Direct ab initio calculation of the dynamical matrix

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In this paper there is presented method for ab initio calculation of the phonon spectra. The method is based upon a direct calculation of the dynamical matrix via second derivatives of the total energy. The pseudopotential technique in plane-wave basis set was used to calculate the total energy within the local density approximation (LDA). For the change of the electron density there is derived the self-consistent equation which is solved analytically with no use of iterations. In this paper the attention is paid only to non-metallic systems.

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I. INTRODUCTION

Increasing accuracy of methods for calculation of the electronic structure of solids enable us to obtain the variety of properties of the solid state. In this paper, there is described new scheme for ab initio calculations of phonon spectra in non-metallic systems.

The problem of phonons as the perturbation of the perfect crystal lattice is used to be studied in different ways. The first one is the so-called direct approach based upon the comparison of the properties of unperturbed and perturbed states. The perturbed state is solved with use of the supercell geometry. This method enable us to study both the linear and nonlinear properties of the crystal lattice. Disadvantage of this method is that for each phonon wavevector \( q \) we need a corresponding supercell. Only a few phonons can be described by the supercell containing only a few cells, and this is the reason why the use of this method is limited only to few special long-wave phonons. Thus, this supercell technique seems to be insufficient as there are a lot of quantities, which must be computed by integrating over phonon frequencies of the whole Brillouin zone.

The second way is to calculate the dynamical matrix which can describe dynamical properties of solids with use of the linear response methods.

In this paper there is presented method for ab initio calculation of phonon spectra of non-metallic systems. At first the self-consistent electron charge density is calculated. Then, the self-consistent variation of charge density for an arbitrary phonon wave-length is calculated. After that, that one is used for calculating of the dynamical matrix. The presented scheme is restricted to non-metallic systems because the variation of the numbers of states with respect to perturbation in non-metallic systems is almost zero. The situation in metals is more complex.

The presented method differs from the other linear response methods, the dielectric matrix method, the method of Baroni et al., the method of King-Smith and Needs and the method of Rignanese, Michenaud and González. The presented method is based on direct calculation of the dynamical matrix via the second derivatives of the total potential energy of the crystal lattice.

Throughout the paper, the hartree units are used.

II. DYNAMICAL MATRIX

In the harmonic approximation the theory of lattice dynamics can be formulated in terms of the dynamical matrix. Then it can be written

\[
[D(q) - \omega^2(q)] W(q) = 0,
\]

where \( D \) stands for the dynamical matrix, \( q \) is the wavevector of the phonon, \( \omega \) is the frequency of the phonon and \( W \) is the eigenvector of the dynamical matrix which represents the polarization of the phonon. The dimension of the dynamical matrix is \( 3N \times 3N \), where \( N \) stands for the number of atoms per cell. Elements of the dynamical matrix can be expressed as

\[
D_{\alpha\beta}(q, \mu \nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_{h} A_{\alpha\beta}(h, \mu \nu) \exp(-i q \cdot h),
\]

where \( M_\mu, M_\nu \) are masses of atom \( \mu \) and \( \nu \), \( \alpha \) and \( \beta \) are Cartesian directions and \( h \) is vector of the translation symmetry. Elements of the matrix \( A \) are defined as

\[
A_{\alpha\beta}(h, \mu \nu) \overset{def}{=} \left. \frac{\partial^2 V_L}{\partial u_{\alpha}^{\mu,0} \partial u_{\beta}^{\nu,h}} \right|_{u=0},
\]

where \( V_L \) stands for the total potential energy of the crystal lattice, \( u_{\nu}^{\mu,0} \) is a vector giving displacement of atom \( \mu \) away from equilibrium in direction of \( \alpha \) axes. The \( u_{\beta}^{\nu,h} \) is a vector of displacement away from equilibrium in the direction of \( \beta \) axes of atom \( \nu \) in elementary cell with the translation vector \( h \) from the cell containing atom \( \mu \). Defining the operator
\[ \frac{\partial}{\partial \mu, \alpha} = \frac{1}{\sqrt{M}} \sum_{q} e^{-i q \cdot \mathbf{h}} \frac{\partial}{\partial u_{\mu, \alpha}^n} \bigg|_{n=0}, \]  

one can write the dynamical matrix as
\[ D_{\alpha \beta}(q, \mu \nu) = \partial_{\mu, \alpha}^* \partial_{\nu, \beta}^2 V_L, \]  

where asterisk means the complex conjugated operator.

To solve the Eq. (1) we have to know elements of the dynamical matrix. They can be calculated on the basis of elements of matrix \( A \). To calculate elements of the matrix \( A \) we need the second derivatives of energy \( V_L \) for which it can be written
\[ V_L = V_{Ew} + E_{el}, \]  

where \( V_{Ew} \) is the Ewald ion-ion interaction energy and \( E_{el} \) stands for energy of the set of electrons.

To find the contribution of the \( V_{Ew} \) to the dynamical matrix is easy because the analytical expressions for that are well known and therefore in the rest of this paper we study only term \( E_{el} \).

### III. THE ELECTRON SYSTEM ENERGY

Using the conventional density functional formalism in the pseudopotential framework, the total energy of the set of electrons is given by
\[ E_{el} = E_e - \frac{1}{2} \int \rho(r) V_c(r) d^3 r - \int \mu_{xc}(r) \rho(r) d^3 r + E_{xc}[\rho], \]  

where \( \rho \) is the charge density, \( V_c \) is the Coulombic potential, \( \mu_{xc} \) is the exchange and correlation potential and \( E_{xc} \) stands for the exchange-correlation energy. The \( E_e \) is the sum of eigenvalues
\[ E_e = \sum_i n_i \varepsilon_i, \]  

where \( \varepsilon_i \) are eigenvalues of the one-particle Kohn-Sham equation
\[ \left( \hat{T} + U + V_c + \mu_{xc} \right) \psi_i = \varepsilon_i \psi_i. \]  

\( \psi_i \) are self-consistent eigenfunctions, \( \hat{T} \) is operator of kinetic energy and \( U \) stands for pseudopotentials of the ionic sites. The exchange-correlation potential \( \mu_{xc} \) is given in the local density approximation by
\[ \mu_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} = \frac{\delta}{\delta \rho(r)} \int \varepsilon_{xc}(r) \rho(r) d^3 r = \varepsilon_{xc}(r) + \frac{\delta \varepsilon_{xc}(r)}{\delta \rho(r)} \rho(r). \]

The variation of \( E_{el} \) can be then expressed as
\[ \delta E_{el} = \delta \sum_i n_i \varepsilon_i - \frac{1}{2} \int \rho(r) V_c(r) d^3 r - \int \delta \varepsilon_{xc}(r) \rho(r) d^3 r + \int \frac{\delta \varepsilon_{xc}(r)}{\delta \rho(r)} \rho(r) d^3 r. \]

The variation of the first term on the right-hand side can be written as
\[ \delta \sum_i n_i \varepsilon_i = \sum_i [n_i \delta \varepsilon_i + \delta n_i (\varepsilon_i + \delta \varepsilon_i)]. \]

In metallic systems the occupancy can change with an additional potential while in the non-metallic systems the occupation number remains unchanged for small perturbation. Thus, for the non-metallic systems one can write
\[ \delta \sum_i n_i \varepsilon_i = \sum_i n_i \delta \varepsilon_i. \]

Having used the perturbation series one obtains
\[ \delta E_e = \sum_i n_i \delta \varepsilon_i = \sum_v \langle v | \delta U + \delta V_c + \delta \mu_{xc} | v \rangle + \sum_{v,c} \langle v | \delta U + \delta V_c + \delta \mu_{xc} | c \rangle \langle c | \delta U + \delta V_c + \delta \mu_{xc} | v \rangle - \varepsilon_v - \varepsilon_c + \Theta(\delta U + \delta V_c + \delta \mu_{xc}), \]

where \( v \) and \( c \) denote the occupied and unoccupied bands, respectively. The \( \Theta \) stands for higher terms. The first term can be expressed as
\[ \sum_v \langle v | \delta U + \delta V_c + \delta \mu_{xc} | v \rangle = \sum_v \langle v | \delta U | v \rangle + \int \rho^0(r) \delta V_c(r) d^3 r + \int \rho^0(r) \delta \mu_{xc}(r) d^3 r. \]

Having used the expression for the variation of the Coulombic potential
\[ V_c(r) = \int \frac{\delta \rho(r')}{|r - r'|} d^3 r', \]

the difference of the second term of Eq.(11) and the second term of Eq.(12) can be written as
\[ \rho^0(r) \delta V_c(r) - \frac{1}{2} \left( \rho(r) V_c(r) \right) = - \frac{1}{2} \int \frac{\delta \rho(r) \delta \rho(r')}{|r - r'|} d^3 r'. \]

Having expressed the exchange and correlation potential from Eq.(14), the difference of the third term of Eq.(11) and the third term of Eq.(12) can be written as
\[ \rho^0 \delta \mu_{xc} - \delta \left( \frac{\delta \varepsilon_{xc}}{\delta \rho} \rho \right) = \delta \left( \rho^0 \varepsilon_{xc} - \left( \rho - \rho^0 \right) \frac{\delta \varepsilon_{xc}}{\delta \rho} \right). \]
For the first order variation we can write
\[ \frac{\delta}{\delta \rho} \left( \rho^0 \epsilon_{xc} - (\rho - \rho^0) \rho \frac{\delta \epsilon_{xc}}{\delta \rho} \right)_0 = 0, \] (19)
and the second order variation can be written as
\[ \frac{\delta^2}{\delta \rho^2} \left( \rho^0 \epsilon_{xc} - (\rho - \rho^0) \rho \frac{\delta \epsilon_{xc}}{\delta \rho} \right)_0 = -\frac{\delta \epsilon_{xc}}{\delta \rho}, \] (20)
where the subscript 0 means that variations are taken for \( \rho = \rho^0 \). The variation of \( E_{el} \) can be finally rewritten into the form
\[ \delta E_{el} = \sum \langle v | \delta U | v \rangle + \sum_{v, c} \langle v | \delta U + \delta V_c + \delta \mu_{xc} + \epsilon | c \rangle \langle c | \delta U + \delta V_c + \delta \mu_{xc} | v \rangle \]
\[ - \frac{1}{2} \int \frac{\delta \rho(r) \delta \rho(r')}{|r - r'|} d^3 r d^3 r'
- \int \frac{\langle \delta \mu_{xc}(r) \rangle}{\delta \rho(r)} \delta \rho(r) d^3 r + \Theta(\delta U + \delta V_c + \delta \mu_{xc}). \] (21)

For the first order variation of the exchange-correlation potential \( \mu_{xc} \) we can write
\[ \delta \mu_{xc}(r) = \left( \frac{\delta \mu_{xc}(r)}{\delta \rho(r)} \right)_0 \delta \rho(r). \] (22)

As it was already mentioned one needs to calculate the second derivatives of energy \( E_{el} \)
\[ \frac{\partial^2 E_{el}}{\partial \mu_{\alpha\sigma} \partial \mu_{\beta\beta}} \bigg|_{\mu=0}, \] (23)
and therefore from Eq. (21) is obvious that only the linear variation of the electron density is needed.

IV. VARIATION OF ELECTRON DENSITY

The charge density \( \rho(r) \) is calculated from
\[ \rho(r) = \sum_i n_i \psi_i^*(r) \psi_i(r), \] (24)
where \( n_i \) is the occupation number and \( \psi_i \) are one-electron wavefunctions, the variation of \( \rho(r) \) is expressed as
\[ \delta \rho = \sum_i (n_i + \delta n_i)(\psi_i^{0*} + \delta \psi_i^*) (\psi_i^0 + \delta \psi_i) - n_i \psi_i^{0*} \psi_i^0. \] (25)
Having supposed that in the non-metallic systems the \( \delta n_i = 0 \) one can write
\[ \delta \rho = \sum_i n_i (\psi_i^{0*} \delta \psi_i + \delta \psi_i^* \psi_i^0 + \delta \psi_i^* \delta \psi_i). \] (26)
The variation of the wave function
\[ \delta \psi_i = \sum_j a_{ij} \psi_j^0, \] (27)
and the variation of the electron density can be written as
\[ \delta \rho = \sum_i n_i \sum_j (\psi_i^{0*} \psi_j^0 a_{ij} + \psi_j^{0*} \psi_i^0 a_{ij}^*) \]
\[ + \sum_i n_i \sum_{jk} (\psi_j^{0*} \psi_k^0 a_{ik} a_{ij}^*). \] (28)
The variation of the wave function is obtained from the Lippmann-Schwinger equation
\[ | \psi_i \rangle = | \psi_i^0 \rangle + G_0(\epsilon_i) \delta V_{KS} | \psi_i \rangle, \] (29)
where \( G_0(\epsilon) \) is the Green function
\[ G_0(\epsilon) = \sum_i | \psi_i \rangle \langle \psi_i |, \] (30)
and \( \delta V_{KS} \) is the variation of the total Kohn-Sham potential
\[ \delta V_{KS} = \delta U + \delta V_c + \delta \mu_{xc}. \] (31)
With the use of Eqs. (22) and (23) it can be written as
\[ \delta V_{KS} = \delta U + \int \frac{\delta \rho(r')}{|r - r'|} d^3 r' + \left( \frac{\delta \mu_{xc}(r)}{\delta \rho(r)} \right)_0 \delta \rho(r). \] (32)
The elements \( a_{ij} \) are then expressed as
\[ a_{ij} = \langle \psi_i^0 | \delta \psi_j \rangle = \langle \psi_i^0 | G_0(\epsilon_i) \delta V_{KS} | \psi_j^0 \rangle. \] (33)

Having combined equations (28) and (33) and applying operator \( \partial_{\mu, \alpha} \), which contains the limit to the zero perturbation (Eq. (4)) we obtain integral equation
\[ \partial_{\mu, \alpha}^0 \rho(r) = \sum_{i,j} n_i \psi_i^{0*}(r) \psi_j^0(r) \]
\[ \times \langle \psi_i^0 | G_0(\epsilon_i) \partial_{\mu, \alpha} (U + V_c + \mu_{xc}) | \psi_j^0 \rangle \]
\[ = \sum_{i,j} n_i \psi_i^{0*}(r) \psi_j^0(r) \langle \psi_i^0 | G_0(\epsilon_i) \partial_{\mu, \alpha} U | \psi_j^0 \rangle \]
\[ + \sum_{i,j} n_i \psi_i^{0*}(r) \psi_j^0(r) \langle \psi_i^0 | G_0(\epsilon_i) \partial_{\mu, \alpha} \rho(r) \rangle \]
\[ \times \left[ \int \frac{\partial_{\mu, \alpha} \rho(r')}{|r - r'|} d^3 r' + \left( \frac{\delta \mu_{xc}(r)}{\delta \rho(r)} \right)_0 \partial_{\mu, \alpha}^0 \rho(r) \right] | \psi_j^0 \rangle, \] (34)
which can be rewritten in form
\[ \partial_{\mu, \alpha}^0 \rho(r) = \partial_{\mu, \alpha}^0 \sigma(r) \]
\[ + \int \Lambda(r, r') \Gamma(r', r'') d^3 r' \partial_{\mu, \alpha}^0 \rho(r'') d^3 r'', \] (35)
where $\sigma$ and $\Lambda$ depend only on eigenfunctions and eigenvalues of the unperturbed state. The quantities from previous equation can be expressed as

$$\partial^q_{\mu,\alpha} \sigma(r) = \sum_{i,j} \frac{n_i - n_j}{\varepsilon_i - \varepsilon_j} \psi_{i}^{\mu,\alpha}(r) \psi_{j}^{\nu,\beta}(r) \delta_{\mu,\nu} U | \psi_{i}^{\nu,\beta}$$

(36)

$$\Lambda(r, r') = \sum_{i,j} \frac{n_i - n_j}{\varepsilon_i - \varepsilon_j} \psi_{i}^{\mu,\alpha}(r) \psi_{j}^{\nu,\beta}(r) \psi_{j}^{\nu,\alpha}(r') \psi_{i}^{\nu,\beta}(r')$$

(37)

$$\Gamma(r, r') = \frac{1}{|r'' - r'|} + \delta(r' - r'') \left( \frac{\delta_{\varepsilon_{xc}(r'')}}{\delta\rho(r'')} \right)_0.$$  

(38)

After expansion into plane waves the integral equation yields the set of algebraic equations. By solving this set we obtain $\partial^q_{\mu,\alpha,\rho}$ which are used for calculation of the dynamical matrix.

The contribution of the variation of the $E_{cl}$ to the dynamical matrix is given by the sum of contributions from four terms on the right-hand side of the Eq. (21), i.e.

$$D^{cl,1}_{\alpha\beta}(q, \mu \nu) = D^{cl,1}_{\alpha\beta}(q, \mu \nu) + D^{cl,2}_{\alpha\beta}(q, \mu \nu) + D^{cl,3}_{\alpha\beta}(q, \mu \nu) + D^{cl,4}_{\alpha\beta}(q, \mu \nu).$$

(39)

The contribution of the fifth term on the right-hand side of the Eq. (21) is zero because $\partial^q_{\mu,\alpha,\rho} \delta_{\varepsilon_{xc}(r'')} U | \varepsilon_{xc} = 0$.

To calculate the term $D^{cl,3}_{\alpha\beta}(q, \mu \nu)$ is quite easy because $\partial^q_{\mu,\alpha,\rho} \delta_{\varepsilon_{xc}(r'')} U | \varepsilon_{xc}$ only. According to Eqs. (21) one can write

$$D^{cl,1}_{\alpha\beta}(q, \mu \nu) = \sum_{\nu, k} \langle \nu, k | \partial^q_{\mu,\alpha} \partial^q_{\nu,\beta} U | \nu, k \rangle.$$  

(40)

More complicated is to calculate $D^{cl,2}_{\alpha\beta}(q, \mu \nu)$. According to the Eq. (21) one can write

$$D^{cl,2}_{\alpha\beta}(q, \mu \nu) = \sum_{\nu, k} \frac{n_{\nu, k} - n_{\nu, k+q}}{\varepsilon_{\nu, k} - \varepsilon_{\nu, k+q}}$$

$$\times \langle \nu, k | \partial^q_{\mu,\alpha} (U + V_{\nu, \beta} \mu_{xc}) | \nu, k + q \rangle$$

$$\times \langle \nu, k + q | \partial^q_{\nu,\beta} (U + V_{\nu, \beta} \mu_{xc}) | \nu, k \rangle.$$  

(41)

The sum over $\nu$ and $c$ in Eq. (11) runs over occupied and unoccupied bands respectively. The $D^{cl,3}_{\alpha\beta}(q, \mu \nu)$ and $D^{cl,4}_{\alpha\beta}(q, \mu \nu)$ can be written in the forms

$$D^{cl,3}_{\alpha\beta}(q, \mu \nu) = - \int \frac{\partial^q_{\mu,\alpha} \rho(r) \partial^q_{\nu,\beta} \rho(r')}{|r - r'|} d^3r d^3r',$$  

(42)

and

$$D^{cl,4}_{\alpha\beta}(q, \mu \nu) = - 2 \int \left( \frac{\delta_{\varepsilon_{xc}(r')}}{\delta\rho(r')} \right)_0 \partial^q_{\mu,\alpha} \rho(r) \partial^q_{\nu,\beta} \rho(r) d^3r.$$  

(43)

V. CALCULATIONS

The calculations were performed with all quantities expanded into plane waves. The set of special $k$-points mesh was used for integration over the Brillouin zone. It corresponds to 10 $k$-points for $\Gamma$ phonon and 128 $k$-points for phonon with general wave-vector. The plane-wave set was selected for each $k$ in the first Brillouin zone such that among the reciprocal-lattice vectors $G$ only those are selected which have a kinetic energy $E_{kin} = \frac{1}{2}(k + G)^2$ less then $E_{cutoff} = 18 Ry$. The sums over unoccupied states went over energies up to cutoff energy $E_{cutoff} = 9 Ry$, which corresponds to 350 unoccupied bands approximately.

VI. RESULTS

The method presented in this paper was applied to silicon crystal with lattice constant $a = 0.543 nm$. Both optical and acoustic branches of phonon frequencies in longitudinal and transverse modes were obtained for $\Gamma$, $X$ and $L$ phonons. Calculated frequencies together with values obtained by other authors and experimental values are summarized in Table 1. The values are expressed in THz.

|     | $\Gamma$ | $L$ | $X$ |
|-----|---------|-----|-----|
|     | (0,0,0) | (1,1,1) | (1,0,0) |
| $TO_{calc}$ | 15.9 | 15.8 | 15.1 |
| $TO_{calc}$ | 15.6 | – | – |
| $TO_{calc}$ | 15.2 | – | 13.5 |
| $TO_{calc}$ | 15.7 | – | – |
| $TO_{calc}$ | 15.5 | 15.0 | 14.2 |
| $LO_{calc}$ | 15.9 | 14.5 | 14.6 |
| $LO_{calc}$ | – | – | 12.1 |
| $LO_{calc}$ | 15.5 | 12.8 | 12.5 |
| $TA_{calc}$ | 0.0 | 6.2 | 7.3 |
| $TA_{calc}$ | – | 3.0 | 4.1 |
| $TA_{calc}$ | 0.0 | 3.6 | 4.4 |
| $LA_{calc}$ | 0.0 | 13.8 | 14.6 |
| $LA_{calc}$ | 0.0 | 11.7 | 12.5 |

a Phonons calculated in this work.

b Reference [13].

c Reference [18].

d Reference [17].

e Reference [18].

TABLE I. The calculated and experimental values of phonon frequencies in the silicon crystal.
VII. DISCUSSION

Having used the presented method a quite good agreement of the calculated frequencies of optical phonons in silicon crystal and experimental ones was reached. We systematically increased the number of unoccupied states taken into account and we have found that the increase over \( \sim 300 \) bands almost doesn’t change the results. Thus, the contribution from states with energy \( \epsilon_i > \epsilon_{\text{cutoff}} \) doesn’t appear essential. The biggest individual contributions to the dynamical matrix come from unoccupied states with energy near the Fermi energy. But the number of these states is small, the density of unoccupied states with energy near the Fermi energy.

The presented method does not need time consuming calculations of inverse matrix as in the inverse dielectric matrix method. Method of Baroni et al. is based on the self-consistent scheme for perturbed eigenfunctions while our method is based on the self-consistent equation (85) for the variation of the electron density and only energies and eigenfunctions of unperturbed states are needed. King-Smith and Needs method used the Hellmann-Feynman forces on all atoms in distorted crystal to construct the dynamical matrix. The method of Gonze et al. is based on variations of the DFT total energy with respect to the first-order perturbations of the wave functions. In this paper, the second derivatives of energy approach is used. The advantage of the presented method is that in contradiction to the both, Baroni et al. method and King-Smith and Needs method, the iteration up to the self-consistency is needed only once for the unperturbed state. In contradiction to the method of Gonze et al., we don’t need any additional minimization of the total energy with respect to the first-order variations of the wave function for each phonon, because all quantities are calculated from quantities of unperturbed state.

Because of avoiding the iterations and minimization the presented method is very suitable for massive parallelization of the computer code.

VIII. CONCLUSION

The method for ab initio calculation of frequency and polarization vector of phonons with an arbitrary wavevector was presented. The density functional theory within the pseudopotential framework was used. As in other linear response methods, the presented one uses the perturbation theory. In contradiction to the other methods the presented one is based upon a direct calculation of the dynamical matrix via second derivatives of the total crystal energy and no calculation of the Hellmann-Feynman forces is needed.

The presented method does not need time consuming calculations of inverse matrix as in the inverse dielectric matrix method. Another advantage is that in contradistinction to the both Baroni et al. method and King-Smith and Needs method, no iteration up to self-consistency for individual phonon is needed. Similarly, we don’t need any total energy minimization as in the case of method of Rignanese, Michenaud and Gonze. The computing time saving due to the parallelization of the computer code is significantly high for the presented method.

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