabla^2 + V_{KS:L}(r))\psi_i(r) + \int V_{KS:NL}(r, r')\psi_i(r')\,dr' = \varepsilon_i\psi_i(r) \qquad (4.1a)$$

where the local Kohn–Sham potential $V_{KS:L}(r)$ is the sum of external, Hartree and exchange–correlation parts given through

$$V_{KS:L}^{\delta}(r) = \sum_{lk} V^k(r - R_l^k) + V_H(r) + \mu_{xc}(r) \qquad (4.1b)$$

and non-local Kohn–Sham potential $V_{KS:NL}$ is defined through the non-local ionic potential as

$$V_{KS:NL}(r, r') = \sum_{lk} V_{NL}^k(r - R_l^k, r' - R_l^k). \qquad (4.1c)$$

The Hartree and exchange–correlation potentials depend self-consistently on the Kohn–Sham wavefunctions $\psi_i(r)$ through the charge density:

$$\rho(r) = \sum_i |\psi_i(r)|^2 \qquad (4.1d)$$

where the sum over i runs over the occupied states of the solid. The Hartree potential is defined by standard expression

$$V_H(r) = \int \frac{\rho(r')}{|r - r'|}\,dr' \qquad (4.1e)$$

while the exchange–correlation potential is defined as the functional derivative with respect to the charge density of the exchange and correlation energy, E_{xc}, as

$$\mu_{xc}(r) = \delta E_{xc}/\delta\rho(r). \qquad (4.1f)$$

The functional dependence of E_{xc} on the charge density is unknown, and in practice it is usually estimated using the local-density approximation.

In the case where the solid has no phonon distortion we shall denote the Kohn–Sham eigenfunctions as $\psi_{pn}(r)$ with a Bloch wavevector p in the first primitive Brillouin zone of the solid, and a band index n. We shall assume in what follows that we are dealing with a semiconductor or insulator and that there are M valence bands at each wavevector p.

Let us now consider how we might formally compute the first order change in the expectation value of a general operator produced by a distortion of the form (3.1). We shall write expand the Kohn–Sham potential as a power series in the parameter λ. Thus we write for the local part

$$V_{KS:L}(r) = V_{KS:L}^0(r) + \lambda V_{KS:L}^1(r) + O(\lambda^2) \qquad (4.2a)$$

and similarly for the non-local ionic contribution

$$V_{KS:NL}(r, r') = V_{KS:NL}^0(r, r') + \lambda V_{KS:NL}^1(r, r') + O(\lambda^2). \qquad (4.2b)$$

Straightforward application of second-order perturbation theory [13] allows one to write the first order charge in the expectation value of any operator Z as

$$\langle Z^1 \rangle = \sum_{pp'} \sum_{n=1}^{M} \sum_{n'=M+1}^{\infty} \frac{\langle \psi_{pn}|V_{KS:L}^1 + V_{KS:NL}^1|\psi_{p'n'}\rangle\langle\psi_{p'n'}|\hat{Z}|\psi_{pn}\rangle}{\varepsilon_{pn} - \varepsilon_{p'n'}} + CC \qquad (4.3a)$$

where $|\psi_{pn}\rangle$ are the ground state Kohn–Sham eigenfunctions of the primitive cell of the

perfect crystal, the sums over p and p' run over the first Brillouin zone and the sums over n and n' runs over the valence and conduction band states respectively. As an alternative to (4.3a) we may equivalently state that the first-order variation in the density matrix is given by

$$\rho^1(r, r') = \sum_{pp'} \sum_{n=1}^{M} \sum_{n'=M+1}^{\infty} \eta^1(r, r' | pn, p'n') + \text{CC} \tag{4.3b}$$

where

$$\eta^1(r, r' | pn, p'n') = \frac{\psi_{pn}(r) \langle \psi_{pn} | V^1_{\text{KS:L}} + V^1_{\text{KS:NL}} | \psi_{p'n'} \rangle \psi^*_{p'n'}(r)}{\varepsilon_{pn} - \varepsilon_{p'n'}} \tag{4.3c}$$

We therefore conclude that the first-order change in the self-consistent Kohn–Sham potential contains sufficient information to compute the variation in the density matrix to first order in λ, and thus contains sufficient information to obtain the dynamical matrix in the harmonic approximation using (3.6).

The formal expression for the first-order change in the density matrix can be simplified by observing that in a crystalline solid the periodicity of the lattice imposes a selection rule on the matrix elements appearing in (4.3). We may write the first-order change in the local part of the Kohn–Sham potential as

$$V^1_{\text{KS:L}}(r) = \tfrac{1}{2} \sum_{lk\alpha} \theta^k_\alpha(r - l - m^k) \zeta^k_\alpha \exp[i q \cdot (l + m^k)] + \text{CC} \tag{4.4a}$$

where

$$\theta^k_\alpha(r - l - m^k) = \left(\partial V_{\text{KS:L}}(r) / \partial u^k_{l\alpha} \right)_0. \tag{4.4b}$$

The form of (4.4a) implies that the first-order change in the Kohn–Sham potential may be written as a Fourier series of the form

$$V^1_{\text{KS:L}}(r) = \sum_G V^1_{\text{KS:L}}(G + q) \exp[i(G + q) \cdot r] + \sum_G V^1_{\text{KS:L}}(G - q) \exp[i(G - q) \cdot r]$$

$$(4.5)$$

where the vectors G are reciprocal-space vectors of the primitive Bravais lattice. We see that, whereas the zeroth-order local component of the Kohn–Sham potential can be written as Fourier series in the primitive wavevectors G, the Fourier expansion of the first-order change in the Kohn–Sham potential is limited to wavevectors of the form $G + q$ or $G - q$. Clearly a potential of the form (4.5) will only couple a state at wavevector p to those at $p + q$ and $p - q$ in (4.3). A similar line of reasoning can be employed to show that the same selection rule also holds true for the non-local part of the potential. Therefore, we may explicitly perform the sum over the wavevector p' in (4.3b) to obtain

$$\rho^1(r, r') = \sum_p \sum_{n=1}^{M} \sum_{n'=M+1}^{\infty} \left(\eta^1(r, r' | pn, p + qn') + \eta^1(r, r' | pn, p - qn') \right) + \text{CC}. \tag{4.6}$$

Direct computation of the first-order variation of any observable using (4.3) and (4.6) for a given Kohn–Sham potential is numerically cumbersome and expensive, requiring evaluation of matrix elements against both conduction and valence band states. However, it is quite straightforward to derive an alternative expression for the first-order variation in any quantity using wavefunctions obtained from a partial diagonalisation of the Kohn–Sham Hamiltonian. Suppose we compute the eigenvectors of the zeroth- and

first-order Kohn–Sham Hamiltonians, using basis states with Bloch wavevectors p and $p + q$. We shall denote valence band eigenfunctions derived by this process by $\varphi_{pi}^{(+)}(r)$ where i is an index running between 1 and $2M$ and the $(+)$ superscript indicates that basis states at p and $p + q$ are included. It is easily shown that

$$
\sum_{i=1}^{2M} |\varphi_{pi}^{(+)}\rangle\langle\varphi_{pi}^{(+)}| = \sum_{n=1}^{M} (|\psi_{pn}\rangle\langle\psi_{pn}| + |\psi_{p+qn}\rangle\langle\psi_{p+qn}|)
$$

$$
+ \lambda \sum_{n=1}^{M} \sum_{n'=M+1}^{\infty} (\eta^1(r, r'|pn, p+qn') + \eta^1(r, r'|p+qn, pn'))
$$

$$
+ \text{cc} + O(\lambda^2)
$$

(4.7)

which is close to what we want. Now consider forming the vector

$$
\bar{\psi}_{pn}^{(+)}(r) = \sum_{i=1}^{2M} \varphi_{pi}^{(+)}(r)\langle\varphi_{pi}^{(+)}|\psi_{pn}\rangle
$$

(4.8)

which is easily computed given $\psi_{pn}(r)$, the Bloch states for the perfect solid. Using (4.3c) and (4.7) we find, to first order λ,

$$
\bar{\psi}_{pn}^{(+)}(r) = \psi_{pn}(r) + \lambda \sum_{n'=M+1}^{\infty} \frac{\psi_{p+qn'}(r)\langle\psi_{p+qn'}|V_{\text{KS:L}}^1 + V_{\text{KS:NL}}^1|\psi_{pn}\rangle}{\varepsilon_{pn} - \varepsilon_{p+qn'}}.
$$

(4.9a)

Obviously we can repeat this whole exercise using basis wavefunctions with Bloch wavevectors p and $p - q$ to derive a second set of wavevectors obeying

$$
\bar{\psi}_{pn}^{(-)}(r) = \psi_{pn}(r) + \lambda \sum_{n'=M+1}^{\infty} \frac{\psi_{p-qn'}(r)\langle\psi_{p-qn'}|V_{\text{KS:L}}^1 + V_{\text{KS:NL}}^1|\psi_{pn}\rangle}{\varepsilon_{pn} - \varepsilon_{p-qn'}}.
$$

(4.9b)

We see therefore using (4.3a), (4.9a) and (4.9b), that the expectation value of any operator can be written, correct to first-order in the displacement parameter λ, as

$$
\langle Z \rangle = \sum_{p} \sum_{n=1}^{M} (\langle\bar{\psi}_{pn}^{(+)}|\hat{Z}|\bar{\psi}_{pn}^{(+)}\rangle + \langle\bar{\psi}_{pn}^{(-)}|\hat{Z}|\bar{\psi}_{pn}^{(-)}\rangle - \langle\psi_{pn}|\hat{Z}|\psi_{pn}\rangle).
$$

(4.10)

Note that the summation over p runs over the primitive Brillouin zone. Evaluation of expression (4.10) for various observables in the super-cell, such as the Hellmann–Feynman forces and the charge density is central to our approach for phonon properties in the harmonic approximation.

5. Computational details

In this section we discuss how the formalism discussed above is turned into an efficient and practical scheme for first-principles calculation of phonon properties in the harmonic approximation. In what follows we shall be specifically concerned with the conventional plane-wave pseudopotential approach, although we believe that many of the ideas presented above are also applicable for other types of total-energy techniques. Our calculation begins with a determination of the form of the Kohn–Sham potential for the crystal in the absence of any phonon distortion. This quantity is routinely obtained using the standard techniques outlined below.

The calculation begins with the construction of the ionic potential of the solid using norm-conserving ionic pseudopotentials [14]. A self-consistent solution for the Hartree and exchange and correlation potentials appearing in the Kohn–Sham equations (4.1a– f) is obtained using an iterative scheme. The cycle starts with a guessed input form for the local Kohn–Sham potential and the corresponding Kohn–Sham eigenfunctions are then computed by solving the eigenvalue equation (4.1a). If we wish to solve for the wavefunctions $\psi_{pn}(r)$ the Bloch condition greatly restricts the size of Hamiltonian which needs to be diagonalised because only basis functions with Bloch wavevector p need to be considered. Thus in a plane-wave pseudopotential program, for example, only basis states of the form

$$\exp[\mathrm{i}(G + p) \cdot r] \tag{5.1a}$$

need be considered to compute the wavefunctions at wavevector p in the zone. The number of basis states implied by (5.1a) is of course still infinite and in practice we must truncate the basis set to some finite size. This is usually achieved by inclining all plane waves obeying

$$(G + p) \cdot (G + p) < G_{\mathrm{max}}^2 \tag{5.1b}$$

where G_{max} is the plane-wave cutoff. It will be convenient to define $N_{\mathrm{w}}(G_{\mathrm{max}})$ to be the number of plane waves selected by this algorithm. Our Hamiltonian thus has dimensions $N_{\mathrm{w}} \times N_{\mathrm{w}}$ and using iterative diagonalisation techniques the M valence band eigenvalues and eigenvectors can be obtained in order MN_{w}^2 operations [15]. Having thus obtained the Kohn–Sham wavefunctions, the charge density and output Kohn–Sham potential are constructed using (4.1d–f). The exchange and correlation contribution to the potential is usually computed in the local-density approximation, using exchange and correlation energies for the free electron gas, taken for example from Ceperley and Alder's [16] calculation. Unless the potentials are at self-consistency the input and output Kohn–Sham potentials will be different. A new input potential is therefore constructed using some type of mixing scheme on the output potential and the old input potential, and the self-consistency cycle is iterated until the input and output potentials have converged to the desired accuracy.

The sums over all the eigenfunctions in the solid, required for example to compute the charge density in (4.1d), cannot be done exactly as this would require a knowledge of the wavefunctions at every point in the zone. In practice this type of sum can be approximated using the special points method to sample the wavefunctions over the zone. Thus we write for any general operator, Z,

$$\langle Z \rangle \simeq \sum_{n=1}^{M} \sum_{j} w_j \langle p_j n | \hat{Z} | p_j n \rangle \tag{5.2}$$

where the special point wavevectors p_j and weights w_j can be generated, for example, by the Brillouin zone integration method of Monkhorst and Pack [17].

Having obtained the Kohn–Sham potential for the crystal with the atoms in their perfect crystalline positions we then choose a super-cell for the phonon of interest, ensuring condition (1.1) is obeyed, and construct the atomic basis of the cell freezing in the displacement pattern generated by our choice of parameters ζ and λ in (3.1). The ionic potential for the cell is then set up in the usual way. The zeroth-order self-consistent Kohn–Sham potential for the super-cell is easily constructed because this potential will

be zero at all reciprocal-lattice vectors, g, of the super-cell, unless g is coincident with a reciprocal-lattice vector of the primitive cell where we have simply

$$V_{\text{KS:L}}^{0\text{super}}(G) = V_{\text{KS:L}}^{0\text{prim}}(G). \tag{5.3}$$

We are therefore left with the problem of computing the first-order change in the self-consistent potential, which we obtain by reapplying the self-consistent iterative procedure. We simply take an input form for $V_{\text{KS:L}}^1(r)$ of the form given in (4.5). The functions $\varphi_p^{(+)}$ and $\varphi_p^{(-)}$ are then computed using the same special points mesh as was employed in the primitive cell calculation to select the vectors p. The symmetry of the phonon cell will usually be lower than that of the primitive cell, and care must be taken to redetermine which points in the mesh are related by symmetry and to recompute the special point weights in (5.3). In the plane-wave pseudopotential calculation we generate $\varphi_p^{(+)}$ by computing the valence band eigenfunctions of the Kohn–Sham Hamiltonian using basis states of the form

$$\exp[\mathrm{i}(G + p) \cdot r] \qquad \exp[\mathrm{i}(G + p + q) \cdot r] \tag{5.4a}$$

including in all waves for which

$$(G + p) \cdot (G + p) < G_{\text{max}}^2. \tag{5.4b}$$

The total number of basis states defined in this procedure will be $2N_w$ and thus using an iterative diagonalisation procedure the $2M$ valence band wavefunctions for $\varphi_{pi}^{(+)}$ can be obtained in order $8MN_w^2$ operations. Having thus obtained $\varphi_{pi}^{(+)}$ and $\varphi_{pi}^{(-)}$ on the special points set the output charge density is then constructed using (4.8)–(4.10), using the special points method to perform the Brillouin Zone integral in (4.10). The new output Kohn–Sham potential is thus obtained and the process iterated to self-consistency in the usual way.

It is clear from the above discussion that the computational effort required to perform the diagonalisation of the Kohn–Sham Hamiltonian with sufficient accuracy to obtain the dynamical matrix in the harmonic approximation is independent of the choice of phonon wavevector. Essentially the calculation of the two sets of valence band states $\varphi_{pi}^{(+)}$ and $\varphi_{pi}^{(-)}$ at each special point is just 16 times as costly as the computation of the primitive valence band Bloch wavefunction ψ_{pn}.

A further advantage of our scheme is that also allows the expectation value of any operator to be evaluated in a time which is independent of q, using equation (4.10). Let us consider, for example, the numerical work required to compute the expectation value of the first term on the right-hand side of (4.10) at any given special point. We have for our general operator $Z(r, r')$

$$\langle \tilde{\psi}_{pn}^{(+)} | \hat{Z} | \tilde{\psi}_{pn}^{(+)} \rangle = \sum_{gg'} \tilde{c}_{p+gn}^* Z(p + g, p + g') \tilde{c}_{p+g'n} \tag{5.5}$$

where,

$$\tilde{\psi}_{pn}^{(+)}(r) = \sum_g \tilde{c}_{p+gn} \exp[\mathrm{i}(p + g) \cdot r] \tag{5.5a}$$

and

$$Z(p + g, p + g') = \int\int \exp[\mathrm{i}(p + g) \cdot r] \, Z(r, r') \exp[\mathrm{i}(p + g') \cdot r'] \, \mathrm{d}r \, \mathrm{d}r' \tag{5.5b}$$

and where the sums over g and g' in (5.5) and (5.5a) need include only wavevectors of

the form G or $G + q$. We see therefore that the number of terms in the summation in (5.5) is of order $4N_w^2$ and which is not a function of q. Thus the computational effort to compute the expectation value of any operator correct to first order in the displacement parameter λ is independent of both the phonon wavevector and N_p.

In principle the total numerical work required to compute the Hellmann–Feynman forces should be independent of q in our approach, because using the results of section 3, the dynamical matrix can be constructed from the forces on just $2s$ atoms, and the arguments of the previous paragraph serve to show the force on a single atom may be derived in a time which does not depend on q. However, we have found in practice that the approach using forces on just $2s$ atoms can lead to rounding error problems, particularly with very long-wavelength phonons, where the total forces produced by a pure acoustic mode distortion will be very small. In this case we have found good numerical results can be obtained by computing the forces on all the atoms in the super-cell and solving for the vector τ in (3.3) by averaging over the forces in the cell using

$$\tau_\alpha^k = \frac{2}{N_p} \sum_{\{l\}} \exp[-\mathrm{i} q \cdot (l + m^k)] F_{l\alpha}^k \qquad (5.6)$$

In (5.6) the summation over the set of primitive vectors $\{l\}$ runs over all atoms of type k in the super-cell. For long-wavelength phonon calculations the time to compute the Hellmann–Feynman forces therefore scales linearly with N_p. It should be borne in mind that the calculation of the forces is only necessary on the final self-consistent cycle, and that the linear increase with N_p is much more favourable than the corresponding N_p^3 scaling of the convential super-cell approach.

We conclude, therefore, that in our frozen phonon technique the time spent in the traditionally expensive parts of plane-waves pseudopotential calculations, namely the diagonalisation of the Kohn–Sham Hamiltonian, and the computation of the non-local parts of the forces, is dramatically reduced. In our experience the amount of reorganisation of a total-energy program required to exploit this scheme is small. Some rearrangement of the special points generation section of the code was found to be necessary. In addition the algorithm for selection of the plane-wave basis set had to be changed and a routine written to perform the vector product in (4.8). However, once these changes had been implemented the major sections of the code, which set up the Hamiltonian, perform the iterative diagonalisation and compute the charge density and Hellmann–Feynman forces, could be run as they stood.

It should be pointed out that the run time of several sections of code will remain a function of q even after the changes outlined above. For example, the exchange and correlation potential is usually computed in real space using fast Fourier transforms (FFT) to convert the charge density reciprocal space to real space. The size of the grid will obviously increase in direct proportion to the super-cell size and therefore the time to transform the charge density to real space will scale as $N_p \ln (N_p)$. However, for the phonons we have studied so far with this technique the most significant part of the time is still spent in matrix diagonalisation.

6. Results and conclusions

We have used the above scheme to perform first-priciples calculations of frequencies and eigenvectors of long-wavelength phonon modes in silicon. The particular modes studied are at points $(\frac{1}{16}, \frac{1}{16}, \frac{1}{16}) 2\pi/a$ and $(\frac{1}{8}, 0, 0) 2\pi/a$ in the Brillouin zone, a, being the

Table 1. Summary of calculation on long-wavelength phonons in silicon

Phonon wavevector $(2\pi/a)$	Real-space basis vectors (a)			Mode	Frequency (experiment) (THz)	Frequency (calculation) (THz)	
$\frac{1}{16}\frac{1}{16}\frac{1}{16}$	0.0	8.0	8.0	TA	1.02†	1.01§	1.02‖
	0.0	−0.5	0.5	LA	1.87†	1.84§	1.88‖
	−0.5	0.0	0.5	TO	15.53‡	14.96§	15.14¶
				LO	15.53‡	14.98§	15.14¶
$\frac{1}{8}00$	8.0	0.0	0.0	TA	1.34†	1.34§	1.38‖
	0.0	0.5	0.5	LA	1.94†	1.92§	1.89‖
	0.0	−0.5	0.5	TO	15.53‡	14.87§	15.14¶
				LO	15.53‡	14.99§	15.14¶

† Value obtained using experimental values for the elastic constants from [18].
‡ Experimental value of zone-centre TO(Γ) phonon [19].
§ Value determined in this calculation.
‖ Frequency computed from calculated elastic constants [21].
¶ Calculated TO(Γ) phonon frequency using same pseudopotential, Monkhorst–Pack mesh and plane-wave cut-off as the long-wavelength calculation.

lattice constant for silicon. Both these modes can be studied using 32 atom super-cells. We used a non-local norm-conserving pseudopotential generated by the method due to Kerker [14]. Our calculation included all plane waves up to 20 Ryd in energy and used the Ceperley–Alder form of the local-density approximation for exchange and correlation [16]. The Brillouin zone integration was performed using a (4,4,4) Monkhorst–Pack mesh [17] which had been symmetrised using the point group operations for the silicon Bravais lattice. The lattice constant was set to its experimental value of 5.429 Å. For the silicon phonons studied here, there is in fact no need to compute the forces for six independent choices of ζ in (3.1); sufficient information can be obtained from a single calculation, because of the symmetry constraints on the dynamical matrix. We chose our values of ζ to be

$$(\zeta_x^1, \zeta_y^1, \zeta_z^1, \zeta_x^{\bar{1}}, \zeta_y^{\bar{1}}, \zeta_z^{\bar{1}}) = (0.001a/\sqrt{1.81})(1.0, 0.0, 0.0, 0.9, 0.0, 0.0) \qquad (6.1a)$$

for the $(\frac{1}{16}, \frac{1}{16}, \frac{1}{16})2\pi/a$ phonon and

$$(\zeta_x^1, \zeta_y^1, \zeta_z^1, \zeta_x^{\bar{1}}, \zeta_y^{\bar{1}}, \zeta_z^{\bar{1}}) = (0.001a/\sqrt{5.43})(1.0, 1.0, 1.0, 0.9, 0.9, 0.9) \qquad (6.1b)$$

for the mode at $(\frac{1}{8}, 0, 0)2\pi/a$. With these forms of displacement vector the distorted super-cells had some residual symmetry, and several points in the Monkhorst–Pack mesh were symmetry related, allowing a significant reduction in the computational effort for each self-consistency cycle. The dynamical matrix was constructed by calculating the Hellmann–Feynman forces on all the atoms in the cell using (5.6) to obtain the vector τ. The above choices of parameters correspond to a value of N_w of about 400 plane waves and thus the largest Hamiltonian which had to be diagonalised in our calculation had dimensions of roughly 800 × 800. By way of contrast, the conventional super-cell frozen phonon method, would entail the diagonalisation of a 6400 × 6400 element array at each special point of the super-cell in the 32 atom cells investigated here.

The results of our calculation together with details of the super-cells employed are summarised in table 1. The frequencies of the acoustic modes are in excellent agreement with those predicted using the experimental elastic constants of silicon assuming that

the dispersion of the modes away from the origin of the zone is linear [18]. The optic modes are slightly softer than the experimental value for the TO(Γ) mode [19], although they do agree well with the calculated TO(Γ) frequency obtained by performing a frozen phonon calculation using a two-atom primitive unit cell with the same basis set cut-off, pseudopotential and Monkhorst–Pack mesh as were employed in the 32-atom calculation. We have also analysed the polarisation vectors of the acoustic modes to compute the size of the internal strain parameter and obtained a value of 0.53 ± 0.1. This is in excellent agreement with the numerical value of 0.53 found by Cardona *et al* [20] using the inter-planar force method, and also agrees with the theoretical value obtained from first-principles macroscopic strain calculations [21] and the recent experimental value of Cousins *et al* [22].

The emphasis in this paper has been on describing a scheme for performing frozen phonon calculations which can be implemented by making a small number of changes to an exisiting total-energy program. It should, however, be pointed out that with further reprogramming there are a number of extensions and uses for the method. The technique could be used to compute efficiently the linear response of the solid to any external potential of the form

$$V_{\text{ext}}(\mathbf{r}) = \sum_{G} V_{\text{ext}}(\mathbf{G} + \mathbf{q}) \exp[\mathrm{i}(\mathbf{G} + \mathbf{q}) \cdot \mathbf{r}] + \text{CC} \tag{6.2}$$

where the $V_{\text{ext}}(\mathbf{G} + \mathbf{q})$ are completely arbitrary, and need not correspond to a potential which can be realised by making small displacements of the ions away from equilibrium. Thus one could, for example, use the approach to compute a column of the static inverse dielectric response function, $\varepsilon^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q})$, by choosing an external potential of the form

$$V_{\text{ext}}(\mathbf{r}) = V(\mathbf{q}) \exp(\mathrm{i}\mathbf{q} \cdot \mathbf{r}) + \text{CC} \tag{6.3}$$

and using the self-consistency procedure described above to compute the induced charge density and the corresponding total potential. Also in the current implementation of the method the size of the potential files, the charge density arrays and the FFT grids for the exchange and correlation potential are all grown linearly with the super-cell size. Memory requirements will therefore eventually place an upper bound on the size of cell which can be addressed in this formulation. However, these limitations are certainly not intrinsic to the method, as the charge density, for example, need only be stored at primitive vectors $\mathbf{G}$ and vectors of the form $\mathbf{G} + \mathbf{q}$ and $\mathbf{G} - \mathbf{q}$. If the method were developed to include such refinements it should be possible to study phonons at completely arbitrary points in the zone and modes, whose wavevectors are incommensurate with the lattice and which therefore cannot be studied in any finite super-cell.

In conclusion we have presented a new method for computing the dynamical properties of solids in the harmonic approximation, which has been found to produce dramatic improvements in the efficiency of frozen phonon calculations. We are currently using the technique described above to compute absolute deformation potentials of long-wavelength phonons [23]. Recently, we successfullly applied the method to compute the temperature dependence of the band gap of silicon, which can be related to the degree to which phonon modes soften upon creation of an electron–hole pair [24].

Acknowledgments

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