

A short introduction: the calculation of phonons with DFPT

Notes for Giulia Canevali

Katalin Gaál-Nagy

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Abstract

In this short introduction the basic principles for the calculation of phonon frequencies within density-functional perturbation theory (DFPT) are summarized. These notes do not have the aim to be complete or explain everything. Nevertheless, they could be used as a guide for the understanding of the theory by reading the given references if necessary.

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1 Introduction

This document will start at the adiabatic approximation and it will one day also contain a short overview of the basics of the density-functional theory (DFT), even if these topics are well known. However, in this way also the necessary notation is introduced. The section about basic functions (here: plane waves) and together with these, the use of pseudopotentials is skipped at the moment and could be read elsewhere, e.g., in the notes from Pasquale Pavone.

In this document we are mainly talking about solids, but the principles described here are also valid for surfaces and molecules, which can be calculated using a slab or a large box.

2 Adiabatic approximation

A solid is a many-body problem, which can be described by a Schrödinger equation of the form

$$H(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) = E(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) \quad (1)$$

where the Hamilton operator of the system H , the corresponding eigenfunctions Ψ , and the self energies E depend on all atomic coordinates \mathbf{R} and all electronic coordinates \mathbf{r} . The Hamilton operator has the form

$$H(\mathbf{r}, \mathbf{R}) = T_K(\dot{\mathbf{R}}) + T_e(\dot{\mathbf{r}}) + V_{KK}(\mathbf{R}) + V_{ee}(\mathbf{r}) + V_{eK}(\mathbf{r}, \mathbf{R}) \quad (2)$$

with

$$T_K(\dot{\mathbf{R}}) = - \sum_{\mathbf{R}} \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{R}^2} \quad (3)$$

being the operator of the kinetic energy of the cores of the atoms with the mass M ,

$$T_e(\dot{\mathbf{r}}) = - \sum_{\mathbf{r}} \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} \quad (4)$$

the operator of the kinetic energy of the electrons with mass m ,

$$V_{KK}(\mathbf{R}) = + \sum_{\mathbf{R}' \neq \mathbf{R}} \frac{1}{2} \frac{ZZ'e^2}{|\mathbf{R} - \mathbf{R}'|} \quad (5)$$

the coulomb repulsion of the cores,

$$V_{ee}(\mathbf{r}) = + \sum_{\mathbf{r}' \neq \mathbf{r}} \frac{1}{2} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \quad (6)$$

the coulomb repulsion of the electrons, and

$$V_{eK}(\mathbf{r}, \mathbf{R}) = - \sum_{\mathbf{R}} \frac{Ze^2}{|\mathbf{R} - \mathbf{r}|} \quad (7)$$

the coulomb attraction of cores and electrons.

This many-body problem can not be solved in this form. Within the adiabatic approximation (often called also Born-Oppenheimer approximation[Bor27]) it is assumed, that the

movement of the electrons does not influence the movement of the atomic cores, whereas the electrons are adiabatically following the movement of the cores, because of the large difference in the masses of electrons and cores. This allows us to solve the electronic problem for a fixed configuration of the cores. Nevertheless, the solution depends on the coordinates of the cores.

With a separation ansatz

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_e(\mathbf{r}, \mathbf{R}) \Psi_K(\mathbf{R}) \quad (8)$$

and the assumption that electron and core motion are not coupled any more, we receive a Schrödinger equation for the electrons for a fixed configuration of the cores \mathbf{R}

$$H_e(\mathbf{r}, \mathbf{R}) \Psi_e(\mathbf{r}, \mathbf{R}) = [T(\dot{\mathbf{r}}) + V_{ee}(\mathbf{r}) + V_{eK}(\mathbf{r}, \mathbf{R})] \Psi_e(\mathbf{r}, \mathbf{R}) = E_e(\mathbf{R}) \Psi_e(\mathbf{r}, \mathbf{R}) \quad (9)$$

and a Schrödinger equation for the cores

$$H_K(\mathbf{R}) \Psi_K(\mathbf{R}) = [T_K(\dot{\mathbf{R}}) + V_{KK}(\mathbf{R}) + E_e(\mathbf{R})] \Psi_K(\mathbf{R}) = E \Psi_K(\mathbf{R}) \quad . \quad (10)$$

3 Density-functional theory (DFT)

The goal is to solve the Schrödinger equation for the electrons (9). The coordinates of the cores are just parameters, and thus we neglect an explicit notation. The problem is now reduced to a system of interacting electrons in an external potential, which comes from the atomic cores, and can be solved within the DFT. The DFT is based on the theorem of Hohenberg and Kohn (section 3.1). From this, the system could be mapped to a model system which is described by one-particle equations, the Kohn-Sham equations (section 3.2), which have to be solved. In these equations everything is well known except the interaction of the electrons (as a function of the electronic density), and so an additional approximation is necessary (section 3.3).

3.1 Hohenberg-Kohn Theorem

(see notes from Pasquale Pavone and [Hoh64])

3.2 Kohn-Sham equations

(see notes from Pasquale Pavone and [Koh65])

Kohn and Sham derived the following one-particle equations:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r}) \right) \psi_j(\mathbf{r}) &= \epsilon_j \psi_j(\mathbf{r}) \\ V_{KS}(\mathbf{r}) &= V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \\ n(\mathbf{r}) &= \sum_{j=1}^{N_j} |\psi_j(\mathbf{r})|^2 \quad , \end{aligned} \quad (11)$$

where N_j is the number of all occupied states with self energies ϵ_j . Here, the effective potential for the electrons V_{KS} is named Kohn-Sham potential and

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} \quad (12)$$

is called exchange-correlation potential.

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \quad (13)$$

is the Hartree potential [Koh85].

The Kohn-Sham equations (11) have to be solved self-consistently, since the Kohn-Sham potential $V_{XC}(\mathbf{r})$ depends on the electronic density. Because the exchange-correlation interaction is part of the effective potential, the system of interacting electrons in an external potential V_{ext} is mapped to a system of non-interacting electrons in an potential $V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}} + V_H + V_{XC}$, and thus, the solution of the many-body problem is reduced to the solution of single-particle equations. The idea to see each electron in the field of all others (mean field theory) goes back to Thomas and Fermi [Tho26, Fer27]. What is missing now is the exchange-correlation potential, which is the only term which can not be calculated explicitly.

3.3 Exchange-correlation potential

The exchange-correlation energy $E_{XC}[n]$ is defined as the difference of the exact energy functional $E[n]$ and the sum of all determined terms like the kinetic energy of the non-interacting electrons $T_s[n]$, the Hartree energy $E_H[n]$, and the energy of the external potential $E_{\text{ext}}[n]$:

$$E_{XC}[n] = E[n] - T_s[n] - E_H[n] - E_{\text{ext}}[n] \quad . \quad (14)$$

This energy will be now approximated.

3.3.1 Local-density approximation (LDA)

(see notes from Pasquale Pavone and [Koh65])

3.3.2 Generalized gradient approximation (GGA)

The GGA is an extension of the LDA (but not necessary for you ...).

4 Basis functions and Pseudopotentials

... skipped here ...

Main point: frozen core approximation: the core electrons are fixed to the cores. This system is described by the pseudopotential. The electrons are now just the “valence” electrons.

5 Lattice dynamics

Besides the ground-state properties we are interested in the dynamical properties of the solids, in particular, the lattice vibrations (phonons). Phonons can be calculated within the harmonic approximation (section 5.1). The calculation of the force constants which yield the phonons, is summarized in section 5.2.

5.1 Harmonic approximation

The cores are described within the adiabatic approximation by the Schrödinger equation for the cores, Eq. (10). The cores are moving in an effective core potential

$$V_{\text{eff}}(\mathbf{R}) = V_{\text{KK}}(\mathbf{R}) + E_{\text{e}}(\mathbf{R}) \quad , \quad (15)$$

which inhibits an electronic contribution $E_{\text{e}}(\mathbf{R})$.

The effective potential depends of the coordinate of the core \mathbf{R} . Now we expand the potential around the equilibrium positions $\mathbf{R}_0 = \mathbf{R}_{(\kappa)}^{(l)} = \{R_{\alpha}^{(l)}(\kappa)\}$, where κ is the sublattice index and l the index of the elementary cell. The expansion is due to the elongation $\mathbf{u} = \{u_{\alpha}^{(l)}(\kappa)\}$ of the atoms in the direction α , which is a cartesian coordinate, $\alpha = x, y, z$:

$$\begin{aligned} V_{\text{eff}}(\mathbf{R}) &= V_{\text{eff}}(\mathbf{R}_0 + \mathbf{u}) \\ &= V_{\text{eff}}(\mathbf{R}_0) + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{u}} V \Big|_{\mathbf{u}=0} + \frac{1}{2!} \left(\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{u}} \right)^2 V \Big|_{\mathbf{u}=0} + \dots \\ &= \Phi_0 + \Phi_1 + \Phi_2 + \dots \quad , \end{aligned} \quad (16)$$

where we use the definition $\frac{\partial}{\partial \mathbf{u}} = \left(\frac{\partial}{\partial u_x}, \frac{\partial}{\partial u_y}, \frac{\partial}{\partial u_z} \right)$. Since the expansion is around the minimum of the potential, the linear term vanishes. The quadratic term is

$$\begin{aligned} \Phi_2 &= \frac{1}{2!} \sum_{l\kappa\alpha} \sum_{l'\kappa'\alpha'} \Phi_{\alpha\alpha'} \binom{l \ l'}{\kappa \ \kappa'} u_{\alpha} \binom{l}{\kappa} u_{\alpha'} \binom{l'}{\kappa'} \\ &= \frac{1}{2!} \sum_{l\kappa\alpha} \sum_{l'\kappa'\alpha'} \frac{\partial^2}{\partial u_{\alpha}^{(l)}(\kappa) \partial u_{\alpha'}^{(l')}(\kappa')} V_{\text{eff}} \left(R_{\alpha} \binom{l}{\kappa} + u_{\alpha} \binom{l}{\kappa} \right) \Big|_{u_{\alpha}=0} \\ &\quad \times u_{\alpha} \binom{l}{\kappa} u_{\alpha'} \binom{l'}{\kappa'} \quad , \end{aligned} \quad (17)$$

Here, $\Phi_{\alpha\alpha'} \binom{l \ l'}{\kappa \ \kappa'}$ is the force-constant matrix. Within the harmonic approximation, all higher-order (anharmonic) terms are neglected. Therefore, the effective potential can be written as

$$V_{\text{eff}}^{\text{harm}}(\mathbf{R}) = V_{\text{eff}}(\mathbf{R}_0) + \frac{1}{2!} \sum_{l\kappa\alpha} \sum_{l'\kappa'\alpha'} \Phi_{\alpha\alpha'} \binom{l \ l'}{\kappa \ \kappa'} u_{\alpha} \binom{l}{\kappa} u_{\alpha'} \binom{l'}{\kappa'} \quad , \quad (18)$$

which is the potential of an harmonic oscillator. The motion of the core κ with mass m_{κ} is described by the classical equation of motion.

$$m_{\kappa} \frac{d^2 u_{\alpha}^{(l)}(\kappa)}{dt^2} = - \sum_{l'\kappa'\alpha'} \Phi_{\alpha\alpha'} \binom{l \ l'}{\kappa \ \kappa'} u_{\alpha'} \binom{l'}{\kappa'} \quad . \quad (19)$$

The equations of motion are coupled for all cores and can not be solved in this form. But since we can assume the solid as infinitely extended, we can apply the Bloch theorem and we can suppose that the elongation can be superimposed by expressions of the form

$$u_\alpha \begin{pmatrix} l \\ \kappa \end{pmatrix} = \frac{1}{\sqrt{m_\kappa}} U_\alpha(\kappa, \mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{R}_{(\kappa)}^{(l)} - \omega(\mathbf{q}) t)} \quad (20)$$

Here, \mathbf{q} is a point in the Brillouin zone, ω a frequency, and t the time. With this, we go to the momentum space, in which the system of equations is decoupled. If we put this into the equation of motion we get

$$\begin{aligned} \omega^2(\mathbf{q}) U_\alpha(\kappa, \mathbf{q}) &= \sum_{l' \kappa'} U_{\alpha'}(\kappa', \mathbf{q}) \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \Phi_{\alpha\alpha'} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} e^{i\mathbf{q} \cdot (\mathbf{R}_{(\kappa')}^{(l')} - \mathbf{R}_{(\kappa)}^{(l)})} \\ &= \sum_{l' \kappa'} U_{\alpha'}(\kappa', \mathbf{q}) D_{\alpha\alpha'} \begin{pmatrix} \mathbf{q} \\ \kappa & \kappa' \end{pmatrix} . \end{aligned} \quad (21)$$

$D_{\alpha\alpha'} \begin{pmatrix} \mathbf{q} \\ \kappa & \kappa' \end{pmatrix}$ is the dynamical matrix and it is the Fourier transform of the matrix of the force constants. It remains to solve the secular equation for the frequencies

$$\left\| \mathbf{D} \begin{pmatrix} \mathbf{q} \\ \kappa & \kappa' \end{pmatrix} - \omega^2(\mathbf{q}) \mathbf{1}_{3N_A} \right\| = 0 \quad (22)$$

where $\mathbf{1}_{3N_A}$ is the $3N_A \times 3N_A$ dimensional unitary matrix. The dynamic of the cores is now reduced to $3N$ independent harmonic oscillators, and the frequencies can be calculated by diagonalizing the dynamical matrix.

5.2 Calculation of the forces

The calculation of the phonon-frequencies requires the force-constant matrix. This matrix can be split into an electronic and a core part,

$$\Phi_{\alpha\alpha'} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} = \Phi_{\alpha\alpha'}^{\text{KK}} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} + \Phi_{\alpha\alpha'}^{\text{e}} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} . \quad (23)$$

The core part is obtained by the derivation of the Ewald sum, see e.g., [Gia91]. The electronic part can be calculated with the help of the density-functional perturbation theory. The electronic part of the force-constant matrix can be written as the second derivative of the electronic energy $E_e(\mathbf{R})$

$$\Phi_{\alpha\alpha'}^{\text{e}} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} = \frac{\partial^2 E_e(\mathbf{R})}{\partial R_\alpha^{(l)} \partial R_{\alpha'}^{(l')}} . \quad (24)$$

This derivative shall be determined now.

5.2.1 Hellman-Feynman theorem

First of all, the first derivative of the energy eigenvalues of a Hamilton operator H_λ , which depends on a parameter λ , is given by the expectation value of the derivative of the Hamiltonian

$$\frac{\partial E_\lambda}{\partial \lambda} = \langle \psi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \psi_\lambda \rangle \quad (25)$$

where ψ_λ is a eigenfunction of H_λ with respect to E_λ .

Within the adiabatic approximation the atomic coordinates are just parameters in the electronic Hamiltonian, and therefore the electronic part of a force on an atom is given by

$$\mathbf{F}(\mathbf{R}_{(\kappa)}^{(l)}) = -\frac{\partial E_e(\mathbf{R})}{\partial \mathbf{R}_{(\kappa)}^{(l)}} = -\left\langle \Psi_e(\mathbf{r}, \mathbf{R}) \left| \frac{\partial H_e(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_{(\kappa)}^{(l)}} \right| \Psi_e(\mathbf{r}, \mathbf{R}) \right\rangle, \quad (26)$$

where $H_e(\mathbf{R})$ is the Hamiltonian from Eq. (9). Here, the definition

$$\frac{\partial}{\partial \mathbf{R}_{(\kappa)}^{(l)}} = \left(\frac{\partial}{\partial R_x^{(l)}}, \frac{\partial}{\partial R_y^{(l)}}, \frac{\partial}{\partial R_z^{(l)}} \right) \quad (27)$$

is used.

According to the Hellmann-Feynman theorem [Hel37, Fey39] this force can be written as

$$\mathbf{F}(\mathbf{R}_{(\kappa)}^{(l)}) = -\int n(\mathbf{R}, \mathbf{r}) \frac{\partial V_{\text{eK}}(\mathbf{R}, \mathbf{r})}{\partial \mathbf{R}_{(\kappa)}^{(l)}} d^3 r \quad (28)$$

with the electronic density of the ground state $n(\mathbf{R}, \mathbf{r})$ at an atomic configuration \mathbf{R} . The electronic part of the force-constant matrix results from a differentiation of the Hellmann-Feynman force $\mathbf{F}(\mathbf{R}_{(\kappa)}^{(l)})$

$$\begin{aligned} \frac{\partial^2 E_e(\mathbf{R})}{\partial \mathbf{R}_{(\kappa)}^{(l)} \partial \mathbf{R}_{(\kappa')}^{(l')}} &\equiv -\frac{\partial \mathbf{F}(\mathbf{R}_{(\kappa)}^{(l)})}{\partial \mathbf{R}_{(\kappa')}^{(l')}} \\ &= \int \frac{\partial n(\mathbf{R}, \mathbf{r})}{\partial \mathbf{R}_{(\kappa')}^{(l')}} \frac{\partial V_{\text{eK}}(\mathbf{R}, \mathbf{r})}{\partial \mathbf{R}_{(\kappa)}^{(l)}} d^3 r + \int n(\mathbf{R}, \mathbf{r}) \frac{\partial^2 V_{\text{eK}}(\mathbf{R}, \mathbf{r})}{\partial \mathbf{R}_{(\kappa)}^{(l)} \partial \mathbf{R}_{(\kappa')}^{(l')}} d^3 r. \end{aligned} \quad (29)$$

The calculation of $\Phi_{\alpha\alpha'}^{(l, l')}(\mathbf{R}_{(\kappa)}^{(l)}, \mathbf{R}_{(\kappa')}^{(l')})$ requires besides the ground state electronic density $n(\mathbf{R}, \mathbf{r})$ also its linear answer to the elongation of the atoms out of their equilibrium positions $\partial n(\mathbf{R}, \mathbf{r})/\partial \mathbf{R}$ [Cic69, Pic70].

The Hellmann-Feynman theorem shows, that the knowledge of the linear change of the electronic density is sufficient in order to calculate the variation of the energy up to second order, after the $2n+1$ theorem [Gon89] also up to third order.

5.2.2 Linear response and density-functional perturbation theory (DFPT)

The calculation of the linear response $\partial n(\mathbf{R}, \mathbf{r})/\partial \mathbf{R} = n^{(1)}(\mathbf{r})$ is performed within density-functional perturbation theory. For this purpose, the external potential of the Kohn-Sham equations (11) is expanded in a perturbation λ ,

$$V_{\text{ext}}(\mathbf{r}) = V_{\text{ext}}^{(0)}(\mathbf{r}) + \lambda V_{\text{ext}}^{(1)}(\mathbf{r}) + \mathcal{O}(\lambda^2) \quad (30)$$

which is here the periodic elongation of the cores. Therewith, also all other quantities in the Kohn-Sham equations are functions of λ and they can be expanded in λ :

$$\begin{aligned} n(\mathbf{r}) &= n^{(0)}(\mathbf{r}) + \lambda n^{(1)}(\mathbf{r}) + \mathcal{O}(\lambda^2) \\ \psi_j(\mathbf{r}) &= \psi_j^{(0)}(\mathbf{r}) + \lambda \psi_j^{(1)}(\mathbf{r}) + \mathcal{O}(\lambda^2) \\ V_{\text{KS}}(\mathbf{r}) &= V_{\text{KS}}^{(0)}(\mathbf{r}) + \lambda V_{\text{KS}}^{(1)}(\mathbf{r}) + \mathcal{O}(\lambda^2) \\ \epsilon_j &= \epsilon_j^{(0)} + \lambda \epsilon_j^{(1)} + \mathcal{O}(\lambda^2). \end{aligned} \quad (31)$$

Now we insert the expansion up to first order into the Kohn-Sham equations (11). A comparison of the order in λ yields the perturbed Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{KS}}^{(0)}(\mathbf{r}) - \epsilon_j^{(0)} \right] \psi_j^{(1)}(\mathbf{r}) = - \left(V_{\text{KS}}^{(1)}(\mathbf{r}) - \epsilon_j^{(1)} \right) \psi_j^{(0)}(\mathbf{r})$$

$$V_{\text{KS}}^{(1)}(\mathbf{r}) = V_{\text{ext}}^{(1)}(\mathbf{r}) + \int \frac{n^{(1)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + n^{(1)}(\mathbf{r}) \left[\frac{\delta E_{\text{XC}}}{\delta n} \right]_{n_0} \quad (32)$$

$$n^{(1)}(\mathbf{r}) = \sum_{j=1}^{N_j} \psi_j^{(0)*}(\mathbf{r}) \psi_j^{(1)}(\mathbf{r}) + \psi_j^{(1)*}(\mathbf{r}) \psi_j^{(0)}(\mathbf{r}) \quad .$$

A multiplication of the first equation by $\psi_j^{(0)}(\mathbf{r})$ leads to the energy $\epsilon^{(1)}$

$$\epsilon^{(1)} = \int \psi_j^{(0)*}(\mathbf{r}) V_{\text{KS}}^{(1)}(\mathbf{r}) \psi_j^{(0)}(\mathbf{r}) d^3 \mathbf{r} \quad . \quad (33)$$

The equations (32) and (33) have to be solved self-consistently like the Kohn-Sham equations. The first equation in (32) is the so called Sternheimer equation [Ste54].

Baroni *et al.* [Bar87, Gia91, Bar01] developed a method in order to solve the perturbed Kohn-Sham equations for semiconductors. Later on, this procedure was extended to metallic systems [Gir95]. The PWscf code base on this.

The phonon calculations with ABINIT software package base on the DFPT, too, but the implementation is slightly different (see references in the attached paper).

References

- [Bor27] M. B. UND R. OPPENHEIMER, Zur Quantentheorie der Molekeln, *Annalen der Physik* **84**, 457 (1927).
- [Hoh64] P. HOHENBERG, and W. KOHN, Inhomogenous Electron Gas, *Phys. Rev.* **136 B**, 864 (1964).
- [Koh65] W. KOHN, and L. J. SHAM, Self-Consistent Equations including exchange and correlation effects, *Phys. Rev.* **140 A**, 1133 (1965).
- [Koh85] W. KOHN, Density Functional Theory: Fundamentals and Applications, in *Highlights of Condensed-Matter Theory, Proceedings of the Int. School of Physics Enrico Fermi, Course LXX-XIX*, Ed. F. BASSANI, F. FUMI, and M. P. TOSI, p. 1, North-Holland, Amsterdam, 1985.
- [Tho26] L. H. THOMAS, Calculation of atomic fields, *Proc. Camb. Phil. Soc.* **23**, 542 (1926).
- [Fer27] E. FERMI, Un metodo statistico per la determinazione di alcune proprieta dell'atome, *Rend. Accad. Naz. Lincei* **6**, 602 (1927).
- [Gia91] P. GIANNOZZI, S. GIRONCOLI, P. PAVONE, and S. BARONI, Ab initio calculation of phonon dispersions in semiconductors, *Phys. Rev. B* **43**, 7231 (1991).
- [Hel37] H. HELLMANN, *Einführung in die Quantenchemie*, Deuticke, Leipzig, 1937.
- [Fey39] R. P. FEYNMAN, Forces in Molecules, *Phys. Rev.* **56**, 340 (1939).
- [Cic69] P. D. DECICCO, and F. A. JOHNSON, The quantum theory of lattice dynamics. IV, *Proc. Roy. Soc. London A* **310**, 111 (1969).
- [Pic70] R. M. PICK, M. H. COHEN, and R. M. MARTIN, Microscopic Theory of Force Constants in Adiabatic Approximation, *Phys. Rev. B* **1**, 910 (1970).
- [Gon89] X. GONZE, and J. P. VIGNERON, Density-functional approach to nonlinear-response coefficients of solids, *Phys. Rev. B* **39**, 13120 (1989).
- [Ste54] R. M. STERNHEIMER, Electronic Polarizabilities of Ions from the Hartree-Fock Wave Functions, *Phys. Rev.* **96**, 951 (1954).
- [Bar87] S. BARONI, P. GIANNOZZI, and A. TESTA, Green's-Function Approach to Linear Response in Solids, *Phys. Rev. Lett.* **58**, 1861 (1987).
- [Bar01] S. BARONI, S. DE GIRONCOLI, A. D. CORSO, and P. GIANNOZZI, Phonons and related crystal properties from density-functional perturbation theory, *Rev. Mod. Phys.* **73**, 515 (2001).
- [Gir95] S. DE GIRONCOLI, Lattice dynamics of metals from density-functional perturbation theory, *Phys. Rev. B* **51**, 6773 (1995).