# *Ab Initio* Calculation of Force Constants and Full Phonon Dispersions

Siqing Wei and M. Y. Chou
*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430*
(Received 2 June 1992)

We present a method to calculate the full phonon spectrum using the local-density approximation and Hellmann-Feynman forces. By a limited number of supercell calculations of the planar force constants, the interatomic force constant matrices are determined. One can then construct the dynamical matrix for any arbitrary wave vector in the Brillouin zone. We describe in detail the procedure for elements in the diamond structure and derive the phonon dispersion curves for Si. The anharmonic effects can also be studied by the present method.

PACS numbers: 63.20.Dj

The energy dispersion of phonons has long been a focus of interest because it provides rich information about the dynamical properties of the material [1]. In particular, it is an essential input in the calculation of heat capacities, thermal expansion coefficients, electron-phonon interactions, etc., for the crystal. Attempts have also been made to study the vibrational properties of complex systems, such as semiconductor alloys and superlattices, based on information about the force constants of the constituent materials [2,3]. *Ab initio* calculations of the force constant matrices and phonon spectra will not only give an accurate database for these applications but also provide stringent tests of various empirical models [4,5].

There are basically two methods in use for the calculations of phonon frequencies within the framework of the local-density approximation (LDA): (1) the linear response theory with dielectric screening in which atomic displacements are treated as perturbations [6] and (2) the "direct" approach which calculates the total energy of the distorted system or the Hellmann-Feynman forces [7] on the atoms using the supercell method. Each of these methods has its advantages and drawbacks. In the first approach, the response to perturbations was calculated in the past by inverting the dielectric matrix [6] which is computationally cumbersome and restrictive. Recently, new schemes have been proposed to obtain the linear response either by iterating up to self-consistency [8] or by solving an integral equation [9] for the change in the electron density. These methods can handle perturbations of arbitrary wave vectors, yet only linear effects are considered.

On the other hand, the direct approach which considers periodic distortions using supercells is computationally straightforward. It handles the perturbed and unperturbed systems on the same footing under the frozen-phonon approximation, and allows one to study, in principle, both linear and nonlinear effects. Phonon frequencies for isolated symmetry points can be easily calculated [10] by the pseudopotential LDA method. However, the supercell size increases rapidly as the symmetry decreases. Only the dispersions along a few high-symmetry directions have been reported [11-14] using this direct approach.

In this paper, we will present a procedure to obtain the full real space interatomic force constant matrices using the direct supercell approach. It is based on the observation that the planar force constants are in fact linear combinations of these matrix elements. Therefore from a limited set of planar force constants for some high-symmetry directions (which can be easily and accurately determined using supercells), the three-dimensional force constant matrices can be constructed. These force constants of the perfect crystal are particularly useful in the study of the dynamical properties of other mixed systems [2,3,15]. In addition, phonon frequencies associated with any wave vector in the Brillouin zone can be obtained from these force constants. The method requires only the standard total energy codes with 10–20 atoms per cell and can be easily applied to both insulators and metals.

One distinct advantage of this method over the linear response theory [8] is its ability to study the anharmonic effects as well. In the force calculation, the relation between the force and the displacement may not be exactly linear, nor along the same direction. Although only the harmonic term will be discussed in the present Letter, information on anharmonicity can be readily available if higher-order terms are kept in the planar force calculation. Following similar procedures outlined below, information on the cubic or higher-order force constants (which will be third- or higher-rank tensors) can be obtained. This will be the subject of further investigations.

In the harmonic approximation, the energy change resulting from small displacements of atoms is usually written in the general form

$$U_{\text{harm}}=\frac{1}{2}\sum_{\mathbf{R},\mathbf{R}',\alpha,\beta}\mathbf{u}^{\alpha}(\mathbf{R})\cdot\mathbf{D}^{\alpha\beta}(\mathbf{R}-\mathbf{R}')\cdot\mathbf{u}^{\beta}(\mathbf{R}')\,, \qquad (1)$$

where $\mathbf{u}^{\alpha}(\mathbf{R})$ is the deviation from equilibrium of atom $\alpha$ in the unit cell associated with lattice vector $\mathbf{R}$, and $\mathbf{D}^{\alpha\beta}(\mathbf{R}-\mathbf{R}')$ is the force constant matrix connecting atom $\alpha$ in unit cell $\mathbf{R}$ and atom $\beta$ in unit cell $\mathbf{R}'$. ($\alpha$ and $\beta$ are indices of atoms in the basis.) There are some general symmetries that must be obeyed by the matrices $\mathbf{D}^{\alpha\beta}(\mathbf{R})$ [16], yet it has not been computationally feasible to calculate these matrices by directly evaluating the LDA total energies for a series of geometries with isolated distortions. However, the one-dimensional (planar) force constants along some high-symmetry directions can be calculated by evaluating the Hellmann-Feynman forces in the presence of a simultaneous displacement of one whole layer of (equivalent) atoms. (For details, see Refs. [13,14].) Translational symmetry is lost only along the direction normal to the displaced layer. It is analogous to a coupled linear chain problem in which the polarization directions of the normal modes are well defined. As long as the interaction decays reasonably fast, the supercell method can be used.

In general (within the harmonic approximation), the force on atom $\alpha$ in the $n$th layer, $\mathbf{F}^{\alpha}(n)$, is proportional to the collective displacement of atom $\beta$ in the $m$th layer, $\mathbf{u}^{\beta}(m)$:

$$-\mathbf{F}^{\alpha}(n)=\sum_{m,\beta}\boldsymbol{\lambda}^{\alpha\beta}(n-m)\cdot\mathbf{u}^{\beta}(m)\,, \tag{2}$$

where $\boldsymbol{\lambda}^{\alpha\beta}(n)$ is the planar force constant matrix for the chosen direction. Normally longitudinal ($L$) or transverse ($T$) displacements of the atomic layer are made in the calculation and the corresponding forces are evaluated. The resulting force constants will then be the projection $\hat{\mathbf{e}}_i\cdot\boldsymbol{\lambda}^{\alpha\beta}(n)\cdot\hat{\mathbf{e}}_j$, where $i$ and $j$ represent the polarization directions ($T$ or $L$). Knowing these projected force constants and polarization vectors, it is straightforward to map out the matrix $\boldsymbol{\lambda}^{\alpha\beta}(n)$ by a unitary transformation.

The relation between $\boldsymbol{\lambda}^{\alpha\beta}(n)$ and $\mathbf{D}^{\alpha\beta}(\mathbf{R})$ is simply

$$\boldsymbol{\lambda}^{\alpha\beta}(n)=\sum_{\mathbf{R},\hat{\mathbf{e}}\cdot(\mathbf{R}+\boldsymbol{\tau}_{\alpha\beta})=d_n}\mathbf{D}^{\alpha\beta}(\mathbf{R})\,, \tag{3}$$

where $\hat{\mathbf{e}}$ is the unit vector normal to the atomic layer, $d_n$ is the distance between the displaced layer and the layer where the force is being considered, and $\boldsymbol{\tau}_{\alpha\beta}=\boldsymbol{\tau}_\alpha-\boldsymbol{\tau}_\beta$ is the vector connecting atoms $\alpha$ and $\beta$ in the basis. By repeating the procedure for other high-symmetry directions, one obtains a set of linear equations for $\mathbf{D}^{\alpha\beta}(\mathbf{R})$. The crystal symmetry can also be used to reduce the number of independent variables and the matrix elements of $\mathbf{D}^{\alpha\beta}(\mathbf{R})$ can be solved if a sufficient number of planar constants are known.

In practice, the summation over $\mathbf{R}$ is limited to those vectors within a sphere of radius $R_{\max}$, which means that only the interaction between atoms separated by a cutoff distance is considered. $R_{\max}$ needs to be determined carefully by the convergence study in the calculation. There are several ways to check it, including inspecting the decay of the planar force constants, checking the sum rule, and the convergence of elastic constants.

We will use the diamond structure as an example which has two atoms in the primitive cell. Following the notations in Refs. [13,14], they are denoted by $a$ and $c$, respectively, with $\boldsymbol{\tau}_{ac}=(a/4,a/4,a/4)$. The four kinds of $3\times3$ interatomic force constant matrices to be considered are $\mathbf{D}^{cc}(\mathbf{R})$, $\mathbf{D}^{ca}(\mathbf{R})$, $\mathbf{D}^{ac}(\mathbf{R})$, and $\mathbf{D}^{aa}(\mathbf{R})$. Taking into account the inversion symmetry and the definition of the force constant as the second derivative of the interaction energy, we have

$$\begin{aligned}&\mathbf{D}^{ac}(\mathbf{R})=\mathbf{D}^{ca}(-\mathbf{R})\,,\\&\mathbf{D}^{cc}(\mathbf{R})=\mathbf{D}^{aa}(-\mathbf{R})^{T}\,,\\&\mathbf{D}^{aa}(\mathbf{R})=D^{cc}(\mathbf{R})^{T}\,,\\&\mathbf{D}^{ca}(\mathbf{R})=\mathbf{D}^{ca}(\mathbf{R})^{T}\,.\end{aligned} \tag{4}$$

Therefore only two of the above four kinds of matrices need to be evaluated. Moreover, the force constant matrix transforms as a second-rank tensor,

$$\mathbf{D}^{\alpha\beta}(\mathbf{R}')=S\cdot\mathbf{D}^{\alpha\beta}(\mathbf{R})\cdot S^{-1}\,, \tag{5}$$

where $S$ is any symmetry operation that maps the atom at $\mathbf{R}+\boldsymbol{\tau}_{\alpha\beta}$ to that at $\mathbf{R}'+\boldsymbol{\tau}_{\alpha\beta}$.

The present calculation for silicon included the interatomic force constants up to the eighth nearest neighbors, which results in *31* independent matrix elements (see Table I). The planar force constants are evaluated for the [100], [110], and [111] directions using the supercell consisting of eight (or twelve), sixteen and eight atoms, respectively. In our calculations we use the Ceperley-Alder [17] exchange-correlation form (parametrized by Perdew-Zunger [18]) with a plane-wave energy cutoff of 12 Ry. The Brillouin zone is sampled by a special $k$-point set equivalent to the 10 special $k$ points in the perfect diamond structure, except for the [100] TA mode where a 28 special $k$ point set is used. The ion-electron interaction is approximated by a soft pseudopotential developed recently [19]. Five different displacements $(0,\pm u,\pm 2u)$

TABLE I. Coordinates of representative neighbors and corresponding force constant matrix elements (with a plane-wave energy cutoff of 12 Ry) for Si. Coordinates are expressed in units of $a/4$ with $a$ being the cubic lattice constant. The notations of the force constant matrix elements follow Ref. [21].

| NN | Coordinates | Force constants ($10^5$ dyn/cm) |
|---|---|---|
| 0 | (0,0,0) | $a_0=2.237$ |
| 1 | (1,1,1) | $\alpha_1=-0.547$, $\beta_1=-0.388$ |
| 2 | (2,2,0) | $\mu_2=-0.035$, $\nu_2=0.068$ |
|  |  | $\delta_2=-0.029$, $\lambda_2=0.017$ |
| 3 | $(\bar{1},\bar{1},\bar{3})$ | $\mu_3=0.007$, $\nu_3=0.001$ |
|  |  | $\delta_3=-0.010$, $\lambda_3=0.008$ |
| 4 | (0,0,4) | $\mu_4=-0.013$, $\lambda_4=0.018$ |
| 5 | (3,3,1) | $\mu_5=-0.002$, $\nu_5=-0.030$ |
|  |  | $\delta_5=-0.001$, $\lambda_5=0.004$ |
| 6 | (2,2,4) | $\mu_6=-0.002$, $\nu_6=0.001$ |
|  |  | $\delta_6=0.006$, $\lambda_6=-0.000$ |
|  |  | $\gamma_6=0.002$, |
| 7 | (1,1,5) | $\mu_7=0.000$, $\nu_7=0.004$ |
|  |  | $\delta_7=0.004$, $\lambda_7=0.002$ |
| 7′ | $(\bar{3},\bar{3},\bar{3})$ | $\alpha_7=0.004$, $\beta_7=-0.002$ |
| 8 | (4,4,0) | $\mu_8=-0.002$, $\nu_8=0.012$ |
|  |  | $\delta_8=-0.002$, $\lambda_8=-0.008$ |

are calculated for each supercell to ensure the anharmonic effect is eliminated for the calculated planar force constants. We use a least-squares fit to solve for the best set of the 31 matrix elements of the interatomic force constants from 51 linear equations. The standard deviation is less than 0.3% of the average planar force constants calculated, indicating the consistency of the calculations for various directions.

The phonon frequency is obtained by solving the eigenvalues of the dynamical matrix, $\Phi(\mathbf{k})$, the Fourier transform of the $6\times6$ real space force constant matrix,

$$[\Phi(\mathbf{k})]=\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}}\begin{bmatrix}\mathbf{D}^{cc}(\mathbf{R}) & \mathbf{D}^{ca}(\mathbf{R})\\ \mathbf{D}^{ac}(\mathbf{R}) & \mathbf{D}^{aa}(\mathbf{R})\end{bmatrix} =\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}}\begin{bmatrix}D^{cc}(\mathbf{R}) & D^{ca}(\mathbf{R})\\ D^{ca}(-\mathbf{R}) & D^{cc}(\mathbf{R})^{T}\end{bmatrix}, \qquad (6)$$

where **k** is a wave vector. Figure 1 shows the calculated phonon dispersion curve, including the lower-symmetry directions *X*-*W*-*L*-*K*, compared with the experimental data [20]. From the figure, we can see that the calculated values are in excellent agreement with experiment, except for the zone-boundary TA modes (*X* and *L* points). As noted by Herman [21], the flatness of the dispersion curve at the zone boundary is the result of the longer-range interactions. To check the real space convergence, we have performed additional calculations for the [100] TA mode; (1) the unit cell is increased from twelve to sixteen atoms to see if there is any long-range interaction contribution; (2) the TA(*X*) mode is calculated directly using a four-atom cell [10] with the frequency evaluated from both the total-energy change and forces. The results, shown in Table II, indicate that the calculated TA(*X*) phonon frequencies are consistently lower than the experimental value, while these calculated frequencies agree well with each other. The comparison indicates that the lower frequency we are getting is related to the LDA or pseudopotential method, or the cutoff of the basis set used. It does not result from the method proposed here for calculating the phonon frequencies. In fact, as the energy cutoff of the plane waves is increased from 12 to 18 Ry, we obtain a better agreement with experiment for the TA frequency at *X* (Table II).

TABLE II. Comparison of TA(*X*) and TA(*L*) phonon frequencies of Si calculated by different methods: direct frozen-phonon calculation of the energy or the forces, planar force constant (PF) calculation with 12 or 16 atomic layers, and dynamical matrix (DM) calculation with interatomic force constants. The energy cutoff of the plane-wave expansion is 12 or 18 Ry. Experimental values [20] are also shown. Frequencies in THz ($10^{12}$ Hz).

| | Frozen phonon | | Planar force | | | |
|---|---|---|---|---|---|---|
| | Energy | Force | 12-layer | 16-layer | DM | EXP |
| | | | 12 Ry | | | |
| TA(*X*) | 4.00 | 4.00 | 4.10 | 4.01 | 4.11 | 4.49 |
| TA(*L*) | 3.12 | 3.12 | 3.06 | | 2.99 | 3.43 |
| | | | 18 Ry | | | |
| TA(*X*) | 4.22 | 4.22 | | | | 4.49 |

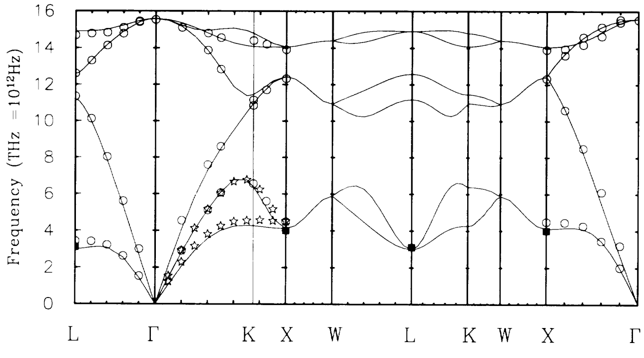

FIG. 1. Phonon dispersion of Si calculated from the interatomic force constant matrices with a plane-wave energy cutoff of 12 Ry. The experimental values [20] are shown by open circles (Dolling, 296 K) and stars (Nilsson and Nelin, 300 K). The phonon frequencies TA(*X*) and TA(*L*) from direct frozen-phonon calculations are marked by solid squares.

We have shown above the real space convergence of TA(*X*) using both the frozen-phonon calculation and a larger unit cell. It has been well recognized that, to achieve the flatness of the TA mode, it is vital to include at least the fifth nearest neighbors [21]. A more recent study [22] found the effect of adding farther interactions to be minimal. We have calculated the force constants up to the eighth nearest neighbors which should be sufficient for Si. We have also checked the bulk modulus calculated from the force constants, which is within 2% of the value obtained directly from the equation of state.

In conclusion, we have presented a new approach to obtain the phonon dispersion over the entire Brillouin zone by calculating the real space interatomic force constant matrices from first principles. The major advantage of this method is that only simple supercell calculations of the planar forces are needed. The calculation is within the framework of the LDA and the pseudopotential method, and hence it has the predicting power for new materials. Although only the harmonic interaction is considered here, the anharmonic effect can also be studied in principle by keeping higher-order terms in the forces. The formalism is general with no restrictions on the crystal structure or electronic structure.

We thank Dr. D. C. Allan for providing some useful references. This work was supported in part by NSF and DOE. M.Y.C. acknowledges the support from the Sloan and Packard Foundations.

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