Ab initio phonon dynamics of rhodium from a generalized supercell approach

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We present a generalization of the supercell approach to the *ab initio* determination of the complete lattice dynamics. Combining force calculations for supercells of arbitrary shapes greatly increases the number of accessible interatomic force constants without the necessity to resort to large supercell sizes. The method allows a systematic *a priori* search for optimal supercell geometries as well as *a posteriori* improvements of calculations already performed. Its ability to efficiently handle systems with longer-range lattice interactions is demonstrated for the transition metal rhodium. The present approach has the potential to extend the applicability of the conceptually simple direct approach to the calculation of the complete phonon spectra for lattices with larger unit cells. [S0163-1829(98)03614-5]

Recent advances in numerical methods and computer technology have reinforced attempts to obtain the complete phonon dispersions of crystalline solids from first principles. An accurate knowledge of the phonon spectrum, or equivalently of the interatomic force constants (IFC), is a prerequisite for the calculation of various dynamical and thermodynamical properties, as, e.g., thermal expansion, heat capacity, or electron-phonon coupling. Basically, two approaches have been considered for an *ab initio* calculation of lattice dynamics, the linear response or dielectric theory and the direct supercell approach. In the linear response method, changes in the electron density arising from atomic displacements are treated perturbationally. Originally, this has been done by inverting the dielectric matrix.[1] This method had only limited success, because it required the inversion of large matrices and numerically expensive summations over many unoccupied states. Recently, alternative approaches have been developed, based on the solid-state version of the Sternheimer equation, that overcome some of the main disadvantages of the dielectric matrix method.[2,3] By Fourier transformation of the dynamical matrix obtained on a regular mesh in reciprocal space, real-space force constants have been calculated for several semiconductors and, more recently, for metallic systems.[2,4]

The direct approach makes no conceptional distinction in the treatment of the unperturbed and the perturbed lattice. Supercell geometries are employed to handle atom displacements, and phonon frequencies are either extracted form differences in the total energy for the undistorted and distorted lattice (frozen phonon) or from forces acting on atoms in the distorted geometry (using the Hellmann-Feynman theorem). This method principally allows the study of anharmonic force constants to any order, but is restricted to phonons with momenta commensurate to the supercell. Because the numerical effort increases drastically with the size of the supercell, the direct approach has been applied mainly to phonons at high-symmetry points or along high-symmetry directions (via interplanar force constants) of the Brillouin zone (BZ). For the same reason, a determination of all relevant IFC's using a single large supercell is only feasible for systems with interactions of very short range.[5,6]

A possible way to circumvent this problem explores the linear relationship (in harmonic approximation) between the forces obtained in a supercell calculation and the IFC's. By combining results for several supercells, the IFC's can be obtained from a least-square fit. Until now, the only implementation of this idea has been presented by Wei and Chou[7] for the insulators silicon and germanium using a combination of planar force constants.

In this work, we generalize this approach to supercells of arbitrary shapes. Taking the fcc transition metal rhodium as an example, we demonstrate that this method allows us to extract all relevant force constants even for systems with lattice interaction of long range in real space, thereby retaining the conceptual simplicity of the direct approach. We find that the proper choice of supercell geometries is crucial for the efficiency of the method, and that supercells with low symmetry are generally favored over those with high symmetry.

In harmonic approximation, the complete information about the lattice dynamics is contained in the real-space force constants, which are given as second derivatives of the total energy of the system with respect to displacements $\mathbf{u}(\ell)$ of atoms at lattice sites $\mathbf{R}(\ell)$ (for simplicity, we restrict the discussion to monoatomic lattices only),

$$\Phi_{\alpha\beta}(\ell,\ell') = \partial^2 E_{\mathrm{tot}} / \partial u_\alpha(\ell)\, \partial u_\beta(\ell'), \tag{1}$$

where α and β denote cartesian coordinates. Φ enters the linear relationship between the force acting on atom ℓ and the displacements for a given lattice deformation,

$$F_\alpha(\ell) = -\sum_{\ell'\beta} \Phi_{\alpha\beta}(\ell,\ell') u_\beta(\ell'). \tag{2}$$

In a supercell calculation, atoms are labeled by two indices, $\ell \rightarrow (m,L)$, where m denotes the atoms inside a supercell, and L denotes the translation vectors of the supercell lattice. When displacing the atom at the origin by $\mathbf{v}$, the force experienced by atom m is given by the linear relationship

$$F_\alpha(m) = -\sum_\beta \tilde{\Phi}_{\alpha\beta}(m) v_\beta , \tag{3}$$

where the supercell force constants $\tilde{\Phi}$ are related to the lattice IFC's by

$$\tilde{\Phi}_{\alpha\beta}(m) = \sum_L \Phi_{\alpha\beta}(m,L). \tag{4}$$

For example, in the case of a supercell stretched along a high-symmetry direction, $\tilde{\Phi}$ can be expressed in terms of the interplanar force constants.

From the knowledge of $\tilde{\Phi}$ for a single supercell, Eq. (4) can be inverted to extract the IFC's only if the interaction is sufficiently short range such that contributions from neighboring cells ($L \neq 0$) can be neglected. This usually requires large supercells even for systems with short-range interactions.

The basic idea of the present approach is to obtain $\tilde{\Phi}$ for several supercells, and to replace Eq. (4) by a set of equations, which may eventually be inverted to obtain all relevant Φ's even for longer-range interactions without the necessity of involving large supercells. In practice, the inversion procedure is done by introducing a cutoff R_c for the lattice interaction, i.e., to set $\Phi_{\alpha\beta}(\ell,\ell') = 0$ for $|\mathbf{R}(\ell) - \mathbf{R}(\ell')| > R_c$. By making use of their transformation properties with respect to the space-group symmetries,[8] one can identify the independent components of the lattice and supercell IFC's.[9] For a given combination of supercells, Eq. (4) is then transformed into a set of linear equations,

$$\eta_i = \sum_{j=1}^{N_L} M_{ij}(R_c)\xi_j , \quad i = 1, \ldots, N_S , \tag{5}$$

which relates the N_L independent components ξ_j of the lattice IFC's to the N_S independent components η_i of the set of supercells. Generally, the inversion of Eq. (5) is replaced by a least-square fit of the IFC's to the calculated supercell components η_i. Each combination of supercells can be characterized by a cutoff $R_c^{\max}$ defined as the largest cutoff for which a unique least-square solution of Eq. (5) still exists. It can be used as a measure for the amount of information extractable from the given supercell set.

The matrix M possesses the important property that it is solely determined by the chosen cutoff R_c and by the geometries of the supercells, but is independent of the force constants. As a consequence, also $R_c^{\max}$ is a plain geometric quantity. This opens the way for (i) *a priori* searches for optimal combinations of supercells before performing any *first-principles* calculation, and (ii) *a posteriori* improvements of existing calculations by adding a suitable supercell geometry, which optimally increases $R_c^{\max}$.

To demonstrate the usefulness of the present approach, we have applied it to the phonon spectrum of the fcc transition metal rhodium. In a recent theoretical and experimental work,[10] it has been shown that the phonon dispersions of Rh exhibit very pronounced anomalies along high-symmetry directions [especially along the (110) direction] indicating a rather long range of the lattice interaction. This is corroborated by the finding that a satisfactory fit of the phonon spectra with a phenomenological force constant model could only be achieved by taking into account interactions up to at least the ninth neighbor. Thus Rh constitutes a stringent test case for the present method.

All calculations reported below were performed within the local-density-functional approximation using a pseudopotential approach. The electronic wave functions are represented in terms of a mixed basis set consisting of a linear combination of plane waves up to a kinetic energy of 10.5 Ry and five localized d orbitals, which are atomic $4d$ pseudoorbitals smoothly cut off at a radius 2.55 a.u.[11] Norm-conserving pseudopotentials of the Hamann-Schlueter-Chiang type (for details see Ref. 10) and the Hedin-Lundqvist parametrization for the exchange and correlation potential have been used. The k-point sampling was performed using a Gaussian broadening with a width of 0.2 eV.[12] The theoretical lattice constant of 3.806 Å has been used throughout. Supercell force constants were derived from force calculations for geometries with a single atom displaced by 0.02 Å. To eliminate spurious contributions arising from the low symmetry of the supercell, forces obtained for the undistorted geometry have been subtracted, and corrections for anharmonic contributions have been taken into account.[13]

As the starting point, we took the *ab initio* supercell calculations along the high-symmetry directions (100), (110), and (111) (18 atomic layers each, 30–200 special k points in the irreducible BZ) already reported in Ref. 10. Despite their large number of independent supercell force constants of $N_S = 70$, the combination of these three supercells allows only to deduce IFC's up to the fourth-neighbor shell. To find an optimal supplement to this set of high-symmetry supercells (HS), we have carried out searches in the space of supercells with a fixed volume, choosing those which resulted in the largest $R_c^{\max}$ when combined with HS. Generally, this procedure leads to supercells with very low symmetry. For the actual calculation, we have chosen a supercell containing 26 atoms (called cell 26 in the following), which is defined by basis vectors $(1\,0\,5), (-5\,0\,1), (1\,-2\,1)$ (in units of $a/2$), and which increases $R_c^{\max}$ to the 22nd-neighbor shell. Some properties of the used cells are summarized in Table I. Adding instead a supercell suitable for obtaining interplanar force constants along lower-symmetry directions, as proposed by Wei and Chou,[7] proved to be less efficient, because they only gradually increase $R_c^{\max}$.

Cell 26 possesses a very low symmetry (only inversion remains) and therefore requires an increased numerical effort for a single force calculation (we used 160 k points in the irreducible BZ). Furthermore, a larger number of atom displacements is needed to obtain the complete set of supercell force constants. Nevertheless, it is by far superior to high-symmetry cells. For example, combining HS with a $5\times5\times5$ fcc supercell with 125 atoms, which possesses the full cubic symmetry, increases $R_c^{\max}$ only to the ninth-neighbor shell (see Table I). Clearly, the disadvantage of a large number of atoms outweighs the reduction in numerical labor due to high symmetry.

TABLE I. Properties of supercells and combinations of supercells used in the calculation of the lattice force constants. HS denotes the combination of the three supercells stretched along high-symmetry directions (100), (110), and (111); fcc5 denotes the $5\times5\times5$ fcc supercell, and cell 26 the low-symmetry cell with 26 atoms as described in the text. $N_{\rm at}$ denotes the number of atoms in the supercell, and $n_{\rm dis}$ is the number of distinct atomic displacements, which have to be considered to obtain the complete set of supercell force constants. N_S and N_L are the number of independent components for the supercells and lattice, respectively. The latter is given for the maximum cutoff $R_c^{\rm max}$.

Cell	$N_{\rm at}$	$n_{\rm dis}$	N_S	NN($R_c^{\rm max}$)	$N_L(R_c^{\rm max})$
(100)	18	2	20		
(110)	18	3	30		
(111)	18	2	20		
fcc5	125	1	27	6	18
cell 26	26	3	84	12	45
Cell combinations					
HS			70	4	12
HS+fcc5			97	9	33
HS+cell 26			154	22	110

Table II shows the IFC's as obtained from fits to the supercell force constants of HS and cell 26. We present results for R_c of 9.5 Å (12th NN) and 11.2 Å (16th NN) (where NN is nearest neighbor), respectively, to demonstrate the sensitivity of the IFC's on the cutoff. Although the number of variables increases from 45 to 72, the standard deviation only drops from 2.5% to 1.7% of the average supercell force constants for the larger cutoff. The most prominent features are the large values found for the (330) IFC's. They are in contrast to the small values of the (411) IFC's, which belong to the same ninth-neighbor shell. Both findings are in full agreement with the analysis of the experimental phonon dispersion.[10]

The importance of the (330) interaction is also born out in a study of the effective interaction range. When performing a series of fits with increasing cutoff R_c, the standard deviation showed a drastic drop when the (330) bond was included. Further increases in R_c resulted in steady but minor improvements only. We also found that it is important to have a sufficient overdeterminancy of the system of linear equations, i.e., to perform fits for $R_c \ll R_c^{\rm max}$ in order to get a numerically stable and physically plausible fit. For $R_c \approx R_c^{\rm max}$, the fit procedure overestimates the IFC's for large distances, giving rise to unphysical oscillating behavior in the phonon dispersions. For this reason, the knowledge of the supercell force constants for cell 26 alone is not sufficient for obtaining reliable IFC's although its related $R_c^{\rm max}$ is beyond the (330) shell.

In Fig. 1, the phonon dispersions obtained from the fitted values of the force constants are compared with results from neutron scattering experiments.[10] Very good agreement with the experimental data is found not only for the high-symmetry directions, where the positions of the anomalies are reproduced correctly, but also along lines near the BZ boundary. The latter represents a more direct test of our method, because none of these phonon frequencies can be extracted from calculations based on only one of the supercells considered above.

As discussed in detail in Ref. 10, the phonon anomalies in the dispersion relations of Rh can be understood as weak Kohn anomalies, and their positions in reciprocal space are linked to the geometrical shape of the Fermi surface. The

TABLE II. Interatomic force constants (in 10^3 dyn/cm) up to the 12th nearest-neighbor shell for two fits taking into account all force constants up to the 12th and 16th nearest-neighbor shells, respectively.

NN	Index	Comp			12th NN			16th NN		
0	000	xx			−193.66			−192.78		
1	110	xx	zz	xy	18.89	−1.28	21.18	18.73	−1.16	21.21
2	200	xx	yy		8.01	−3.29		8.38	−3.43	
3	211	xx	yy	xz	3.04	1.44	1.56	3.11	1.43	1.43
		yz			−0.16			−0.28		
4	220	xx	zz	xy	−0.03	−0.21	−0.28	−0.24	−0.47	−0.04
5	310	xx	yy	zz	0.06	0.02	0.21	0.11	−0.05	0.17
		xy			−0.16			0.01		
6	222	xx	xy		0.40	0.25		−0.01	0.08	
7	321	xx	yy	zz	−0.87	−0.01	−0.37	0.80	0.20	−0.23
		xy	xz	yz	−0.22	−0.78	−0.31	−0.20	−0.69	−0.20
8	400	xx	yy		−0.71	−0.58		−0.50	−0.52	
9	411	xx	yy	xy	−0.08	0.13	0.02	−0.08	0.25	−0.08
		yz			0.07			0.17		
9′	330	xx	zz	xy	2.27	0.07	2.12	2.32	−0.06	2.65
10	420	xx	yy	zz	−0.66	0.31	−0.06	−0.42	0.40	0.04
		xy			0.04			−0.09		
11	332	xx	zz	xy	−0.16	−0.27	−0.13	−0.02	−0.12	−0.17
		xz			−0.03			0.08		
12	422	xx	yy	xy	0.47	0.08	0.16	0.46	0.07	−0.03
		yz			0.02			0.05		

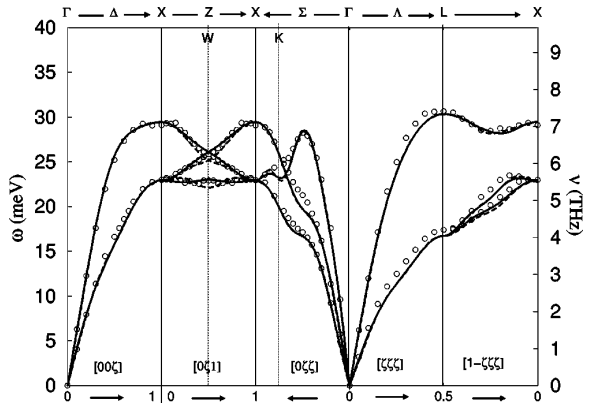

FIG. 1. Phonon dispersion of rhodium. Solid and dashed lines represent the theoretical results for the 12th NN and 16th NN fits, respectively. Experimental data from Ref. 10 are shown as open circles.

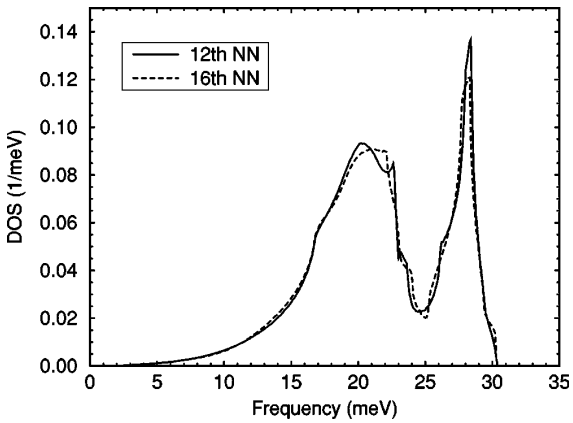

FIG. 2. Calculated phonon density of states of rhodium for the two cutoffs.

large values of the (330) IFC's are necessary for an adequate description of the strong anomalies along [110].

The phonon density of states is shown in Fig. 2 for the two cutoffs. The positions of the two main peaks agree well with maxima found in point contact spectra.[14] As in the case of the phonon dispersion, only marginal differences for the two cutoffs are observed, indicating a weak dependence on the chosen interaction range beyond the ninth NN shell.

The present scheme differs from the perturbational approach in several respects. First, a perturbative calculation of the dynamical matrix on a regular k mesh is a numerically very efficient equivalent (in harmonic approximations) of a force constant calculation using a single large supercell of high symmetry. Our approach instead involves a combination of smaller supercells with low symmetry. Second, as a k-space method, the perturbative approach is better suited for treating strongly localized anomalies in the phonon spectrum. However, as demonstrated above for rhodium, more shallow anomalies are well within reach of the direct method. Third, the direct approach has the practical advantage that it can be performed with any standard total-energy software package. On the other hand, a perturbative calculation requires the development of additional computer code, which, depending on the underlying band-structure method, can be a highly nontrivial task.

In summary, we have presented a generalization of the direct supercell approach to the calculation of interatomic force constants. For a given lattice, it allows a systematic search for appropriate supercell geometries before performing any *ab initio* calculation. As demonstrated for the transition metal rhodium, taking into account low-symmetry supercells leads to a drastic reduction of the numerical effort necessary to obtain all significant interatomic force constants even for systems with rather long-range interaction. An application of this method to the phonon spectrum of iridium is in progress.

The present approach can be straightforwardly extended to lattices with a general atomic basis. Furthermore, it is not restricted to metallic systems, but can be applied to polar insulators as well, if the long-range dipole-dipole interaction present in the latter case is treated properly. This could be achieved by calculating the Born-effective charges and the static dielectric permittivity, which allows us to separate explicitly the long-range part of the interaction from the short-range part,[2,15] the latter being tractable by the present direct method. Thus our scheme opens the way for the direct approach to access the complete phonon dynamics of complex compounds or surfaces.

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