Aspects of Frozen-Phonon Calculations: Theory and Application to High Temperature Superconductors

Dissertation

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Contents

Symbols and abbreviations

$\mathbf{T}$	Real-space lattice vector
$\mathbf{S}_\alpha$	Undistorted position vector of nucleus α
Ω	Volume of primitive unit cell
Ω_s	Volume of super-cell
N	Number of primitive unit cells contained within the super-cell
MT_α	Atomic (Muffin-tin) sphere of atom α
Int	Interstitial
R_α	Radius of atomic sphere around nucleus α
Z_α	Nuclear charge of atom α
$V_{eff}(\mathbf{r})$	Unperturbed effective potential
$V_{nuc}(\mathbf{r})$	Unperturbed Coulomb potential of nuclei
$V_c(\mathbf{r})$	Unperturbed total Coulomb potential (nuclei and electrons)
$V_{xc}(\mathbf{r})$	Unperturbed exchange-correlation potential
$n, \mathbf{k}$	Band and $\mathbf{k}$-point index
$\Psi_{n,\mathbf{k}}(\mathbf{r})$	Kohn-Sham orbital
$\varepsilon_{n,\mathbf{k}}$	Kohn-Sham eigenvalue
$\mathbf{G}$	Lattice vector in reciprocal space
$G_{\max}$	Maximum length of $(\mathbf{k}+\mathbf{G})$ in the Kohn-Sham eigenvalue problem
$C_{n,\mathbf{k}}(\mathbf{G})$	Variational coefficient in the Kohn-Sham eigenvalue problem
$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$	LAPW basis function
$Y_{LM}(\mathbf{r})$	Complex spherical harmonic
$\rho_v(\mathbf{r})$	Unperturbed charge density of valence electrons
$\rho_c(\mathbf{r})$	Unperturbed charge density of core electrons
$\rho(\mathbf{r})$	Unperturbed total charge density
$\rho^{ph}(\mathbf{r})$	Total charge density of perturbed (phonon-distorted) crystal
δ^+	Change in the forward-traveling-wave representation
δ^-	Change in the backward-traveling-wave representation
$\delta^+\mathbf{S}_\alpha$	Complex polarization vector of a phonon-related displacement
$\mathbf{q}$	Wave-vector of the perturbation
$\delta^+\check{V}(\mathbf{r})$	Soft change of potential
$\delta^+\check{\rho}(\mathbf{r})$	Soft change of density
$\Theta(\mathbf{r}), \Theta_0(\mathbf{r})$	Step function of unperturbed crystal
$\Theta_{\delta\mathbf{S}}(\mathbf{r})$	Step function with regard to the perturbed super-cell

$\mathbf{F}_\alpha$	Atomic force on nucleus α in the standing-wave representation
$\delta^+\mathbf{F}_\alpha$	First-order change of the atomic force $\mathbf{F}_\alpha$
BZ	Brillouin zone
DFT	density functional theory
LAPW	linearized augmented plane-wave
LDA	local density approximation
SCF	self-consistent field
KS	Kohn-Sham

Introduction

The atoms in a solid are continuously oscillating about their equilibrium positions with an energy which is determined by the chemical composition of the material, the structural parameters and the temperature. In periodic lattices these oscillations are called lattice vibrations or, if viewed as lattice waves in a quantum mechanical framework, phonons. They are, entirely or in part, responsible for a very large number of properties, such as the specific heat, optical and dielectric properties and electrical resistance. For this reason the interest in the theoretical determination of eigenfrequencies and eigenvectors of phonons has already emerged as a scientific challenge several decades ago. Although the early approaches had to rely very much on empirical or semi-empirical models for interatomic potentials they have been and still are quite successful at complementing available experimental data. However, with the appearance of realistic self-consistent band structure calculations within the framework of density functional theory (DFT) [1, 2] twenty years ago the door was opened to calculate lattice vibrations from *first-principles.* Under the assumptions of (i) an ideal crystalline structure implying perfect translational symmetry, and (ii) the adiabatic approximation providing a clear and physically founded framework to separate the motion of the electrons from the dynamics of the nuclei the potentials governing the lattice vibrations could be established by the so called frozen-phonon technique [3]. In practical terms this is traditionally realized by the following procedure. First a super-cell commensurate with the wave-vector of the phonon is set up. It will contain a specific number N of primitive unit cells. Next, the atoms in this super-cell are slightly displaced from their perfect crystalline lattice sites in accordance with the translational requirements of the phonon mode. For this frozen-in ionic configuration the total energy of the crystal is then calculated. Repeating the last step for a whole series of different displacement patterns yields a set of discrete total energy values which are subsequently fitted to a polynomial function around the equilibrium structure. This polynomial function is called energy surface and its harmonic contributions describe the phonon potentials. In general excellent agreement is found between the thus derived phonon frequencies and the corresponding experimental data for all types of materials. Nevertheless with regard to computational efficiency and even accessibility there are severe restrictions in this approach. Phonons with a low-symmetry wave-vector will generate a large super-cell. As the computational effort to perform a self-consistent band structure calculation at one displacement pattern roughly scales with N^3 this approach is very much limited to high-symmetry phonons. Additionally the number of fit parameters to be determined for a harmonic energy surface scales with N_F^2, where N_F represents the number of degrees of freedom (number of atoms) within the primitive unit cell. This scaling behaviour thus also applies to the number of different displacement patterns at which band structure calculations have to be carried out. The later argument implies that the application of the method to highly complex materials (like high-temperature superconductors) is computationally extremely costly even at high symmetry-points in the Brillouin zone.

Two main strategies have been developed to overcome these limitations. On the one hand analytic expressions for the calculation of atomic forces [4, 5] acting on the nuclei in a non-equilibrium configuration have been formulated and subsequently implemented in all main band structure programs. The atomic force related to a specific nuclear coordinate is defined as the negative partial derivative of the energy surface with respect to this coordinate. The resulting information on the gradient of the energy surface supplements the calculated total energy data of the frozen-phonon calculations and in this way significantly lowers the required number of displacement patterns. In fact this number now only scales linearly with N_F. Additionally the knowledge of atomic forces in the vicinity of the equilibrium structure is also very well suited to extract more detailed information on the shape of the energy surface. In this way it serves to obtain a quantitative picture of anharmonicities which affect important physical quantities like thermal expansion coefficients, the thermal conductivity of insulators or the life-time of phonons.

On the other hand the conventional frozen-phonon technique has been coupled to the concepts of first-order perturbation theory. In this approach the phonon-related small displacements of the ionic coordinates are viewed to generate a dipole potential to which the electrons respond by rearranging their spatial distribution. Within the linear regime this response can mathematically be described by first-order perturbation theory on the wave functions of the electrons appearing in the band structure calculations. Imposing the self-consistency requirement between first-order changes in the potentials and densities analytically in this formalism results in the necessity to explicitly calculate the dielectric matrix (DM) of the system (DM-approach) [6]. Alternatively the self-consistency requirement can also be fulfilled by a numerical process which very much resembles the concepts of the conventional band structure programs. In this approach the first-order counterparts to the main equations appearing in the unperturbed SCF-cycle (e.g. Poisson equation, Kohn-Sham equation, etc.) are formulated and programmed thus providing an *iterative cycle* through which the self-consistency between perturbing potential and charge response can be obtained [7, 8]. The key advantage of both perturbative methods lies in the fact that the associated computational effort can be met *independently of the length and symmetry of the wave-vector* $\mathbf{q}$.

This thesis is partitioned into two main chapters. In the first one, a complete derivation of the linear-response formalism based on the aforementioned iterative process is presented for the full-potential LAPW method. As a prerequisite the procedure to set up the dynamical matrix from first-order atomic-forces is established. In the second chapter, detailed frozen-phonon calculations of Raman frequencies in the high-temperature superconductor $YBa_2Cu_3O_7$ are presented and discussed in comparison to related experimental data.

Chapter 1

Ab-initio phonon calculations based on linear-response theory

1.1 Determination of the dynamical matrix

The ab-initio calculation of the frequencies and eigenvectors of lattice vibrations in a crystal assumes the validity of the Born-Oppenheimer approximation [9]. This approximation introduces the adiabatic principle, which states that due to the large difference in mass between the crystal's electrons and nuclei the electrons will accommodate themselves almost instantaneously to any motion of the nuclei. As a result the system of electrons is permanently found in its quantum mechanical ground state, which itself only depends on the position vectors of the atomic nuclei. In this scenario the effective potential governing the motion of the nuclei then consists of two contributions: (i) the direct electrostatic potential between the point charges of the nuclei, and (ii) the total energy of the quantum mechanical ground state of the electronic system given as a sole function of the nuclear coordinates. Whereas the first contribution can be calculated in the framework of classical electrostatics the determination of the second one is more complex and is traditionally based on the following procedure: First the system of nuclei is frozen in a certain configuration. The resulting bare nuclear Coulomb potential is treated as an external potential in the electronic Hamiltonian. The ground state charge distribution and energy related to this Hamiltonian are then found within the framework of density functional theory (DFT) [1, 2]. Repeating this procedure for a whole set of different nuclear configurations yields a discrete set of energy values depending on the nuclear coordinates. Finally by numerical interpolation of these data the continuous energy function described in (ii) can be constructed.

This function in combination with the contribution from (i) yields a total energy surface which represents the effective potential responsible for the dynamics of the nuclei. Its minima determine the stable structures (phases) of the crystalline system. The gradient of the energy surface yields the atomic forces exerted on the nuclei. In the vicinity of the minima these forces will give rise to lattice vibrations which are termed phonons when viewed as collective excitations in a quantum mechanical sense. In the framework of these ideas we will now review the mathematical concepts and certain calculational methods to describe vibronic properties of periodic structures.

1.1.1 Basic concepts: energy surface and atomic forces

The starting point is the Taylor expansion of the energy surface around an equilibrium configuration of the nuclei located at $\mathbf{S}$:

$$E(\mathbf{S}+\mathbf{u}) = E_0 + \frac{1}{2}\sum_{\mathbf{T},\mathbf{T}'}\sum_{\alpha,\alpha'}\sum_{x,x'} u^{\mathbf{T}}_{\alpha,x}\left[\frac{\partial^2 E}{\partial u^{\mathbf{T}}_{\alpha,x} u^{\mathbf{T}'}_{\alpha',x'}}\right]_{\mathbf{S}} u^{\mathbf{T}'}_{\alpha',x'} + O(u^3), \tag{1.1}$$

where the general position vector $\mathbf{S}^{\mathbf{T}}_{\alpha}$ of an atomic nucleus with index α (and mass m_α) located in the primitive unit cell $\mathbf{T}$ is given by,

$$\mathbf{S}^{\mathbf{T}}_{\alpha} = \mathbf{T} + \mathbf{S}_\alpha + \mathbf{u}_\alpha. \tag{1.2}$$

$\mathbf{S}_\alpha$ is the position vector of the nucleus measured from the origin of the cell $\mathbf{T}$ when there are no displacements present in the crystal. The collection of all vectors $\{\mathbf{T}+\mathbf{S}_\alpha\}$ has been denoted by the symbol $\mathbf{S}$. $\mathbf{u}_\alpha$ is a vector describing the displacement of the nucleus away from equilibrium. The displacements are assumed small enough so that third- and higher-order terms in the Taylor expansion (1.1) are negligible. This assumption is called the harmonic approximation. The second partial derivatives of the energy surface are called real-space force constants and are commonly abbreviated in the following way:

$$\Phi^{\alpha\alpha'}_{xx'}(\mathbf{T},\mathbf{T}') \equiv \left[\frac{\partial^2 E}{\partial u^{\mathbf{T}}_{\alpha,x} u^{\mathbf{T}'}_{\alpha',x'}}\right]_{\mathbf{S}}. \tag{1.3}$$

The translational invariance of the undistorted crystal leads to the condition that with regard to the cell vectors $\mathbf{T}$ and $\mathbf{T}'$ the force constants can only depend on the relative vector $(\mathbf{T}-\mathbf{T}')$, i.e.,

$$\Phi^{\alpha\alpha'}_{xx'}(\mathbf{T},\mathbf{T}') = \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T}-\mathbf{T}'). \tag{1.4}$$

If $E(\mathbf{S}+\mathbf{u})$ is now combined with the kinetic energy of the nuclei we obtain the total Hamiltonian of the system,

$$H = E_0 + \frac{1}{2}\sum_{\mathbf{T},\mathbf{T}'}\sum_{\alpha,\alpha'}\sum_{x,x'} u^{\mathbf{T}}_{\alpha,x}\Phi^{\alpha\alpha'}_{xx'}(\mathbf{T},\mathbf{T}')u^{\mathbf{T}'}_{\alpha',x'} + \frac{1}{2}\sum_{\mathbf{T},\alpha,x} m_\alpha(\dot{u}^{\mathbf{T}}_{\alpha,x})^2, \tag{1.5}$$

which gives the following equations of motion for the nuclei:

$$m_\alpha \ddot{u}^{\mathbf{T}}_{\alpha,x} = F^{\mathbf{T}}_{\alpha,x} = -\frac{\partial E}{\partial u^{\mathbf{T}}_{\alpha,x}} = -\sum_{\alpha',x',\mathbf{T}'} \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T},\mathbf{T}')u^{\mathbf{T}'}_{\alpha',x'}, \tag{1.6}$$

with $\mathbf{F}^{\mathbf{T}}_\alpha$ being the atomic force. This system of differential equations couples $3 \times N_{tot} \times s$ degrees of freedom, with N_{tot} being the number of primitive unit cells in the crystal defined by the periodic boundary conditions and s being the number of atoms in one unit cell. To simplify the problem, the motions of the atoms can be decomposed into lattice waves characterized by a wave-vector $\mathbf{q}$. This is achieved by the following ansatz:

$$\mathbf{u}^{\mathbf{T}}_\alpha = \frac{1}{\sqrt{m_\alpha}}\mathbf{U}_\alpha e^{i\mathbf{q}\mathbf{T}} e^{-i\omega(\mathbf{q})t} \tag{1.7}$$

where $\mathbf{U}_\alpha$ denotes a complex polarization vector which is independent of the unit-cell index $\mathbf{T}$. Inserting (1.7) into (1.6) leads to the coupled system of equations,

$$\omega^2(\mathbf{q})U_{\alpha,x} = \sum_{\alpha' x'} D^{\alpha\alpha'}_{xx'}(\mathbf{q})U_{\alpha',x'}. \tag{1.8}$$

For a given $\mathbf{q}$-vector, $D^{\alpha\alpha'}_{xx'}(\mathbf{q})$ is a matrix of dimension $3s \times 3s$ which is called the dynamical matrix:

$$D^{\alpha\alpha'}_{xx'}(\mathbf{q}) = \frac{1}{\sqrt{m_\alpha m_{\alpha'}}}\sum_{\mathbf{T}'} \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T}',0)e^{-i\mathbf{q}\mathbf{T}'}. \tag{1.9}$$

It is a Hermitian matrix, i.e.,

$$D^{\alpha'\alpha}_{x'x}(\mathbf{q}) = [D^{\alpha\alpha'}_{xx'}(\mathbf{q})]^*, \tag{1.10}$$

and also fulfils the relationship

$$D^{\alpha\alpha'}_{xx'}(-\mathbf{q}) = [D^{\alpha\alpha'}_{xx'}(\mathbf{q})]^*. \tag{1.11}$$

Further relationships may be obtainable on the basis of the space group symmetry of the crystal under consideration [10]. By diagonalizing the dynamical matrix for a given $\mathbf{q}$-vector a total of $3 \times s$ different eigenmodes (phonon modes), characterized by eigenfrequencies $\omega_j(\mathbf{q})$ and corresponding eigenvectors $\mathbf{e}_j(\mathbf{q})$ are obtained. The index j runs from 1 to $3 \times s$ and labels the different modes. To accomplish the correct total number of modes in the whole crystal the values of $\mathbf{q}$ are restricted by the condition:

$$\mathbf{q} = n_1(\frac{\mathbf{G}_1}{N_1}) + n_2(\frac{\mathbf{G}_2}{N_2}) + n_3(\frac{\mathbf{G}_3}{N_3}), \qquad n_i = 0, ..., (N_i - 1); \tag{1.12}$$

with N_i denoting the number of primitive unit cells composing the crystal (Born-van Karman boundary conditions) in the direction of one primitive lattice vector.

1.1.2 The super-cell approach

The direct employment of Eq.(1.1) to set up the dynamical matrix requires the knowledge of the entire energy surface. To establish it according to the traditional method based on the interpolation of energy values is only possible for very simple crystal structures where the value of the force constants is negligible beyond the second or third neighbour shells. The application of the method to more complex structures is limited by the computer capacities available today. We therefor want to turn now to alternative ab-initio techniques based on atomic-force calculations to numerically determine the dynamical matrix if the energy surface and thus the force constants are not known.

In the super-cell approach based on atomic forces [11] the starting point to compute $D^{\alpha\alpha'}_{xx'}(\mathbf{q})$ would be to relax the internal coordinates of the primitive unit cell to their equilibrium positions $\mathbf{S}$. In this configuration the atomic forces will be vanishing, i.e.,

$$\left.\frac{\partial E}{\partial u^{\mathbf{T}}_{\alpha,x}}\right|_{\mathbf{S}} = 0 \qquad \text{for all } \mathbf{T}, \alpha \text{ and } x.$$

Next a series of lattice distortions of the form,

$$\mathbf{u}^{\mathbf{T}}_{\alpha} = \delta^{+}\mathbf{S}_{\alpha} e^{i\mathbf{q}\mathbf{T}} + [\delta^{+}\mathbf{S}_{\alpha}]^{*} e^{-i\mathbf{q}\mathbf{T}}, \tag{1.13}$$

would be frozen in. $\delta^{+}\mathbf{S}_{\alpha}$ is a complex polarization vector. This vector is assumed to be small enough to conform to the requirements of the harmonic approximation. The resulting change of the atomic force acting on atom α in the primitive unit cell located at lattice vector $\mathbf{T}$ will then be given by:

$$\delta F^{\mathbf{T}}_{\alpha,x} = -\left.\frac{\partial E}{\partial u^{\mathbf{T}}_{\alpha,x}}\right|_{\mathbf{S}+\mathbf{u}} + \left.\frac{\partial E}{\partial u^{\mathbf{T}}_{\alpha,x}}\right|_{\mathbf{S}} = -\sum_{\alpha',x',\mathbf{T}'} \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T}-\mathbf{T}') u^{\mathbf{T}'}_{\alpha',x'}$$

$$\begin{aligned}
&= -\sum_{\alpha',x',\mathbf{T}'} \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T}-\mathbf{T}')[\delta^+S_{\alpha',x'}e^{i\mathbf{q}\mathbf{T}'} + [\delta^+S_{\alpha',x'}]^* e^{-i\mathbf{q}\mathbf{T}'}] \\
&= -e^{i\mathbf{q}\mathbf{T}}\left[\sum_{\alpha',x',\mathbf{T}'} \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T}-\mathbf{T}')e^{-i\mathbf{q}(\mathbf{T}-\mathbf{T}')}\right]\delta^+S_{\alpha',x'} \\
&\quad -e^{-i\mathbf{q}\mathbf{T}}\left[\sum_{\alpha',x',\mathbf{T}'} \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T}-\mathbf{T}')e^{-i\mathbf{q}(\mathbf{T}-\mathbf{T}')}\right]^* [\delta^+S_{\alpha',x'}]^* \\
&= -\left[e^{i\mathbf{q}\mathbf{T}}\sum_{\alpha',x'} \tilde{\Phi}^{\alpha\alpha'}_{xx'}(\mathbf{q})\delta^+S_{\alpha',x'} + e^{-i\mathbf{q}\mathbf{T}}\sum_{\alpha',x'}[\tilde{\Phi}^{\alpha\alpha'}_{xx'}(\mathbf{q})]^*[\delta^+S_{\alpha',x'}]^*\right], \qquad (1.14)
\end{aligned}$$

where

$$\tilde{\Phi}^{\alpha\alpha'}_{xx'}(\mathbf{q}) = \sum_{\mathbf{T}} \Phi^{\alpha\alpha'}_{xx'}(\mathbf{T}-\mathbf{0})e^{-i\mathbf{q}\mathbf{T}} = \sqrt{m_\alpha m_{\alpha'}}D^{\alpha\alpha'}_{xx'}(\mathbf{q}) \qquad (1.15)$$

is the Fourier transform of the real-space force constants. By employing the mathematical tool of the complex-valued change in the force vector,

$$\delta^+F^{\mathbf{T}}_{\alpha,x} \equiv -e^{i\mathbf{q}\mathbf{T}}\sum_{\alpha',x'} \tilde{\Phi}^{\alpha\alpha'}_{xx'}(\mathbf{q})\delta^+S_{\alpha',x'}, \qquad (1.16)$$

displaying the translational property,

$$\delta^+\mathbf{F}^{\mathbf{T}}_{\alpha} = e^{i\mathbf{q}\mathbf{T}}\delta^+\mathbf{F}^{\mathbf{0}}_{\alpha}, \qquad (1.17)$$

Eq.(1.14) can also be written as:

$$\delta F^{\mathbf{T}}_{\alpha,x} = \delta^+F^{\mathbf{T}}_{\alpha,x} + [\delta^+F^{\mathbf{T}}_{\alpha,x}]^* = e^{i\mathbf{q}\mathbf{T}}\delta^+F^{\mathbf{0}}_{\alpha,x} + e^{-i\mathbf{q}\mathbf{T}}[\delta^+F^{\mathbf{0}}_{\alpha,x}]^*. \qquad (1.18)$$

On the basis of these definitions and relations the $3 \times s$ elements of the dynamical matrix can now be evaluated by the following algorithm: (i) $3 \times s$ linearly independent polarization vectors $\delta^+\mathbf{S}$ are constructed. (ii) For each resulting displacement pattern (denoted by index $j = 1...3 \times s$) the change in the atomic forces $\delta\mathbf{F}^{\mathbf{T},j}_{\alpha}$ on all atoms in two different primitive unit cells within the super-cell are calculated. For convenience we choose the first ($\mathbf{T} = \mathbf{0}$) and the second ($\mathbf{T} = \mathbf{T}_1$) cell. We want to stress that $\delta\mathbf{F}^{\mathbf{T},j}_{\alpha}$ is calculated here on the basis of a 'finite-difference-method' implying the following computational procedure: In the phonon-distorted crystal the ground-state electronic wave-function and the corresponding potential are determined by standard DFT techniques. From these data the atomic forces $\mathbf{F}^{\mathbf{T},j}_{\alpha}\big|_{\mathbf{S}+\mathbf{u}}$ for this configuration are calculated analytically as the sum of the Hellmann-Feynman forces [4] and corrective terms (Pulay forces [5]) where the latter depend on the band structure method employed [12, 13]. The numerical difference between $\mathbf{F}_\alpha^{\mathbf{T},j}\big|_{\mathbf{S}+\mathbf{u}}$ and the corresponding force at equilibrium $\mathbf{F}_\alpha^{\mathbf{T},j}\big|_{\mathbf{S}}$ yields $\delta\mathbf{F}_\alpha^{\mathbf{T}} + O(u^2)$. As $\mathbf{F}_\alpha^{\mathbf{T},j}\big|_{\mathbf{S}}$ is zero we obtain:

$$\delta\mathbf{F}_\alpha^{\mathbf{T},j} + O(u^2) = \mathbf{F}_\alpha^{\mathbf{T},j}\big|_{\mathbf{S}+\mathbf{u}}, \tag{1.19}$$

or in the harmonic approximation:

$$\delta\mathbf{F}_\alpha^{\mathbf{T},j} = \mathbf{F}_\alpha^{\mathbf{T},j}\big|_{\mathbf{S}+\mathbf{u}}. \tag{1.20}$$

The so constructed real-value force vectors $\left\{\delta\mathbf{F}_\alpha^{\mathbf{0},j}\right\}$ and $\left\{\delta\mathbf{F}_\alpha^{\mathbf{T}_1,j}\right\}$ are now converted to the complex-valued force vector $\{\delta^+\mathbf{F}_\alpha^{\mathbf{0},j}\}$ by the following relations:

$$\begin{aligned}
\mathrm{Re}(\delta^+\mathbf{F}_\alpha^{\mathbf{0},j}) &= \frac{1}{2}\delta\mathbf{F}_\alpha^{\mathbf{0},j}, && (1.21)\\
\mathrm{Im}(\delta^+\mathbf{F}_\alpha^{\mathbf{0},j}) &= \frac{\delta\mathbf{F}_\alpha^{\mathbf{0},j}\cos(\mathbf{q}\mathbf{T}_1) - \delta\mathbf{F}_\alpha^{\mathbf{T}_1,j}}{2\sin(\mathbf{q}\mathbf{T}_1)}. && (1.22)
\end{aligned}$$

(iii) By defining the following set of data,

$$\begin{aligned}
\mathbf{f}_1^j &\equiv \mathrm{Re}(\delta^+\mathbf{F}^{\mathbf{0},j}), & \mathbf{f}_2^j &\equiv \mathrm{Im}(\delta^+\mathbf{F}^{\mathbf{0},j}), && (1.23)\\
\tilde{\mathbf{\Phi}}_1(\mathbf{q}) &\equiv \mathrm{Re}(\tilde{\mathbf{\Phi}}(\mathbf{q})), & \tilde{\mathbf{\Phi}}_2(\mathbf{q}) &\equiv \mathrm{Im}(\tilde{\mathbf{\Phi}}(\mathbf{q})), && (1.24)\\
\delta^+\mathbf{S}_{\mathrm{Re}}^j &\equiv \mathrm{Re}(\delta^+\mathbf{S}^j), & \delta^+\mathbf{S}_{\mathrm{Im}}^j &\equiv \mathrm{Im}(\delta^+\mathbf{S}^j), && (1.25)
\end{aligned}$$

the coefficients of $\tilde{\mathbf{\Phi}}(\mathbf{q})$ (and thus via Eq.(1.15) also the coefficients of the dynamical matrix $\mathbf{D}(\mathbf{q})$) can finally be computed by solving the coupled set of linear matrix equations:

$$\begin{aligned}
\mathbf{f}_1^j &= -\tilde{\mathbf{\Phi}}_1(\mathbf{q})\delta^+\mathbf{S}_{\mathrm{Re}}^j + \tilde{\mathbf{\Phi}}_2(\mathbf{q})\delta^+\mathbf{S}_{\mathrm{Im}}^j, && (1.26)\\
\mathbf{f}_2^j &= -\tilde{\mathbf{\Phi}}_2(\mathbf{q})\delta^+\mathbf{S}_{\mathrm{Re}}^j - \tilde{\mathbf{\Phi}}_1(\mathbf{q})\delta^+\mathbf{S}_{\mathrm{Im}}^j, && (1.27)
\end{aligned}$$

which directly result from setting $\mathbf{T} = \mathbf{0}$ in Eq.(1.16). In some cases it will be possible to choose real-value polarization vectors and thus avoid all parts of the algorithm which involve imaginary quantities. It is obvious that this will become relevant as soon as the dynamical matrix can be chosen to be real (for example in the case of zone-center or zone-boundary phonons; for further examples see [10]).

1.1.3 The linear-response approach

In general, the algorithm described in the previous section will be suitable for practical applications as long as the number of primitive cells and the related number of atoms

(N_{at}) contained within the super-cell will not be too large. This is due to the fact that within band structure calculations the computational effort to obtain the electrons' wave-functions roughly scales as N^3_{basis}, where N_{basis} denotes the number of basis functions in the wave-function expansion. As N_{basis} scales linearly with N_{at} only phonons characterized by a $\mathbf{q}$-vector which is not too small and at least preserves some symmetry elements of the unperturbed lattice[1] will lend itself to super-cell calculations. From these considerations it is obvious that the bottle neck in our algorithm lies in step (ii) where the atomic forces are determined on the basis of band structure data. This automatically raises the question on the existence of an alternative strategy to determine $\delta\mathbf{F}^{\mathbf{T},j}_{\alpha}$ where the related computational effort is independent of the particular $\mathbf{q}$-value. The affirmative answer to this question is based on the observation that within the harmonic and adiabatic approximations the electronic contribution to the Fourier-space force constants can be related to the inverse static dielectric matrix $\epsilon^{-1}(\mathbf{q}+\mathbf{G}',\mathbf{q}+\mathbf{G})$ given by

$$\delta V(\mathbf{q}+\mathbf{G}) = \sum_{\mathbf{G}'} \epsilon^{-1}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')\delta V_{ext}(\mathbf{q}+\mathbf{G}'), \qquad (1.28)$$

[14][2]. $\delta V_{ext}(\mathbf{q}+\mathbf{G})$ denotes the first-order perturbing potential (in our case the change in the Coulomb potential caused by the displaced nuclei) whereas the first-order potential change $\delta V(\mathbf{q}+\mathbf{G})$ includes the perturbing potential, the screening of the charge response and also the first-order changes of the exchange-correlation potential. Thus the regime of linear response is sufficient to set up the dynamical matrix of a material. This automatically implies that the analytical calculation of the linear change in the atomic forces $\delta\mathbf{F}^{\mathbf{T},j}_{\alpha}$ only requires the knowledge of the linear changes in the density, the potentials and the wave-functions. In fact this is only a special case of the much more general '$(2n+1)$-theorem' which states: The knowledge of the change in the wave-function of a quantum mechanical system up to n^{th}-order in the perturbation parameter suffices to analytically determine the change in the total energy up to $(2n+1)^{th}$-order [15, 16]. In our problem n is equal to 1 and the perturbation parameter is the total displacement vector $\{\mathbf{u}_{\alpha}\}$. Explicit formulas for the analytic calculation of $\delta^{+}\mathbf{F}^{\mathbf{T},j}_{\alpha}$ (including the bare Coulomb interaction between the nuclei) will be derived in section (1.3.7).

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[1] The actual number will depend on the complexity of the investigated material.

[2] The full mathematical relation between the force constants and the inverse *total* static dielectric matrix including the effects of the bare nuclear interaction is rather involved. As it does not influence the main arguments which are relevant for the present work, we are not going to ouline it.

We have now introduced the notion that linear-response quantities provide the foundation for the calculation of the dynamical matrix. Thus the most obvious choice to simplify step (ii) of our algorithm would be to directly calculate the dielectric matrix $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$ in a one-particle picture as proposed by Adler and Wiser [17, 18] and invert the resulting matrix (DM-approach). The simplest expression, where exchange-correlation (xc) effects are neglected would read:

$$\begin{aligned}\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}') &= \delta_{\mathbf{G},\mathbf{G}'} + \frac{4\pi e^2}{\Omega\,|\mathbf{q}+\mathbf{G}|\,|\mathbf{q}+\mathbf{G}'|} \\ &\quad \times \sum_{c,v,\mathbf{k}} \frac{\left\langle \mathbf{k}+\mathbf{q},c \left| e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}} \right| \mathbf{k},v \right\rangle \left\langle \mathbf{k},v \left| e^{-i(\mathbf{G}'+\mathbf{q})\mathbf{r}} \right| \mathbf{k}+\mathbf{q},c \right\rangle}{\varepsilon_c(\mathbf{k}+\mathbf{q})-\varepsilon_v(\mathbf{k})},\end{aligned} \tag{1.29}$$

involving the occupied (v) and unoccupied (c) eigenstates of the unperturbed Hamiltonian of the electronic system. Expression (1.29) assumes that the first-order potentials felt by the electrons as well as the charge response can be well described by a Fourier series up to $2G_{\mathrm{max}}$ with[3] G,$G' \leq 2G_{\mathrm{max}}$. As already indicated $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$ has to be inverted to obtain the relevant matrix for the calculation of the first-order potential change (Eq.(1.28)). The underlying theoretical reason for this procedure is found in the derivation of Eq.(1.29) where the requirement of self-consistency between charge response and potential change is analytically imposed. The extension of the Adler-Wiser expression, Eq.(1.29), to include exchange and correlation effects and at the same time keeping its relative simple formal structure is only possible within local approximations of the xc-potential (LDA, GGA) [19, 20].

Although the whole procedure is largely independent of the selected $\mathbf{q}$-vector it displays a series of drawbacks in the context of band structure calculations: (i) Formula (1.29) can be handled easily only in the case of a plane-wave basis set. Thus the application to materials which also require a localized part in the basis set (e.g. materials containing heavy elements) is complicated. (ii) The set up of $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$ requires the knowledge of the entire eigenvalue spectrum (valence and conduction bands) of the unperturbed crystal. (iii) The inversion of $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$ is computationally a time consuming step. (iv) The possibilities to include non-local exchange correlation potentials in the formulas describing $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$ are limited and complicated.

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[3] We have choosen $2G_{\mathrm{max}}$ in order to conform with the conventions used in later chapters.

The method to circumvent these drawbacks is the direct application of first-order perturbation theory to the ground-state wave-function of the unperturbed crystal where the interplay between charge- and potential-response (self-consistency requirement) is treated numerically rather than analytically. This method will be described in detail in the next chapter. For now we only state that as in the DM-approach it also avoids the unfavourable scaling behaviour of the super-cell calculation with respect to the **q**-vector. Similar as in the DM-approach a 'price' has to be paid for this advantage: (i) Extra programming work has to be done (super-cell calculations can be performed without code-alterations of standard band structure programs) and (ii) information on possible higher-order responses of the system is lost – an information which is intrinsically available in super-cell calculations (compare with Eq.(1.19)) but not utilized in the harmonic approximation.

1.2 Density-functional linear-response theory

To set up the dynamical matrix for an arbitrary wave-vector **q** the first-order change of the atomic forces upon displacement patterns of the nuclei commensurate with this wave-vector have to be known. In the general framework of the Kohn-Sham (KS) scheme [2] within density functional theory (DFT) [1] the explicit calculation of these first-order forces will primarily require the knowledge of the electronic density, the Kohn-Sham orbitals (KS orbitals), the KS eigenvalues and the effective potential up to first-order in a perturbation expansion with respect to the polarization vector of the phonon-induced displacement patterns. In this section we want to review a well established and efficient iterative algorithm to calculate these four quantities for a periodic solid [7, 8, 21, 22, 23]. Its advantages compared to the DM approach and super-cell calculations will be summarized. For now, we are not going to make reference to a specific basis-set representation for wave-functions, potentials and densities but rather concentrate on the outline of general principles of the algorithm which is termed the 'iterative linear-response' (ILR) scheme. It was first introduced independently by Baroni et al. [7] and Zein et al. [8].

1.2.1 The iterative linear-response (ILR) scheme

The essential idea behind it can be summarized as follows: Within ground-state band structure calculations the electronic charge density is constructed on the basis of the occupied KS orbitals:

$$\rho(\mathbf{r}) = \sum_{n,\mathbf{k}} w(n,\mathbf{k}) \Psi^*_{n,\mathbf{k}}(\mathbf{r}) \Psi_{n,\mathbf{k}}(\mathbf{r}). \tag{1.30}$$

These orbitals are the solutions of the KS equations, which are formally single-particle Schrödinger equations with an effective potential depending on the charge density:

$$(-\nabla^2 + V_{eff}(\mathbf{r}) - \varepsilon_{n\mathbf{k}})\Psi_{n,\mathbf{k}}(\mathbf{r}) = 0 \qquad \mathbf{k} \in \text{I. BZ} \tag{1.31}$$

with

$$V_{eff}(\mathbf{r}) = V_{nuc}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + V_{xc}[\rho(\mathbf{r})]. \tag{1.32}$$

The effective potential consists of the bare Coulomb potential $V_{nuc}(\mathbf{r})$ stemming from the spatially fixed atomic nuclei, the Hartree potential of the electronic charge density and the exchange-correlation potential, assumed here to be described by the local density approximation (LDA). The three equations (1.30), (1.32) and (1.31) are solved iteratively until self-consistency is reached. At the end of the iteration process a charge density is thus obtained which has the following property: It generates an effective potential that when inserted into the KS equations yields orbitals which reproduce this density.

The phonon-related displacements of the nuclei are now treated as a first-order perturbation to the unperturbed self-consistent-field (SCF) cycle. The unperturbed quantities, i.e., charge density, effective potential and KS orbitals will thus experience a linear variation:

$$\rho(\mathbf{r}) \longrightarrow \rho(\mathbf{r}) + \delta\rho(\mathbf{r}), \tag{1.33}$$

$$V_{eff}(\mathbf{r}) \longrightarrow V_{eff}(\mathbf{r}) + \delta V_{eff}(\mathbf{r}), \tag{1.34}$$

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) \longrightarrow \Psi_{n,\mathbf{k}}(\mathbf{r}) + \delta\Psi_{n,\mathbf{k}}(\mathbf{r}). \tag{1.35}$$

By linearizing Eqs.(1.30),(1.31) and (1.32) we obtain a new set of equations, which are suitable to determine the first-order changes of these quantities:

$$\delta V_{eff}(\mathbf{r}) = \delta V_{nuc}(\mathbf{r}) + \int \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \delta\rho(\mathbf{r}) \left.\frac{dV_{xc}}{d\rho}\right|_{\rho(\mathbf{r})}, \tag{1.36}$$

$$(-\nabla^2 + V_{eff}(\mathbf{r}) - \varepsilon_{n\mathbf{k}})\delta\Psi_{n,\mathbf{k}}(\mathbf{r}) = -(\delta V_{eff}(\mathbf{r}) - \delta\varepsilon_{n\mathbf{k}})\Psi_{n,\mathbf{k}}(\mathbf{r}), \tag{1.37a}$$

$$\delta \left\langle \Psi_{n,\mathbf{k}}(\mathbf{r}) \middle| \Psi_{n,\mathbf{k}}(\mathbf{r}) \right\rangle = 0, \tag{1.37b}$$

$$\delta\rho(\mathbf{r}) = \sum_{n,\mathbf{k}} w(n,\mathbf{k})[\delta\Psi^*_{n,\mathbf{k}}(\mathbf{r})\Psi_{n,\mathbf{k}}(\mathbf{r}) + \Psi^*_{n,\mathbf{k}}(\mathbf{r})\delta\Psi_{n,\mathbf{k}}(\mathbf{r})], \tag{1.38}$$

where Eq.(1.37a) is called Sternheimer equation [24] and the constraint given in Eq.(1.37b) guarantees the conservation of the electronic charge in the system. The change in the effective potential consists of the 'external' perturbing potential $\delta V_{nuc}(\mathbf{r})$ screened by the induced charge density and supplemented by the related change in the exchange-correlation potential. For simplicity we have assumed that there is no change in the occupation number $w(n,\mathbf{k})$ upon the perturbation; a condition rigorously fulfilled by semiconductors and insulators. In close analogy to the unperturbed case, Eqs.(1.36), (1.37a), and (1.38) are solved by iteration until self-consistency is reached for the first-order effective potential and the density response. Note that the unperturbed KS orbitals and eigenvalues as well as the unperturbed effective potential are required as input quantities for the Sternheimer equation. Further, Eq.(1.36) requires the knowledge of the original charge distribution. Thus these quantities have to be calculated before the iterative linear-response process can be started.

We now review and discuss several aspects of this scheme in more detail [23]. We consider a lattice with several atoms in the unit cell. If a superposition of frozen-in phonons at wave-vector $\mathbf{q}$ are present in the crystal the atoms are displaced from their equilibrium position by a small amount

$$\begin{aligned}\delta\mathbf{S}_\alpha^{\mathbf{T}} &= \delta^+\mathbf{S}_\alpha e^{+i\mathbf{qT}} + \delta^-\mathbf{S}_\alpha e^{-i\mathbf{qT}} \\ &= \delta^+\mathbf{S}_\alpha e^{+i\mathbf{qT}} + [\delta^+\mathbf{S}_\alpha]^* e^{-i\mathbf{qT}}, \qquad (1.39)\end{aligned}$$

where $\delta^+\mathbf{S}_\alpha$ is a complex polarization vector and $\mathbf{T}$ is a lattice vector of the unperturbed crystal. The presence of such a displacement field will primarily give rise to a change in the bare Coulomb potential of the atomic nuclei. The first-order contribution to this change is the dipole field of the nuclei:

$$\begin{aligned}\delta V_{nuc}(\mathbf{r}) &= \sum_{\mathbf{T}} e^{+i\mathbf{qT}} \sum_\alpha \delta^+\mathbf{S}_\alpha \nabla \frac{-Z_\alpha}{|\mathbf{r}-\mathbf{S}_\alpha-\mathbf{T}|} \\ &\quad + \sum_{\mathbf{T}} e^{-i\mathbf{qT}} \sum_\alpha [\delta^+\mathbf{S}_\alpha]^* \nabla \frac{-Z_\alpha}{|\mathbf{r}-\mathbf{S}_\alpha-\mathbf{T}|} \\ &\equiv \delta^+ V_{nuc}(\mathbf{r}) + \delta^- V_{nuc}(\mathbf{r}). \qquad (1.40)\end{aligned}$$

It consists of a superposition of two traveling waves with wave-vector $+\mathbf{q}$ and $-\mathbf{q}$. The forward-traveling contribution $\delta^+ V_{nuc}(\mathbf{r})$ is related to the backward-traveling counterpart $\delta^- V_{nuc}(\mathbf{r})$ by the relation

$$\delta^+ V_{nuc}(\mathbf{r}) = [\delta^- V_{nuc}(\mathbf{r})]^*. \qquad (1.41)$$

From Eq.(1.40) we see that with regard to the unperturbed lattice the two contributions translate like Bloch-waves for wave-vectors $+\mathbf{q}$ and $-\mathbf{q}$, i.e.,

$$\begin{aligned}\delta^+ V_{nuc}(\mathbf{r}+\mathbf{T}) &= e^{+i\mathbf{q}\mathbf{T}}\delta^+ V_{nuc}(\mathbf{r}), &(1.42)\\ \delta^- V_{nuc}(\mathbf{r}+\mathbf{T}) &= e^{-i\mathbf{q}\mathbf{T}}\delta^- V_{nuc}(\mathbf{r}). &(1.43)\end{aligned}$$

The Bloch-type character of the contributions implies that they can also be written in the following way:

$$\begin{aligned}\delta^+ V_{nuc}(\mathbf{r}) &= e^{+i\mathbf{q}\mathbf{r}}\delta^+ v_{nuc}(\mathbf{r}), &(1.44)\\ \delta^- V_{nuc}(\mathbf{r}) &= e^{-i\mathbf{q}\mathbf{r}}\delta^- v_{nuc}(\mathbf{r}), &(1.45)\end{aligned}$$

with $\delta^+ v_{nuc}(\mathbf{r})$ and $\delta^- v_{nuc}(\mathbf{r})$ being periodic functions with respect to the undistorted lattice. In the first cycle of iteration this dipole field can be chosen to describe the change in the effective potential.

We now turn to the solution of the Sternheimer equation. If the potential change given by (1.40) is inserted into Eq.(1.37a) and we use the expressions from standard (non-degenerate) perturbation theory to calculate $\delta\Psi_{n,\mathbf{k}}(\mathbf{r})$ we obtain:

$$\delta\Psi_{n,\mathbf{k}}(\mathbf{r}) = \delta^+\Psi_{n,\mathbf{k}}(\mathbf{r}) + \delta^-\Psi_{n,\mathbf{k}}(\mathbf{r}), \tag{1.46}$$

with

$$\begin{aligned}\delta^+\Psi_{n,\mathbf{k}}(\mathbf{r}) &= \sum_m \frac{\langle\Psi_{m,\mathbf{k}+\mathbf{q}}(\mathbf{r})|\,\delta^+ V_{nuc}(\mathbf{r})\,|\Psi_{n,\mathbf{k}}(\mathbf{r})\rangle_\Omega}{\varepsilon_{n,\mathbf{k}} - \varepsilon_{m,\mathbf{k}+\mathbf{q}}}\Psi_{m,\mathbf{k}+\mathbf{q}}(\mathbf{r}), &(1.47)\\ \delta^-\Psi_{n,\mathbf{k}}(\mathbf{r}) &= \sum_m \frac{\langle\Psi_{m,\mathbf{k}-\mathbf{q}}(\mathbf{r})|\,\delta^- V_{nuc}(\mathbf{r})\,|\Psi_{n,\mathbf{k}}(\mathbf{r})\rangle_\Omega}{\varepsilon_{n,\mathbf{k}} - \varepsilon_{m,\mathbf{k}-\mathbf{q}}}\Psi_{m,\mathbf{k}-\mathbf{q}}(\mathbf{r}). &(1.48)\end{aligned}$$

with Ω denoting the volume of the unperturbed unit cell. It is evident from expressions (1.47) and (1.48) that $\delta^\pm\Psi_{n,\mathbf{k}}(\mathbf{r})$ translate like Bloch-waves of wave-vector $(\mathbf{k}\pm\mathbf{q})$:

$$\begin{aligned}\delta^+\Psi_{n,\mathbf{k}}(\mathbf{r}) &= \delta^+ u_{n,\mathbf{k}}(\mathbf{r})e^{i(\mathbf{k}+\mathbf{q})\mathbf{r}}, &(1.49)\\ \delta^-\Psi_{n,\mathbf{k}}(\mathbf{r}) &= \delta^- u_{n,\mathbf{k}}(\mathbf{r})e^{i(\mathbf{k}-\mathbf{q})\mathbf{r}}. &(1.50)\end{aligned}$$

The sums in Eqs.(1.47) and (1.48) should in principle go over all band states of the first Brillouin zone. However, if we take into account the translational properties of the KS orbitals and of the potential change, the matrix element $\langle\Psi_{m,\mathbf{k}'}(\mathbf{r})|\,\delta^\pm V_{nuc}(\mathbf{r})\,|\Psi_{n,\mathbf{k}}(\mathbf{r})\rangle_\Omega$

will be non-vanishing only in the case of $\mathbf{k}' = \mathbf{k} \pm \mathbf{q}$:

$$\begin{aligned}
\langle \Psi_{m,\mathbf{k}+\mathbf{q}}(\mathbf{r})|\, \delta^{\pm} V_{nuc}(\mathbf{r})\, |\Psi_{n,\mathbf{k}}(\mathbf{r})\rangle_{\Omega} &\equiv \frac{1}{N} \langle \Psi_{m,\mathbf{k}'}(\mathbf{r})|\, \delta^{\pm} V_{nuc}(\mathbf{r})\, |\Psi_{n,\mathbf{k}}(\mathbf{r})\rangle_{\Omega_s} \\
&= \frac{1}{N} \int_{\Omega_s} e^{-i\mathbf{k}'\mathbf{r}} u^*_{\mathbf{k}',m}(\mathbf{r}) e^{\pm i\mathbf{q}\mathbf{r}} \delta^{\pm} v_{nuc}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k},n}(\mathbf{r}) d^3\mathbf{r} \\
&= \frac{1}{N} \sum_{\mathbf{T}} e^{i(\mathbf{k}-\mathbf{k}'\pm\mathbf{q})\mathbf{T}} \\
&\quad \times \int_{\Omega} e^{i(\mathbf{k}-\mathbf{k}'\pm\mathbf{q})\mathbf{r}} u^*_{\mathbf{k}',m}(\mathbf{r}) \delta^{\pm} v_{nuc}(\mathbf{r}) u_{\mathbf{k},n}(\mathbf{r}) d^3\mathbf{r} \\
&= \delta_{\mathbf{k}',\mathbf{k}\pm\mathbf{q}} \int_{\Omega} u^*_{\mathbf{k}',m}(\mathbf{r}) \delta^{\pm} v_{nuc}(\mathbf{r}) u_{\mathbf{k},n}(\mathbf{r}) d^3\mathbf{r}. \qquad (1.51)
\end{aligned}$$

with Ω_s denoting the volume of the smallest possible supercell commensurate with the phonon wave-vector $\mathbf{q}$ and N being the number of unperturbed unit cells within this cell. On a similar line of reasoning we demonstrate that the change in the KS eigenvalue vanishes for $\mathbf{q} \neq \mathbf{0}$:

$$\begin{aligned}
\delta\varepsilon_{n\mathbf{k}} &= \frac{1}{N} \langle \Psi_{n,\mathbf{k}}(\mathbf{r})|\, \delta^{+} V_{nuc}(\mathbf{r}) + \delta^{-} V_{nuc}(\mathbf{r})\, |\Psi_{n,\mathbf{k}}(\mathbf{r})\rangle_{\Omega_s} \\
&= \frac{1}{N} \sum_{\mathbf{T}} e^{+i\mathbf{q}\mathbf{T}} \int_{\Omega} e^{+i\mathbf{q}\mathbf{r}} \left|u_{\mathbf{k},n}(\mathbf{r})\right|^2 \delta^{+} v_{nuc}(\mathbf{r}) d^3\mathbf{r} \\
&\quad + \frac{1}{N} \sum_{\mathbf{T}} e^{-i\mathbf{q}\mathbf{T}} \int_{\Omega} e^{-i\mathbf{q}\mathbf{r}} \left|u_{\mathbf{k},n}(\mathbf{r})\right|^2 \delta^{-} v_{nuc}(\mathbf{r}) d^3\mathbf{r} \\
&= 0. \qquad (1.52)
\end{aligned}$$

Given the change in the KS orbitals the first-order change in the charge density can be constructed by inserting Eqs.(1.49) and (1.50) into Eq.(1.38):

$$\begin{aligned}
\delta\rho(\mathbf{r}) &= \sum_{n,\mathbf{k}} w(n,\mathbf{k}) \{ [\delta^{+}\Psi_{n,\mathbf{k}}(\mathbf{r})]^* \Psi_{n,\mathbf{k}}(\mathbf{r}) + [\delta^{-}\Psi_{n,\mathbf{k}}(\mathbf{r})]^* \Psi_{n,\mathbf{k}}(\mathbf{r}) \\
&\quad + \Psi^*_{n,\mathbf{k}}(\mathbf{r}) \delta^{+} \Psi_{n,\mathbf{k}}(\mathbf{r}) + \Psi^*_{n,\mathbf{k}}(\mathbf{r}) \delta^{-} \Psi_{n,\mathbf{k}}(\mathbf{r}) \} \\
&= \sum_{n,\mathbf{k}} w(n,\mathbf{k}) \left\{ [\delta^{-} u_{n,\mathbf{k}}(\mathbf{r})]^* u_{n,\mathbf{k}}(\mathbf{r}) + u^*_{n,\mathbf{k}}(\mathbf{r}) \delta^{+} u_{n,\mathbf{k}}(\mathbf{r}) \right\} e^{+i\mathbf{q}\mathbf{r}} \\
&\quad + \sum_{n,\mathbf{k}} w(n,\mathbf{k}) \{ [\delta^{+} u_{n,\mathbf{k}}(\mathbf{r})]^* u_{n,\mathbf{k}}(\mathbf{r}) + u^*_{n,\mathbf{k}}(\mathbf{r}) \delta^{-} u_{n,\mathbf{k}}(\mathbf{r}) \} e^{-i\mathbf{q}\mathbf{r}} \\
&\equiv \delta^{+}\varrho(\mathbf{r}) e^{+i\mathbf{q}\mathbf{r}} + \delta^{-}\varrho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}}. \qquad (1.53)
\end{aligned}$$

We see that the first-order modification in the charge density exhibits the same translational properties as the dipole field. In fact if we insert expressions (1.53), (1.44) and (1.45) into Eq.(1.36) this statement can be generalized: All potential and charge disturbances calculated in the ILR scheme are composed of two contributions: One that is forward-traveling ($e^{+i\mathbf{qr}}$) and another one that is backward-traveling ($e^{-i\mathbf{qr}}$). The two contributions are complex-conjugate to each other. This opens up the possibility of restricting the ILR scheme from a standing-wave representation to a traveling-wave representation. Inspection of the three equations reveals that in the solution of the Sternheimer equation as well as in the construction of the effective potential change there is no mixing between forward- and backward-traveling quantities. Only with regard to the charge response (Eq.(1.53)) we see that the calculation of the forward- (backward-)traveling part requires the knowledge of $\delta^+\Psi_{n,\mathbf{k}}(\mathbf{r})$ *and* of $\delta^-\Psi_{n,\mathbf{k}}(\mathbf{r})$. To also decouple this part of the SCF cycle we use Kramer's theorem (time reversal symmetry) [25] for the unperturbed and perturbed KS orbitals. It shows that the following relations hold:

$$\begin{aligned}\Psi_{n,\mathbf{k}}(\mathbf{r}) &= \Psi^*_{n,-\mathbf{k}}(\mathbf{r}) \quad\Longrightarrow\quad u_{n,\mathbf{k}}(\mathbf{r}) = u^*_{n,-\mathbf{k}}(\mathbf{r}), &(1.54)\\ \delta^+\Psi_{n,\mathbf{k}}(\mathbf{r}) &= [\delta^-\Psi_{n,-\mathbf{k}}(\mathbf{r})]^* \quad\Longrightarrow\quad \delta^+u_{n,\mathbf{k}}(\mathbf{r}) = [\delta^-u_{n,-\mathbf{k}}(\mathbf{r})]^*. &(1.55)\end{aligned}$$

We now restrict ourselves to the forward-traveling-wave representation: Applying relations (1.54) and (1.55) to Eq.(1.53) and reordering the summation over the Brillouin-zone we obtain:

$$\begin{aligned}\delta^+\rho(\mathbf{r}) &\equiv \delta^+\varrho(\mathbf{r})e^{+i\mathbf{qr}}\\ &= e^{+i\mathbf{qr}}\sum_{n,\mathbf{k}} w(n,\mathbf{k})\{[\delta^-u_{n,\mathbf{k}}(\mathbf{r})]^*u_{n,\mathbf{k}}(\mathbf{r}) + u^*_{n,\mathbf{k}}(\mathbf{r})\delta^+u_{n,\mathbf{k}}(\mathbf{r})\}\\ &= e^{+i\mathbf{qr}}\sum_{n,-\mathbf{k}} w(n,-\mathbf{k})[\delta^+u_{n,-\mathbf{k}}(\mathbf{r})u^*_{n,-\mathbf{k}}(\mathbf{r})] + e^{+i\mathbf{qr}}\sum_{n,\mathbf{k}} w(n,\mathbf{k})[\delta^+u_{n,\mathbf{k}}(\mathbf{r})u^*_{n,\mathbf{k}}(\mathbf{r})]\\ &= 2e^{+i\mathbf{qr}}\sum_{n,\mathbf{k}} w(n,\mathbf{k})[\delta^+u_{n,\mathbf{k}}(\mathbf{r})u^*_{n,\mathbf{k}}(\mathbf{r})] = 2\sum_{n,\mathbf{k}} w(n,\mathbf{k})[\delta^+\Psi_{n,\mathbf{k}}(\mathbf{r})\Psi^*_{n,\mathbf{k}}(\mathbf{r})]. \quad (1.56)\end{aligned}$$

We can thus avoid the perturbation summation (1.48) for $\delta^-\Psi_{n,\mathbf{k}}(\mathbf{r})$ and instead calculate the required quantity with the help of the perturbation summation (1.47) at the band state $(n,-\mathbf{k})$. The formulation of the ILR scheme in terms of purely forward-traveling quantities is thus completed. For the case $\mathbf{q} \neq \mathbf{0}$ it can be summarized as follows:

$$\delta^+V_{eff}(\mathbf{r}) = \delta^+V_{nuc}(\mathbf{r}) + \int \frac{\delta^+\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d^3r' + \delta^+\rho(\mathbf{r})\left.\frac{dV_{xc}}{d\rho}\right|_{\rho(\mathbf{r})}, \qquad (1.57)$$

$$(-\nabla^2 + V_{eff}(\mathbf{r}) - \varepsilon_{n\mathbf{k}})\delta^+\Psi_{n,\mathbf{k}}(\mathbf{r}) = -\delta^+V_{eff}(\mathbf{r})\Psi_{n,\mathbf{k}}(\mathbf{r}) \qquad (1.58)$$

$$\Longrightarrow \quad \delta^+\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{m\neq n} \frac{\langle \Psi_{m,\mathbf{k}+\mathbf{q}}(\mathbf{r})|\, \delta^+ V_{eff}(\mathbf{r})\, |\Psi_{n,\mathbf{k}}(\mathbf{r})\rangle_\Omega}{\varepsilon_{n,\mathbf{k}} - \varepsilon_{m,\mathbf{k}+\mathbf{q}}} \Psi_{m,\mathbf{k}+\mathbf{q}}(\mathbf{r}), \tag{1.59}$$

$$\delta^+\rho(\mathbf{r}) = 2\sum_{n,\mathbf{k}} w(n,\mathbf{k})\delta^+\Psi_{n,\mathbf{k}}(\mathbf{r})\Psi^*_{n,\mathbf{k}}(\mathbf{r}). \tag{1.60}$$

With regard to practical calculations it is important to realize that the sum appearing in the perturbation expression (1.59) is only one way to determine the change in the KS orbitals. A powerful alternative would be to directly integrate the Sternheimer equation as given by Eq.(1.58). As only the occupied states are of interest for the charge response, this technique, in contrast to the employment of expression (1.59), will not require the knowledge of the unoccupied states of the band structure [7, 23]. Nevertheless, in case of crystalline solids the situation is complicated by the fact that the numerically computed eigenstates are only variational but not exact solutions of the KS equations. As these eigenstates are necessary input data for the Sternheimer equation it is clear that the solution for this differential equation will also have to comply with the Rayleigh-Ritz variational principle. The construction of this solution will be the topic of the next section.

1.2.2 The variational solution of the Sternheimer equation

We assume that the KS orbitals are expanded in terms of a set of non-orthogonal basis functions $\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$, which at least partly depend on the location of the atomic nuclei. Bloch sums of atom-centered localized orbitals constituting the basis functions of the LMTO and the LCAO method would comply with this criterion. Another example is the LAPW method, where atomic-like orbitals confined to a certain sphere volume are augmentations to a plane-wave basis set valid in the interstitial region between the atoms. The KS wavefunction will now read:

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}}(\mathbf{G})\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \tag{1.61}$$

We denote the number of terms in the sum by N_{basis}. The expansion coefficients $C_{n,\mathbf{k}}(\mathbf{G})$ are determined by the solutions of the generalized eigenvalue equations,

$$\sum_{\mathbf{G}'} (H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n,\mathbf{k}} S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}) C_{n,\mathbf{k}}(\mathbf{G}') = 0, \qquad \mathbf{k} \in \text{I.BZ} \tag{1.62}$$

with

$$H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \;\equiv\; \left\langle \phi_{\mathbf{k}+\mathbf{G}} \right| \hat{H} \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle, \tag{1.63}$$

$$S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \equiv \langle \phi_{\mathbf{k}+\mathbf{G}} | \phi_{\mathbf{k}+\mathbf{G}'} \rangle, \tag{1.64}$$

denoting the Hamiltonian and overlap matrix, respectively. Eq.(1.62) results from the variational minimization of the KS eigenvalues with respect to the expansion coefficients. In setting it up use had been made of the fact that in the unperturbed crystal there is no mixing between Bloch functions at different **k**-points of the first Brillouin zone. This implies that with respect to this zone the Hamiltonian and overlap matrix are block-diagonal, i.e.,

$$H_{\mathbf{k}+\mathbf{G},\mathbf{k}'+\mathbf{G}'} = \langle \phi_{\mathbf{k}+\mathbf{G}} | \hat{H} | \phi_{\mathbf{k}'+\mathbf{G}'} \rangle \delta_{\mathbf{k},\mathbf{k}'} \tag{1.65}$$

$$S_{\mathbf{k}+\mathbf{G},\mathbf{k}'+\mathbf{G}'} = \langle \phi_{\mathbf{k}+\mathbf{G}} | \phi_{\mathbf{k}'+\mathbf{G}'} \rangle \delta_{\mathbf{k},\mathbf{k}'} \tag{1.66}$$

and the eigenvalue problem can thus be solved for each **k**-point separately. We now introduce a phonon-induced displacement pattern of wave-vector **q** in the standing-wave representation (Eq.(1.39)). This will lead to a Hermitian change in the effective potential of the crystalline system, i.e.,

$$\delta V_{eff}(\mathbf{r}) = \delta^{+} V_{eff}(\mathbf{r}) + \delta^{-} V_{eff}(\mathbf{r}). \tag{1.67}$$

Additionally, the displacement of the atomic nuclei will also modify the basis functions in the variational scheme. This is due to our assumption of dealing with atom-centered orbitals in the basis set. The total first-order change in the KS orbital caused by the perturbation will thus be well described by the following expression [23, 26]:

$$\delta\Psi_{n,\mathbf{k}}(\mathbf{r}) = \delta^{+}\Psi_{n,\mathbf{k}}(\mathbf{r}) + \delta^{-}\Psi_{n,\mathbf{k}}(\mathbf{r}), \tag{1.68}$$

with

$$\delta^{\pm}\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \delta^{\pm} C_{n,\mathbf{k}}(\mathbf{G}) \phi_{\mathbf{k}\pm\mathbf{q}+\mathbf{G}}(\mathbf{r}) + \sum_{\mathbf{G}} C_{n,\mathbf{k}}(\mathbf{G}) \delta^{\pm}\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \tag{1.69}$$

where one contribution originates from the change of the variational coefficient and the second contribution describes the change of the wave-function due to the shift of the unperturbed localized orbitals. Although in this section we will not use an explicit formula for $\delta^{\pm}\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ (as this depends on the specific basis set used) two aspects should be born in mind: (i) The change in the basis function has to translate like a Bloch wave of wave-vector $(\mathbf{k} \pm \mathbf{q})$. This results from the requirements on the translational behaviour of $\delta^{\pm}\Psi_{n,\mathbf{k}}(\mathbf{r})$ as given by Eqs.(1.49) and (1.50). (ii) The functions $\delta^{\pm}\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ are obtained by an ansatz appropriate to the physical situation of the phonon distortion and are spatially fixed prior to the solution of the Sternheimer equation. In a crude physical picture the change in the basis set will have a significant contribution from the rigid movement of the localized orbitals. This will obviously be best described by the first-order term in a Taylor expansion of the shifted orbitals with respect to the coordinate system of the undisplaced nuclei.

We now want to find the first-order change of the matrix equation (1.62). The result will be the Sternheimer equation within the variational scheme and will provide a linear system of equations suitable to determine the change in the variational coefficients $\delta^{\pm}C_{n,\mathbf{k}}(\mathbf{G})$. We restrict our analysis to the case $\mathbf{q} \neq \mathbf{0}$ under the assumption of non-degeneracy between $\Psi_{n,\mathbf{k}}(\mathbf{r})$ and $\Psi_{n,\mathbf{k}\pm\mathbf{q}}(\mathbf{r})$. Concerning the structure of the H- and S-matrix with regard to the entire first Brillouin zone, a perturbation of type (1.67) will give rise to a first-order modification of the elements coupling the basis functions at point $\mathbf{k}$ with those at points $(\mathbf{k} \pm \mathbf{q})$. As a first explicit example we consider the H-matrix elements in the Block $(\mathbf{k}+\mathbf{q}, \mathbf{k})$. For this and later purposes we introduce the following convention to describe first-order changes within a matrix element:

$$\delta^{\pm}H_{i,j} \equiv \left\langle \delta^{\pm}\phi_i \middle| \hat{H} \middle| \phi_j \right\rangle + \left\langle \phi_i \middle| \delta^{\pm}\hat{H} \middle| \phi_j \right\rangle + \left\langle \phi_i \middle| \hat{H} \middle| \delta^{\pm}\phi_j \right\rangle \tag{1.70}$$

The changes in the various quantities related to the standing-wave representation of the phonon distortion will then modify the H-matrix elements in the following way:

$$\begin{aligned}
\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} &\equiv \delta^{+}H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} + \delta^{-}H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \\
&= \delta^{+}\left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| H \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \delta^{-}\left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| H \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \\
&= \left\langle \delta^{+}\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| H \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| \delta^{+}H \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \\
&\quad + \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| H \left| \delta^{+}\phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \left\langle \delta^{-}\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| H \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \\
&\quad + \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| \delta^{-}H \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \right| H \left| \delta^{-}\phi_{\mathbf{k}+\mathbf{G}'} \right\rangle .
\end{aligned} \tag{1.71}$$

The integrational region for each matrix element is the super-cell commensurate with the wave-vector of the perturbation. Thus for the value of a specific matrix element to be non-vanishing the respective total function to be integrated has to be periodic with the *undistorted* lattice[4]. In a more formal language this means that the product of all exponential factors $e^{\pm i\mathbf{q}\mathbf{T}}$ in the function has to amount to $e^{0} = 1$. Taking into account the translational properties of the basis functions, of the effective potential and of their respective first-order counterparts we now see that only three out of six contributions will remain

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[4] This is equivalent to the argument used in the derivation of Eq.(1.51).

in expression (1.71):

$$\delta H_{\mathbf{k+q+G},\mathbf{k+G'}} = \langle \phi_{\mathbf{k+q+G}} | \, \delta^{+} H \, | \phi_{\mathbf{k+G'}} \rangle + \langle \phi_{\mathbf{k+q+G}} | \, H \, | \delta^{+} \phi_{\mathbf{k+G'}} \rangle + \langle \delta^{-} \phi_{\mathbf{k+q+G}} | \, H \, | \phi_{\mathbf{k+G'}} \rangle . \tag{1.72}$$

In close analogy we can find the first-order change of the S-matrix:

$$\begin{aligned} \delta S_{\mathbf{k+q+G},\mathbf{k+G'}} &\equiv \delta^{+} S_{\mathbf{k+q+G},\mathbf{k+G'}} + \delta^{-} S_{\mathbf{k+q+G},\mathbf{k+G'}} \\ &= \delta^{+} \langle \phi_{\mathbf{k+q+G}} \, | \phi_{\mathbf{k+G'}} \rangle + \delta^{-} \langle \phi_{\mathbf{k+q+G}} \, | \phi_{\mathbf{k+G'}} \rangle \\ &= \langle \phi_{\mathbf{k+q+G}} \, | \delta^{+} \phi_{\mathbf{k+G'}} \rangle + \langle \delta^{-} \phi_{\mathbf{k+q+G}} \, | \phi_{\mathbf{k+G'}} \rangle . \end{aligned} \tag{1.73}$$

Similar derivations can be made for δH and δS in the three matrix blocks $(\mathbf{k}, \mathbf{k+q})$, $(\mathbf{k}, \mathbf{k-q})$ and $(\mathbf{k-q}, \mathbf{k})$. Applying the same line of reasoning to the block-diagonal parts of the H- and S-matrices will immediately reveal that these elements will not experience any first-order change, i.e.,

$$\begin{aligned} \delta H_{\mathbf{k+G},\mathbf{k+G'}} &= \langle \delta^{+} \phi_{\mathbf{k+G}} | \, H \, | \phi_{\mathbf{k+G'}} \rangle + \langle \phi_{\mathbf{k+G}} | \, \delta^{+} H \, | \phi_{\mathbf{k+G'}} \rangle + \langle \phi_{\mathbf{k+G}} | \, H \, | \delta^{+} \phi_{\mathbf{k+G'}} \rangle \\ &\quad + \langle \delta^{-} \phi_{\mathbf{k+G}} | \, H \, | \phi_{\mathbf{k+G'}} \rangle + \langle \phi_{\mathbf{k+G}} | \, \delta^{-} H \, | \phi_{\mathbf{k+G'}} \rangle + \langle \phi_{\mathbf{k+G}} | \, H \, | \delta^{-} \phi_{\mathbf{k+G'}} \rangle \\ &= 0, \end{aligned} \tag{1.74}$$

and

$$\begin{aligned} \delta S_{\mathbf{k+G},\mathbf{k+G'}} &= \langle \delta^{+} \phi_{\mathbf{k+G}} \, | \phi_{\mathbf{k+G'}} \rangle + \langle \phi_{\mathbf{k+G}} \, | \delta^{+} \phi_{\mathbf{k+G'}} \rangle \\ &\quad + \langle \delta^{-} \phi_{\mathbf{k+G}} \, | \phi_{\mathbf{k+G'}} \rangle + \langle \phi_{\mathbf{k+G}} \, | \delta^{-} \phi_{\mathbf{k+G'}} \rangle \\ &= 0. \end{aligned} \tag{1.75}$$

This also implies that the first-order change of the KS eigenvalue given by the expression [13, 26],

$$\delta \varepsilon_{n\mathbf{k}} = \sum_{\mathbf{G},\mathbf{G'}} C^{*}_{n,\mathbf{k}}(\mathbf{G}) (\delta H_{\mathbf{k+G},\mathbf{k+G'}} - \varepsilon_{n\mathbf{k}} \delta S_{\mathbf{k+G},\mathbf{k+G'}}) C_{n,\mathbf{k}}(\mathbf{G'}), \tag{1.76}$$

will be vanishing. Summarizing the results (1.71) – (1.76) the linearization of the eigenvalue equation (1.62) with regard to the unperturbed eigenvector $C_{n,\mathbf{k}}(\mathbf{G})$ will be given by:

$$\left(\begin{bmatrix} 0 & \delta\mathbf{H}_{\mathbf{k-q,k}} & 0 \\ \delta\mathbf{H}_{\mathbf{k,k-q}} & 0 & \delta\mathbf{H}_{\mathbf{k,k+q}} \\ 0 & \delta\mathbf{H}_{\mathbf{k+q,k}} & 0 \end{bmatrix} - \varepsilon_{n\mathbf{k}} \begin{bmatrix} 0 & \delta\mathbf{S}_{\mathbf{k-q,k}} & 0 \\ \delta\mathbf{S}_{\mathbf{k,k-q}} & 0 & \delta\mathbf{S}_{\mathbf{k,k+q}} \\ 0 & \delta\mathbf{S}_{\mathbf{k+q,k}} & 0 \end{bmatrix}\right) \times \begin{pmatrix} 0 \\ \mathbf{C}_{n,\mathbf{k}} \\ 0 \end{pmatrix}$$
$$= -\left(\begin{bmatrix} \mathbf{H}_{\mathbf{k-q,k-q}} & 0 & 0 \\ 0 & \mathbf{H}_{\mathbf{k,k}} & 0 \\ 0 & 0 & \mathbf{H}_{\mathbf{k+q,k+q}} \end{bmatrix} - \varepsilon_{n\mathbf{k}} \begin{bmatrix} \mathbf{S}_{\mathbf{k-q,k-q}} & 0 & 0 \\ 0 & \mathbf{S}_{\mathbf{k,k}} & 0 \\ 0 & 0 & \mathbf{S}_{\mathbf{k+q,k+q}} \end{bmatrix}\right) \times \begin{pmatrix} \delta^{-}\mathbf{C}_{n,\mathbf{k}} \\ 0 \\ \delta^{+}\mathbf{C}_{n,\mathbf{k}} \end{pmatrix} \tag{1.77}$$

where whole matrices and vectors (in contrast to individual elements) are denoted by bold letters. Eq. (1.77) decouples into two separately solvable matrix equations which are of the same dimension as the original eigenvalue problem:

$$[\delta\mathbf{H}_{\mathbf{k-q,k}} - \varepsilon_{n\mathbf{k}}\delta\mathbf{S}_{\mathbf{k-q,k}}]\mathbf{C}_{n,\mathbf{k}} = [\varepsilon_{n\mathbf{k}}\mathbf{S}_{\mathbf{k-q,k-q}} - \mathbf{H}_{\mathbf{k-q,k-q}}]\delta^{-}\mathbf{C}_{n,\mathbf{k}}, \tag{1.78}$$

$$[\delta\mathbf{H}_{\mathbf{k+q,k}} - \varepsilon_{n\mathbf{k}}\delta\mathbf{S}_{\mathbf{k+q,k}}]\mathbf{C}_{n,\mathbf{k}} = [\varepsilon_{n\mathbf{k}}\mathbf{S}_{\mathbf{k+q,k+q}} - \mathbf{H}_{\mathbf{k+q,k+q}}]\delta^{+}\mathbf{C}_{n,\mathbf{k}}. \tag{1.79}$$

In the framework of the variational principle applied to the KS formalism, Eq.(1.78) and (1.79) represent the Sternheimer equations in the backward- and forward-traveling wave representation, respectively. As we will work in the forward-traveling-wave representation when introducing the LAPW basis functions, we finally formulate Eq.(1.79) in more detail:

$$\begin{aligned} &\sum_{\mathbf{G}'} \left\langle \phi_{\mathbf{k+q+G}} \middle| \varepsilon_{n\mathbf{k}} - \hat{H} \middle| \phi_{\mathbf{k+q+G}'} \right\rangle \delta^{+}C_{n\mathbf{k}}(\mathbf{G}') \\ = &\sum_{\mathbf{G}'} [\left\langle \phi_{\mathbf{k+q+G}} \middle| \delta^{+}\hat{H} \middle| \phi_{\mathbf{k+G}'} \right\rangle + \left\langle \delta^{-}\phi_{\mathbf{k+q+G}} \middle| \hat{H} - \varepsilon_{n\mathbf{k}} \middle| \phi_{\mathbf{k+G}'} \right\rangle \\ &+ \left\langle \phi_{\mathbf{k+q+G}} \middle| \hat{H} - \varepsilon_{n\mathbf{k}} \middle| \delta^{+}\phi_{\mathbf{k+G}'} \right\rangle] C_{n\mathbf{k}}(\mathbf{G}'). \end{aligned} \tag{1.80}$$

Eq.(1.80) represents a system of inhomogeneous linear equations, which only involve the occupied states of the unperturbed system. It can be solved by matrix inversion with the number of numerical operations being proportional to N_{basis}^3. A more efficient procedure would be to use an iterative algorithm which scales with $N_{band} \times N_{basis}^3$ where N_{band} is the number of filled bands. Just for completion we want to mention that the change in the variational coefficient could also be calculated via a perturbation sum similar to the one given in Eq.(1.59). It would read:

$$\delta^{+}C_{n\mathbf{k}}(\mathbf{G}) = \sum_{m} \frac{\mathbf{C}^{\dagger}_{m,\mathbf{k+q}}(\delta\mathbf{H}_{\mathbf{k+q,k}} - \varepsilon_{n\mathbf{k}}\delta\mathbf{S}_{\mathbf{k+q,k}})\mathbf{C}_{n,\mathbf{k}}}{\varepsilon_{n,\mathbf{k}} - \varepsilon_{m,\mathbf{k+q}}} C_{m,\mathbf{k+q}}(\mathbf{G}). \tag{1.81}$$

1.2.3 The ILR scheme in comparison to alternative methods

Compared to super-cell calculations the main advantage of the ILR scheme lies in the fact that the size of the Sternheimer matrix equation (Eq.(1.80)) is *independent* of the wave-vector $\mathbf{q}$ and is the same as the size of the matrices in the eigenvalue problem of the unperturbed crystal. If a consistent[5] calculation with regard to $\mathbf{k}$-space integration is required the computational effort of the ILR scheme will nevertheless scale linearly with $|\mathbf{q}|$. This is founded in the fact that the projection of the $\mathbf{k}$-points used in a super-cell calculation onto the BZ of the corresponding primitive unit cell will generate a mesh where the distance between neighbouring $\mathbf{k}$-points is smaller or equal to $|\mathbf{q}|$. Consequently a decrease of $|\mathbf{q}|$ will proportionally increase the number of $\mathbf{k}$-points for which the Sternheimer equation has to be solved. At least for pseudo-potential calculations it has explicitly been reported [27] that the error introduced by using a 'non-compatible' $\mathbf{k}$-point mesh (this means that the point $\mathbf{k} \pm \mathbf{q}$ may not be part of the mesh used in the unperturbed band structure calculation underlying the ILR scheme) should be small.

As has already been mentioned at the end of section (1.1) the ILR scheme circumvents many of the drawbacks of the DM approach. Here we want to discuss these aspects in more detail: (i) The DM approach is tailored to the employment of a plane-wave basis set. Only in this case the resulting formulas are simple and numerically fairly easy to handle. In contrast, as the ILR scheme is oriented by the structure of the unperturbed SCF cycle the employment of basis sets other than plane waves is not complicating the algorithm too drastically. It is thus possible to perform realistic response calculations for materials where orbitals localized on the atomic sites play a central role for the band structure (transition metals, f-electron systems). The most prominent methods used in this respect are the LAPW and the LMTO method. It is worth mentioning that both of them are full-potential methods where the charge distribution of the core electrons is based on the solutions of the radial Dirac equation in the spherical potential around each nucleus. If required it is thus possible to also include the core-level response in the ILR scheme. (ii) The calculation of the dielectric matrix (Eq. (1.29)) necessitates the knowledge of the entire band structure of the unperturbed crystal. Ground-state eigenvalues and eigenvectors have to be calculated for all occupied and unoccupied states. The same is true if equation (1.81) is used to obtain the first-order change of the KS orbitals in the ILR scheme. However if the Sternheimer

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[5] In this context 'consistent' means that the first-order part of the response quantities calculated in a super-cell calculation on a chosen $\mathbf{k}$-point mesh is equivalent to the solutions of the ILR-scheme.

equation (1.80) is solved directly by matrix inversion (or even more efficiently by an iterative scheme) *only the occupied* energy bands have to be known. (iii) In the ILR scheme the self-consistency between the charge response and the first-order change in the effective potential is obtained by iteration. Although this substitutes the time consuming step of inverting the dielectric matrix this apparent advantage might be outweighed by the requirement of having to solve the Sternheimer equation several times (iteration process). This will at least be true for the LAPW method. (iv) In contrast to the DM approach it should be possible to quite naturally include non-local exchange correlation potentials in the ILR scheme. In fact one only needs to formulate the expression for the first-order change of the xc-potential.

A final remark has to be made on the 'content of information' intrinsically available in the DM and ILR approach: It can be seen from Eq.(1.28) that once the elements of the inverse of the dielectric matrix have been calculated the response to *any* external potential perturbation at wave-vector $\mathbf{q}$ is straight forwardly obtainable. In contrast the ILR scheme provides the specific response of the crystal to only *one particular* external perturbation. This implies that carrying out one ILR calculation up to self-consistency can only determine one row of the corresponding dielectric matrix. The establishment of the dielectric matrix via the ILR scheme would thus also be a formidable task in terms of required computer time. Luckily this realization is not too severe in practical terms because most problems posed in material science require the response to a number of specific external perturbations which is much smaller than the dimension of the dielectric matrix. In this sense one might say that the knowledge of the entire dielectric matrix represents 'too much information'.

1.3 The ILR scheme within the LAPW formalism

In this section we will give a detailed account of all formulas necessary to set up the ILR scheme within the full potential LAPW method [28]. As a perturbation we assume a phonon-like displacement pattern with wave-vector $\mathbf{q} \neq \mathbf{0}$. We further assume a 'non-degenerate' band structure meaning that $\Psi_{n,\mathbf{k}}$ (n denoting an occupied band state) displays no degeneracy with any of the states $\Psi_{m,\mathbf{k}\pm\mathbf{q}}$.

After a brief introduction into the LAPW formalism (section (1.3.1)) we specify the particular representations used for the linear change of the total potential (section (1.3.2)). This is a necessary prerequisite for the next section (1.3.3) where we deal with the linear changes of the Hamiltonian and overlap matrices of the Sternheimer equation. In this context a simple and efficient scheme to evaluate certain atomic sphere integrals involving gradients of wave-functions and potentials is developed. In sections (1.3.4) and (1.3.5) the charge response formulas for valence as well as for core electrons are derived. The latter one are linked to the presentation of the first-order perturbation theory for the radial Dirac equation in a spherical-symmetric potential. To complete the SCF cycle the linear change of the total potential is formulated (section (1.3.6)). With respect to the electrostatic contribution the first-order change is derived within the Weinert formalism [29] based on the coordinate system of the displaced atomic nuclei. For the xc-potential an LDA-type functional is assumed. In section (1.3.7) we finally give a complete derivation of the first-order LAPW forces (Hellmann-Feynman force, Core correction, IBS correction) which are the essential ingredients to calculate the dynamical matrix via the system of linear equations (1.26) and (1.27) presented in section (1.1.2).

1.3.1 The LAPW formalism

The application of the Rayleigh-Ritz variational principle to solve the KS equation requires the definition of a set of basis functions in which the KS orbitals are expanded. Within the full potential linearized augmented plane-wave (LAPW) method the elementary cell is partitioned into two types of regions: These are (i) non-overlapping atomic spheres (also termed muffin-tin spheres) which are centered at the nuclear coordinates $\{\mathbf{S}_\alpha\}$ and are characterized by sphere radii $\{R_\alpha\}$, and (ii) the space between the spheres, called 'interstitial'. In the interstitial region the KS orbitals are expected to be rather smooth, hence an appropriate basis set are normalized plane waves, i.e.,

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \qquad \mathbf{r} \in \text{Int}. \tag{1.82}$$

On the other hand within the spheres the wave-functions of the electrons will be similar to those in an atom. Therefore the basis functions are chosen to be linear combinations of atom centered orbitals:

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{lm} [A^{\alpha}_{lm}(\mathbf{k}+\mathbf{G}) u^{\alpha}_{l}(r,\varepsilon_l) + B^{\alpha}_{lm}(\mathbf{k}+\mathbf{G}) \dot{u}^{\alpha}_{l}(r,\varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}), \qquad |\mathbf{r}| \leq R_\alpha, \tag{1.83}$$

with

$$\dot{u}_l \equiv \frac{\partial u_l}{\partial \varepsilon}.$$

The functions $u_l^\alpha(r,\varepsilon_l)$ and $\dot{u}_l^\alpha(r,\varepsilon_l)$ are determined by numerical integration of the radial part of the Schrödinger equation (1.84) and the energy derivative of it (1.85). The potential $V_{eff}^s(r)$ is spherical symmetric and the integrational region spans the sphere radius:

$$\begin{aligned}
[\hat{T} + V_{eff}^s(r)]u_l^\alpha(r,\varepsilon_l)Y_{lm}(\hat{\mathbf{r}}) &= \varepsilon_l u_l^\alpha(r,\varepsilon_l)Y_{lm}(\hat{\mathbf{r}}), && (1.84)\\
[\hat{T} + V_{eff}^s(r)]\dot{u}_l^\alpha(r,\varepsilon_l)Y_{lm}(\hat{\mathbf{r}}) &= [\varepsilon_l \dot{u}_l^\alpha(r,\varepsilon_l) + u_l^\alpha(r,\varepsilon_l)]Y_{lm}(\hat{\mathbf{r}}). && (1.85)
\end{aligned}$$

The parameter ε_l is a chosen linearization energy which is an input parameter for Eqs.(1.84) and (1.85). The radial functions $u_l^\alpha(r,\varepsilon_l)$ and $\dot{u}_l^\alpha(r,\varepsilon_l)$ fulfil the following conditions:

$$\begin{aligned}
\int_0^{R_\alpha} |u_l^\alpha(r,\varepsilon_l)|^2 r^2 dr &= 1, && (1.86)\\
\int_0^{R_\alpha} u_l^\alpha(r,\varepsilon_l)\dot{u}_l^\alpha(r,\varepsilon_l) r^2 dr &= 0. && (1.87)
\end{aligned}$$

Additionally the abbreviation,

$$N_l \equiv \int_0^{R_\alpha} |\dot{u}_l^\alpha(r,\varepsilon_l)|^2 r^2 dr, \tag{1.88}$$

is introduced. The matching coefficients $A_{lm}^\alpha(\mathbf{k}+\mathbf{G})$ and $B_{lm}^\alpha(\mathbf{k}+\mathbf{G})$ are chosen in such a way that on the sphere surface the basis functions (1.83) are equal in value and slope to the corresponding plane wave of the interstitial. The resulting formulas read:

$$\begin{aligned}
A_{lm}(\mathbf{k}+\mathbf{G}) &= \frac{4\pi}{\sqrt{\Omega}} i^l Y_{lm}^*(\widehat{\mathbf{k}+\mathbf{G}}) a_l(\mathbf{k}+\mathbf{G}) R_\alpha^2 e^{i(\mathbf{k}+\mathbf{G})\mathbf{S}_\alpha}, && (1.89)\\
B_{lm}(\mathbf{k}+\mathbf{G}) &= \frac{4\pi}{\sqrt{\Omega}} i^l Y_{lm}^*(\widehat{\mathbf{k}+\mathbf{G}}) b_l(\mathbf{k}+\mathbf{G}) R_\alpha^2 e^{i(\mathbf{k}+\mathbf{G})\mathbf{S}_\alpha}, && (1.90)
\end{aligned}$$

with

$$\begin{aligned}
a_l(\mathbf{k}+\mathbf{G}) &= j_l'(|\mathbf{k}+\mathbf{G}|R_\alpha)\dot{u}_l(R_\alpha) - j_l(|\mathbf{k}+\mathbf{G}|R_\alpha)\dot{u}_l'(R_\alpha), && (1.91)\\
b_l(\mathbf{k}+\mathbf{G}) &= j_l(|\mathbf{k}+\mathbf{G}|R_\alpha)u_l'(R_\alpha) - j_l'(|\mathbf{k}+\mathbf{G}|R_\alpha)u_l(R_\alpha). && (1.92)
\end{aligned}$$

$j_l(x)$ is the Bessel function of the first kind, $j'(x), u'(r)$, etc. symbolize the partial derivatives $\partial j(x)/\partial r$, $\partial u(r)/\partial r$, etc. In order to simplify the notation we have neglected the atomic index on A_{lm}, B_{lm}, u_l and $\dot{u}_l$. Additionally we have dropped the linearization energy in the radial functions.

To find numerical solutions to the various equations appearing in an SCF cycle (Poisson's equation, KS equation, etc.) it is practicable that besides the KS orbitals also the charge density and the potentials (electrostatic and exchange-correlation potential) are represented in terms of basis functions. In the LAPW method the natural choice are spherical harmonics for the sphere regions,

$$\begin{aligned} V(\mathbf{S}_\alpha + \mathbf{r}) &= \sum_{LM} V_{LM}(r) Y_{LM}(\hat{\mathbf{r}}), \qquad |\mathbf{r}| \le R_\alpha, && (1.93) \\ \rho(\mathbf{S}_\alpha + \mathbf{r}) &= \sum_{LM} \rho_{LM}(r) Y_{LM}(\hat{\mathbf{r}}), \qquad |\mathbf{r}| \le R_\alpha, && (1.94) \end{aligned}$$

and plane waves for the interstitial:

$$\begin{aligned} V(\mathbf{r}) &= \sum_{\mathbf{G}} V(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}, \qquad \mathbf{r} \in \text{Int.}, && (1.95) \\ \rho(\mathbf{r}) &= \sum_{\mathbf{G}} \rho(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}, \qquad \mathbf{r} \in \text{Int.} && (1.96) \end{aligned}$$

The corresponding representations for the first-order wave-functions, potentials and densities will be introduced in the following sections, where the equations of the ILR scheme are specified for the LAPW method.

1.3.2 The change of the total effective potential: an overview

We consider a lattice with several atoms in the primitive unit cell. If a frozen in phonon is present in the crystal the atoms are displaced from their equilibrium positions by a small amount $\delta^+\mathbf{S}_\alpha^\mathbf{T}$:

$$\delta^+\mathbf{S}_\alpha^\mathbf{T} = \delta^+\mathbf{S}_\alpha e^{i\mathbf{q}\mathbf{T}}, \tag{1.97}$$

where $\delta^+\mathbf{S}_\alpha$ is a complex polarization vector and the forward-traveling-wave representation has been chosen. As has already been discussed in section (1.2.1) the presence of such a displacement field primarily causes a change in the bare coulomb potential of the atomic nuclei $\delta^+V_{nuc}(\mathbf{r})$ which alters the total effective potential $V_{eff}(\mathbf{r})$. The unperturbed electronic charge density will respond to this perturbation by rearranging its spatial distribution. The resulting induced charge density $\delta^+\rho(\mathbf{r})$ consisting of valence and core electrons, i.e.,

$$\delta^+\rho(\mathbf{r}) = \delta^+\rho_v(\mathbf{r}) + \delta^+\rho_c(\mathbf{r}), \tag{1.98}$$

screens the external potential. This in turn leads to an additional change of the total effective potential, i.e.,

$$\delta^+V_{eff}(\mathbf{r}) = \delta^+V_{nuc}(\mathbf{r}) + \int \frac{\delta^+\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' + \delta^+\rho(\mathbf{r}) \left. \frac{dV_{xc}(\mathbf{r})}{d\rho} \right|_{\rho_0(\mathbf{r})}. \tag{1.99}$$

With regard to the dual representation of $\delta^+ V_{eff}(\mathbf{r})$ in terms of plane-waves (interstitial region) and spherical harmonics (atomic spheres) it is necessary to account for the displacements of the atomic nuclei which redefine the locations of the atomic spheres. Refering to the coordinate system of the unperturbed problem the following expression is obtained [30]:

$$\delta^+ V_{eff}^{\alpha,\mathbf{T}}(\mathbf{r}) = \underbrace{\sum_{LM} \delta^+ \check{V}_{eff,LM}^{\alpha,\mathbf{T}}(r') Y_{LM}(\hat{\mathbf{r}}')}_{\equiv \delta^+ \check{V}_{eff}^{\alpha,\mathbf{T}}(\mathbf{r}')} + \delta^+ \mathbf{S}_\alpha^{\mathbf{T}} \nabla \underbrace{\sum_{LM} V_{eff,LM}^{\alpha}(r') Y_{LM}(\hat{\mathbf{r}}')}_{= V_{eff}^{\alpha}(\mathbf{r}')}, \qquad |r'| \leq R_\alpha, \tag{1.100}$$

where $\mathbf{r} = \mathbf{T} + \mathbf{S}_\alpha + \mathbf{r}'$ is a position vector within an atomic sphere. The first term on the right hand side of Eq.(1.100) is the 'soft' contribution [12] to the change in the effective potential. It represents the first-order difference between the effective potentials evaluated at point $\mathbf{r} = \mathbf{T} + \mathbf{S}_\alpha + \delta^+ \mathbf{S}_\alpha^{\mathbf{T}} + \mathbf{r}'$ with the perturbation being applied and at point $\mathbf{r} = \mathbf{T} + \mathbf{S}_\alpha + \mathbf{r}'$ when no perturbation is present. The second term originates from the fact that the atomic sphere has been rigidly shifted by the position vector $\delta^+ \mathbf{S}_\alpha^{\mathbf{T}}$. We note that second- and higher-order terms in Eq.(1.100) with respect to the displacement have been dropped. In the interstitial region where plane-waves are the natural choice of basis functions $\delta^+ V_{eff}^{int}(\mathbf{r})$ reads:

$$\delta^+ V_{eff}^{int}(\mathbf{r}) = \sum_{G \leq 2G_{\max}} \delta^+ V_{eff}(\mathbf{G} + \mathbf{q}) e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}. \tag{1.101}$$

At this point we want to clarify the summation conventions used in the following derivations. When summations over the number of basis functions constituting a KS orbital (N_{basis}) are needed we use the symbol $\sum_{G \leq G_{\max}}$ meaning that all $\mathbf{G}$-vectors fulfilling the relation $|\mathbf{k} + \mathbf{G}| \leq G_{\max}$ are included. On the other hand summations over the Fourier coefficients describing the interstitial part of the valence density or the total effective potential are abbreviated by the symbol $\sum_{G \leq 2G_{\max}}$. As the valence density is constructed from the KS orbitals the corresponding sum will exactly consist of $2N_{basis}$ terms. In the case of the total potential the set of $\mathbf{G}$-vectors constituting the $2N_{basis}$ terms is the minimum requirement to obtain potential values consistent with the electrons' charge distribution . However, to reach a converged description also with regard to the Coulomb potential of the nuclei the set is usually enlarged significantly in practical calculations.

1.3.3 The elements of the Sternheimer equation

By solving the Sternheimer equation (1.80) on the basis of $\delta^+V_{eff}(\mathbf{r})$ the first-order change of the KS orbitals in the forward-traveling-wave representation is obtainable. If we remember that this change is represented by the following ansatz,

$$\delta^+\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{G\leq G_{\max}} \delta^+C_{n,\mathbf{k}}(\mathbf{G})\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) + C_{n,\mathbf{k}}(\mathbf{G})\delta^+\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \tag{1.102}$$

it is evident that we now have to provide an explicit formula for $\delta^+\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ which is suitable to describe the changes of the LAPW basis functions upon a displacement by $\delta^+\mathbf{S}^{\mathbf{T}}_\alpha$. This formula has already been worked by Yu et al. [26] and can be summarized as follows. First of all, the first-order shift $\delta^+\mathbf{S}^{\mathbf{T}}_\alpha$ of the atomic spheres only alters the contribution given by Eq.(1.83) whereas the plane-wave basis set remains unaltered. Thus it is only non-vanishing inside the atomic spheres and in this region is composed of two additive contributions: (i) The basis function $\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{T}+\mathbf{S}_\alpha+\mathbf{r}')$ primarily undergoes a *rigid* movement by the displacement vector $\delta^+\mathbf{S}^{\mathbf{T}}_\alpha$. If the shifted basis function is expanded in a Taylor series at the undisplaced position vector of the nucleus the first-order term in this expansion will properly describe this change of the basis function, i.e.,

$$\delta^+_1\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{T}+\mathbf{S}_\alpha+\mathbf{r}') \equiv -\delta^+\mathbf{S}^{\mathbf{T}}_\alpha\nabla\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha+\mathbf{r}'), \qquad |\mathbf{r}'| \leq R_\alpha\,. \tag{1.103}$$

(ii) Due to the shift of the nucleus the surface of the corresponding atomic sphere is also shifted by $\delta^+\mathbf{S}^{\mathbf{T}}_\alpha$. This alters the matching conditions between the plane-waves and the basis functions inside the sphere. Consequently, the matching parameters A_{lm} and B_{lm} change by the phase factor $e^{i(\mathbf{k}+\mathbf{G})\delta^+\mathbf{S}^{\mathbf{T}}_\alpha}$ [26]. Expanding this phase factor in a Taylor series and only considering terms up to first order the second contribution to $\delta^+\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{T}+\mathbf{S}_\alpha+\mathbf{r}')$ is obtained:

$$\delta^+_2\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{T}+\mathbf{S}_\alpha+\mathbf{r}') \equiv i[(\mathbf{k}+\mathbf{G})\delta^+\mathbf{S}^{\mathbf{T}}_\alpha]\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha+\mathbf{r}'), \qquad |\mathbf{r}'| \leq R_\alpha. \tag{1.104}$$

Combining (1.103) with (1.104) and summing over all atoms comprising the super-cell induced by the phonon distortion then leads to:

$$\delta^+\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \equiv \frac{\partial\phi_{\mathbf{k}+\mathbf{G}}}{\partial\{\delta\mathbf{S}\}}\delta^+\mathbf{S} = -\sum_{\mathbf{T}}\sum_{\alpha}[\nabla\phi^\alpha_{\mathbf{k}+\mathbf{G}}(\mathbf{r})]\delta^+\mathbf{S}^{\mathbf{T}}_\alpha + \sum_{\mathbf{T}}\sum_{\alpha} i[(\mathbf{k}+\mathbf{G})\delta^+\mathbf{S}^{\mathbf{T}}_\alpha]\phi^\alpha_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \tag{1.105}$$

which displays the correct translational property:

$$\delta^{+}\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}+\mathbf{T}) = e^{i(\mathbf{k}+\mathbf{q})\mathbf{T}}\delta^{+}\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}). \tag{1.106}$$

The area of definition for the position vector $\mathbf{r}$ is the super-cell. To be completely precise, a third contribution should be incorporated in expression (1.105). It stems from the fact that the spherical part of the soft contribution to $\delta^{+}V_{eff}^{\alpha,\mathbf{T}}(\mathbf{r})$ (first term on the right-hand side of Eq.(1.100)) will induce a relaxation of the radial basis functions $u_l(r)$ and $\dot{u}_l(r)$ and in this way alters the matching parameters A_{lm} and B_{lm}. However, with regard to frozen-phonon calculations it has been argued (and partly numerically verified) [23, 26] that the motions of the atoms mainly distort the dipole part of the potential and the relaxations are thus negligible in comparison to the contributions (1.103) and (1.104). This approximation is called the rigid muffin-tin orbital approximation [26] and is also adopted in this work.

If expression (1.105) is now inserted into the Sternheimer equation as derived in section (1.2.2), i.e.,

$$\begin{aligned}
& \sum_{G'\leq G_{\max}} \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \varepsilon_{n\mathbf{k}} - \hat{H} \right| \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \right\rangle \delta^{+}C_{n\mathbf{k}}(\mathbf{G}') \\
= & \sum_{G'\leq G_{\max}} [\left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \delta^{+}\hat{H} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \left\langle \delta^{-}\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \\
& + \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \delta^{+}\phi_{\mathbf{k}+\mathbf{G}'} \right\rangle] C_{n\mathbf{k}}(\mathbf{G}'),
\end{aligned} \tag{1.107}$$

the result will be the specific Sternheimer equation suitable for the LAPW basis set [26]:

$$\begin{aligned}
& \sum_{G'\leq G_{\max}} \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \varepsilon_{n\mathbf{k}} - \hat{H} \right| \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \right\rangle_{\Omega_s} \delta C_{n\mathbf{k}}(\mathbf{G}') \\
= & \sum_{G'\leq G_{\max}} \underbrace{[\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \delta^{+}V_{eff}(\mathbf{r}) \right| \phi_{\mathbf{k}+\mathbf{G}'} \rangle_{\Omega_s}}_{R1} \\
& \underbrace{+ \left\langle \frac{\partial \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}}{\partial\{\delta\mathbf{S}\}} (\delta^{+}\mathbf{S})^{*} \left| \hat{H} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT(\Omega_s)}}_{R2} \\
& \underbrace{+ \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} \right| \frac{\partial \phi_{\mathbf{k}+\mathbf{G}'}}{\partial\{\delta\mathbf{S}\}} \delta^{+}\mathbf{S} \right\rangle_{MT(\Omega_s)}}_{R3} \\
& -\varepsilon_{n\mathbf{k}} \underbrace{\left\langle \frac{\partial \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}}{\partial\{\delta\mathbf{S}\}} (\delta^{+}\mathbf{S})^{*} | \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT(\Omega_s)}}_{R4}
\end{aligned} \tag{1.108}$$

$$\underbrace{-\varepsilon_{n\mathbf{k}} \left\langle \phi_{\mathbf{k+q+G}} \middle| \frac{\partial \phi_{\mathbf{k+G'}}}{\partial\{\delta \mathbf{S}\}} \delta^{+}\mathbf{S} \right\rangle_{MT(\Omega_s)}}_{R5}$$

$$\underbrace{+\delta^{+} \left\langle \phi_{\mathbf{k+q+G}} \left| \hat{T} \right| \phi_{\mathbf{k+G'}} \right\rangle}_{R6}]\, C_{n\mathbf{k}}(\mathbf{G'}). \tag{1.109}$$

The region of integration on the left-hand side of Eq.(1.109) as well as in the matrix element $R1$ is the entire volume of the super-cell (Ω_s), whereas the terms $R2 \rightarrow R5$ are integrated over the volume of the atomic spheres only. The last term $R6$ is a surface integral over the atomic spheres, i.e.,

$$\begin{aligned} \delta^{+} \left\langle \phi_{\mathbf{k+q+G}} \left| \hat{T} \right| \phi_{\mathbf{k+G'}} \right\rangle \equiv & \sum_{\mathbf{T}} \sum_{\alpha} \delta^{+} \mathbf{S}_{\alpha}^{\mathbf{T}} \oint_{MT_\alpha} [\phi^{*\alpha}_{\mathbf{k+q+G}}(\mathbf{r}) \nabla^2 \phi^{\alpha}_{\mathbf{k+G'}}(\mathbf{r})|_{MT_\alpha} \\ & -\phi_{\mathbf{k+q+G}}(\mathbf{r}) \nabla^2 \phi_{\mathbf{k+G'}}(\mathbf{r})|_{Int}] d\mathbf{A}_{\alpha}, \end{aligned} \tag{1.110}$$

where MT_α and Int indicate that in the respective kinetic energy term the basis functions appropriate for the denoted region have to be inserted. The term $R6$ will have a non-vanishing value because the second derivative of the LAPW basis functions are discontinues on the surface of the atomic spheres [13, 26].

By analytical evaluation we now want to simplify the terms appearing in Eq.(1.109). For the accomplishment of this task we are guided by two criteria: (i) Whenever possible the resulting formulas should utilize formal similarities to matrix elements and algorithms used in standard LAPW band structure programs. In this context we specifically refer to the LAPW program WIEN97 [31]. (ii) The numerical evaluation of the formulas on a computer should be as efficient as possible.

For reasons of simplicity we introduce the symbol δ from now on denoting the change in the forward-traveling-wave representation δ^{+}. The matrix elements on the left-hand side of Eq.(1.109) are composed of the Hamiltonian and overlap matrix elements at point $(\mathbf{k}+\mathbf{q})$ and are thus calculated like in the eigenvalue problem for the unperturbed system. We refer to Ref.[32] for the respective formulas. If we assume that the super-cell with volume Ω_s is composed of N primitive unit cells each having volume Ω it is apparent that

$$\left\langle \phi_{\mathbf{k+q+G}} \left| \varepsilon_{n\mathbf{k}} - \hat{H} \right| \phi_{\mathbf{k+q+G'}} \right\rangle_{\Omega_s} = N \left\langle \phi_{\mathbf{k+q+G}} \left| \varepsilon_{n\mathbf{k}} - \hat{H} \right| \phi_{\mathbf{k+q+G'}} \right\rangle_{\Omega}. \tag{1.111}$$

Next we separate the interstitial from the atomic-sphere contribution in the term $R1$ and subsequently insert expressions (1.100) for the change of the effective potential within the spheres:

$$\begin{aligned}\left\langle \phi_{\mathbf{k+q+G}} \left| \delta V_{eff} \right| \phi_{\mathbf{k+G'}} \right\rangle_{\Omega_s} &= \left\langle \phi_{\mathbf{k+q+G}} \left| \delta V_{eff}^{int} \right| \phi_{\mathbf{k+G'}} \right\rangle_{Int(\Omega_s)} \\ &+ \sum_{\mathbf{T}} \sum_{\alpha} \left\langle \phi_{\mathbf{k+q+G}}^{\alpha,\mathbf{T}} \left| \delta \check{V}_{eff}^{\alpha,\mathbf{T}} \right| \phi_{\mathbf{k+G'}}^{\alpha,\mathbf{T}} \right\rangle_{MT_\alpha} \\ &- \sum_{\mathbf{T}} \sum_{\alpha} \delta \mathbf{S}_{\alpha}^{\mathbf{T}} \left\langle \phi_{\mathbf{k+q+G}}^{\alpha,\mathbf{T}} \left| \nabla V_{eff}^{\alpha} \right| \phi_{\mathbf{k+G'}}^{\alpha,\mathbf{T}} \right\rangle_{MT_\alpha} . \quad (1.112)\end{aligned}$$

The contribution from the interstitial region can be further simplified by using the plane wave basis functions and the expression (1.101) for $\delta V_{eff}^{int}(\mathbf{r})$:

$$\begin{aligned}&\left\langle \phi_{\mathbf{k+q+G}} \left| \delta V_{eff}^{int}(\mathbf{r}) \right| \phi_{\mathbf{k+G'}} \right\rangle_{Int(\Omega_s)} \\ &= \frac{1}{\Omega} \int_{Int(\Omega_s)} e^{i(\mathbf{G'}-\mathbf{G}-\mathbf{q})\mathbf{r}} \sum_{G'' \leq 2G_{\max}} \delta V_{eff}(\mathbf{G''}+\mathbf{q}) e^{i(\mathbf{G''}+\mathbf{q})\mathbf{r}} d^3\mathbf{r} \\ &= \frac{1}{\Omega} \sum_{G'' \leq 2G_{\max}} \delta V_{eff}(\mathbf{G''}+\mathbf{q}) \int_{Int(\Omega_s)} e^{i(\mathbf{G'}-\mathbf{G}+\mathbf{G''})\mathbf{r}} d^3\mathbf{r} \\ &= \frac{N}{\Omega} \sum_{G'' \leq 2G_{\max}} \delta V_{eff}(\mathbf{G''}+\mathbf{q}) \int_{Int} e^{i(\mathbf{G'}-\mathbf{G}+\mathbf{G''})\mathbf{r}} d^3\mathbf{r} \equiv N \Delta V_{eff}^{int}(\mathbf{G},\mathbf{G'}). \quad (1.113)\end{aligned}$$

Due to the fact that the plane-wave function under the integral is periodic within the primitive unperturbed lattice the integrational range can be reduced from the **interstitial**[6] region of the super-cell to the interstitial region of the primitive cell, a procedure being displayed in line three and four of Eq.(1.113). From a practical point of view this simplification is very important as it implies that the computational effort for the numerical evaluation of this matrix element does not exceed the one needed for the unperturbed counterpart, i.e.,

$$\left\langle \phi_{\mathbf{k+G}} \left| V_{eff}^{int} \right| \phi_{\mathbf{k+G'}} \right\rangle_{Int(\Omega)} . \quad (1.114)$$

In fact this reduction of the integrational range is a general principle of the Sternheimer equation and thus applies to all matrix elements appearing in it (compare to Eq.(1.51)). As a last illustration we explicitly demonstrate this reduction for the two **atomic-sphere** contributions of Eq.(1.112). From then on we will use it without explicitly mentioning it. The general translational property of the perturbed effective potential

$$\delta V_{eff}^{\alpha,\mathbf{T}}(\mathbf{r}) = e^{i\mathbf{q}\mathbf{T}} \delta V_{eff}^{\alpha}(\mathbf{r})$$

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[6] For orientation within the large number of partly cross referenced formulas we will sometimes emphasize the words 'interstitial' and 'atomic sphere'.

implies for the soft contribution of Eq.(1.100) that

$$\delta\check{V}^{\alpha,\mathbf{T}}_{eff,LM}(r') = e^{i\mathbf{qT}}\delta\check{V}^{\alpha}_{eff,LM}(r'). \tag{1.115}$$

Inserting Eq.(1.115) and the translational property of the Bloch-type basis function

$$\phi^{\alpha}_{\mathbf{k+G}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{kT}}\phi^{\alpha}_{\mathbf{k+G}}(\mathbf{r}) \tag{1.116}$$

into the second line of Eq.(1.112) leads to:

$$\begin{aligned} & \sum_{\mathbf{T}}\sum_{\alpha}\left\langle \phi^{\alpha,\mathbf{T}}_{\mathbf{k+q+G}} \left| \delta\check{V}^{\alpha,\mathbf{T}}_{eff} \right| \phi^{\alpha,\mathbf{T}}_{\mathbf{k+G'}} \right\rangle_{MT_\alpha} \\ = & \sum_{\mathbf{T}}\sum_{\alpha}\left\langle e^{i(\mathbf{k+q})\mathbf{T}}\phi^{\alpha}_{\mathbf{k+q+G}} \left| e^{i\mathbf{qT}}\delta\check{V}^{\alpha}_{eff} \right| e^{i\mathbf{kT}}\phi^{\alpha}_{\mathbf{k+G'}} \right\rangle_{MT_\alpha} \\ = & \; N\sum_{\alpha}\left\langle \phi^{\alpha}_{\mathbf{k+q+G}} \left| \delta\check{V}^{\alpha}_{eff} \right| \phi^{\alpha}_{\mathbf{k+G'}} \right\rangle_{MT_\alpha} \equiv N\Delta\check{V}^{MT}_{eff}(\mathbf{G},\mathbf{G'}). \end{aligned} \tag{1.117}$$

For the matrix element involving the gradient of the effective potential (third line of Eq.(1.112)) we additionally use the definition (1.97) and thus immediately obtain:

$$\begin{aligned} & -\sum_{\mathbf{T}}\sum_{\alpha}\delta\mathbf{S}^{\mathbf{T}}_{\alpha}\left\langle \phi^{\alpha,\mathbf{T}}_{\mathbf{k+q+G}} \left| \nabla V^{\alpha}_{eff} \right| \phi^{\alpha,\mathbf{T}}_{\mathbf{k+G'}} \right\rangle_{MT_\alpha} \\ = & \; -\sum_{\mathbf{T}}\sum_{\alpha}e^{i\mathbf{qT}}\delta\mathbf{S}_{\alpha}\left\langle e^{i(\mathbf{k+q})\mathbf{T}}\phi^{\alpha}_{\mathbf{k+q+G}} \left| \nabla V^{\alpha}_{eff} \right| e^{i\mathbf{kT}}\phi^{\alpha}_{\mathbf{k+G'}} \right\rangle_{MT_\alpha} \\ = & \; -N\sum_{\alpha}\delta\mathbf{S}_{\alpha}\left\langle \phi^{\alpha}_{\mathbf{k+q+G}} \left| \nabla V^{\alpha}_{eff} \right| \phi^{\alpha}_{\mathbf{k+G'}} \right\rangle_{MT_\alpha}. \end{aligned} \tag{1.118}$$

We now return to the evaluation of expression (1.113). The integral over the **interstitial** region is considered as the difference between the respective integrals over the entire unit cell and the atomic-sphere volumes. As the plane-wave is characterized by a reciprocal space vector $\mathbf{K} \equiv (\mathbf{G'} - \mathbf{G} + \mathbf{G''})$ the unit-cell integration leads to:

$$\int_{\Omega} e^{i\mathbf{Kr}} d^3\mathbf{r} = \Omega\delta_{\mathbf{K},\mathbf{0}}. \tag{1.119}$$

The integration over the atomic spheres can also be carried out analytically by using the spherical-harmonics expansion (Rayleigh-expansion) of a plane-wave in each sphere, i.e.,

$$e^{i\mathbf{Kr}} = 4\pi e^{i\mathbf{KS}_\alpha}\sum_{lm} i^l j_l(r'K)Y^{*}_{lm}(\hat{\mathbf{K}})Y_{lm}(\hat{\mathbf{r}}') \quad \text{with} \quad \mathbf{r}' = \mathbf{r} - \mathbf{S}_\alpha. \tag{1.120}$$

The integral thus evaluates to:

$$\sum_{\alpha}\int_{MT_\alpha} e^{i\mathbf{Kr}} d^3\mathbf{r} = \begin{cases} \frac{4\pi}{3}\sum_\alpha R^3_\alpha & \text{for} \quad \mathbf{K} = \mathbf{0} \\ \frac{4\pi}{|\mathbf{K}|}\sum_\alpha R^2_\alpha j_1(R_\alpha|\mathbf{K}|)e^{i\mathbf{KS}_\alpha} & \text{for} \quad \mathbf{K} \neq \mathbf{0} \end{cases}, \tag{1.121}$$

with $j_1(x)$ being the first-order Bessel function. Taking now the difference between (1.119) and (1.121) we arrive at the final expression for $\Delta V_{eff}^{int}(\mathbf{G},\mathbf{G}')$:

$$\begin{aligned}\Delta V_{eff}^{Int}(\mathbf{G},\mathbf{G}') \;=\; & \sum_{G''\leq 2G_{\max}} \{\delta V_{eff}(\mathbf{G}''+\mathbf{q})(1-\frac{4\pi}{3\Omega}\sum_{\alpha} R_\alpha^3)\delta_{\mathbf{G}'',\mathbf{G}-\mathbf{G}'} \\ & -[1-\delta_{\mathbf{G}'',\mathbf{G}-\mathbf{G}'}]\delta V_{eff}(\mathbf{G}''+\mathbf{q})\frac{4\pi}{\Omega|\mathbf{K}|}\sum_{\alpha} R_\alpha^2 j_1(R_\alpha|\mathbf{K}|)e^{i\mathbf{K}\mathbf{S}_\alpha}\}. \end{aligned} \tag{1.122}$$

Although the formulas of expression (1.122) are easy to handle in practical programming work their numerical evaluation is computationally fairly costly. An alternative scheme which is mathematically equivalent but computationally more efficient is based on the following idea [33]. We assume that the integral

$$\int_\Omega F(\mathbf{r})\Theta(\mathbf{r})d^3\mathbf{r} \tag{1.123}$$

has to be calculated. The function $F(\mathbf{r})$ is regular in the entire unit cell and has a finite Fourier series,

$$F(\mathbf{K}) = \frac{1}{\Omega}\int_\Omega F(\mathbf{r})e^{-i\mathbf{K}r}d^3\mathbf{r},$$

with a maximum cut-off $K_{\max}$. $\Theta(\mathbf{r})$ is the unit step function defined as being zero inside the spheres and one in the interstitial region. It can be shown by inserting the respective Fourier series of both functions into expression (1.123) that the following equality holds:

$$\int_\Omega F(\mathbf{r})\Theta(\mathbf{r})d^3\mathbf{r} = \int_\Omega F(\mathbf{r})\tilde{\Theta}(\mathbf{r})d^3\mathbf{r}, \tag{1.124}$$

if

$$\tilde{\Theta}(\mathbf{K}) = \begin{cases} \Theta(\mathbf{K}) & \text{for} \quad |\mathbf{K}| \leq K_{\max} \\ 0 & \text{for} \quad |\mathbf{K}| > K_{\max} \end{cases}, \tag{1.125}$$

and

$$\Theta(\mathbf{K}) = \begin{cases} 1-\frac{4\pi}{3\Omega}\sum_\alpha R_\alpha^3 & \text{for} \quad \mathbf{K}=\mathbf{0} \\ -\frac{4\pi}{\Omega|\mathbf{K}|}\sum_\alpha R_\alpha^2 j_1(R_\alpha|\mathbf{K}|)e^{-i\mathbf{K}\mathbf{S}_\alpha} & \text{for} \quad \mathbf{K}\neq\mathbf{0} \end{cases}, \tag{1.126}$$

This equality implies that although the Fourier series of $\Theta(\mathbf{r})$ is very slowly convergent only its Fourier coefficients up to $K_{\max}$ have to be known in order to evaluate the integral (1.123) exactly. For higher Fourier coefficients ($|\mathbf{K}| > K_{\max}$) an arbitrary value can be chosen, the simplest one in practical terms being zero. In the context of evaluating $\Delta V_{eff}^{int}(\mathbf{G},\mathbf{G}')$ these facts open up the possibility of utilizing efficient fast Fourier transform (FFT) algorithms.

The coarseness of the respective grids in real and reciprocal space will only be determined by the number of reciprocal space vectors lying within the sphere of radius $K_{\max}$. The implementation of this idea runs as follows [33]: First we see that the integral $\Delta V^{int}_{eff}(\mathbf{G},\mathbf{G}')$ can be cast into the form (1.123):

$$\Delta V^{Int}_{eff}(\mathbf{G},\mathbf{G}') = \frac{1}{\Omega}\int_{\Omega} \underbrace{e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}[\sum_{G''\leq 2G_{\max}} \delta V_{eff}(\mathbf{G}''+\mathbf{q})e^{i\mathbf{G}''\mathbf{r}}]}_{F_{\mathbf{G},\mathbf{G}'}(\mathbf{r})}\,\Theta(\mathbf{r})d^3\mathbf{r}. \qquad (1.127)$$

Under the assumption that $|\mathbf{G}|$ and $|\mathbf{G}'|$ are smaller or equal $G_{\max}$ the highest Fourier component possible for the function $F_{\mathbf{G},\mathbf{G}'}(\mathbf{r})$ will be $4G_{\max}$. Therefor replacing the function $\Theta(\mathbf{r})$ by the function $\tilde{\Theta}(\mathbf{r})$ composed of the Fourier components (1.125) up to $K_{\max} = 4G_{\max}$ will reproduce the exact values $\Delta V^{int}_{eff}(\mathbf{G},\mathbf{G}')$ for all possible $\mathbf{G}$ and $\mathbf{G}'$. In practical calculations we first use FFT-algorithms to transform $\delta V^{int}_{eff}(\mathbf{G})$ and $\tilde{\Theta}(\mathbf{G})$ to real space, where the density of the real-space-grid is determined by $4G_{\max}$. On this grid the two functions are then point wise multiplied with each other. The resulting product is back transformed to reciprocal space. The resulting Fourier components truncated at $K_{\max} = 2G_{\max}$ provide the values for the matrix elements $\Delta V^{int}_{eff}(\mathbf{G},\mathbf{G}')$.

We now proceed by evaluating the matrix element describing the soft contribution of the potential change,

$$\Delta \check{V}^{MT}_{eff}(\mathbf{G},\mathbf{G}') \equiv \sum_{\alpha} \langle \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}} | \delta \check{V}^{\alpha}_{eff} | \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \rangle_{MT_{\alpha}}. \qquad (1.128)$$

We recall that the basis functions within the muffin-tin spheres are atomic-orbital-like wavefunctions. Using the abbreviation $\mathbf{Q}_{\mathbf{q}} \equiv \mathbf{k}+\mathbf{q}+\mathbf{G}$ they are defined as[7]

$$\phi_{\mathbf{Q}_{\mathbf{q}}}(\mathbf{S}_{\alpha}+\mathbf{r}) = \sum_{lm}[A_{lm}(\mathbf{Q}_{\mathbf{q}})u_l(r) + B_{lm}(\mathbf{Q}_{\mathbf{q}})\dot{u}_l(r)]Y_{lm}(\hat{\mathbf{r}}), \qquad |\mathbf{r}| \leq R_{\alpha}, \qquad (1.129)$$

with

$$\begin{aligned}
A_{lm}(\mathbf{Q}_{\mathbf{q}}) &= \frac{4\pi}{\sqrt{\Omega}} i^l Y^{*}_{lm}(\hat{\mathbf{Q}}_{\mathbf{q}}) a_l(\mathbf{Q}_{\mathbf{q}}) R^2_{\alpha} e^{i\mathbf{Q}\mathbf{S}_{\alpha}}, \\
B_{lm}(\mathbf{Q}_{\mathbf{q}}) &= \frac{4\pi}{\sqrt{\Omega}} i^l Y^{*}_{lm}(\hat{\mathbf{Q}}_{\mathbf{q}}) b_l(\mathbf{Q}_{\mathbf{q}}) R^2_{\alpha} e^{i\mathbf{Q}\mathbf{S}_{\alpha}}, \\
a_l(\mathbf{Q}_{\mathbf{q}}) &= j_l'(|\mathbf{Q}_{\mathbf{q}}|R_{\alpha})\dot{u}_l(R_{\alpha}) - j_l(|\mathbf{Q}_{\mathbf{q}}|R_{\alpha})\dot{u}_l'(R_{\alpha}), \\
b_l(\mathbf{Q}_{\mathbf{q}}) &= j_l(|\mathbf{Q}_{\mathbf{q}}|R_{\alpha})u_l'(R_{\alpha}) - j_l'(|\mathbf{Q}_{\mathbf{q}}|R_{\alpha})u_l(R_{\alpha}).
\end{aligned}$$

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[7] For simplicity we again omit the superscript α on A_{lm}, B_{lm}, u_l and $\dot{u}_l$.

In order to make formal similarities between $\Delta\check{V}^{MT}_{eff}(\mathbf{G},\mathbf{G}')$ and the corresponding formulas of the unperturbed Hamiltonian as transparent as possible we separate the soft change of the effective potential into the spherical and non-spherical contribution, i.e.,

$$\delta\check{V}^{\alpha}_{eff}(\mathbf{r}) = \delta\check{V}^{\alpha}_{00}(r)\frac{1}{\sqrt{4\pi}} + \sum_{L>0,M} \delta\check{V}^{\alpha}_{LM}(r)Y_{LM}(\hat{\mathbf{r}}). \tag{1.130}$$

We define the corresponding separation in the potential matrix element as

$$\Delta\check{V}^{MT}_{eff} = \Delta\check{V}^{s,MT}_{eff} + \Delta\check{V}^{ns,MT}_{eff}. \tag{1.131}$$

Inserting the spherical part of (1.130) and the wave-functions at points $\mathbf{Q_q} \equiv \mathbf{k}+\mathbf{q}+\mathbf{G}$ and $\mathbf{Q}'_0 \equiv \mathbf{k}+\mathbf{G}'$ constructed according to Eq.(1.129) into Eq.(1.128) leads to:

$$\begin{aligned}\Delta\check{V}^{s,MT}_{eff}(\mathbf{G},\mathbf{G}') &= \sum_{\alpha}\frac{1}{\sqrt{4\pi}}\int_{MT_\alpha}\{\sum_{l,m}[A^{*}_{lm}(\mathbf{Q_q})u_l(r)+B^{*}_{lm}(\mathbf{Q_q})\dot{u}_l(r)]Y^{*}_{lm}(\hat{\mathbf{r}})\}\delta\check{V}^{\alpha}_{00}(r)\\ &\times\{\sum_{l',m'}[A_{l'm'}(\mathbf{Q}'_0)u_{l'}(r)+B_{l'm'}(\mathbf{Q}'_0)\dot{u}_{l'}(r)]Y_{l'm'}(\hat{\mathbf{r}})\}d^3\mathbf{r}.\end{aligned} \tag{1.132}$$

Applying the orthogonality relation for spherical harmonics and introducing the radial integrals

$$\begin{aligned}IS1(l) &\equiv \frac{1}{\sqrt{4\pi}}\int_{r=0}^{R_\alpha} u_l^2(r)\delta\check{V}^{\alpha}_{00}(r)r^2dr, &(1.133)\\ IS2(l) &\equiv \frac{1}{\sqrt{4\pi}}\int_{r=0}^{R_\alpha} u_l(r)\dot{u}_l(r)\delta\check{V}^{\alpha}_{00}(r)r^2dr, &(1.134)\\ IS3(l) &\equiv \frac{1}{\sqrt{4\pi}}\int_{r=0}^{R_\alpha} \dot{u}_l^2(r)\delta\check{V}^{\alpha}_{00}(r)r^2dr, &(1.135)\end{aligned}$$

simplifies Eq.(1.132) to

$$\begin{aligned}\Delta\check{V}^{s,MT}_{eff}(\mathbf{G},\mathbf{G}') &= \sum_{\alpha}\sum_{lm}\{A^{*}_{lm}(\mathbf{Q_q})A_{lm}(\mathbf{Q}'_0)IS1(l)\\ &+[A^{*}_{lm}(\mathbf{Q_q})B_{lm}(\mathbf{Q}'_0)+B^{*}_{lm}(\mathbf{Q_q})A_{lm}(\mathbf{Q}'_0)]IS2(l)\\ &+B^{*}_{lm}(\mathbf{Q_q})B_{lm}(\mathbf{Q}'_0)IS3(l)\}.\end{aligned} \tag{1.136}$$

Proceeding along the same path of derivation the non-spherical contribution is found to be:

$$\begin{aligned}\Delta\check{V}^{ns,MT}_{eff}(\mathbf{G},\mathbf{G}') &= \sum_{\alpha}\int_{MT_\alpha}\{\sum_{l,m}[A^{*}_{lm}(\mathbf{Q_q})u_l(r)+B^{*}_{lm}(\mathbf{Q_q})\dot{u}_l(r)]Y^{*}_{lm}(\hat{\mathbf{r}})\}\\ &\times\sum_{L>0,M}\delta\check{V}^{\alpha}_{LM}(r)Y_{LM}(\hat{\mathbf{r}})\end{aligned}$$

$$
\begin{aligned}
&\times\{\sum_{l',m'}[A_{l'm'}(\mathbf{Q}'_0)u_{l'}(r)+B_{l'm'}(\mathbf{Q}'_0)\dot{u}_{l'}(r)]Y_{l'm'}(\hat{\mathbf{r}})\}d^3\mathbf{r} \\
= \; & \frac{(4\pi)^2R_\alpha^4}{\Omega}e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{S}_\alpha}\sum_{l,m}\sum_{L>0,M}\sum_{l'm'}i^{(l'-l)}Y_{lm}(\hat{\mathbf{Q}}_\mathbf{q})Y^*_{l'm'}(\hat{\mathbf{Q}}'_0) \\
&\times[a_l(\mathbf{Q}_\mathbf{q})a_{l'}(\mathbf{Q}'_0)INS1(l,L,M,l')+b_l(\mathbf{Q}_\mathbf{q})b_{l'}(\mathbf{Q}'_0)INS3(l,L,M,l') \\
&+a_l(\mathbf{Q}_\mathbf{q})b_{l'}(\mathbf{Q}'_0)INS2(l,L,M,l')+b_l(\mathbf{Q}_\mathbf{q})a_{l'}(\mathbf{Q}'_0)INS2(l',L,M,l)] \\
&\times G(l,m,L,M,l',m'), \qquad (1.137)
\end{aligned}
$$

where the Gaunt-coefficient $G(l,m,L,M,l',m')$ denotes the surface integral of the product $Y^*_{lm}(\hat{\mathbf{r}})Y_{LM}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})$ over the unit sphere. The symbols chosen to represent radial integrals involving potential coefficients and orbital functions are defined as follows:

$$
\begin{aligned}
INS1(l,L,M,l') &\equiv \int_{r=0}^{R_\alpha} u_l(r)\delta\check{V}^\alpha_{LM}(r)u_{l'}(r)r^2dr, \qquad (1.138)\\
INS2(l,L,M,l') &\equiv \int_{r=0}^{R_\alpha} u_l(r)\delta\check{V}^\alpha_{LM}(r)\dot{u}_{l'}(r)r^2dr, \qquad (1.139)\\
INS3(l,L,M,l') &\equiv \int_{r=0}^{R_\alpha} \dot{u}_l(r)\delta\check{V}^\alpha_{LM}(r)\dot{u}_{l'}(r)r^2dr. \qquad (1.140)
\end{aligned}
$$

The gradient of the effective potential within the atomic spheres provides the next contribution to the first-order Hamilton matrix:

$$
\Delta V^{MT}_{grad}(\mathbf{G},\mathbf{G}') \equiv -\sum_\alpha \delta\mathbf{S}_\alpha \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \nabla V^\alpha_{eff} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha}. \qquad (1.141)
$$

The most obvious choice for resolving the integrals constituting $\Delta V^{MT}_{grad}(\mathbf{G},\mathbf{G}')$ would be to explicitly apply the gradient operator onto the spherical-harmonics representation of the effective potential. For illustration we restrict ourselves to the third component of the operator $(\frac{\partial}{\partial z})$ [34]:

$$
\begin{aligned}
\frac{\partial V^\alpha_{eff}(\mathbf{r})}{\partial z} = & \sum_{L,M}\frac{\partial V^{\alpha,eff}_{LM}(r)}{\partial r}\cos(\vartheta)Y_{LM}(\hat{\mathbf{r}}) \\
& +\sum_{L,M}V^{\alpha,eff}_{LM}(r)\frac{1}{r}(L+1)\sqrt{\frac{(L-M)(L+M)}{(2L-1)(2L+1)}}Y_{L-1,M}(\hat{\mathbf{r}}) \\
& -\sum_{L,M}V^{\alpha,eff}_{LM}(r)\frac{1}{r}L\sqrt{\frac{(L-M+1)(L+M+1)}{(2L+1)(2L+3)}}Y_{L+1,M}(\hat{\mathbf{r}}). \qquad (1.142)
\end{aligned}
$$

Inserting expression (1.142) and the wave-functions at points $(\mathbf{k}+\mathbf{q}+\mathbf{G})$ and $(\mathbf{k}+\mathbf{G}')$ constructed according to Eq.(1.129) into Eq.(1.141) would lead to several terms involving cumbersome summations over Gaunt-coefficients. The formal structure of these terms would be similar to Eq.(1.137). From practical experiences in LAPW band structure calculations it is known that the computational evaluation of such terms is very time consuming in comparison to other steps in the set up procedure of the Hamilton matrix. Fortunately there exists an alternative approach which is computationally much more efficient and also with regard to the simplicity of the resulting formulas superior to the method just described. To explain it we first need to prove the following relation: A continuous function $G(\mathbf{r})$ is defined in the entire unit cell. At least its first derivative is also continuous throughout space. If the value of this function remains unchanged in every point of the entire cell and at the same time the atomic spheres $\{\alpha\}$ experience a first-order displacement $\{\delta\mathbf{S}_\alpha\}$ it is true that:

$$-\sum_\alpha \delta\mathbf{S}_\alpha \int_{MT_\alpha} \nabla G(\mathbf{r}) d^3\mathbf{r} = \int_{Int(\delta\mathbf{S})} G(\mathbf{r}) d^3\mathbf{r} - \int_{Int(0)} G(\mathbf{r}) d^3\mathbf{r}, \tag{1.143}$$

where $Int(0)$ and $Int(\delta\mathbf{S})$ denote the interstitial region before and after the displacement of the spheres respectively. The proof uses the fact that the integral over the entire cell is independent of the position of the spheres:

$$\begin{aligned}
\int_{\Omega(0)} G(\mathbf{r}) d^3\mathbf{r} &= \int_{\Omega(\delta\mathbf{S})} G(\mathbf{r}) d^3\mathbf{r}, \\
\int_{Int(0)} G(\mathbf{r}) d^3\mathbf{r} + \sum_\alpha \int_{MT_\alpha(0)} G(\mathbf{r}) d^3\mathbf{r} &= \int_{Int(\delta\mathbf{S})} G(\mathbf{r}) d^3\mathbf{r} + \sum_\alpha \int_{MT_\alpha(\delta\mathbf{S})} G(\mathbf{r}) d^3\mathbf{r}, \\
\int_{Int(0)} G(\mathbf{r}) d^3\mathbf{r} + \sum_\alpha \int_{MT_\alpha(0)} G(\mathbf{r}) d^3\mathbf{r} &= \int_{Int(\delta\mathbf{S})} G(\mathbf{r}) d^3\mathbf{r} + \sum_\alpha \int_{MT_\alpha(0)} G(\mathbf{r}) d^3\mathbf{r} \\
&\quad + \sum_\alpha \int_{MT_\alpha(0)} [\delta\mathbf{S}_\alpha \nabla G(\mathbf{r}) + O(\delta\mathbf{S}_\alpha^2)] d^3\mathbf{r}.
\end{aligned} \tag{1.144}$$

As we assumed a first-order change in the position vectors $\{\delta\mathbf{S}_\alpha\}$ higher order terms in the second integral of the right-hand side of Eq.(1.144) are negligible. Thus we arrive at Eq.(1.143). The mathematical and computational advantages offered by this relation with respect to the LAPW formalism are evident: It enables the transfer of sphere integrals over the gradient of a function to the first-order difference between respective integrals over the interstitial. As in the latter region the basis set for potentials, densities and wave-functions are plane waves a substantial simplification in the formal evaluation of the integrals will be achievable. Further on, efficient FFT algorithms (see previous section) are at hand to subsequently evaluate the integrals numerically.

Applying (1.143) to the evaluation of (1.141) is not directly possible as we can not identify the function $G(\mathbf{r})$ within the matrix element. This only becomes possible when (1.141) is combined with those matrix elements embedded in expression $R2$ and $R3$ of Eq.(1.109) which include the gradient of the wave-functions. They are found by inserting the first part of (1.105) into $R2$ and $R3$ and restricting the subsequent evaluation to the potential operator of the Hamiltonian:

$$\begin{aligned}\Delta S^{V,MT}_{grad}(\mathbf{G},\mathbf{G}') \equiv & -\sum_{\alpha}\langle \delta\mathbf{S}^{*}_{\alpha}(\nabla\phi^{\alpha}_{\mathbf{k+q+G}})\,|V^{\alpha}_{eff}|\,\phi^{\alpha}_{\mathbf{k+G}'}\rangle_{MT_\alpha} \\ & -\sum_{\alpha}\langle\phi^{\alpha}_{\mathbf{k+q+G}}\,|V^{\alpha}_{eff}|\,\delta\mathbf{S}_{\alpha}(\nabla\phi^{\alpha}_{\mathbf{k+G}'})\rangle_{MT_\alpha}\,. \end{aligned} \qquad (1.145)$$

Adding (1.141) and (1.145) and using the chain rule for the gradient operator we obtain:

$$\begin{aligned} & \Delta S^{V,MT}_{grad}(\mathbf{G},\mathbf{G}') + \Delta V^{MT}_{grad}(\mathbf{G},\mathbf{G}') \\ = & -\frac{1}{N}\sum_{\mathbf{T}}\sum_{\alpha}\delta\mathbf{S}^{\mathbf{T}}_{\alpha}\int_{MT_\alpha}\nabla\,\underbrace{[\phi^{*\alpha,\mathbf{T}}_{\mathbf{k+q+G}}(\mathbf{r})V^{\alpha,\mathbf{T}}_{eff}(\mathbf{r})\phi^{\alpha,\mathbf{T}}_{\mathbf{k+G}'}(\mathbf{r})]}_{\equiv G(\mathbf{r})}\,d^3\mathbf{r}, \end{aligned} \qquad (1.146)$$

where the product of the potential and the wave-functions defines the function $G(\mathbf{r})$. In the interstitial region it is given by the plane-wave representation of the wave-functions and the potential. In the critical region of the sphere surface $G(\mathbf{r})$ is continuous in value and slope. Note that in order to provide higher clarity in the following argumentation we have extended the integrational range over the entire super-cell by introducing the weighted summation $\frac{1}{N}\sum_{\mathbf{T}}$. Applying relation (1.143) to Eq.(1.146) and inserting the plane-wave representations for the potential and the wave-functions leads to:

$$\begin{aligned} & \Delta S^{V,MT}_{grad}(\mathbf{G},\mathbf{G}') + \Delta V^{MT}_{grad}(\mathbf{G},\mathbf{G}') \\ = & \frac{1}{\Omega_s}\int_{\Omega_s} e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}}\sum_{G''\leq 2G_{\max}} V(\mathbf{G}'')e^{i\mathbf{G}''\mathbf{r}}\Theta_{\delta\mathbf{S}}(\mathbf{r})d^3\mathbf{r} \\ & -\frac{1}{\Omega_s}\int_{\Omega_s} e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}}\sum_{G''\leq 2G_{\max}} V(\mathbf{G}'')e^{i\mathbf{G}''\mathbf{r}}\Theta_{0}(\mathbf{r})d^3\mathbf{r}, \end{aligned} \qquad (1.147)$$

with $\Theta_0(\mathbf{r})$ and $\Theta_{\delta\mathbf{S}}(\mathbf{r})$ denoting the respective step function operators before and after the displacement of the atoms. To simplify the first integral the representation of $\Theta_{\delta\mathbf{S}}(\mathbf{r})$ in momentum space is needed. Within the linear regime the function can be written as

$$\Theta_{\delta\mathbf{S}}(\mathbf{r}) = \Theta_0(\mathbf{r}) + \sum_{\mathbf{G}}\Theta_{\delta\mathbf{S}}(\mathbf{q}+\mathbf{G})e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}, \qquad (1.148)$$

with

$$\begin{aligned}
\Theta_{\delta\mathbf{S}}(\mathbf{G}+\mathbf{q}) &\equiv \frac{1}{\Omega_s}\int_{Int(\Omega_s)} e^{-i(\mathbf{G}+\mathbf{q})\mathbf{r}}d^3\mathbf{r} \\
&= -\frac{4\pi}{\Omega_s|\mathbf{G}+\mathbf{q}|}\sum_{\mathbf{T}}\sum_{\alpha} R_\alpha^2 j_1(R_\alpha|\mathbf{G}+\mathbf{q}|)e^{-i(\mathbf{G}+\mathbf{q})(\mathbf{S}_\alpha^{\mathbf{T}}+\delta\mathbf{S}_\alpha^{\mathbf{T}})} \\
&= -\frac{4\pi}{\Omega_s|\mathbf{G}+\mathbf{q}|}\sum_{\mathbf{T}}\sum_{\alpha}\{R_\alpha^2 j_1(R_\alpha|\mathbf{G}+\mathbf{q}|)e^{-i(\mathbf{G}+\mathbf{q})(\mathbf{S}_\alpha+\mathbf{T})} \\
&\quad \times(1-i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha e^{i\mathbf{q}\mathbf{T}})\} \\
&= -\frac{4\pi}{\Omega_s|\mathbf{G}+\mathbf{q}|}\underbrace{\sum_{\mathbf{T}} e^{-i(\mathbf{G}+\mathbf{q})\mathbf{T}}}_{0}\sum_{\alpha} R_\alpha^2 j_1(R_\alpha|\mathbf{G}+\mathbf{q}|)e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \\
&\quad +\frac{4\pi}{\Omega_s|\mathbf{G}+\mathbf{q}|}\underbrace{\sum_{\mathbf{T}} e^{-i\mathbf{G}\mathbf{T}}}_{N}\sum_{\alpha} R_\alpha^2 j_1(R_\alpha|\mathbf{G}+\mathbf{q}|)e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha \\
&= \frac{4\pi}{\Omega|\mathbf{G}+\mathbf{q}|}\sum_{\alpha} R_\alpha^2 j_1(R_\alpha|\mathbf{G}+\mathbf{q}|)e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha. \qquad (1.149)
\end{aligned}$$

Inserting Eq.(1.148) into the first integral of Eq.(1.147) leads to:

$$\begin{aligned}
&\Delta S_{grad}^{V,MT}(\mathbf{G},\mathbf{G}') + \Delta V_{grad}^{MT}(\mathbf{G},\mathbf{G}') \\
=\; &\frac{1}{\Omega_s}\int_{\Omega_s} e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}} \sum_{G''\leq 2G_{\max}} V(\mathbf{G}'')e^{i\mathbf{G}''\mathbf{r}}[\Theta_0(\mathbf{r}) \\
&+\sum_{\mathbf{G}'''}\Theta_{\delta\mathbf{S}}(\mathbf{q}+\mathbf{G}''')e^{i(\mathbf{q}+\mathbf{G}''')\mathbf{r}}]d^3\mathbf{r} \\
&-\frac{1}{\Omega_s}\int_{\Omega_s} e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}} \sum_{G''\leq 2G_{\max}} V(\mathbf{G}'')e^{i\mathbf{G}''\mathbf{r}}\Theta_0(\mathbf{r}) \\
=\; &\frac{1}{\Omega}\int_{\Omega} \underbrace{e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} \sum_{G''\leq 2G_{\max}} V(\mathbf{G}'')e^{i\mathbf{G}''\mathbf{r}}}_{\equiv Q_{\mathbf{G}'\mathbf{G}}(\mathbf{r})}\underbrace{\sum_{\mathbf{G}'''}\Theta_{\delta\mathbf{S}}(\mathbf{q}+\mathbf{G}''')e^{i\mathbf{G}'''\mathbf{r}}}_{\equiv\Gamma(\mathbf{r})}\, d^3\mathbf{r}, \qquad (1.150)
\end{aligned}$$

The periodicity of $Q_{\mathbf{G}'\mathbf{G}}(\mathbf{r})$ and $\Gamma(\mathbf{r})$ with respect to the unperturbed lattice enabled us to reduce the integrational range back to the primitive unit cell. The most essential aspect of our final result is provided by its formal structure which is identical with the one displayed by Eq.(1.127). We recall that it is possible to replace the step function $\Theta(\mathbf{r})$ by the finite Fourier series $\tilde{\Theta}(\mathbf{r})$ in the integral (1.124) leaving the value of the integral unchanged. It is straight forwardly shown that this is not a specific property of the step function but can be applied to any regular function representable by a Fourier series. In the context of

Eq.(1.150) this would be the 'first-order' step function $\Gamma(\mathbf{r})$. To summarize mathematically:

$$\frac{1}{\Omega}\int_{\Omega} Q_{\mathbf{G}'\mathbf{G}}(\mathbf{r})\Gamma(\mathbf{r})d^3\mathbf{r} = \frac{1}{\Omega}\int_{\Omega} Q_{\mathbf{G}'\mathbf{G}}(\mathbf{r})\,\tilde{\Gamma}\,(\mathbf{r})d^3\mathbf{r} \qquad \text{for all } |\mathbf{G}'|,|\mathbf{G}| \leq G_{\max}, \tag{1.151}$$

with

$$\tilde{\Gamma}\,(\mathbf{G}) = \begin{cases} \frac{4\pi}{\Omega|\mathbf{G}+\mathbf{q}|}\sum_\alpha R_\alpha^2 j_1(R_\alpha|\mathbf{G}+\mathbf{q}|)e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha & \text{for} \quad |\mathbf{G}| \leq 4G_{\max} \\ 0 & \text{for} \quad |\mathbf{G}| > 4G_{\max} \end{cases}.$$

Using FFT algorithms the right-hand side of Eq.(1.151) is numerically evaluated in exactly the same manner as has been described for the functions $F_{\mathbf{G}'\mathbf{G}}(\mathbf{r})$ and $\tilde{\Theta}(\mathbf{r})$ following Eq.(1.127).

The gradient of wave-functions also appears in the matrix elements $R4$ and $R5$ which explicitly represent the change in the overlap matrix due to the phonon distortion. Once more the transfer of the integrational procedure from the spheres to the interstitial region based on relation (1.143) is possible. The following formulas summarize the results:

$$\begin{aligned} \Delta S_{grad}^{MT}(\mathbf{G},\mathbf{G}') \equiv & -\sum_\alpha \langle \delta\mathbf{S}_\alpha^*(\nabla\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^\alpha)|\phi_{\mathbf{k}+\mathbf{G}'}^\alpha\rangle_{MT_\alpha} \\ & -\sum_\alpha \langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^\alpha|\delta\mathbf{S}_\alpha(\nabla\phi_{\mathbf{k}+\mathbf{G}'}^\alpha)\rangle_{MT_\alpha} \\ = & -\sum_\alpha \delta\mathbf{S}_\alpha \int_{MT_\alpha} \nabla\, \underbrace{[\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^{*\alpha}(\mathbf{r})\phi_{\mathbf{k}+\mathbf{G}'}^\alpha(\mathbf{r})]}_{\equiv G(\mathbf{r})}\, d^3\mathbf{r} \\ = & \ \frac{1}{\Omega}\int_\Omega e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}}[\Theta_{\delta\mathbf{S}}(\mathbf{r}) - \Theta_0(\mathbf{r})]d^3\mathbf{r} & (1.152) \\ = & \ \frac{1}{\Omega}\int_\Omega e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}\sum_{\mathbf{G}''}\Theta_{\delta\mathbf{S}}(\mathbf{q}+\mathbf{G}'')e^{i\mathbf{G}''\mathbf{r}}d^3\mathbf{r} \\ = & \ \sum_{\mathbf{G}''}\Theta_{\delta\mathbf{S}}(\mathbf{q}+\mathbf{G}'')\frac{1}{\Omega}\int_\Omega e^{i(\mathbf{G}'-\mathbf{G}+\mathbf{G}'')\mathbf{r}}d^3\mathbf{r} \\ = & \ \sum_{\mathbf{G}''}\Theta_{\delta\mathbf{S}}(\mathbf{q}+\mathbf{G}'')\delta_{\mathbf{G}-\mathbf{G}',\mathbf{G}''} = \Theta_{\delta\mathbf{S}}(\mathbf{q}+\mathbf{G}-\mathbf{G}') \\ = & \ \frac{4\pi}{\Omega|\mathbf{G}-\mathbf{G}'+\mathbf{q}|}\sum_\alpha\{R_\alpha^2 j_1(R_\alpha|\mathbf{G}-\mathbf{G}'+\mathbf{q}|) \\ & \times e^{-i(\mathbf{G}-\mathbf{G}'+\mathbf{q})\mathbf{S}_\alpha} i(\mathbf{G}-\mathbf{G}'+\mathbf{q})\delta\mathbf{S}_\alpha\}. & (1.153) \end{aligned}$$

Next we deal with the kinetic energy operator in combination with the gradients of the wave-functions displayed in terms $R2$ and $R3$:

$$\Delta T_{grad}^{MT}(\mathbf{G},\mathbf{G}') \equiv -\sum_\alpha \langle \delta\mathbf{S}_\alpha^*(\nabla\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^\alpha)|\nabla^2|\phi_{\mathbf{k}+\mathbf{G}'}^\alpha\rangle_{MT_\alpha}$$

$$\begin{aligned} & -\sum_{\alpha} \langle \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}} | \nabla^2 | \delta\mathbf{S}_{\alpha} (\nabla \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}) \rangle_{MT_{\alpha}} \\ = & -\sum_{\alpha} \delta\mathbf{S}_{\alpha} \int_{MT_{\alpha}} \nabla [\phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^2 \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})] d^3\mathbf{r}. \end{aligned} \tag{1.154}$$

Using the theorem of Gauss ΔT^{MT}_{grad} can also be written as a surface integral:

$$\Delta T^{MT}_{grad}(\mathbf{G},\mathbf{G}') = -\sum_{\alpha} \delta\mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \underbrace{\phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^2 \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})}_{\equiv TS(\mathbf{r})} \, d\mathbf{A}_{\alpha}, \tag{1.155}$$

with $\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}$ and $\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}$ being the LAPW basis functions inside the atomic spheres. Combing Eq.(1.155) with the term $R6$ given in its explicit form through Eq.(1.110) we notice that the surface integrals involving the basis functions from the spheres cancel each other:

$$\begin{aligned} & \Delta T^{MT}_{grad} + \delta^{+} \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{T} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \\ = & -\sum_{\alpha} \delta\mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^{*}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^2 \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) |_{Int} d\mathbf{A}_{\alpha} \equiv \Delta T^{Int}_{grad}(\mathbf{G},\mathbf{G}') \end{aligned} \tag{1.156}$$

with $\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}$ and $\phi_{\mathbf{k}+\mathbf{G}'}$ now denoting plane waves, the interstitial representation of the LAPW basis set. In order to use the mathematical tools already developed, the spatial validity of the plane-wave basis set is artificially extended into the spheres. We can then use the theorem of Gauss to transfer the surface integrals back to volume integrals over the spheres. Using the explicit plane-wave representation we obtain:

$$\begin{aligned} \Delta T^{Int}_{grad}(\mathbf{G},\mathbf{G}') &= -\sum_{\alpha} \delta\mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^{*}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^2 \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) |_{Int} d\mathbf{A}_{\alpha} \\ &= -\frac{1}{\Omega} \sum_{\alpha} \delta\mathbf{S}_{\alpha} \int_{MT_{\alpha}} \nabla [e^{-i(\mathbf{k}+\mathbf{q}+\mathbf{G})\mathbf{r}} \nabla^2 e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}}] d^3\mathbf{r} \\ &= \frac{1}{\Omega} |\mathbf{k}+\mathbf{G}'|^2 \sum_{\alpha} \delta\mathbf{S}_{\alpha} \int_{MT_{\alpha}} \nabla [e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}}] d^3\mathbf{r} \\ &= -\frac{1}{\Omega} i |\mathbf{k}+\mathbf{G}'|^2 \sum_{\alpha} \delta\mathbf{S}_{\alpha} (\mathbf{G}-\mathbf{G}'+\mathbf{q}) \int_{MT_{\alpha}} e^{-i(\mathbf{G}-\mathbf{G}'+\mathbf{q})\mathbf{r}} d^3\mathbf{r} \end{aligned} \tag{1.157}$$

Finally using the explicit formula (1.121) for the sphere integrals over plane-waves the kinetic energy term is found to be:

$$\begin{aligned} \Delta T^{Int}_{grad}(\mathbf{G},\mathbf{G}') = & -\frac{4\pi |\mathbf{k}+\mathbf{G}'|^2}{\Omega |\mathbf{G}-\mathbf{G}'+\mathbf{q}|} \sum_{\alpha} \{ R^2_{\alpha} j_1(R_{\alpha} |\mathbf{G}-\mathbf{G}'+\mathbf{q}|) \\ & \times e^{-i(\mathbf{G}-\mathbf{G}'+\mathbf{q})\mathbf{S}_{\alpha}} i (\mathbf{G}-\mathbf{G}'+\mathbf{q}) \delta\mathbf{S}_{\alpha} \}. \end{aligned} \tag{1.158}$$

The similarity to the matrix element ΔS^{MT}_{grad} is evident. In fact ΔT^{int}_{grad} can be related to ΔS^{MT}_{grad} in a very simple way[8]:

$$\Delta T^{int}_{grad}(\mathbf{G},\mathbf{G}') = -|\mathbf{k}+\mathbf{G}'|^2 \Delta S^{MT}_{grad}(\mathbf{G},\mathbf{G}'). \tag{1.159}$$

So far, only the gradient of the wave-functions has been taken into account when matrix elements involving $\delta\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}$ or $\delta\phi_{\mathbf{k}+\mathbf{G}}$ have been evaluated. As has been demonstrated in the second term of Eq.(1.105) another contribution to the change in the wave-function is caused by the phase shift of the matching parameters A_{lm} and B_{lm}. Inserting this contribution into $R2$ and $R3$ leads to:

$$\begin{aligned}
\Delta H_{MT}(\mathbf{G},\mathbf{G}') &\equiv \sum_\alpha \left\langle i(\mathbf{k}+\mathbf{q}+\mathbf{G})\delta\mathbf{S}^*_\alpha \phi^\alpha_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\
&\quad + \sum_\alpha \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} \right| i(\mathbf{k}+\mathbf{G}')\delta\mathbf{S}_\alpha \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\
&= i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta\mathbf{S}_\alpha \sum_\alpha \int_{MT_\alpha} \phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})[\nabla^2 + V^\alpha_{eff}(\mathbf{r})]\phi^\alpha_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})d^3\mathbf{r} \\
&= i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta\mathbf{S}_\alpha \sum_\alpha \int_{MT_\alpha} \phi^{\alpha *}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \\
&\quad \times[\nabla^2 + V^s_{eff,\alpha}(\mathbf{r}) + V^{ns}_{eff,\alpha}(\mathbf{r})]\phi^\alpha_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})d^3\mathbf{r},
\end{aligned} \tag{1.160}$$

where the spherical part of the effective potential has been separated from the non-spherical one. Repeating this insertion in $R4$ and $R5$ gives the corresponding change in the overlap matrix:

$$\begin{aligned}
\Delta S_{MT}(\mathbf{G},\mathbf{G}') &\equiv \sum_\alpha \langle i(\mathbf{k}+\mathbf{q}+\mathbf{G})\delta\mathbf{S}^*_\alpha \phi^\alpha_{\mathbf{k}+\mathbf{q}+\mathbf{G}} | \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \rangle_{MT_\alpha} \\
&\quad + \sum_\alpha \langle \phi^\alpha_{\mathbf{k}+\mathbf{q}+\mathbf{G}} | i(\mathbf{k}+\mathbf{G}')\delta\mathbf{S}_\alpha \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \rangle_{MT_\alpha} \\
&= i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta\mathbf{S}_\alpha \sum_\alpha \int_{MT_\alpha} \phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\phi^\alpha_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})d^3\mathbf{r}.
\end{aligned} \tag{1.161}$$

The formal structure of the integrals in (1.160) and (1.161) is very similar to the integrals appearing in the matrix elements

$$H^\alpha_{\mathbf{G}\mathbf{G}'} = \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}} \left| \hat{H} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \tag{1.162}$$

---

[8] The 'mathematical trick' to artificially extend the validity of the plane-waves into the sphere regions and then employ the theorem of Gauss is actually an alternative description of the concepts used to derive Eq.(1.153) and also Eq.(1.150).

and

$$S^{\alpha}_{\mathbf{GG}'} = \langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} | \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \rangle_{MT_\alpha} \tag{1.163}$$

of the eigenvalue problem in a regular LAPW band structure calculation. The formulas describing (1.162) and (1.163) are well established and have been derived in detail in many works (see for instance [32]). In order to evaluate (1.160) and (1.161) correctly it suffices to substitute the vector-argument $(\mathbf{k}+\mathbf{G})$ by $(\mathbf{k}+\mathbf{G}+\mathbf{q})$ in these formulas and subsequently multiply the results by the first-order phase factor $i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta\mathbf{S}_\alpha$. If we once more adopt the definitions $\mathbf{Q}_\mathbf{q} = \mathbf{k}+\mathbf{q}+\mathbf{G}$ and $\mathbf{Q}'_0 = \mathbf{k}+\mathbf{G}'$ this procedure leads to the following set of formulas:

$$\begin{aligned}
\Delta H^{s}_{MT}(\mathbf{G},\mathbf{G}') &\equiv i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\sum_\alpha \delta\mathbf{S}_\alpha \int_{MT_\alpha} \phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})[\nabla^2 + V^{s}_{eff,\alpha}(\mathbf{r})]\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})d^3\mathbf{r} \\
&= i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\sum_\alpha \delta\mathbf{S}_\alpha \frac{4\pi}{\Omega} R^4_\alpha e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{S}_\alpha} \sum_l (2l+1) P_l(\beta_{\mathbf{Q}_\mathbf{q},\mathbf{Q}'_0}) \\
&\quad \times [\varepsilon_l s_l(\mathbf{Q}_\mathbf{q},\mathbf{Q}'_0) + a_l(\mathbf{Q}_\mathbf{q}) b_l(\mathbf{Q}'_0)],
\end{aligned} \tag{1.164}$$

with

$$s_l(\mathbf{Q}_\mathbf{q},\mathbf{Q}'_0) \equiv a_l(\mathbf{Q}_\mathbf{q}) a_l(\mathbf{Q}'_0) + b_l(\mathbf{Q}_\mathbf{q}) b_l(\mathbf{Q}'_0) N_l.$$

P_l denotes the Legendre polynomial and $\beta_{\mathbf{Q}_\mathbf{q},\mathbf{Q}'_0}$ denotes the cosine of the angel between the vectors $\mathbf{Q}_\mathbf{q}$ and $\mathbf{Q}'_0$. Further more ε_l is the linearization energy for the orbital function $u_l(r)$ and N_l abbreviates the norm of the orbital function $\dot{u}_l(r)$ $(= \int_0^{R_\alpha} \dot{u}_l^2(r) r^2 dr)$.

$$\begin{aligned}
\Delta H^{ns}_{MT}(\mathbf{G},\mathbf{G}') &= i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\sum_\alpha \delta\mathbf{S}_\alpha \int_{MT_\alpha} \phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) V^{ns}_{eff,\alpha}(\mathbf{r}) \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})d^3\mathbf{r} \\
&= i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\sum_\alpha \delta\mathbf{S}_\alpha \frac{(4\pi)^2 R^4_\alpha}{\Omega} e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{S}_\alpha} \sum_{l,m}\sum_{L>0,M}\sum_{l'm'} i^{(l'-l)} Y_{lm}(\hat{\mathbf{Q}}_\mathbf{q}) \\
&\quad \times Y^*_{l'm'}(\hat{\mathbf{Q}}'_0)\{a_l(\mathbf{Q}_\mathbf{q}) a_{l'}(\mathbf{Q}'_0) VNS1(l,L,M,l') \\
&\quad + b_l(\mathbf{Q}_\mathbf{q}) b_{l'}(\mathbf{Q}'_0) VNS3(l,L,M,l') \\
&\quad + a_l(\mathbf{Q}_\mathbf{q}) b_{l'}(\mathbf{Q}'_0) VNS2(l,L,M,l') \\
&\quad + b_l(\mathbf{Q}_\mathbf{q}) a_{l'}(\mathbf{Q}'_0) VNS2(l',L,M,l)\} \times G(l,m,L,M,l',m'),
\end{aligned} \tag{1.165}$$

with

$$\begin{aligned}
VNS1(l,L,M,l') &\equiv \int_{r=0}^{R_\alpha} u_l(r) V^{\alpha}_{LM}(r) u_{l'}(r) r^2 dr, \\
VNS2(l,L,M,l') &\equiv \int_{r=0}^{R_\alpha} u_l(r) V^{\alpha}_{LM}(r) \dot{u}_{l'}(r) r^2 dr,
\end{aligned}$$

$$VNS3(l,L,M,l') \equiv \int_{r=0}^{R_\alpha} \dot{u}_l(r) V_{LM}^{\alpha}(r) \dot{u}_{l'}(r) r^2 dr.$$

$$\begin{aligned}\Delta S_{MT}(\mathbf{G},\mathbf{G}') &\equiv i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\sum_\alpha \delta\mathbf{S}_\alpha \int_{MT_\alpha} \phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})d^3\mathbf{r} \\ &= i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\sum_\alpha \delta\mathbf{S}_\alpha \frac{4\pi}{\Omega} R_\alpha^4 e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{S}_\alpha} \\ &\quad \times \sum_l (2l+1) P_l(\beta_{\mathbf{Q}_\mathbf{q},\mathbf{Q}'_0}) s_l(\mathbf{Q}_\mathbf{q},\mathbf{Q}'_0). \end{aligned} \tag{1.166}$$

Having completed the analysis of the various matrix elements of the Sternheimer equation we will now summarize them in order to provide a comprehensive description of this first-order perturbation equation for phonon-distorted wave-functions:

$$\sum_{G'\leq G_{\max}} \langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} | \epsilon_{n\mathbf{k}} - H | \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \rangle_\Omega \delta C_{n\mathbf{k}}(\mathbf{G}') = \sum_{G'\leq G_{\max}} M_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\delta\mathbf{S}) C_{n\mathbf{k}}(\mathbf{G}'), \tag{1.167}$$

with

$$\begin{aligned}\mathbf{M}(\mathbf{q},\delta\mathbf{S}) &= \Delta\mathbf{V}^{Int}_{eff} + \Delta\check{\mathbf{V}}^{s,MT}_{eff} + \Delta\check{\mathbf{V}}^{ns,MT}_{eff} + \Delta\mathbf{S}^{V,MT}_{grad} + \Delta\mathbf{V}^{MT}_{grad} \\ &\quad -\varepsilon_{n\mathbf{k}}(\Delta\mathbf{S}^{MT}_{grad} + \Delta\mathbf{S}_{MT}) + \Delta\mathbf{T}^{Int}_{grad} + \Delta\mathbf{H}^{s}_{MT} + \Delta\mathbf{H}^{ns}_{MT}.\end{aligned}$$

and the various matrix contributions being given by equations (1.127), (1.136), (1.137), (1.150), (1.153), (1.166), (1.158), (1.164) and (1.165).

1.3.4 The density change for valence electrons

The first-order response of the electron density can be constructed from the knowledge of the unperturbed KS orbitals and their first-order change as given by Eq.(1.102):

$$\delta\rho_v(\mathbf{r}) = 2\sum_{n,\mathbf{k}} \Psi^*_{n,\mathbf{k}}(\mathbf{r})\delta\Psi_{n,\mathbf{k}}(\mathbf{r}). \tag{1.168}$$

In the **interstitial** region the contribution at point **k** to the density response is obtained by the product of the plane-wave representation of $\Psi^*_{n,\mathbf{k}}(\mathbf{r})$ and $\delta\Psi_{n,\mathbf{k}}(\mathbf{r})$, i.e.,

$$\begin{aligned}\Psi^*_{n,\mathbf{k}}(\mathbf{r})\delta\Psi_{n,\mathbf{k}}(\mathbf{r}) &= \frac{1}{\Omega}\sum_{G,G'\leq G_{\max}} C^*_{n,\mathbf{k}}(\mathbf{G})\delta C_{n,\mathbf{k}}(\mathbf{G}') e^{i(\mathbf{G}'-\mathbf{G}+\mathbf{q})\mathbf{r}} \\ &= \frac{1}{\Omega} e^{i\mathbf{q}\mathbf{r}} \sum_{G,G'\leq G_{\max}} C^*_{n,\mathbf{k}}(\mathbf{G})\delta C_{n,\mathbf{k}}(\mathbf{G}') e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}.\end{aligned} \tag{1.169}$$

As expected, the density response in this region of the unit cell is composed of a lattice-periodical Fourier series modulated by $e^{i\mathbf{qr}}$, i.e.,

$$\Psi^*_{n,\mathbf{k}}(\mathbf{r})\delta\Psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{qr}} \sum_{G''\leq 2G_{\max}} \delta\rho_{n,\mathbf{k}}(\mathbf{G}''+\mathbf{q})e^{i\mathbf{G}''\mathbf{r}}, \tag{1.170}$$

where the coefficient $\delta\rho(\mathbf{G}''+\mathbf{q})$ is obtained as the Fourier transform of the double sum in Eq.(1.169), i.e.,

$$\delta\rho_{n,\mathbf{k}}(\mathbf{G}''+\mathbf{q}) = \frac{1}{\Omega^2}\sum_{G,G'\leq G_{\max}}\int_\Omega C^*_{n,\mathbf{k}}(\mathbf{G})\delta C_{n,\mathbf{k}}(\mathbf{G}')e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{G}'')\mathbf{r}}. \tag{1.171}$$

Using the orthogonality relation for plane waves,

$$\frac{1}{\Omega}\int_\Omega e^{i\mathbf{Kr}}d^3\mathbf{r} = \delta_{\mathbf{K},\mathbf{0}},$$

the coefficient reads

$$\delta\rho_{n,\mathbf{k}}(\mathbf{G}''+\mathbf{q}) = \frac{1}{\Omega}\sum_{G\leq G_{\max}} C^*_{n,\mathbf{k}}(\mathbf{G})\delta C_{n,\mathbf{k}}(\mathbf{G}''+\mathbf{G}). \tag{1.172}$$

We note from Eq.(1.172) that the Fourier coefficients $\delta\rho_{n,\mathbf{k}}(\mathbf{G}''+\mathbf{q})$ will extend up to $G''\leq 2G_{\max}$ whereas the variational coefficient and its first-order counterpart only extend up to $G\leq G_{\max}$. Finally the entire first-order change in the density response is obtained by summing up terms as given by Eq.(1.172) over the entire Brillouin zone and all occupied states, i.e.,

$$\delta\rho_v(\mathbf{r}) = e^{i\mathbf{qr}}\sum_{G\leq 2G_{\max}}\delta\rho(\mathbf{G}+\mathbf{q})e^{i\mathbf{Gr}}, \tag{1.173}$$

with

$$\delta\rho(\mathbf{G}+\mathbf{q}) \equiv 2\sum_{n,\mathbf{k}}\delta\rho_{n,\mathbf{k}}(\mathbf{G}+\mathbf{q}). \tag{1.174}$$

Within the atomic spheres the KS orbital is given by

$$\Psi_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r}) = \sum_{lm}[(AS)^{n,\mathbf{k}}_{lm}u_l(r) + (BS)^{n,\mathbf{k}}_{lm}\dot{u}_l(r)]Y_{lm}(\hat{\mathbf{r}}), \qquad |\mathbf{r}|\leq R_\alpha \tag{1.175}$$

with the abbreviations

$$\begin{aligned}(AS)^{n,\mathbf{k}}_{lm} &\equiv \sum_{G\leq G_{\max}} C_{n,\mathbf{k}}(\mathbf{G})A_{lm}(\mathbf{k}+\mathbf{G}),\\ (BS)^{n,\mathbf{k}}_{lm} &\equiv \sum_{G\leq G_{\max}} C_{n,\mathbf{k}}(\mathbf{G})B_{lm}(\mathbf{k}+\mathbf{G}).\end{aligned}$$

The first-order change of the KS orbital reads:

$$
\begin{aligned}
\delta\Psi_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r}) &= \sum_{G\leq G_{\max}} \delta C_{n,\mathbf{k}}(\mathbf{G})\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) + C_{n,\mathbf{k}}(\mathbf{G})\delta\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \\
&= \sum_{G\leq G_{\max}} \{\delta C_{n,\mathbf{k}}(\mathbf{G})\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) + C_{n,\mathbf{k}}(\mathbf{G})i[(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_\alpha]\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\} \\
&\quad - \sum_{G\leq G_{\max}} C_{n,\mathbf{k}}(\mathbf{G})\nabla\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\delta\mathbf{S}_\alpha. \qquad (1.176)
\end{aligned}
$$

Inserting the **atomic-sphere** representation of the basis functions for the first two terms on the right-hand side of expression (1.176) leads to:

$$
\begin{aligned}
\delta\Psi_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r}) &= \sum_{lm}\{(DAS)^{n,\mathbf{k}+\mathbf{q}}_{lm}u_l(r) + (DBS)^{n,\mathbf{k}+\mathbf{q}}_{lm}\dot{u}_l(r)\}Y_{lm}(\hat{\mathbf{r}}) \\
&\quad + \sum_{lm}\{(PAS)^{n,\mathbf{k}}_{lm}u_l(r) + (PBS)^{n,\mathbf{k}}_{lm}\dot{u}_l(r)\}Y_{lm}(\hat{\mathbf{r}}) \\
&\quad - \delta\mathbf{S}_\alpha\nabla\Psi_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r}), \qquad (1.177)
\end{aligned}
$$

with the abbreviations

l2main

$$
\begin{aligned}
(DAS)^{n,\mathbf{k}+\mathbf{q}}_{lm} &\equiv \sum_{G\leq G_{\max}} \delta C_{n,\mathbf{k}}(\mathbf{G})A_{lm}(\mathbf{k}+\mathbf{q}+\mathbf{G}), \qquad \text{DCALM} \\
(DBS)^{n,\mathbf{k}+\mathbf{q}}_{lm} &\equiv \sum_{G\leq G_{\max}} \delta C_{n,\mathbf{k}}(\mathbf{G})B_{lm}(\mathbf{k}+\mathbf{q}+\mathbf{G}), \qquad \text{DCBLM} \\
(PAS)^{n,\mathbf{k}}_{lm} &\equiv \sum_{G\leq G_{\max}} C_{n,\mathbf{k}}(\mathbf{G})i[(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_\alpha]A_{lm}(\mathbf{k}+\mathbf{G}), \\
(PBS)^{n,\mathbf{k}}_{lm} &\equiv \sum_{G\leq G_{\max}} C_{n,\mathbf{k}}(\mathbf{G})i[(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_\alpha]B_{lm}(\mathbf{k}+\mathbf{G}).
\end{aligned}
$$

Expressions (1.175) and (1.177) are inserted into (1.168), i.e.,

$$
\begin{aligned}
\delta\rho_v(\mathbf{S}_\alpha+\mathbf{r}) &= 2\sum_{n,\mathbf{k}}\Psi^*_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r})\delta\Psi_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r}) \\
&= 2\sum_{n,\mathbf{k}}\sum_{G,G'\leq G_{\max}}\{C^*_{n,\mathbf{k}}(\mathbf{G})\delta C_{n,\mathbf{k}}(\mathbf{G}')\phi^{*\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}(\mathbf{r}) \\
&\quad + C^*_{n,\mathbf{k}}(\mathbf{G})C_{n,\mathbf{k}}(\mathbf{G}')i[(\mathbf{k}+\mathbf{G}')\delta\mathbf{S}_\alpha]\phi^{*\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})\} \\
&\quad - \delta\mathbf{S}_\alpha[2\sum_{n,\mathbf{k}}\Psi^*_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r})\nabla\Psi_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r})] \qquad (1.178a) \\
&= 2\sum_{n,\mathbf{k}}\sum_{l,m}\sum_{l,'m'}\{[AS^{n,\mathbf{k}}_{lm}]^*[DAS^{n,\mathbf{k}+\mathbf{q}}_{l'm'}]u_l(r)u_{l'}(r) \\
&\quad + [AS^{n,\mathbf{k}}_{lm}]^*[DBS^{n,\mathbf{k}+\mathbf{q}}_{l'm'}]u_l(r)\dot{u}_{l'}(r) + [BS^{n,\mathbf{k}}_{lm}]^*[DAS^{n,\mathbf{k}+\mathbf{q}}_{l'm'}]\dot{u}_l(r)u_{l'}(r)
\end{aligned}
$$

$$
\begin{aligned}
&+[BS^{n,\mathbf{k}}_{lm}]^*[DBS^{n,\mathbf{k}+\mathbf{q}}_{l'm'}]\dot{u}_l(r)\dot{u}_{l'}(r)\}Y^*_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}}) \\
&+2\sum_{n,\mathbf{k}}\sum_{l,m}\sum_{l,'m'}\{[AS^{n,\mathbf{k}}_{lm}]^*[PAS^{n,\mathbf{k}}_{l'm'}]u_l(r)u_{l'}(r) \\
&+[AS^{n,\mathbf{k}}_{lm}]^*[PBS^{n,\mathbf{k}}_{l'm'}]u_l(r)\dot{u}_{l'}(r)+[BS^{n,\mathbf{k}}_{lm}]^*[PAS^{n,\mathbf{k}}_{l'm'}]\dot{u}_l(r)u_{l'}(r) \\
&+[BS^{n,\mathbf{k}}_{lm}]^*[PBS^{n,\mathbf{k}}_{l'm'}]\dot{u}_l(r)\dot{u}_{l'}(r)\}Y^*_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}}) \\
&-\delta\mathbf{S}_\alpha[2\sum_{n,\mathbf{k}}\Psi^*_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r})\nabla\Psi_{n,\mathbf{k}}(\mathbf{S}_\alpha+\mathbf{r})]. \qquad (1.178b)
\end{aligned}
$$

For the last term involving the gradient operator we have not used the explicit **atomic-sphere** representation for the wave-functions. It is more advantageous at this stage to evaluate it without explicit reference to a particular wave-function expansion. We now demonstrate that this term actually represents the gradient of the unperturbed electron density distribution. For this purpose we reduce the sum over the entire Brillouin zone $\sum_{n,\mathbf{k}}$ to a sum over half the Brillouin zone denoted by $\sum_{n,\mathbf{k}>0}$ where the points excluded can be generated by applying the inversion operator onto the **k** points of this new zone. The evaluation of the last term of expression (1.178b) thus reads:

$$
\begin{aligned}
2\sum_{n,\mathbf{k}}\Psi^*_{n,\mathbf{k}}(\mathbf{r}')\nabla\Psi_{n,\mathbf{k}}(\mathbf{r}') &= 2\sum_{n,\mathbf{k}>0}[\Psi^*_{n,\mathbf{k}}(\mathbf{r}')\nabla\Psi_{n,\mathbf{k}}(\mathbf{r}')+\Psi^*_{n,-\mathbf{k}}(\mathbf{r}')\nabla\Psi_{n,-\mathbf{k}}(\mathbf{r}')] \\
&= 2\sum_{n,\mathbf{k}>0}[\Psi^*_{n,\mathbf{k}}(\mathbf{r}')\nabla\Psi_{n,\mathbf{k}}(\mathbf{r}')+\Psi_{n,\mathbf{k}}(\mathbf{r}')\nabla\Psi^*_{n,\mathbf{k}}(\mathbf{r}')] \\
&= 2\sum_{n,\mathbf{k}>0}\nabla[\Psi^*_{n,\mathbf{k}}(\mathbf{r}')\Psi_{n,\mathbf{k}}(\mathbf{r}')] = 2\sum_{n,\mathbf{k}>0}\nabla[\rho_{n,\mathbf{k}}(\mathbf{r}')] \\
&= \nabla\rho_v(\mathbf{r}'), \qquad (1.179)
\end{aligned}
$$

with $\mathbf{r}'=\mathbf{r}+\mathbf{S}_\alpha$. In the evaluation displayed in (1.179) Kramer's theorem (see for instance [25]) and its implications for the density distribution of the electrons have been utilized:

$$
\Psi_{n,-\mathbf{k}}(\mathbf{r})=\Psi^*_{n,\mathbf{k}}(\mathbf{r}) \quad\Longrightarrow\quad \rho_{n,\mathbf{k}}(\mathbf{r})=\rho_{n,-\mathbf{k}}(\mathbf{r}). \qquad (1.180)
$$

With the result obtained in Eq.(1.179) the density response within the spheres can be separated into a soft contribution $\delta\breve{\rho}_v(\mathbf{S}_\alpha+\mathbf{r})$ and the contribution stemming from the rigid shift of the unperturbed density. The former shall be expanded into spherical harmonics:

$$
\delta\rho_v(\mathbf{S}_\alpha+\mathbf{r})=\sum_{LM}\delta\breve{\rho}^\alpha_{v,LM}(r)Y_{LM}(\hat{\mathbf{r}})-\delta\mathbf{S}_\alpha\nabla\rho_v(\mathbf{S}_\alpha+\mathbf{r}). \qquad (1.181)
$$

structure calculation have to be independent of the choice of atomic sphere radius ranging from $R1 \rightarrow R2$. This condition implies that in the shell just defined the plane waves are interchangeable with the atomic-orbital-functions of the LAPW basis set.

With respect to the calculation of the density response we can state that due to this 'interchangeability' of the basis set in these shells the validity of the Fourier series (1.173) can be specified to extend over the interstitial region of the perturbed crystal configuration. This will become relevant when we solve Poisson's equation in section (1.3.6).

1.3.5 The density change for core electrons

Core-electron states $\Psi^{\alpha}_{l,n,m}(\mathbf{r})$ in the unperturbed problem are obtained by numerical integration of the radial KS equation within the atomic spheres,

$$\begin{aligned} [-\nabla_r^2 + \frac{l(l+1)}{r^2} + V_s^{\alpha}(r)]u^{\alpha}_{n,l}(r) &= \varepsilon^{\alpha}_{n,l}u^{\alpha}_{n,l}(r), && (1.184) \\ \Psi^{\alpha}_{n,l,m}(\mathbf{r}) &= u^{\alpha}_{n,l}(r)Y_{lm}(\hat{\mathbf{r}}), && (1.185) \end{aligned}$$

with

$$\nabla_r^2 = \frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr}),$$

and $\mathbf{r}$ being the position vector of the electron relative to the center of the atomic sphere. The effective potential for the core electrons is spherical symmetric with respect to the atomic nucleus. The same applies to the charge density of the core electrons. The latter is a direct consequence of the condition that within the LAPW formalism only atomic orbitals of closed shells are allowed to be treated as core-electron states [34]. Further more the core charge is completely localized within the atomic sphere. If we now apply a perturbing potential we assume that all these properties are also valid for the respective perturbed quantities. This implies that we have to determine the change of the core orbitals upon a first-order change of the spherical potential. In fact, as the origin of our calculation is the center of the atomic sphere the change of the orbital function will only be influenced by the spherical part of the soft change $\delta\check{V}^{\alpha,\mathbf{T}}_{eff}(\mathbf{r})$. We denote it $\delta\check{V}^{\alpha,\mathbf{T}}_{s}(r)$. The radial Sternheimer equation is obtained by linearizing Eq.(1.184):

$$\begin{aligned} [-\nabla_r^2 + \frac{l(l+1)}{r^2} + V_s^{\alpha}(r) - \varepsilon^{\alpha}_{n}]\delta u^{\mathbf{T},\alpha}_{n,l}(r) &= [\delta\varepsilon^{\mathbf{T},\alpha}_{n,l} - \delta\check{V}^{\alpha,\mathbf{T}}_{s}(r)]u^{\alpha}_{n,l}(r), && (1.186) \\ \delta\Psi^{\mathbf{T},\alpha}_{n,l,m}(\mathbf{r}) &= \delta u^{\mathbf{T},\alpha}_{n,l}(r)Y_{lm}(\hat{\mathbf{r}}), && (1.187) \\ \delta\varepsilon^{\mathbf{T},\alpha}_{n,l} &= \int_{r=0}^{R_\alpha} u^{\alpha}_{l,n}(r)\delta\check{V}^{\alpha,\mathbf{T}}_{s}(r)u^{\alpha}_{l,n}(r)r^2dr. && (1.188) \end{aligned}$$

A superscript $\mathbf{T}$ indicating an arbitrary lattice vector of the unperturbed crystal has been introduced. It distinguishes between atomic spheres which are equivalent in the unperturbed case but are characterized by differing perturbing potentials if a frozen-phonon distortion is imposed. It is directly deducible from the general translational properties of $\delta\check{V}_{eff}(\mathbf{r})$ that the spherical soft change in the potential $\delta\check{V}_s^{\alpha,\mathbf{T}}(r)$ and the change of the energy parameter $\delta\varepsilon_{n,l}^{\mathbf{T},\alpha}$ fulfil the relations:

$$\delta\check{V}_s^{\alpha,\mathbf{T}}(r) = e^{i\mathbf{q}\mathbf{T}}\delta\check{V}_s^{\alpha}(r), \tag{1.189}$$

$$\delta\varepsilon_{n,l}^{\mathbf{T},\alpha} = e^{i\mathbf{q}\mathbf{T}}\delta\varepsilon_{n,l}^{\alpha}. \tag{1.190}$$

It can thus be seen that solving the differential equation (1.186) within the first unit cell $(\mathbf{T}=\mathbf{0})$ produces atomic core state solutions for the entire crystal:

$$\begin{aligned} \delta u_{n,l}^{\mathbf{T},\alpha}(r) &= e^{i\mathbf{q}\mathbf{T}}\delta u_{n,l}^{\alpha}(r), && (1.191)\\ \delta\Psi_{n,l,m}^{\mathbf{T},\alpha}(\mathbf{r}) &= e^{i\mathbf{q}\mathbf{T}}\delta\Psi_{n,l,m}^{\alpha}(\mathbf{r}). && (1.192) \end{aligned}$$

To obtain the charge response in the forward-traveling-wave representation, i.e.,

$$\begin{aligned} \delta^+\check{\rho}_c^{\alpha,\mathbf{T}}(\mathbf{r}) &= \sum_{n,l,m}\{[\Psi_{n,l,m}^{\alpha}(\mathbf{r})]^*\delta^+\Psi_{n,l,m}^{\alpha,\mathbf{T}}(\mathbf{r}) + [\delta^-\Psi_{n,l,m}^{\alpha,\mathbf{T}}(\mathbf{r})]^*\Psi_{n,l,m}^{\alpha}(\mathbf{r})\}\\ &= e^{i\mathbf{q}\mathbf{T}}\sum_{n,l}\{u_{n,l}^{\alpha}(r)\delta^+u_{n,l}^{\alpha}(r) + [\delta^-u_{n,l}^{\alpha}(r)]^*u_{n,l}^{\alpha}(r)\}\sum_{m}Y_{lm}^*(\hat{\mathbf{r}})Y_{lm}(\hat{\mathbf{r}}) \end{aligned} \tag{1.193}$$

we can exploit the fact that

$$[\delta^-u_{n,l}^{\alpha}(r)]^* = \delta^+u_{n,l}^{\alpha}(r). \tag{1.194}$$

Relation (1.194) is straight forwardly proved by taking the complex conjugate of Eq.(1.186) and taking into account that $\delta^+\check{V}_s^{\alpha}(\hat{\mathbf{r}}) = [\delta^-\check{V}_s^{\alpha}(\hat{\mathbf{r}})]^*$. We thus arrive at the final expression for the core-charge response:

$$\delta^+\check{\rho}_c^{\alpha,\mathbf{T}}(\mathbf{r}) = 2\sum_{n,l,m}[\Psi_{n,l,m}^{\alpha}(\mathbf{r})]^*\delta^+\Psi_{n,l,m}^{\alpha,\mathbf{T}}(\mathbf{r}). \tag{1.195}$$

For clarity we have so far presented the general treatment of perturbed core states within the non-relativistic KS equation. In actual calculations within the all-electron LAPW scheme core electrons are treated by solving the stationary Dirac equation within a spherical symmetric potential,

$$[c\boldsymbol{\alpha}\widehat{\mathbf{p}} + c^2\boldsymbol{\beta} + V_s^{\alpha}(r)\overline{\mathbf{1}}]\Psi_c^{\alpha}(\mathbf{r}) = \varepsilon^{\alpha}\Psi_c^{\alpha}(\mathbf{r}) \tag{1.196}$$

with

$$\begin{aligned} \boldsymbol{\alpha} &= (\alpha_1, \alpha_2, \alpha_3), \qquad \widehat{p}_i = i\frac{\partial}{\partial x_i}, \qquad c = 137.03599, \\ \alpha_i &= \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \qquad \mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \overline{\mathbf{1}} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & \mathbf{1} \end{pmatrix}, \qquad \boldsymbol{\beta} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}, \end{aligned}$$

and σ_i denoting the Pauli spin matrices. For simplicity we have dropped the index of the atomic sphere. It can be shown (see for instance [35]) that the spatial part of the stationary solutions for equation (1.196) can be written the following way:

$$\Psi^{\alpha}_{njlm}(\mathbf{r}) = \begin{pmatrix} \frac{i}{r} G^{\alpha}_{nl\kappa}(r) \Omega_{jlm}(\hat{\mathbf{r}}) \\ -\frac{1}{r} F^{\alpha}_{nl\kappa}(r) \Omega_{jl'm}(\hat{\mathbf{r}}) \end{pmatrix}, \tag{1.197}$$

where $G_{n\kappa}(r)$ and $F_{n\kappa}(r)$ are the big and small component of the radial function corresponding to the quantum numbers n and κ. The total angular momentum j ($j \geq \frac{1}{2}$) can take on either the value $(l + \frac{1}{2})$ or $(l - \frac{1}{2})$. The respective angular component of the wave-function is given by:

$$\Omega_{jlm}(\hat{\mathbf{r}}) = \begin{pmatrix} \sqrt{\frac{j+m}{2j}} Y_{l,m-\frac{1}{2}}(\hat{\mathbf{r}}) \\ \sqrt{\frac{j-m}{2j}} Y_{l,m+\frac{1}{2}}(\hat{\mathbf{r}}) \end{pmatrix}, \tag{1.198}$$

for the case

$$j = l + \frac{1}{2}, \qquad \kappa = -(l+1), \qquad l' = l + 1,$$

and

$$\Omega_{jlm}(\hat{\mathbf{r}}) = \begin{pmatrix} -\sqrt{\frac{j-m+1}{2j+2}} Y_{l,m-\frac{1}{2}}(\hat{\mathbf{r}}) \\ \sqrt{\frac{j+m+1}{2j+2}} Y_{l,m+\frac{1}{2}}(\hat{\mathbf{r}}) \end{pmatrix}, \tag{1.199}$$

for the case

$$j = l - \frac{1}{2}, \qquad \kappa = l, \qquad l' = l - 1.$$

For both values of j the restrictions on the quantum numbers l and m are the following:

$$l = 0, 1, ..., n-1, \qquad m = -j, (-j+1), ..., (j-1), j.$$

The radial parts of the solutions are constructed by numerical integration of the coupled differential equations given by:

$$\begin{aligned} c\frac{dG^{\alpha}_{nl\kappa}(r)}{dr} + c\frac{\kappa}{r} G^{\alpha}_{nl\kappa}(r) - [\varepsilon^{\alpha}_{nl\kappa} + c^2 - V^{\alpha}_s(r)] F^{\alpha}_{nl\kappa}(r) &= 0, & (1.200) \\ c\frac{dF^{\alpha}_{nl\kappa}(r)}{dr} - c\frac{\kappa}{r} F^{\alpha}_{nl\kappa}(r) + [\varepsilon^{\alpha}_{nl\kappa} - c^2 - V^{\alpha}_s(r)] G^{\alpha}_{nl\kappa}(r) &= 0. & (1.201) \end{aligned}$$

From Eq.(1.198) and Eq.(1.199) as well as from the normalized radial solutions of Eq.(1.200) and Eq.(1.201) the charge density can be constructed:

$$\rho_c^\alpha(r) = \sum_{nlmj} w(n,l,m,j)[\Psi_{njlm}^\alpha(\mathbf{r})]^*\Psi_{njlm}(\mathbf{r}) = \sum_{nl\kappa} w'(n,l,\kappa)\left\{\frac{[G_{nl\kappa}^\alpha(r)]^2}{r^2} + \frac{[F_{nl\kappa}^\alpha(r)]^2}{r^2}\right\}. \tag{1.202}$$

In Eq.(1.202) the occupation numbers $w(n,l,m,j)$ and $w'(n,l,\kappa)$ have been introduced. It has been assumed that a shell referenced by the quantum numbers n, l, and j is either fully occupied (and thus representing a closed shell) or completely empty. In the former case $w'(n,l,\kappa)$ is given by:

$$w'(n,l,\kappa) = 2|\kappa|. \tag{1.203}$$

Under this condition the core charge density is spherical symmetric.

If the core potential is now perturbed by a small amount $\delta\check{V}_s^\alpha(r)$ the change in eigenstates will only be caused by a change in the radial functions $G_{nl\kappa}^\alpha(r)$ and $F_{nl\kappa}^\alpha(r)$ of the occupied states. These changes, denoted by $\delta G_{nl\kappa}^\alpha(r)$ and $\delta F_{nl\kappa}^\alpha(r)$, are obtained by solving the following system of coupled inhomogeneous differential equations:

$$c\frac{d[\delta G^\alpha(r)]}{dr} + c\frac{\kappa}{r}[\delta G^\alpha(r)] - [\varepsilon^\alpha + c^2 - V_s^\alpha(r)]\delta F^\alpha(r) = [\delta\varepsilon^\alpha - \delta\check{V}_s^\alpha(r)]F^\alpha(r), \tag{1.204}$$

$$c\frac{d[\delta F^\alpha(r)]}{dr} - c\frac{\kappa}{r}[\delta F^\alpha(r)] + [\varepsilon^\alpha - c^2 - V_s^\alpha(r)]\delta G^\alpha(r) = -[\delta\varepsilon^\alpha - \delta\check{V}_s^\alpha(r)]G^\alpha(r). \tag{1.205}$$

where for simplicity we have dropped the quantum number index (l,n,κ). The first-order change of the eigenstate has to be calculated prior to the integration of Eqs.(1.204) and (1.205). Similarly like in the perturbation theory for the Schrödinger equation it is given as the expectation value of the perturbing potential with respect to the four-spinor wave-function $\Psi_{njlm}^\alpha(\mathbf{r})$ [36]:

$$\begin{aligned}\delta\varepsilon_{nl\kappa}^\alpha &= <\Psi_{njlm}^\alpha(\mathbf{r})|\delta\check{V}_s^\alpha(r)|\Psi_{njlm}^\alpha(\mathbf{r})>_{MT_\alpha} \\ &= \int_{r=0}^{R_\alpha}\left\{[G_{nl\kappa}^\alpha(r)]^2 + [F_{nl\kappa}^\alpha(r)]^2\right\}\delta\check{V}_s^\alpha(r)dr \end{aligned} \tag{1.206}$$

To construct the first-order charge density the solutions of Eqs.(1.204) and (1.205) are inserted into Eq.(1.195) leading to:

$$\delta^+\check{\rho}_c^\alpha(r) = 2\sum_i[\Phi_i^\alpha(\mathbf{r})]^*\delta^+\Phi_i^\alpha(\mathbf{r}) = 2\sum_{n,l,\kappa} w'(n,l,\kappa)\left[\frac{G_{nl\kappa}^\alpha(r)\delta^+G_{nl\kappa}^\alpha(r)}{r^2} + \frac{F_{nl\kappa}^\alpha(r)\delta^+F_{nl\kappa}^\alpha(r)}{r^2}\right]. \tag{1.207}$$

One comment should be made on the first-order change of the eigenvalue of a core-electron state: In our calculation we have implicitly utilized the fact that core states have no dispersion in reciprocal space. This gave us the possibility to calculate the first-order wave-function centered at one atom within an atomic picture where we obtained a finite complex value $\delta\varepsilon^{\alpha}_{nl\kappa}$. This result seems to contradict the finding of section (1.2.1) that the first-order change of the eigenvalue is zero in the case $\mathbf{q} \neq \mathbf{0}$. This can be resolved by first remembering that the crystal core state $\Psi^{\mathbf{k},\alpha}_{njlm}(\mathbf{r})$ will have to fulfil the Bloch-condition and will thus read:

$$\Psi^{\mathbf{k},\alpha}_{njlm}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\mathbf{T}} \Psi^{\alpha}_{njlm}(\mathbf{r} - \mathbf{T} - \mathbf{S}_\alpha), \tag{1.208}$$

with $\mathbf{r}$ now being a position vector in the super-cell. The actual change in the eigenvalue of the crystal electron state is now defined as the expectation value of the soft change in the potential (standing-wave representation) with respect to the core state wave-function $\Psi^{\mathbf{k},\alpha}_{njlm}(\mathbf{r})$. This quantity vanishes:

$$\begin{aligned}
\delta\varepsilon^{\mathbf{k},\alpha}_{nl\kappa} &= < \Psi^{\mathbf{k},\alpha}_{njlm}(\mathbf{r}) | \delta^{+}\check{V}^{\alpha}_{s}(\mathbf{r}) + \delta^{-}\check{V}^{\alpha}_{s}(\mathbf{r}) | \Psi^{\mathbf{k},\alpha}_{njlm}(\mathbf{r}) >_{\Omega_s} \\
&= \sum_{\mathbf{T}} e^{i\mathbf{q}\mathbf{T}} < \Psi^{\alpha}_{njlm}(\mathbf{r}) | \delta^{+}\check{V}^{\alpha}_{s}(|\mathbf{r} - \mathbf{S}_\alpha|) | \Psi^{\alpha}_{njlm}(\mathbf{r}) >_{MT_\alpha} \\
&+ \sum_{\mathbf{T}} e^{-i\mathbf{q}\mathbf{T}} < \Psi^{\alpha}_{njlm}(\mathbf{r}) | \delta^{-}\check{V}^{\alpha}_{s}(|\mathbf{r} - \mathbf{S}_\alpha|) | \Psi^{\alpha}_{njlm}(\mathbf{r}) >_{MT_\alpha} \\
&= [\sum_{\mathbf{T}} e^{i\mathbf{q}\mathbf{T}}] \delta^{+}\varepsilon^{\alpha}_{nl\kappa} + [\sum_{\mathbf{T}} e^{-i\mathbf{q}\mathbf{T}}] \delta^{-}\varepsilon^{\alpha}_{nl\kappa} = 0.
\end{aligned} \tag{1.209}$$

As indicated the essential point is that the finite value quantity $\delta\varepsilon^{\alpha}_{nl\kappa}$ is not to be identified with the first-order change of the KS eigenvalue. It merely represents an energy parameter which occurs through the specific method in which the Bloch-states for core electrons are calculated.

1.3.6 The change of the total effective potential

The change of the total effective potential can be divided into three contributions. These are (i) the change of the Coulomb potential due to the displacement of the atomic nuclei, (ii) the change of the electrostatic potential caused by the response of the electronic density distribution, and (iii) the change of the exchange-correlation potential also stemming from the density response. It is advantageous for the evaluation of all three contributions to change the spatial reference and coordinate system according to the following idea: In the calculation of the valence density response within the spheres (Eq.(1.181)) the center of the spherical-harmonic functions was taken to be the location of the atomic nuclei in the unperturbed situation. We thus obtained a soft contribution and a term involving the gradient of the unperturbed density distribution. Within this reference system we have to add the soft change of the core electron density (Eq.(1.207)) and the gradient of the respective unperturbed density to obtain the total density response:

$$\delta\rho(\mathbf{S}_\alpha+\mathbf{T}+\mathbf{r}) = \sum_{LM} \delta\check{\rho}^{\alpha,\mathbf{T}}_{LM}(r)Y_{LM}(\hat{\mathbf{r}}) - \delta\mathbf{S}^{\mathbf{T}}_\alpha \nabla\rho(\mathbf{S}_\alpha+\mathbf{r}), \qquad |\mathbf{r}| \le R_\alpha, \qquad (1.210)$$

with

$$\begin{aligned}
\delta\rho &\equiv \delta\rho_v + \delta\rho_c, \\
\delta\check{\rho}^{\alpha,\mathbf{T}}_{00}(r) &= \delta\check{\rho}^{\alpha,\mathbf{T}}_{v,00}(r) + \sqrt{4\pi}\,\delta\check{\rho}^{\alpha,\mathbf{T}}_{c}(r), \\
\delta\check{\rho}^{\alpha,\mathbf{T}}_{LM}(r) &= \delta\check{\rho}^{\alpha,\mathbf{T}}_{v,LM}(r), \qquad L>0, \\
\rho^{\alpha}_{00}(r) &= \rho^{\alpha}_{v,00}(r) + \sqrt{4\pi}\,\rho^{\alpha}_{c}(r), \\
\rho^{\alpha}_{LM}(r) &= \rho^{\alpha}_{v,LM}(r), \qquad L>0.
\end{aligned}$$

For the calculation of the potential change we shift the origin for the expansion into the displaced center of the atomic sphere located at $(\mathbf{S}_\alpha + \mathbf{T} + \delta\mathbf{S}_\alpha)$. This would also be the origin in the corresponding frozen-phonon super-cell calculation. If we now ask for the total density distribution expanded up to first-order within the displaced sphere (forward-traveling-wave representation) we would obtain:

$$\rho^{ph}(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha + \mathbf{T} + \mathbf{r}) = \sum_{LM} \rho^{\alpha}_{LM}(r)Y_{LM}(\hat{\mathbf{r}}) + \sum_{LM} \delta\check{\rho}^{\alpha,\mathbf{T}}_{LM}(r)Y_{LM}(\hat{\mathbf{r}}). \qquad (1.211)$$

Having moved into the reference system of the super-cell calculation we have correspondingly extended the interstitial region by those sections of the undisplaced sphere volumes which are not covered by the shifted spheres. At the same time the interstitial has been reduced by those parts of the shifted spheres which are not overlapping with the undisplaced ones. As our polarization vectors $\{\delta\mathbf{S}_\alpha\}$ are small in magnitude the total density distribution in this newly defined interstitial will be given by :

$$\rho^{ph}(\mathbf{r}) = \sum_{G \le 2G_{\max}} [\rho(\mathbf{G})e^{i\mathbf{G}\mathbf{r}} + \delta\rho(\mathbf{G}+\mathbf{q})e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}}], \qquad \mathbf{r} \in \text{Int}. \qquad (1.212)$$

with $\rho(\mathbf{G})$ being the Fourier coefficient of the unperturbed charge density and $\delta\rho(\mathbf{G}+\mathbf{q})$ being described by Eqs.(1.174) and (1.172). We refer to the end of section (1.3.4) for a critical discussion of this change of reference system.

We are now in a position to apply the formalism proposed by Weinert [29] to evaluate the first-order change of the total electrostatic potential encompassing the effects of the displaced atomic nuclei and of the density response. For this purpose we will first solve Poisson's equation for the total electrostatic potential within the perturbed super-cell up to first order in the displacement. At the end of this procedure we will identify the zero-order terms in the potential and subtract them. As it turned out this 'finite-difference-approach' displays a methodical structure which is clearer and more transparent than if we applied the Weinert-formalism [29] directly to the first-order density response $\delta\rho(\mathbf{r})$ and the dipole field of the nuclei.

Starting with the **interstitial** region of the perturbed super-cell Poisson's equation would read:

$$\nabla^2[V_c^{ph}(\mathbf{r})] = -8\pi[\rho^{ph}(\mathbf{r})], \qquad \mathbf{r} \in \text{Int}. \tag{1.213}$$

Within the linear regime the electrostatic potential $V_c^{ph}(\mathbf{r})$ is expanded into a Fourier series of the form:

$$V_c^{ph}(\mathbf{r}) = \sum_{G\leq 2G_{\max}} V_c^{ph}(\mathbf{G})e^{i\mathbf{G}\mathbf{r}} + \sum_{G\leq 2G_{\max}} \delta V_c^{ph}(\mathbf{G}+\mathbf{q})e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}}, \qquad \mathbf{r} \in \text{Int}. \tag{1.214}$$

To determine the interstitial potential caused by the charge distribution in the interstitial as well as in the atomic spheres we will first insert expansions (1.212) and (1.214) into Poisson's equation (1.213) and carry out the double integration over the entire super-cell. The potential zero within the cell is determined by setting the component $V_c^{ph}(\mathbf{G}=\mathbf{0})$ equal to zero. The procedure leads to:

$$\begin{aligned}
&\nabla^2\{\sum_{0<G\leq 2G_{\max}} V_c^{ph}(\mathbf{G})e^{i\mathbf{G}\mathbf{r}} + \sum_{G\leq 2G_{\max}} \delta V_c^{ph}(\mathbf{G}+\mathbf{q})e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}}\} \\
=\;& -8\pi\{\sum_{G\leq 2G_{\max}} \rho(\mathbf{G})e^{i\mathbf{G}\mathbf{r}} + \sum_{G\leq 2G_{\max}} \delta\rho(\mathbf{G}+\mathbf{q})e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}}\}, && (1.215)\\
\Rightarrow\;& V_c^{ph}(\mathbf{G}) = \frac{8\pi\rho(\mathbf{G})}{|\mathbf{G}|^2} \quad \text{for } G>0, && (1.216)\\
\Rightarrow\;& \delta V_c^{ph}(\mathbf{G}+\mathbf{q}) = \frac{8\pi\delta\rho(\mathbf{G}+\mathbf{q})}{|\mathbf{G}+\mathbf{q}|^2} \quad \text{for } G\geq 0, && (1.217)
\end{aligned}$$

A careful examination of the potential Fourier components (1.216) and (1.217) reveals that when inserted into Eq.(1.214) they describe two contributions: First, the potential in the interstitial caused by the charge distribution in the interstitial. Second, the potential in the interstitial caused by a density distribution inside the spheres which is constructed by extending the validity of Eq.(1.212) into the spheres. Obviously the latter contribution does not describe the physical situation correctly. Thus we have to subtract it and instead add a contribution from the proper charge distribution inside the spheres as given by Eq.(1.211) supplemented by the bare Coulomb potential of the atomic nuclei. Our aim is to accomplish this task in momentum space where the Poisson equation can be solved straight forwardly. Unfortunately near the nucleus the core charge density is rapidly varying and the nuclear charge exhibits the behaviour of a delta function. Consequently the corresponding Fourier series is non-convergent. A way out is based on the fact that the sole knowledge of the multipole moments of the charge distribution confined to the atomic sphere, i.e.,

$$p_{00}^{0,\alpha} + \delta\breve{p}_{00}^{\alpha,\mathbf{T}} \equiv Z_\alpha + \int_{r=0}^{R_\alpha} r^L \rho_{00}^{\alpha}(r) r^2 dr + \int_{r=0}^{R_\alpha} r^L \delta\breve{\rho}_{00}^{\alpha,\mathbf{T}}(r) r^2 dr, \tag{1.218}$$

$$p_{LM}^{0,\alpha} + \delta\breve{p}_{LM}^{\alpha,\mathbf{T}} \equiv \int_{r=0}^{R_\alpha} r^L \rho_{LM}^{\alpha}(r) r^2 dr + \int_{r=0}^{R_\alpha} r^L \delta\breve{\rho}_{LM}^{\alpha,\mathbf{T}}(r) r^2 dr \qquad \text{for} \quad L > 0, \tag{1.219}$$

is sufficient to determine the electrostatic potential caused by it outside the spheres. This implies the possibility of mathematically altering the charge distribution inside the spheres without affecting the potential caused by it in the interstitial. We only have to make sure that in this alteration the value of the multipole moments as given by Eq.(1.218) and Eq.(1.219) remain unaffected. Utilizing this freedom we replace the charge distribution within the spheres by a pseudo-charge distribution $\tilde{\rho}(\mathbf{r})$ which has to fulfil the following conditions: (A) Its value is non-zero only inside the atomic spheres smoothly vanishing on the sphere surfaces. (B) Its multipole moments $\Delta\tilde{p}_{lm}^{\alpha,\mathbf{T}}$ in the sphere $(\alpha, \mathbf{T})$ must be the difference between $p_{LM}^{0,\alpha} + \delta\breve{p}_{LM}^{\alpha,\mathbf{T}}$ and the multipole moments of the charge distribution created by extending Eq.(1.212) into the spheres. (C) There exists a well convergent Fourier series,

$$\tilde{\rho}(\mathbf{r}) = \sum_{\mathbf{T},\alpha} \left[\sum_{0 \le G \le 2G_{\max}} \tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} + \sum_{G \le 2G_{\max}} \delta\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q}) e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}} \right], \tag{1.220}$$

for the pseudo-charge distribution. The pseudo-charge given by Eq.(1.220) can now be added to the interstitial charge (Eq.(1.212)) enabling us to directly find the correct solution of the corresponding Poisson equation in momentum space:

$$\begin{aligned} V_c^{ph}(\mathbf{0}) &= 0, && (1.221) \\ V_c^{ph}(\mathbf{G}) &= 8\pi[\frac{\rho(\mathbf{G})}{|\mathbf{G}|^2} + \sum_{\mathbf{T},\alpha} \frac{\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G})}{|\mathbf{G}|^2}] \quad \text{for } G > 0, && (1.222) \end{aligned}$$

$$V_c^{ph}(\mathbf{G}+\mathbf{q}) \quad = \quad \frac{8\pi}{|\mathbf{G}+\mathbf{q}|^2}[\delta\rho(\mathbf{G}+\mathbf{q}) + \sum_{\mathbf{T},\alpha}\delta\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q})] \quad \text{for} \quad G \geq 0. \quad (1.223)$$

When inserting (1.221)-(1.223) into Eq.(1.214) the correct electrostatic potential in the interstitial is obtained.

An algorithm for the determination of the Fourier coefficients $\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G})$ has been proposed by Weinert [29]. According to his idea the pseudo-charge density around each nucleus α located in the unit cell $\mathbf{T}$ is first represented by an expansion in spherical harmonics. The ansatz for the radial expansion coefficients is such that the Fourier transform of $\tilde{\rho}_{\alpha,\mathbf{T}}$ can be calculated analytically:

$$\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha + \mathbf{T} + \mathbf{r}) = \sum_{lm} Q_{lm}^{\alpha,\mathbf{T}} \frac{1}{R_\alpha^{l+3}} (\frac{r}{R_\alpha})^l (1 - \frac{r^2}{R_\alpha^2})^n Y_{lm}(\hat{\mathbf{r}}), \qquad (1.224)$$

with n being a cut-off parameter chosen to optimize the convergence behaviour of the corresponding Fourier series. In a second step Eq.(1.224) is Fourier transformed with respect to $\mathbf{G}$ where the Rayleigh expansion is used to express the plane-wave $e^{-i\mathbf{G}\mathbf{r}}$ in terms of spherical harmonics around the center of the sphere. Subsequently imposing condition (A) and (B) formulated above determines the Fourier coefficient of the pseudo-charge density. It can be shown [29] that $\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G})$ reads:

$$\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}) = \frac{4\pi}{\Omega_s} \sum_{lm} P_{lm}^\alpha(\mathbf{G}) [\Delta\tilde{p}_{lm}^{\alpha,\mathbf{T}}] e^{-i\mathbf{G}(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha^{\mathbf{T}} + \mathbf{T})}, \qquad (1.225)$$

with

$$P_{lm}^\alpha(\mathbf{G}) = \frac{(-i)^l}{R_\alpha^l} \frac{(2l+2n+3)!!}{(2l+1)!!} \frac{j_{l+n+1}(|\mathbf{G}|R_\alpha)}{(|\mathbf{G}|R_\alpha)^{n+1}} Y_{lm}^*(\hat{\mathbf{G}}). \qquad (1.226)$$

In contrast to a regular undistorted lattice the exponential phase factor has to incorporate the atomic displacement $\delta\mathbf{S}_\alpha^{\mathbf{T}}$. In close analogy we find for the Fourier components $\delta\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q})$:

$$\delta\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q}) = \frac{4\pi}{\Omega_s} \sum_{lm} P_{lm}^\alpha(\mathbf{G}+\mathbf{q}) [\Delta\tilde{p}_{lm}^{\alpha,\mathbf{T}}] e^{-i(\mathbf{G}+\mathbf{q})(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha^{\mathbf{T}} + \mathbf{T})}, \qquad (1.227)$$

with

$$P_{lm}^\alpha(\mathbf{G}+\mathbf{q}) \equiv \frac{(-i)^l}{R_\alpha^l} \frac{(2l+2n+3)!!}{(2l+1)!!} \frac{j_{l+n+1}(|\mathbf{G}+\mathbf{q}|R_\alpha)}{(|\mathbf{G}+\mathbf{q}|R_\alpha)^{n+1}} Y_{lm}^*(\widehat{\mathbf{G}+\mathbf{q}}). \qquad (1.228)$$

As already indicated earlier $\Delta\tilde{p}_{lm}^{\alpha,\mathbf{T}}$ represents the difference between the true charge multipoles (defined by Eq.(1.218) and Eq.(1.219)) and the plane-wave multipoles created by extending the Fourier series of the interstitial density (Eq.(1.212)) into the spheres, i.e.,

$$\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm} = p^{0,\alpha}_{lm} + \delta\tilde{p}^{\alpha,\mathbf{T}}_{lm} - p^{pw,\alpha,\mathbf{T}}_{lm}, \tag{1.229}$$

with

$$\begin{aligned} p^{pw,\alpha,\mathbf{T}}_{lm} &= \frac{\sqrt{4\pi}}{3}R^3_\alpha\rho(\mathbf{0})\delta_{l,0} + \sum_{0<G\leq 2G_{\max}} \rho(\mathbf{G})H^\alpha_{lm}(\mathbf{G})e^{i\mathbf{G}(\mathbf{S}_\alpha+\delta\mathbf{S}^\mathbf{T}_\alpha+\mathbf{T})} \\ &+ \sum_{G\leq 2G_{\max}} \delta\rho(\mathbf{G}+\mathbf{q})H^\alpha_{lm}(\mathbf{G}+\mathbf{q})e^{i(\mathbf{G}+\mathbf{q})(\mathbf{S}_\alpha+\delta\mathbf{S}^\mathbf{T}_\alpha+\mathbf{T})}, \end{aligned} \tag{1.230}$$

and

$$H^\alpha_{lm}(\mathbf{G}) \equiv 4\pi i^l\frac{R^{l+2}_\alpha}{|\mathbf{G}|}j_{l+1}(|\mathbf{G}|R_\alpha)Y^*_{lm}(\hat{\mathbf{G}}), \tag{1.231}$$

$$H^\alpha_{lm}(\mathbf{G}+\mathbf{q}) \equiv 4\pi i^l\frac{R^{l+2}_\alpha}{|\mathbf{G}+\mathbf{q}|}j_{l+1}(|\mathbf{G}+\mathbf{q}|R_\alpha)Y^*_{lm}(\widehat{\mathbf{G}+\mathbf{q}}). \tag{1.232}$$

In the regime of linear response we are restricted to the zero- and first-order terms of $p^{pw,\alpha,\mathbf{T}}_{lm}$ with respect to the displacement $\delta\mathbf{S}^\mathbf{T}_\alpha$. Making a first-order expansion of the phase factors $e^{i\mathbf{G}\delta\mathbf{S}^\mathbf{T}_\alpha}$ and $e^{i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}^\mathbf{T}_\alpha}$ and using the definition (1.97) for $\delta\mathbf{S}^\mathbf{T}_\alpha$ the plane wave multipoles are now given by:

$$\begin{aligned} p^{pw,\alpha,\mathbf{T}}_{lm} &= \frac{\sqrt{4\pi}}{3}R^3_\alpha\rho(\mathbf{0})\delta_{l,0} + \sum_{0<G\leq 2G_{\max}} \rho(\mathbf{G})H^\alpha_{lm}(\mathbf{G})e^{i\mathbf{G}\mathbf{S}_\alpha}[1 + i\mathbf{G}\delta\mathbf{S}^\mathbf{T}_\alpha + ...] \\ &+ \sum_{G\leq 2G_{\max}} \delta\rho(\mathbf{G}+\mathbf{q})H^\alpha_{lm}(\mathbf{G}+\mathbf{q})e^{i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha}e^{i\mathbf{q}\mathbf{T}}[1 + i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}^\mathbf{T}_\alpha + ...] \\ &= \underbrace{\frac{\sqrt{4\pi}}{3}R^3_\alpha\rho(\mathbf{0})\delta_{l,0} + \sum_{0<G\leq 2G_{\max}} \rho(\mathbf{G})H^\alpha_{lm}(\mathbf{G})e^{i\mathbf{G}\mathbf{S}_\alpha}}_{=p^{0,pw,\alpha}_{lm}} \\ &+e^{i\mathbf{q}\mathbf{T}} \sum_{0<G\leq 2G_{\max}} i[\mathbf{G}\delta\mathbf{S}_\alpha]\rho(\mathbf{G})H^\alpha_{lm}(\mathbf{G})e^{i\mathbf{G}\mathbf{S}_\alpha} \\ &+e^{i\mathbf{q}\mathbf{T}} \sum_{G\leq 2G_{\max}} \delta\rho(\mathbf{G}+\mathbf{q})H^\alpha_{lm}(\mathbf{G}+\mathbf{q})e^{i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \qquad (1.233) \\ &\equiv p^{0,pw,\alpha}_{lm} + e^{i\mathbf{q}\mathbf{T}}\delta p^{pw,\alpha}_{lm}. \qquad (1.234) \end{aligned}$$

The first two terms on the right-hand side of Eq.(1.233) are the plane-wave multipoles $p^{0,pw,\alpha}_{lm}$ of the undistorted lattice. The term including the phase factor $i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}^\mathbf{T}_\alpha$ is already of second order and thus neglected. In a next step we also expand the Fourier components

$\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G})$ and $\delta\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q})$ to first-order in the displacement:

$$\begin{aligned}
\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}) &= \frac{4\pi}{\Omega_s}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G})[\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha}[1 - i\mathbf{G}\delta\mathbf{S}^{\mathbf{T}}_{\alpha} + ...] \\
&= \frac{4\pi}{\Omega_s}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G})[\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha} \\
&\quad -\frac{4\pi}{\Omega_s}e^{i\mathbf{q}\mathbf{T}}\sum_{lm} i[\mathbf{G}\delta\mathbf{S}_\alpha]P^{\alpha}_{lm}(\mathbf{G})[\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha}, \qquad (1.235)
\end{aligned}$$

$$\begin{aligned}
\delta\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q}) &= \frac{4\pi}{\Omega_s}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha}e^{-i\mathbf{q}\mathbf{T}}[1 - i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}^{\mathbf{T}}_{\alpha} + ...] \\
&= \frac{4\pi}{\Omega_s}e^{-i\mathbf{q}\mathbf{T}}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \\
&\quad -\frac{4\pi}{\Omega_s}\sum_{lm} i[(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha]P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha}. \qquad (1.236)
\end{aligned}$$

Replacing $\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}$ in (1.235) by the expressions (1.229) and (1.233) and neglecting resulting terms in $\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G})$ which are higher than first order in the displacement we obtain:

$$\begin{aligned}
\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}) &= \frac{4\pi}{\Omega_s}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G})[p^{0,\alpha}_{lm} + \delta\breve{p}^{\alpha,\mathbf{T}}_{lm} - p^{0,pw,\alpha}_{lm} - e^{i\mathbf{q}\mathbf{T}}\delta p^{pw,\alpha}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha} \\
&\quad -\frac{4\pi}{\Omega_s}e^{i\mathbf{q}\mathbf{T}}\sum_{lm} i[\mathbf{G}\delta\mathbf{S}_\alpha]P^{\alpha}_{lm}(\mathbf{G})[p^{0,\alpha}_{lm} + \delta\breve{p}^{\alpha,\mathbf{T}}_{lm} - p^{0,pw,\alpha}_{lm} - e^{i\mathbf{q}\mathbf{T}}\delta p^{pw,\alpha}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha} \\
&= \underbrace{\frac{4\pi}{\Omega_s}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G})[p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha}}_{=\tilde{\rho}^0_\alpha(\mathbf{G})\frac{\Omega}{\Omega_s}} \\
&\quad +\frac{4\pi}{\Omega_s}e^{i\mathbf{q}\mathbf{T}}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G})[\delta\breve{p}^{\alpha}_{lm} - \delta p^{pw,\alpha}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha} \\
&\quad -\frac{4\pi}{\Omega_s}e^{i\mathbf{q}\mathbf{T}}\sum_{lm} i[\mathbf{G}\delta\mathbf{S}_\alpha]P^{\alpha}_{lm}(\mathbf{G})[p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm}]e^{-i\mathbf{G}\mathbf{S}_\alpha}, \qquad (1.237)
\end{aligned}$$

with $\tilde{\rho}^0_\alpha(\mathbf{G})$ being the Fourier component of the pseudo charge in the undistorted lattice (see for instance [32]). In (1.237) we have used the translational property of the soft change $\delta\breve{p}^{\alpha,\mathbf{T}}_{lm}(r)$ which also applies to the corresponding multipole moment:

$$\delta\breve{p}^{\alpha,\mathbf{T}}_{lm}(r) = e^{i\mathbf{q}\mathbf{T}}\delta\breve{p}^{\alpha}_{lm}(r) \quad \Rightarrow \quad \delta\breve{p}^{\alpha,\mathbf{T}}_{lm} = e^{i\mathbf{q}\mathbf{T}}\delta\breve{p}^{\alpha}_{lm} \qquad (1.238)$$

For the Fourier component $\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q})$ the same replacement of $\Delta\tilde{p}^{\alpha,\mathbf{T}}_{lm}$ leads to:

$$\tilde{\rho}_{\alpha,\mathbf{T}}(\mathbf{G}+\mathbf{q}) = \frac{4\pi}{\Omega_s}e^{-i\mathbf{q}\mathbf{T}}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm}$$

$$\begin{aligned}
& +e^{i\mathbf{q}\mathbf{T}}(\delta\check{p}^{\alpha}_{lm} - \delta p^{pw,\alpha}_{lm})]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \\
& -\frac{4\pi}{\Omega_s}\sum_{lm} i[(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha]P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm} \\
& +e^{i\mathbf{q}\mathbf{T}}(\delta\check{p}^{\alpha}_{lm} - \delta p^{pw,\alpha}_{lm})]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha}
\end{aligned} \tag{1.239}$$

$$\begin{aligned}
= \; & \frac{4\pi}{\Omega_s}e^{-i\mathbf{q}\mathbf{T}}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \\
& +\frac{4\pi}{\Omega_s}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[\delta\check{p}^{\alpha}_{lm} - \delta p^{pw,\alpha}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \\
& -\frac{4\pi}{\Omega_s}\sum_{lm} i[(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha]P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha}.
\end{aligned} \tag{1.240}$$

Finally, to obtain $V_c(\mathbf{G})$ and $V_c(\mathbf{G}+\mathbf{q})$ we insert expression (1.237) into (1.222) and (1.240) into (1.223). Remembering that the lattice sum $\sum_{\mathbf{T}} e^{\pm i\mathbf{q}\mathbf{T}}$ vanishes for $\mathbf{q} \neq \mathbf{0}$ we obtain:

$$\begin{aligned}
V^{ph}_c(\mathbf{G}) \; = \; & 8\pi[\frac{\rho(\mathbf{G})}{|\mathbf{G}|^2} + \sum_{\mathbf{T}}\sum_{\alpha}\frac{\tilde{\rho}^0_\alpha(\mathbf{G})}{|\mathbf{G}|^2}\frac{\Omega}{\Omega_s}] \\
& +\sum_{\alpha} e^{-i\mathbf{G}\mathbf{S}_\alpha}[\sum_{\mathbf{T}} e^{i\mathbf{q}\mathbf{T}}]\frac{32\pi^2}{\Omega_s}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G})[\delta\check{p}^{\alpha}_{lm} - \delta p^{pw,\alpha}_{lm} \\
& -i\mathbf{G}\delta\mathbf{S}_\alpha(p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm})] \\
= \; & 8\pi[\frac{\rho^0(\mathbf{G})}{|\mathbf{G}|^2} + \sum_{\alpha}\frac{\tilde{\rho}^0_\alpha(\mathbf{G})}{|\mathbf{G}|^2}] = V^0_c(\mathbf{G}) \qquad \text{for} \quad G > 0.
\end{aligned} \tag{1.241}$$

$$\begin{aligned}
\delta V^{ph}_c(\mathbf{G}+\mathbf{q}) \; = \; & \frac{8\pi}{|\mathbf{G}+\mathbf{q}|^2}\{\delta\rho(\mathbf{G}+\mathbf{q}) \\
& +\frac{4\pi}{\Omega_s}\sum_{\mathbf{T}}\sum_{\alpha} e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[\delta\check{p}^{\alpha}_{lm} - \delta p^{pw,\alpha}_{lm} \\
& -i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha(p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm})] \\
& +\frac{4\pi}{\Omega_s}\sum_{\alpha}[\sum_{\mathbf{T}} e^{-i\mathbf{q}\mathbf{T}}]\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \\
= \; & \frac{8\pi}{|\mathbf{G}+\mathbf{q}|^2}\{\delta\rho(\mathbf{G}+\mathbf{q}) \\
& +\frac{4\pi}{\Omega}\sum_{\alpha}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[\delta\check{p}^{\alpha}_{lm} - \delta p^{pw,\alpha}_{lm}]e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha} \\
& -\frac{4\pi}{\Omega}\sum_{\alpha}\sum_{lm} P^{\alpha}_{lm}(\mathbf{G}+\mathbf{q})[i(\mathbf{G}+\mathbf{q})\delta\mathbf{S}_\alpha] \\
& \times(p^{0,\alpha}_{lm} - p^{0,pw,\alpha}_{lm})e^{-i(\mathbf{G}+\mathbf{q})\mathbf{S}_\alpha}\}
\end{aligned} \tag{1.242}$$

As we expected from the general linear-response theory the Fourier component $V_c^{ph}(\mathbf{G})$ in the super-cell calculation up to first-order in the displacement is identical with the Fourier component $V_c^0(\mathbf{G})$ of the unperturbed crystal. The change of the electrostatic potential $\delta V_c(\mathbf{r})$ in the interstitial region comprising the dipole field of the displaced atomic nuclei and the response of the electronic density distribution is thus exclusively described by

$$\delta V_c(\mathbf{r}) = \sum_{G \leq 2G_{\max}} \delta V_c(\mathbf{G}+\mathbf{q}) e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}}, \tag{1.243}$$

with the Fourier coefficient being given by (1.242).

The evaluation of $\delta V_c(\mathbf{r})$ in the interstitial implies that we also know the values of this potential change on the surfaces of the atomic spheres. Therefor solving Poisson's equation inside the **spheres** is identical with solving a Dirichlet boundary value problem well known from electrostatics [29, 37]. In this case the change of the Coulomb potential inside the atomic sphere $(\alpha, \mathbf{T})$ is determined via a Greens-function method. As we have chosen to work in the reference system of the displaced atoms it suffices to apply this method to the soft change of the spheres density. Note that in contrast to the interstitial the zero-order term of the potential inside the spheres is excluded right from the beginning. The formula for the soft change can be summarized as follows [29]:

$$\begin{aligned} \delta \check{V}_c^{\alpha,\mathbf{T}}(\mathbf{r}) &= \int_{\phi'=0}^{2\pi} \int_{\vartheta'=0}^{\pi} \int_{r'=0}^{R_\alpha} \delta \check{\rho}_\alpha^{\mathbf{T}}(\mathbf{r}') G(\mathbf{r},\mathbf{r}') d^3\mathbf{r}' \\ & -\frac{R_\alpha^2}{8\pi} \int_{\phi'=0}^{2\pi} \int_{\vartheta'=0}^{\pi} \delta V_c^{\mathbf{T}}(\mathbf{R}'_\alpha) \frac{\partial G(\mathbf{r},\mathbf{r}')}{\partial \mathbf{r}'} d\Omega'. \end{aligned} \tag{1.244}$$

As the regions for integration are a sphere and its surface, the natural choice of basis functions to represent the Greens function $G(\mathbf{r},\mathbf{r}')$ and its first normal derivative $\frac{\partial G(\mathbf{r},\mathbf{r}')}{\partial \mathbf{r}'}$ are spherical harmonics:

$$G(\mathbf{r},\mathbf{r}') = 8\pi \sum_{lm} \frac{Y_{lm}^*(\hat{\mathbf{r}}') Y_{lm}(\hat{\mathbf{r}})}{(2l+1)} \frac{r_<^l}{r_>^{l+1}} [1 - (\frac{r_>}{R_\alpha})^{2l+1}], \tag{1.245}$$

$$\frac{\partial G(\mathbf{r},\mathbf{r}')}{\partial \mathbf{r}'} = -\frac{8\pi}{R_\alpha^2} \sum_{lm} (\frac{r}{R_\alpha})^l Y_{lm}^*(\hat{\mathbf{r}}') Y_{lm}(\hat{\mathbf{r}}). \tag{1.246}$$

with $r_<$ and $r_>$ having the following meaning:

$$r_< = r \quad \text{for} \quad r < r', \qquad r_< = r' \quad \text{for} \quad r > r',$$

$$r_> = r \quad \text{for} \quad r > r', \qquad r_> = r' \quad \text{for} \quad r < r'.$$

To simplify Eq.(1.244) we first use the expansion of the total density response as given by Eqs.(1.183) and (1.207) to carry out the angular integration within the volume integral of Eq.(1.244):

$$\int_{MT_{\alpha,\mathbf{T}}} \delta\breve{\rho}_{\alpha}^{\mathbf{T}}(\mathbf{r}')G(\mathbf{r},\mathbf{r}')d^3\mathbf{r}' = e^{i\mathbf{q}\mathbf{T}}\sum_{lm} \underbrace{\{\int_{r=0}^{R_\alpha} \frac{8\pi(r')^2}{(2l+1)}\delta\breve{\rho}_{lm}^{\alpha}(r')\frac{1}{r_>}(\frac{r_<}{r_>})^l[1-(\frac{r_>}{R_\alpha})^{2l+1}]dr'\}}_{\equiv C1_{\alpha,lm}(r)}\, Y_{lm}(\hat{\mathbf{r}}). \tag{1.247}$$

Then the surface integral in Eq.(1.244) is evaluated analytically by substituting the values of the change of the Coulomb potential on the surface of the displaced atomic sphere ($\delta V_c^{\mathbf{T}}(\mathbf{R}'_\alpha)$) by the corresponding Fourier expansion of the interstitial. One contribution will directly come from the Fourier components $\delta V_c(\mathbf{G}+\mathbf{q})$. Maybe less obvious but equally important is a second term related to the unperturbed Fourier components $V_c(\mathbf{G})$: The sphere surface has been displaced and at the same time the zero-order Coulomb potential of the interstitial has remained spatially unaltered. This implies that the surface value related to a specific Fourier component $V_c(\mathbf{G})$ will differ from the corresponding value on the undisplaced sphere by a phase factor $e^{+i\mathbf{G}\delta\mathbf{S}_{\alpha}^{\mathbf{T}}}$. Using the Rayleigh expansion for plane-waves and restricting the overall evaluation to first-order terms we obtain for the sum of both contributions:

$$\begin{aligned}\delta V_c^{\mathbf{T}}(\mathbf{R}'_\alpha) \;=\; & e^{+i\mathbf{q}\mathbf{T}}\{\sum_{G\leq 2G_{\max}} \delta V_c(\mathbf{G}+\mathbf{q})e^{+i(\mathbf{q}+\mathbf{G})\mathbf{S}_\alpha}\sum_{lm}4\pi i^l j_l(R_\alpha|\mathbf{q}+\mathbf{G}|)Y_{lm}^*(\widehat{\mathbf{q}+\mathbf{G}}) \\ & + \sum_{0<G\leq 2G_{\max}} V_c(\mathbf{G})i[\mathbf{G}\delta\mathbf{S}_\alpha]e^{+i\mathbf{G}\mathbf{S}_\alpha}\sum_{lm}4\pi i^l j_l(R_\alpha|\mathbf{G}|)Y_{lm}^*(\hat{\mathbf{G}})\}Y_{lm}(\hat{\mathbf{r}}'),\end{aligned} \tag{1.248}$$

with

$$\mathbf{R}'_\alpha = \hat{\mathbf{r}}' R_\alpha.$$

Inserting Eq.(1.248) and (1.246) into the surface integral of Eq.(1.244) leads to:

$$\begin{aligned} & -\frac{R_\alpha^2}{8\pi}\int_{MT_\alpha} \delta V_c^{\mathbf{T}}(\mathbf{R}'_\alpha)\frac{\partial G(\mathbf{r},\mathbf{r}')}{\partial \mathbf{r}'}d\Omega' \\ = \;& e^{+i\mathbf{q}\mathbf{T}}\, \underbrace{4\pi\sum_{lm}\{\sum_{G\leq 2G_{\max}} \delta V_c(\mathbf{G}+\mathbf{q})i^l j_l(R_\alpha|\mathbf{q}+\mathbf{G}|)Y_{lm}^*(\widehat{\mathbf{q}+\mathbf{G}})(\frac{r}{R_\alpha})^l e^{+i(\mathbf{q}+\mathbf{G})\mathbf{S}_\alpha}\}}_{\equiv C2_{\alpha,lm}(r)}\, Y_{lm}(\hat{\mathbf{r}})\end{aligned}$$

$$+e^{+i\mathbf{qT}}\underbrace{4\pi\sum_{lm}\{\sum_{G\leq 2G_{\max}} V_c(\mathbf{G})i^l j_l(R_\alpha|\mathbf{G}|)Y^*_{lm}(\hat{\mathbf{G}})(\frac{r}{R_\alpha})^l i[\mathbf{G}\delta\mathbf{S}_\alpha]e^{+i\mathbf{GS}_\alpha}\}}_{\equiv C3_{\alpha,lm}(r)}\,Y_{lm}(\hat{\mathbf{r}}). \quad (1.249)$$

Finally we expand $\delta\check{V}_c^{\alpha,\mathbf{T}}(\mathbf{r})$ into spherical harmonics, i.e.,

$$\delta\check{V}_c^{\alpha,\mathbf{T}}(\mathbf{r}) = e^{i\mathbf{qT}}\sum_{LM}\delta\check{V}^{\alpha}_{c,LM}(r)Y_{LM}(\hat{\mathbf{r}}), \quad (1.250)$$

and compare the radial expansion coefficient $\delta\check{V}^{\alpha}_{c,lm}(r)$ with the corresponding quantities of Eq.(1.247) and Eq.(1.249). It is thus finally given by:

$$\delta\check{V}^{\alpha}_{c,LM}(r) = C1_{\alpha,LM}(r) + C2_{\alpha,LM}(r) + C3_{\alpha,LM}(r). \quad (1.251)$$

Besides the change in the electrostatic potential the density response also changes the exchange-correlation part of the total potential:

$$\delta V_{xc}(\mathbf{r}) = \delta\rho(\mathbf{r})[\underbrace{\frac{dV_x(\mathbf{r})}{d\rho} + \frac{dV_c(\mathbf{r})}{d\rho}}_{=\frac{dV_{xc}(\mathbf{r})}{d\rho}}]_{\rho=\rho_0(\mathbf{r})}. \quad (1.252)$$

We are restricting our work to a non-spin polarized calculation, where the Slater-exchange potential,

$$V_x(\mathbf{r}) = -2[\frac{3}{\pi}\rho(\mathbf{r})]^{1/3}, \quad (1.253)$$

and the correlation potential according to Perdew and Wang [38],

$$V_c(\mathbf{r}) = \varepsilon_c(r_s) - \frac{r_s}{3}\frac{\partial\varepsilon_c(r_s)}{\partial r_s}, \quad (1.254)$$

with

$$\begin{aligned}
r_s &= [\frac{3}{4\pi\rho(\mathbf{r})}]^{1/3},\\
\varepsilon_c(r_s) &= Q_0\ln(1+\frac{1}{Q_1}),\\
\frac{\partial\varepsilon_c(r_s)}{\partial r_s} &= -2c_0\alpha_1\ln(1+\frac{1}{Q_1}) - \frac{Q_0Q_2}{Q_1(Q_1+1)},\\
Q_0 &= -2c_0(1+\alpha_1 r_s),\\
Q_1 &= 2c_0(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2),\\
Q_2 &= \frac{\partial Q_1}{\partial r_s} = c_0(\beta_1 r_s^{-1/2} + 2\beta_2 + 3\beta_3 r_s^{1/2} + 4\beta_4 r_s),\\
c_0 &= 0.0310907, \qquad \alpha_1 = 0.2137,\\
\beta_1 &= 7.5957, \qquad \beta_2 = 3.5876,\\
\beta_3 &= 1.6382, \qquad \beta_4 = 0.49294,
\end{aligned}$$

are used. For the derivatives of these potentials with respect to the charge density we obtain:

$$\frac{dV_x(\mathbf{r})}{d\rho} = -\frac{2}{3}(\frac{3}{\pi})^{1/3}[\rho(\mathbf{r})]^{-2/3}, \tag{1.255}$$

and

$$\begin{aligned} \frac{dV_c(\mathbf{r})}{d\rho} &= \frac{\partial r_s}{\partial \rho}[-2c_0\alpha_1 \ln(1+\frac{1}{Q_1}) - \frac{Q_0Q_2}{Q_1(Q_1+1)} - \frac{1}{3}\frac{\partial \varepsilon_c(r_s)}{\partial r_s} \\ &+\frac{2}{3}\frac{r_s c_0 \alpha_1 Q_2}{Q_1(Q_1+1)} + \frac{r_s}{3Q_1(Q_1+1)}(-2c_0\alpha_1 Q_2 + Q_0Q_3) \\ &-\frac{r_s Q_0 Q_2^2}{3(Q_1+Q_1^2)^2}(2Q_1+1)], \qquad (1.256) \\ \frac{\partial r_s}{\partial \rho} &= -\frac{1}{3}(\frac{3}{4\pi})^{1/3}[\rho(\mathbf{r})]^{-4/3}, \\ Q_3 &= \frac{\partial Q_2}{\partial r_s} = c_0(-\frac{1}{2}\beta_1 r_s^{-3/2} + \frac{3}{2}\beta_3 r_s^{-1/2} + 4\beta_4), \end{aligned}$$

The dual representation of $\delta V_{xc}(\mathbf{r})$ in real space is achieved in the following way: In analogy to the calculation of the electrostatic potential we chose to work in the reference system of the super-cell, i.e., the separation of the interstitial and the atomic sphere regions assumes the sphere centers to be located at $\{\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha\}$. Within the spheres we fix a radial value r at which we want to determine the set of radial expansion coefficients $\delta\check{V}^{\alpha}_{xc,LM}(r)$ for the soft change of the exchange-correlation potential. Next we evaluate $\delta\check{V}^{\alpha}_{xc}(\mathbf{r})$ on a set of randomly chosen angular grid points which are located on the sphere surface of radius r. For this purpose we employ Eq.(1.252) in conjunction with the soft contribution of the density change displayed in Eq.(1.181) supplemented by the core contribution (Eq.(1.207)). The value of the unperturbed density needed for the evaluation of Eq.(1.252) is given by

$$\rho(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{LM} \rho_{LM}(r) Y_{LM}(\hat{\mathbf{r}}). \tag{1.257}$$

As we are keeping r constant the obtained set of potential values $\delta\check{V}^{\alpha}_{xc}(\mathbf{r})$ can be approximated by basis functions which only depend on the angular arguments ϕ and ϑ. The natural choice for these functions are spherical harmonics $Y_{LM}(\hat{\mathbf{r}})$. The approximation is carried out by least-square fitting the values $\delta\check{V}^{\alpha}_{xc}(\mathbf{r})$ to the spherical harmonics. The fitting parameters represent the expansion coefficients $\delta\check{V}^{\alpha}_{xc,LM}(r)$. By repeating this procedure on a fine grid of r-values ranging from 0 to R_α we obtain a complete representation of the first-order exchange-correlation potential (soft contribution) inside the spheres,

$$\delta\check{V}_{xc}(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha + \mathbf{r}) = \sum_{LM} \delta\check{V}^{\alpha}_{xc,LM}(r) Y_{LM}(\hat{\mathbf{r}}). \tag{1.258}$$

In the **interstitial** region the ansatz for $\delta V_{xc}(\mathbf{r})$ reads:

$$\delta V_{xc}(\mathbf{r}) = \sum_{G \leq 2G_{\max}} \delta V_{xc}(\mathbf{G}+\mathbf{q}) e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}}, \qquad \mathbf{r} \in \mathrm{Int}. \tag{1.259}$$

To determine $\delta V_{xc}(\mathbf{G}+\mathbf{q})$ we use Eqs.(1.259), (1.252) and (1.173):

$$e^{i\mathbf{q}\mathbf{r}} \sum_{G \leq 2G_{\max}} \delta V_{xc}(\mathbf{G}+\mathbf{q}) e^{i\mathbf{G}\mathbf{r}} = e^{i\mathbf{q}\mathbf{r}} \underbrace{\sum_{G \leq 2G_{\max}} \delta\rho(\mathbf{G}+\mathbf{q}) e^{i\mathbf{G}\mathbf{r}} [\frac{dV_{xc}(\mathbf{r})}{d\rho}]_{\rho=\rho_0(\mathbf{r})}}_{\equiv \delta\bar{V}_{xc}(\mathbf{r})}. \tag{1.260}$$

The modulation factor $e^{i\mathbf{q}\mathbf{r}}$ cancels and thus the problem of calculating $\delta V_{xc}(\mathbf{G}+\mathbf{q})$ amounts to finding the Fourier transform of the function $\delta\bar{V}_{xc}(\mathbf{r})$ which displays the periodicity of the unperturbed crystal. Thus the procedure runs as follows: First, the real-space representation of the unperturbed charge density

$$\rho_v(\mathbf{r}) = \sum_{G \leq 2G_{\max}} \rho(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}, \tag{1.261}$$

and of the function,

$$\delta\bar{\rho}(\mathbf{r}) \equiv \sum_{G \leq 2G_{\max}} \delta\rho(\mathbf{G}+\mathbf{q}) e^{i\mathbf{G}\mathbf{r}}, \tag{1.262}$$

are obtained via a Fast Fourier transform (FFT). Next the derivative of the exchange-correlation potential,

$$[\frac{dV_{xc}(\mathbf{r})}{d\rho}]_{\rho=\rho_0(\mathbf{r})},$$

is evaluated for each point on the real space grid. In a third step these values are multiplied pointwise with the corresponding values of $\delta\bar{\rho}(\mathbf{r})$. In this way discrete values of the function $\delta\bar{V}_{xc}(\mathbf{r})$ in the entire unit cell are obtained. Finally an FFT is used again to back-transform $\delta\bar{V}_{xc}(\mathbf{r})$ to the required plane-wave representation.

1.3.7 First-order atomic forces

It has been shown that the knowledge of the first-order atomic forces $\delta\mathbf{F}_\alpha$ provides enough information to efficiently set up the dynamical matrix at wave-vector $\mathbf{q}$. In this section we will describe a complete derivation of practical formulas for all contributions of the first-order forces. We start from expressions describing the Hellmann-Feynman force, the Core correction and the IBS correction as proposed by Yu et al. [13] and analytically evaluated by Kouba [34] and Kohler et al. [39]. We assume that there is no degeneracy between the KS orbitals at point $\mathbf{k}$ and at point $(\mathbf{k}+\mathbf{q})$. The first-order force $\delta\mathbf{F}_\alpha$ is given as the difference between the atomic force $\mathbf{F}_\alpha$ acting on the nucleus α located at $\mathbf{S}_\alpha$ in the unperturbed crystal and the force acting on the same nucleus located at $(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha)$ in the phonon-distorted system. We want to remind the reader that in the current context δ abbreviates δ^+.

The Hellmann-Feynman force The Hellmann-Feynman force [4, 40] $\mathbf{F}_\alpha^{HF}$ is defined as the electrostatic force on the nucleus α exerted by all other charges (electrons and nuclei) of the crystal. Within the framework of all-electron band structure calculations it reads for the unperturbed structure [13, 34]:

$$\mathbf{F}_\alpha^{HF} = Z_\alpha \lim_{r\to 0} \sum_{m=-1}^{+1} \frac{V_{c,1,M}^{\alpha}(R_\alpha)}{r} \nabla[rY_{1,M}(\hat{\mathbf{r}})], \tag{1.263}$$

or alternatively,

$$\begin{aligned}
F_\alpha^{HF,x} &= 4\sqrt{\frac{\pi}{3}} Z_\alpha \{ \int_{r=0}^{R_\alpha} \rho_{1,1}^{\cos,\alpha}(r)[1-(\frac{r}{R_\alpha})^3]dr + \frac{V_{c,1,1}^{\cos,\alpha}(R_\alpha)}{R_\alpha} \}, &(1.264)\\
F_\alpha^{HF,y} &= 4\sqrt{\frac{\pi}{3}} Z_\alpha \{ \int_{r=0}^{R_\alpha} \rho_{1,1}^{\sin,\alpha}(r)[1-(\frac{r}{R_\alpha})^3]dr + \frac{V_{c,1,1}^{\sin,\alpha}(R_\alpha)}{R_\alpha} \}, &(1.265)\\
F_\alpha^{HF,z} &= 4\sqrt{\frac{\pi}{3}} Z_\alpha \{ \int_{r=0}^{R_\alpha} \rho_{1,0}^{\cos,\alpha}(r)[1-(\frac{r}{R_\alpha})^3]dr + \frac{V_{c,1,0}^{\cos,\alpha}(R_\alpha)}{R_\alpha} \}, &(1.266)
\end{aligned}$$

with the position vector $\mathbf{r}$ being taken relative to the sphere center $\mathbf{S}_\alpha$. The coordinate system for the force components is cartesian and identical to the one defined for the complex spherical harmonic functions $Y_{1,M}(\hat{\mathbf{r}})$. Additionally, the expansion coefficients $\rho_{L,M}^{\cos,\alpha}(r)$ and $\rho_{L,M}^{\sin,\alpha}(r)$ with respect to real spherical harmonic functions have been used. They are linked to the respective coefficients of the complex spherical harmonics by:

$$\begin{aligned}
\rho_{L,M}^{\cos}(r) &= \frac{(-1)^M}{\sqrt{2}}[\rho_{L,M}(r) + (-1)^M \rho_{L,-M}(r)], \qquad M>0, &(1.267)\\
\rho_{L,M}^{\sin}(r) &= i\frac{(-1)^M}{\sqrt{2}}[\rho_{L,M}(r) - (-1)^M \rho_{L,-M}(r)], \qquad M>0, &(1.268)\\
\rho_{L,0}^{\cos}(r) &= \rho_{L,0}(r). &(1.269)
\end{aligned}$$

The same transformations (1.267) - (1.269) are to be applied to the coefficients of the electrostatic potential on the sphere boundary $V_{c,LM}^{\alpha}(R_\alpha)$ in Eqs.(1.264) - (1.266). To calculate the first-order force we first would have to evaluate (1.264) – (1.266) in the perturbed system where the position vector is taken relative to the distorted location $(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha)$. It is evident that due to this shift the gradient of the density does not have to be taken into account. The same applies to the gradient of the electrostatic potential. The quantities entirely responsible for altering the Hellmann-Feynman force upon a lattice distortion are the soft contributions in the spherical expansions of the electrostatic potential and the density. The first-order Hellmann-Feynman force is thus given by:

$$\begin{aligned}
\delta F_\alpha^{HF,x} &= 4\sqrt{\frac{\pi}{3}}Z_\alpha\{\int_{r=0}^{R_\alpha}\delta\check{\rho}_{1,1}^{\cos,\alpha}(r)[1-(\frac{r}{R_\alpha})^3]dr+\frac{\delta\check{V}_{c,1,1}^{\cos,\alpha}(R_\alpha)}{R_\alpha}\}, && (1.270)\\
\delta F_\alpha^{HF,y} &= 4\sqrt{\frac{\pi}{3}}Z_\alpha\{\int_{r=0}^{R_\alpha}\delta\check{\rho}_{1,1}^{\sin,\alpha}(r)[1-(\frac{r}{R_\alpha})^3]dr+\frac{\delta\check{V}_{c,1,1}^{\sin,\alpha}(R_\alpha)}{R_\alpha}\}, && (1.271)\\
\delta F_\alpha^{HF,z} &= 4\sqrt{\frac{\pi}{3}}Z_\alpha\{\int_{r=0}^{R_\alpha}\delta\check{\rho}_{1,0}^{\cos,\alpha}(r)[1-(\frac{r}{R_\alpha})^3]dr+\frac{\delta\check{V}_{c,1,0}^{\cos,\alpha}(R_\alpha)}{R_\alpha}\}, && (1.272)
\end{aligned}$$

where the expansion coefficients are determined on the basis of Eqs.(1.181), (1.251) and (1.267) – (1.269).

The Core correction

The fact, that the KS equations for the core states is only solved for the spherical part of the effective potential induces a corrective force which has to be added to the Hellmann-Feynman force. It reads [13, 34, 39]:

$$\mathbf{F}_\alpha^{core} = \int_{MT_\alpha}\rho_{core}^\alpha(r)\nabla V_{eff}^\alpha(\mathbf{r})d^3\mathbf{r}, \qquad (1.273)$$

$$\begin{aligned}
F_\alpha^{core,x} &= \frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha}\rho_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial V_{eff,1,1}^{\cos,\alpha}(r)}{\partial r}+2rV_{eff,1,1}^{\cos,\alpha}(r)]dr, && (1.274)\\
F_\alpha^{core,y} &= \frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha}\rho_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial V_{eff,1,1}^{\sin,\alpha}(r)}{\partial r}+2rV_{eff,1,1}^{\sin,\alpha}(r)]dr, && (1.275)\\
F_\alpha^{core,z} &= \frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha}\rho_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial V_{eff,1,0}^{\cos,\alpha}(r)}{\partial r}+2rV_{eff,1,0}^{\cos,\alpha}(r)]dr, && (1.276)
\end{aligned}$$

Following the same formal line of argumentation as for the change in the Hellmann-Feynman force the first-order correspondence to Eq.(1.273) will read:

$$\delta\mathbf{F}_\alpha^{core} = \int_{MT_\alpha}\delta\check{\rho}_{core}^\alpha(r)\nabla V_{eff}^\alpha(\mathbf{r})d^3\mathbf{r}+\int_{MT_\alpha}\rho_{core}^\alpha(r)\nabla[\delta\check{V}_{eff}^\alpha(\mathbf{r})]d^3\mathbf{r}, \qquad (1.277)$$

or given explicitly,

$$\begin{aligned}
\delta F_{\alpha}^{core,x} &= \frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha} \delta\check{\rho}_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial V_{eff,1,1}^{\cos,\alpha}(r)}{\partial r} + 2rV_{eff,1,1}^{\cos,\alpha}(r)]dr \\
&+\frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha} \rho_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial[\delta\check{V}_{eff,1,1}^{\cos,\alpha}(r)]}{\partial r} + 2r[\delta\check{V}_{eff,1,1}^{\cos,\alpha}(r)]]dr, \quad (1.278) \\
\delta F_{\alpha}^{core,y} &= \frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha} \delta\check{\rho}_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial V_{eff,1,1}^{\sin,\alpha}(r)}{\partial r} + 2rV_{eff,1,1}^{\sin,\alpha}(r)]dr \\
&+\frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha} \rho_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial[\delta\check{V}_{eff,1,1}^{\sin,\alpha}(r)]}{\partial r} + 2r[\delta\check{V}_{eff,1,1}^{\sin,\alpha}(r)]]dr, \quad (1.279) \\
\delta F_{\alpha}^{core,z} &= \frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha} \delta\check{\rho}_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial V_{eff,1,0}^{\cos,\alpha}(r)}{\partial r} + 2rV_{eff,1,0}^{\cos,\alpha}(r)]dr \\
&+\frac{1}{\sqrt{3}}\int_{r=0}^{R_\alpha} \rho_{core,0,0}^{\cos,\alpha}(r)[r^2\frac{\partial[\delta\check{V}_{eff,1,0}^{\cos,\alpha}(r)]}{\partial r} + 2r[\delta\check{V}_{eff,1,0}^{\cos,\alpha}(r)]]dr, \quad (1.280)
\end{aligned}$$

with

$$\delta\check{\rho}_{core}^{\alpha}(r) = Y_{00}\delta\check{\rho}_{core,0,0}^{\alpha}(r) = \frac{1}{\sqrt{4\pi}}\delta\check{\rho}_{core,0,0}^{\alpha}(r), \qquad r \leq R_\alpha.$$

The IBS correction

Within band structure calculations the determination of the wave-functions for valence electrons is based on the variational minimization of the energy parameters $\varepsilon_{n\mathbf{k}}$ appearing in the KS equations. As the basis set in the resulting eigenvalue problem is necessarily finite the expression

$$(\hat{T} + \hat{V}_{eff}(\mathbf{r}) - \varepsilon_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}), \tag{1.281}$$

with

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\sum_{G\leq G_{\max}} C_{n\mathbf{k}}(\mathbf{G})\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \tag{1.282}$$

will in general be non-vanishing. This deviation of the numerically calculated solution for the KS equation from the corresponding exact solution induces a further corrective force called 'incomplete basis set' (IBS) correction [5]. To be completely precise, the IBS correction will only be non-vanishing if a further condition is fulfilled by the basis set: It has to be dependent on the location of the nuclear coordinates meaning that upon the displacement of the atoms the basis functions $\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ have to change their value at least in some regions of the unit cell. In the case of linearized-augmented plane waves this condition is fulfilled due to the shift of the orbital basis functions within the atomic spheres. To first order in the displacement the change of the basis functions within the spheres reads [13, 41]:

$$\begin{aligned}\frac{\delta\phi_{\mathbf{k+G}}(\mathbf{r})}{\delta\mathbf{S}_\alpha} &= i(\mathbf{k}+\mathbf{G})\phi^\alpha_{\mathbf{k+G}}(\mathbf{r}) - \nabla\phi^\alpha_{\mathbf{k+G}}(\mathbf{r}) \\ &= \hat{\mathbf{P}}_h\phi^\alpha_{\mathbf{k+G}}(\mathbf{r}) - \nabla\phi^\alpha_{\mathbf{k+G}}(\mathbf{r}), \qquad (1.283)\end{aligned}$$

where we have introduced the operator $\hat{\mathbf{P}}_h$ acting on the basis functions and being defined as:

$$\hat{\mathbf{P}}_h\phi^\alpha_{\mathbf{K}} = i\mathbf{K}\phi^\alpha_{\mathbf{K}}. \qquad (1.284)$$

In the context of our shifted atomic sphere the operator $\hat{\mathbf{P}}_h$ is obviously connected to the first-order phase change $i\delta\mathbf{S}_\alpha(\mathbf{k}+\mathbf{G})$ of the matching parameters $A_{lm}(\mathbf{k}+\mathbf{G})$ and $B_{lm}(\mathbf{k}+\mathbf{G})$ of the LAPW within the sphere. It can now be shown [13, 41] that the IBS-correction consists of three terms:

$$\mathbf{F}^{IBS}_\alpha = \mathbf{F}_{\alpha 1} + \mathbf{F}_{\alpha 2} + \mathbf{F}_{\alpha 3}, \qquad (1.285)$$

with

$$\begin{aligned}\mathbf{F}_{\alpha 1} &= \int_{MT_\alpha} V^\alpha_{eff}(\mathbf{r})\nabla\rho^\alpha_v(\mathbf{r})d^3\mathbf{r}, \qquad (1.286)\\ \mathbf{F}_{\alpha 2} &= -\sum_{n,\mathbf{k}} w(n,\mathbf{k}) \sum_{\mathbf{G},\mathbf{G}'} [\left\langle C_{n\mathbf{k}}(\mathbf{G})\hat{\mathbf{P}}_h\phi^\alpha_{\mathbf{k+G}}(\mathbf{r}) \middle| \hat{H} - \varepsilon_{n\mathbf{k}} \middle| C_{n\mathbf{k}}(\mathbf{G}')\phi^\alpha_{\mathbf{k+G}'}(\mathbf{r})\right\rangle_{MT_\alpha} \\ &\quad + \left\langle C_{n\mathbf{k}}(\mathbf{G})\phi^\alpha_{\mathbf{k+G}}(\mathbf{r}) \middle| \hat{H} - \varepsilon_{n\mathbf{k}} \middle| C_{n\mathbf{k}}(\mathbf{G}')\hat{\mathbf{P}}_h\phi^\alpha_{\mathbf{k+G}'}(\mathbf{r})\right\rangle_{MT_\alpha}], \qquad (1.287)\\ \mathbf{F}_{\alpha 3} &= \sum_{n,\mathbf{k}} w(n,\mathbf{k}) \oint \Psi^*_{n\mathbf{k}}(\mathbf{r})(-\nabla^2 - \varepsilon_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r})|_{Int}d\mathbf{A}_\alpha. \qquad (1.288)\end{aligned}$$

The term denoted by $\mathbf{F}_{\alpha 1}$ is a consequence of the gradient of the basis function appearing in Eq.(1.283) whereas the phase change described by the operator $\hat{\mathbf{P}}_h$ causes the force component $\mathbf{F}_{\alpha 2}$. The kinetic energy term in $\mathbf{F}_{\alpha 3}$ is very specific to the LAPW-basis set and stems from the fact that the second derivative of $\phi_{\mathbf{k+G}}(\mathbf{r})$ displays a discontinuity on the sphere surfaces [13, 41]. The surface integral constituting $\mathbf{F}_{\alpha 3}$ has to be evaluated with the interstitial basis functions being used for $\Psi_{n\mathbf{k}}(\mathbf{r})$, i.e.,

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{G \le G_{\max}} C_{n\mathbf{k}}(\mathbf{G})e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}. \qquad (1.289)$$

For completion we note that the contribution to the IBS correction originating in a change of the orbital occupation number $w(n,\mathbf{k})$ has been neglected. With regard to insulators and semiconductors it will be exactly zero as the gap will prevent any change of $w(n, \mathbf{k})$. In the case of metals and when the tetrahedron method [42] is used for the BZ-integration the very small contribution could be systematically reduced by increasing the number of **k**-points in the Brillouin zone. With regard to the same integrational method it can analytically be shown [23] that the second-order change of $w(n, \mathbf{k})$ will be exactly zero when the wave-vector **q** of the perturbation is non-vanishing. This additionally justifies to neglect the contribution of the occupation numbers also in the first-order force-terms.

The term $\mathbf{F}_{\alpha 1}$ and its first-order change $\delta\mathbf{F}_{\alpha 1}$: Eq.(1.286) can largely be evaluated analytically [34] if we substitute the effective potential and the valence density by their respective expansions in terms of spherical harmonics. $\mathbf{F}_{\alpha 1}$ is then given by:

$$
\begin{aligned}
F^{x}_{\alpha 1} = {} & \frac{1}{2} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [C_{L,M}^{L+1,M-1} + C_{L+1,M-1}^{L,M}] f_5(L,M) \\
& -\frac{1}{2} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [C_{L,M}^{L+1,M+1} + C_{L+1,M+1}^{L,M}] f_3(L,M) \\
& +\frac{1}{2} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [(L+2)D_{L,M}^{L+1,M-1} - L D_{L+1,M-1}^{L,M}] f_5(L,M) \\
& -\frac{1}{2} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [(L+2)D_{L,M}^{L+1,M+1} - L D_{L+1,M+1}^{L,M}] f_3(L,M),
\end{aligned}
\tag{1.290}
$$

$$
\begin{aligned}
F^{y}_{\alpha 1} = {} & \frac{1}{2i} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [C_{L,M}^{L+1,M-1} - C_{L+1,M-1}^{L,M}] f_5(L,M) \\
& +\frac{1}{2i} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [C_{L,M}^{L+1,M+1} - C_{L+1,M+1}^{L,M}] f_3(L,M) \\
& +\frac{1}{2i} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [(L+2)D_{L,M}^{L+1,M-1} + L D_{L+1,M-1}^{L,M}] f_5(L,M) \\
& +\frac{1}{2i} \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [(L+2)D_{L,M}^{L+1,M+1} + L D_{L+1,M+1}^{L,M}] f_3(L,M),
\end{aligned}
\tag{1.291}
$$

$$
\begin{aligned}
F^{z}_{\alpha 1} = {} & \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [C_{L,M}^{L+1,M} + C_{L+1,M}^{L,M}] f_1(L,M) \\
& + \sum_{L=0}^{L_{\max}-1} \sum_{M=-L}^{+L} [(L+2)D_{L,M}^{L+1,M} - L D_{L+1,M}^{L,M}] f_1(L,M),
\end{aligned}
\tag{1.292}
$$

where the following abbreviations have been used:

$$C_{L,M}^{L',M'} \equiv \int_0^{R_\alpha} V^*_{eff,LM}(r)\frac{\partial\rho^{val}_{L'M'}(r)}{\partial r}r^2dr, \tag{1.293}$$

$$D_{L,M}^{L',M'} \equiv \int_0^{R_\alpha} V^*_{eff,LM}(r)\rho^{val}_{L'M'}(r)rdr, \tag{1.294}$$

$$f_1(L,M) \equiv \sqrt{\frac{(L-M+1)(L+M+1)}{(2L+1)(2L+3)}}, \tag{1.295}$$

$$f_3(L,M) \equiv \sqrt{\frac{(L+M+1)(L+M+2)}{(2L+1)(2L+3)}}, \tag{1.296}$$

$$f_5(L,M) \equiv \sqrt{\frac{(L-M+1)(L-M+2)}{(2L+1)(2L+3)}}. \tag{1.297}$$

$L_{\max}$ is the maximum value of L in the spherical-harmonics expansions of the potential and the density. Comparing (1.286) with (1.273) we notice their formal similarity. In analogy to (1.277) the first-order change $\delta\mathbf{F}_{\alpha 1}$ is thus composed of two terms: one stemming from the soft change of the effective potential $\delta\check{V}^\alpha_{eff}(\mathbf{r})$ and a second one stemming from the soft change of the valence density $\delta\check{\rho}^\alpha_v(\mathbf{r})$:

$$\delta\mathbf{F}_{\alpha 1} = \int_{MT_\alpha} \delta\check{V}^\alpha_{eff}(\mathbf{r})\nabla\rho^\alpha_v(\mathbf{r})d^3\mathbf{r} + \int_{MT_\alpha} V^\alpha_{eff}(\mathbf{r})\nabla[\delta\check{\rho}^\alpha_v(\mathbf{r})]d^3\mathbf{r} \tag{1.298}$$

For the analytic evaluation of the integrals on the right-hand side of Eq.(1.298) we simply substitute the integrals $C_{L,M}^{L',M'}$ and $D_{L,M}^{L',M'}$ in the expressions (1.290) – (1.292) by the integral abbreviations $c_{L,M}^{L',M'}$ and $d_{L,M}^{L',M'}$ defined as

$$c_{L,M}^{L',M'} \equiv \int_0^{R_\alpha} \left[\delta\check{V}^*_{eff,LM}(r)\frac{\partial\rho^{val}_{L'M'}(r)}{\partial r} + V^*_{eff,LM}(r)\frac{\partial[\delta\check{\rho}^{val}_{L'M'}(r)]}{\partial r}\right] r^2dr, \tag{1.299}$$

$$d_{L,M}^{L',M'} \equiv \int_0^{R_\alpha} \left[\delta\check{V}^*_{eff,LM}(r)\rho^{val}_{L'M'}(r) + V^*_{eff,LM}(r)\delta\check{\rho}^{val}_{L'M'}(r)\right] rdr. \tag{1.300}$$

$\delta\mathbf{F}_{\alpha 1}$ thus reads:

$$\begin{aligned} F^x_{\alpha 1} &= \frac{1}{2}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[c_{L,M}^{L+1,M-1} + c_{L+1,M-1}^{L,M}]f_5(L,M) \\ &-\frac{1}{2}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[c_{L,M}^{L+1,M+1} + c_{L+1,M+1}^{L,M}]f_3(L,M) \\ &+\frac{1}{2}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[(L+2)d_{L,M}^{L+1,M-1} - Ld_{L+1,M-1}^{L,M}]f_5(L,M) \end{aligned}$$

$$-\frac{1}{2}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[(L+2)d_{L,M}^{L+1,M+1}-Ld_{L+1,M+1}^{L,M}]f_3(L,M), \tag{1.301}$$

$$\begin{aligned}
F_{\alpha 1}^{y} &= \frac{1}{2i}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[c_{L,M}^{L+1,M-1}-c_{L+1,M-1}^{L,M}]f_5(L,M)\\
&+\frac{1}{2i}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[c_{L,M}^{L+1,M+1}-c_{L+1,M+1}^{L,M}]f_3(L,M)\\
&+\frac{1}{2i}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[(L+2)d_{L,M}^{L+1,M-1}+Ld_{L+1,M-1}^{L,M}]f_5(L,M)\\
&+\frac{1}{2i}\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[(L+2)d_{L,M}^{L+1,M+1}+Ld_{L+1,M+1}^{L,M}]f_3(L,M),
\end{aligned} \tag{1.302}$$

$$\begin{aligned}
F_{\alpha 1}^{z} &= \sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[c_{L,M}^{L+1,M}+c_{L+1,M}^{L,M}]f_1(L,M)\\
&+\sum_{L=0}^{L_{\max}-1}\sum_{M=-L}^{+L}[(L+2)d_{L,M}^{L+1,M}-Ld_{L+1,M}^{L,M}]f_1(L,M).
\end{aligned} \tag{1.303}$$

The term $\mathbf{F}_{\alpha 2}$ and its first-order change $\delta\mathbf{F}_{\alpha 2}$: So far the formulas for the first-order force contributions $\delta\mathbf{F}_{\alpha 1}$, $\delta\mathbf{F}_{\alpha}^{core}$ and $\delta\mathbf{F}_{\alpha}^{HF}$ could simply be derived by substituting radial expansion coefficients for the appropriate potentials and densities in $\mathbf{F}_{\alpha 1}$, $\mathbf{F}_{\alpha}^{core}$ and $\mathbf{F}_{\alpha}^{HF}$ by their respective soft changes. In the case $\delta\mathbf{F}_{\alpha 2}$ the procedure is not so simple any more. Instead it appears more transparent and logical to start the derivation of $\delta\mathbf{F}_{\alpha 2}$ directly from expression (1.287). Necessary formulas from $\mathbf{F}_{\alpha 2}$ will then be introduced at appropriate steps in our line of reasoning. In this section we follow very closely the ideas proposed by Yu et al. [26].

If we use the part of the KS orbital spatially given for a specific atomic sphere, i.e.,

$$\Psi_{n\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{G}}C_{n\mathbf{k}}(\mathbf{G})\phi_{\mathbf{k}+\mathbf{G}}^{\alpha}(\mathbf{r}), \qquad |\mathbf{r}-\mathbf{S}_{\alpha}|\leq R_{\alpha}, \tag{1.304}$$

expression (1.287) can be written in the following simplified way (for clarity the occupation number $w(n,\mathbf{k})$ is temporarily omitted):

$$\mathbf{F}_{\alpha 2} = -\sum_{n,\mathbf{k}}[\left\langle \hat{\mathbf{P}}_h\Psi_{n\mathbf{k}}\middle|\hat{H}-\varepsilon_{n\mathbf{k}}\middle|\Psi_{n\mathbf{k}}\right\rangle_{MT_{\alpha}}$$

$$+\left\langle \Psi_{n\mathbf{k}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha}]. \tag{1.305}$$

We note that the operator $\hat{\mathbf{P}}_h$ is still defined to act on the basis functions constituting the KS orbital, i.e.,

$$\hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \equiv \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) \hat{\mathbf{P}}_h \phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}). \tag{1.306}$$

Making a first-order change in the various terms of expression (1.305) we obtain:

$$\begin{aligned}
\delta \mathbf{F}_{\alpha 2} &= -\sum_{n,\mathbf{k}} \left\langle \hat{\mathbf{P}}_h [\delta \Psi_{n\mathbf{k}}] \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} && (1.307)\\
&\quad -\sum_{n,\mathbf{k}} \left\langle \Psi_{n\mathbf{k}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \hat{\mathbf{P}}_h [\delta \Psi_{n\mathbf{k}}] \right\rangle_{MT_\alpha} && (1.308)\\
&\quad -\sum_{n,\mathbf{k}} \left\langle \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \delta \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} && (1.309)\\
&\quad -\sum_{n,\mathbf{k}} \left\langle \delta \Psi_{n\mathbf{k}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} && (1.310)\\
&\quad -\sum_{n,\mathbf{k}} \left\langle \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \left| \delta \hat{H} \right| \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} && (1.311)\\
&\quad -\sum_{n,\mathbf{k}} \left\langle \Psi_{n\mathbf{k}} \left| \delta \hat{H} \right| \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} && (1.312)\\
&\quad +\delta \varepsilon_{n\mathbf{k}} \sum_{n,\mathbf{k}} \left\langle \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} | \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} && (1.313)\\
&\quad +\delta \varepsilon_{n\mathbf{k}} \sum_{n,\mathbf{k}} \left\langle \Psi_{n\mathbf{k}} | \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} . && (1.314)
\end{aligned}$$

Terms (1.313) and (1.314) vanish because $\delta \varepsilon_{n\mathbf{k}}$ is equal to zero for $\mathbf{q} \neq \mathbf{0}$. For all other matrix elements the evaluation is guided by the following principle: All zero-order quantities appearing in a matrix element are thought of as being rigidly shifted with the sphere when the phonon displacement is imposed. In this concept, all first-order quantities are then to be understood as the additional changes occurring after the rigid shift has been carried out. With regard to potentials this first-order change is the well known soft change already encountered several times. We thus obtain for terms (1.311) and (1.312):

$$\begin{aligned}
\delta \mathbf{F}'_{\alpha 2} &\equiv -\sum_{n,\mathbf{k}} \left[\left\langle \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \left| \delta \hat{H} \right| \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} + \left\langle \Psi_{n\mathbf{k}} \left| \delta \hat{H} \right| \hat{\mathbf{P}}_h \Psi_{n\mathbf{k}} \right\rangle_{MT_\alpha} \right] \\
&= -\sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} [-i(\mathbf{k}+\mathbf{G}) C^*_{n\mathbf{k}}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \left| \delta \check{V}^{\alpha}_{eff} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\
&\quad +i(\mathbf{k}+\mathbf{G}') C^*_{n\mathbf{k}}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \left| \delta \check{V}^{\alpha}_{eff} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha}]
\end{aligned}$$

$$= -i\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')\left\langle\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}\left|\delta\check{V}^{\alpha}_{eff}\right|\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}\right\rangle_{MT_\alpha}. \qquad (1.315)$$

With respect to the KS orbitals we have to subtract the rigid shift in the ansatz for the change in the basis function (1.105). Mathematically this means dropping the term involving the gradient of the unperturbed basis set. Inserting the remaining phase change of the basis functions into (1.102) we obtain the soft change of the total KS orbital needed for the evaluation of $\delta\mathbf{F}_{\alpha 2}$:

$$\delta\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{G\leq G_{\max}}\delta C_{n\mathbf{k}}(\mathbf{G})\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) + C_{n\mathbf{k}}(\mathbf{G})i(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_\alpha\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}). \qquad (1.316)$$

If, for the moment, we only consider the term involving the change in the variational coefficient $\delta C_{n\mathbf{k}}(\mathbf{G})$ and insert it into expressions (1.307) – (1.310) we obtain:

$$\begin{aligned}
\delta\mathbf{F}''_{\alpha 2} \equiv\ & -\sum_{n,\mathbf{k}}[\left\langle\hat{\mathbf{P}}_h[\delta\Psi_{n\mathbf{k}}]\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\Psi_{n\mathbf{k}}\right\rangle_{MT_\alpha} \\
& +\left\langle\delta\Psi_{n\mathbf{k}}\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\hat{\mathbf{P}}_h\Psi_{n\mathbf{k}}\right\rangle_{MT_\alpha}] \\
& -\sum_{n,\mathbf{k}}[\left\langle\Psi_{n\mathbf{k}}\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\hat{\mathbf{P}}_h[\delta\Psi_{n\mathbf{k}}]\right\rangle_{MT_\alpha} \\
& +\left\langle\hat{\mathbf{P}}_h\Psi_{n\mathbf{k}}\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\delta\Psi_{n\mathbf{k}}\right\rangle_{MT_\alpha}] \\
=\ & -\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}[\delta C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')\left\langle\hat{\mathbf{P}}_h\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}\right\rangle_{MT_\alpha} \\
& +\delta C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')\left\langle\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\hat{\mathbf{P}}_h\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}\right\rangle_{MT_\alpha}] \\
& -\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}[C^{*}_{n\mathbf{k}}(\mathbf{G})\delta C_{n\mathbf{k}}(\mathbf{G}')\left\langle\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\hat{\mathbf{P}}_h\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}\right\rangle_{MT_\alpha} \\
& +C^{*}_{n\mathbf{k}}(\mathbf{G})\delta C_{n\mathbf{k}}(\mathbf{G}')\left\langle\hat{\mathbf{P}}_h\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}\right\rangle_{MT_\alpha}] \\
=\ & -\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}\{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}') \\
& \times\left\langle\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}\right\rangle_{MT_\alpha}\} \qquad (1.317) \\
& -\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}\{i(\mathbf{G}'-\mathbf{G}+\mathbf{q})C^{*}_{n\mathbf{k}}(\mathbf{G})\delta C_{n\mathbf{k}}(\mathbf{G}') \\
& \times\left\langle\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\left|\hat{H}-\varepsilon_{n\mathbf{k}}\right|\phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}\right\rangle_{MT_\alpha}\}. \qquad (1.318)
\end{aligned}$$

An important point at this stage concerns the translational properties of the atomic force. As we are working in the forward-traveling-wave representation the corresponding first-order changes in the potentials and densities will translate like a Bloch-wave of wave-vector $+\mathbf{q}$:

$$\delta^{+}V(\mathbf{r}+\mathbf{T}) = e^{+i\mathbf{q}\mathbf{T}}\delta^{+}V(\mathbf{r}), \qquad \delta^{+}\rho(\mathbf{r}+\mathbf{T}) = e^{+i\mathbf{q}\mathbf{T}}\delta^{+}\rho(\mathbf{r}). \tag{1.319}$$

It has been shown in section (1.2.1) that a first-order change of the wave-function $\delta^{+}\Psi_{n\mathbf{k}}(\mathbf{r})$ at a certain **k**-point will contribute to the forward- as well as to the backward-traveling part of the density response and restricted to one **k**-point these two contributions are independent of each other. This property is also inherent in $\delta^{-}\Psi_{n\mathbf{k}}(\mathbf{r})$. Only by exploiting time reversal symmetry for the contributions stemming from the Brillouin zone points $\mathbf{k}$ and $-\mathbf{k}$ it was possible to construct the density response $\delta^{+}\rho(\mathbf{r})$ from the sole knowledge of $\delta^{+}\Psi_{n\mathbf{k}}(\mathbf{r})$ (for all **k**-points in the entire Brillouin zone).

Returning to the atomic forces and still restricting ourselves to the forward-traveling-wave representation the first-order force has to conform to the translational condition,

$$\delta^{+}\mathbf{F}_{\alpha}^{\mathbf{T}} = e^{+i\mathbf{q}\mathbf{T}}\delta^{+}\mathbf{F}_{\alpha}^{\mathbf{0}} = e^{+i\mathbf{q}\mathbf{T}}\delta^{+}\mathbf{F}_{\alpha}, \tag{1.320}$$

with $\delta^{+}\mathbf{F}_{\alpha}^{\mathbf{T}}$ being the force acting on atom α in the unperturbed unit cell located at lattice vector $\mathbf{T}$. The contributions $\delta^{+}\mathbf{F}_{\alpha 1}$, $\delta^{+}\mathbf{F}_{\alpha}^{core}$ and $\delta^{+}\mathbf{F}_{\alpha}^{HF}$ (Eqs.(1.270) - (1.272), (1.278) - (1.280) and (1.301) - (1.303)) fulfil this requirement as the radial expansion coefficients of the soft contributions display the correct translational properties (compare with Eq.(1.115) of section (1.3.3)). On the other hand term (1.317) as part of $\delta^{+}\mathbf{F}_{\alpha 2}$ translates like a Bloch-wave with wave-vector $-\mathbf{q}$ and thus actually represents a force contribution in the backward-traveling-wave representation. Therefore, if we take this term, assume that the change in the wave-function stems from the solution of the Sternheimer equation in the backward-traveling-wave representation, i.e.,

$$\delta^{-}\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{G\leq G_{\max}} \delta^{-}C_{n\mathbf{k}}(\mathbf{G})\phi^{\alpha}_{\mathbf{k}-\mathbf{q}+\mathbf{G}}(\mathbf{r}) + C_{n\mathbf{k}}(\mathbf{G})i[\delta^{+}\mathbf{S}_{\alpha}]^{*}(\mathbf{k}+\mathbf{G})\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \tag{1.321}$$

(and thus also exchange $\mathbf{q}$ by $-\mathbf{q}$) we will obtain the correct contribution to $\delta^{+}\mathbf{F}_{\alpha 2}$. After this correction the sum of (1.317) and (1.318) will now read:

$$\begin{aligned} \delta\mathbf{F}''_{\alpha 2} &= -\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'} \{ i(\mathbf{G}'-\mathbf{G}+\mathbf{q})\delta^{-}C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}') \\ &\quad \times \left\langle \phi^{\alpha}_{\mathbf{k}-\mathbf{q}+\mathbf{G}}(\mathbf{r}) \middle| \hat{H} - \varepsilon_{n\mathbf{k}} \middle| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_{\alpha}} \} \end{aligned}$$

$$-\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}\{i(\mathbf{G}'-\mathbf{G}+\mathbf{q})C^{*}_{n\mathbf{k}}(\mathbf{G})\delta^{+}C_{n\mathbf{k}}(\mathbf{G}') \times \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \left| \hat{H}-\varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \right\rangle_{MT_\alpha}\}. \tag{1.322}$$

By simple index manipulation for $\mathbf{G}, \mathbf{G}'$ and $\mathbf{k}$ in the sums over reciprocal space and over the Brillouin zone respectively we obtain the following identity:

$$\begin{aligned} &\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'} i(\mathbf{G}'-\mathbf{G}+\mathbf{q})\delta^{-}C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}') \left\langle \phi^{\alpha}_{\mathbf{k}-\mathbf{q}+\mathbf{G}} \left| \hat{H}-\varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\ = &\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'} i(\mathbf{G}'-\mathbf{G}+\mathbf{q})\delta^{-}C^{*}_{n,-\mathbf{k}}(-\mathbf{G}')C_{n,-\mathbf{k}}(-\mathbf{G}) \left\langle \phi^{\alpha}_{-\mathbf{k}-\mathbf{q}-\mathbf{G}'} \left| \hat{H}-\varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{-\mathbf{k}-\mathbf{G}} \right\rangle_{MT_\alpha}. \end{aligned} \tag{1.323}$$

Using (1.323) and Kramer's theorem [25],

$$C_{n,-\mathbf{k}}(-\mathbf{G}) = C^{*}_{n,\mathbf{k}}(\mathbf{G}) \qquad \text{and} \qquad \delta C^{-\mathbf{q}}_{n,-\mathbf{k}}(-\mathbf{G}) = \delta C^{*,+\mathbf{q}}_{n,\mathbf{k}}(\mathbf{G}), \tag{1.324}$$

$\delta\mathbf{F}''_{\alpha 2}$ can now finally be constructed having only solved the Sternheimer equation in the forward-traveling-wave representation:

$$\begin{aligned} \delta\mathbf{F}''_{\alpha 2} = &-\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'} i(\mathbf{G}'-\mathbf{G}+\mathbf{q})C^{*}_{n\mathbf{k}}(\mathbf{G})\delta^{+}C_{n\mathbf{k}}(\mathbf{G}') \\ &[\left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \left| \hat{H}-\varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \right\rangle_{MT_\alpha} + \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \left| \hat{H}-\varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \right\rangle^{*}_{MT_\alpha}]. \end{aligned} \tag{1.325}$$

We now turn to the second contribution of the change of the wave-function in (1.316), i.e.,

$$C_{n\mathbf{k}}(\mathbf{G})i(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_{\alpha}\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}). \tag{1.326}$$

Replacing $\delta\Psi_{n\mathbf{k}}$ in (1.307) – (1.310) by (1.326) we obtain:

$$\begin{aligned} \delta\mathbf{F}'''_{\alpha 2} \equiv &\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}-\mathbf{G}')[(\mathbf{k}+\mathbf{G})\delta\mathbf{S}^{*}_{\alpha}]C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}') \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \left| \hat{H}-\varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\ &+\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})[(\mathbf{k}+\mathbf{G}')\delta\mathbf{S}_{\alpha}]C^{*}_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}') \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \left| \hat{H}-\varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha}. \end{aligned} \tag{1.327}$$

With regard to the required translational properties of the first-order force we see that in the first term of the right hand side of expression (1.327) we have to replace $\delta\mathbf{S}^{*}_{\alpha}$ by $\delta\mathbf{S}_{\alpha}$. This action produces the contribution from the first-order wave-function,

$$\delta^{-}\Psi_{n\mathbf{k}} = C_{n\mathbf{k}}(\mathbf{G})i(\mathbf{k}+\mathbf{G})[\delta^{+}\mathbf{S}_{\alpha}]^{*}\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}).$$

In a second step we apply simple index manipulation for $\mathbf{G}, \mathbf{G}'$ and $\mathbf{k}$ in the second term of expression (1.327). Subsequent exploitation of Kramer's theorem (1.324) enables us to combine the two terms of expression (1.327):

$$\begin{aligned} \delta\mathbf{F}'''_{\alpha 2} &= \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} \{(\mathbf{G}-\mathbf{G}')[(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_\alpha] C^*_{n\mathbf{k}}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') \\ &\quad \times [\left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} + \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}} \right\rangle^*_{MT_\alpha}]\}. \end{aligned} \tag{1.328}$$

Summarizing, the contribution $\delta\mathbf{F}_{\alpha 2}$ is given by:

$$\begin{aligned} \delta\mathbf{F}_{\alpha 2} &= \delta\mathbf{F}'_{\alpha 2} + \delta\mathbf{F}''_{\alpha 2} + \delta\mathbf{F}'''_{\alpha 2} \\ &= -i \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} (\mathbf{G}'-\mathbf{G}) C^*_{n\mathbf{k}}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}} \left| \delta\check{V}^\alpha_{eff} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\ &\quad -i \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} \{(\mathbf{G}'-\mathbf{G}+\mathbf{q}) C^*_{n\mathbf{k}}(\mathbf{G}) \delta^+ C_{n\mathbf{k}}(\mathbf{G}') \\ &\quad \times [\left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \phi^\alpha_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \right\rangle_{MT_\alpha} + \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}} \right\rangle^*_{MT_\alpha}]\} \\ &\quad + \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} \{(\mathbf{G}-\mathbf{G}')[(\mathbf{k}+\mathbf{G})\delta^+\mathbf{S}_\alpha] C^*_{n\mathbf{k}}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') \\ &\quad \times [\left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} + \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \left| \hat{H} - \varepsilon_{n\mathbf{k}} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}} \right\rangle^*_{MT_\alpha}]\}. \end{aligned} \tag{1.329}$$

Using the abbreviations and definitions:

$$a^{n,\mathbf{k}}_{lm} \equiv \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) A^\alpha_{lm}(\mathbf{k}+\mathbf{G}), \tag{1.330}$$

$$b^{n,\mathbf{k}}_{lm} \equiv \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) B^\alpha_{lm}(\mathbf{k}+\mathbf{G}), \tag{1.331}$$

$$\mathbf{a}^{n,\mathbf{k}}_{lm} \equiv \sum_{\mathbf{G}} \mathbf{G} C_{n\mathbf{k}}(\mathbf{G}) A^\alpha_{lm}(\mathbf{k}+\mathbf{G}), \tag{1.332}$$

$$\mathbf{b}^{n,\mathbf{k}}_{lm} \equiv \sum_{\mathbf{G}} \mathbf{G} C_{n\mathbf{k}}(\mathbf{G}) B^\alpha_{lm}(\mathbf{k}+\mathbf{G}), \tag{1.333}$$

$$\delta\check{V}^\alpha_{eff}(\mathbf{r}) = \delta\check{V}^\alpha_{00}(r) \frac{1}{\sqrt{4\pi}} + \sum_{L>0,M} \delta\check{V}^\alpha_{LM}(r) Y_{LM}(\hat{\mathbf{r}}), \tag{1.334}$$

the first term of (1.329) can be evaluated by implementing the following formulas:

$$\begin{aligned} & -i\frac{1}{\sqrt{4\pi}} \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} (\mathbf{G}'-\mathbf{G}) C^*_{n\mathbf{k}}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') \left\langle \phi^\alpha_{\mathbf{k}+\mathbf{G}} \left| \delta\check{V}^\alpha_{00} \right| \phi^\alpha_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\ = \; & -i\frac{1}{\sqrt{4\pi}} \sum_{n,\mathbf{k}} \sum_{l,m} \left([a^{n,\mathbf{k}}_{lm}]^* \mathbf{a}^{n,\mathbf{k}}_{lm} - [\mathbf{a}^{n,\mathbf{k}}_{lm}]^* a^{n,\mathbf{k}}_{lm} \right) \int_0^{R_\alpha} \delta\check{V}^\alpha_{00}(r) u^2_l(r) r^2 dr \end{aligned}$$

$$
\begin{aligned}
&-i\frac{1}{\sqrt{4\pi}}\sum_{n,\mathbf{k}}\sum_{l,m}\left([a_{lm}^{n,\mathbf{k}}]^*\mathbf{b}_{lm}^{n,\mathbf{k}}-[\mathbf{a}_{lm}^{n,\mathbf{k}}]^*b_{lm}^{n,\mathbf{k}}+[b_{lm}^{n,\mathbf{k}}]^*\mathbf{a}_{lm}^{n,\mathbf{k}}-[\mathbf{b}_{lm}^{n,\mathbf{k}}]^*a_{lm}^{n,\mathbf{k}}\right)\\
&\times\int_0^{R_\alpha}\delta\check{V}_{00}^{\alpha}(r)u_l(r)\dot{u}_l(r)r^2dr\\
&-i\frac{1}{\sqrt{4\pi}}\sum_{n,\mathbf{k}}\sum_{l,m}\left([b_{lm}^{n,\mathbf{k}}]^*\mathbf{b}_{lm}^{n,\mathbf{k}}-[\mathbf{b}_{lm}^{n,\mathbf{k}}]^*b_{lm}^{n,\mathbf{k}}\right)\int_0^{R_\alpha}\delta\check{V}_{00}^{\alpha}(r)\dot{u}_l^2(r)r^2dr, \qquad (1.335)
\end{aligned}
$$

and

$$
\begin{aligned}
&-i\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}\sum_{L>0,M}(\mathbf{G}'-\mathbf{G})C_{n\mathbf{k}}^*(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')\left\langle\phi_{\mathbf{k}+\mathbf{G}}^{\alpha}\left|\delta\check{V}_{LM}^{\alpha}Y_{LM}\right|\phi_{\mathbf{k}+\mathbf{G}'}^{\alpha}\right\rangle_{MT_\alpha}\\
=\;&-i\sum_{n,\mathbf{k}}\sum_{l,m,,l',m'}\sum_{L>0,M}G(l,m,L,M,l',m')\\
&\times\{\int_0^{R_\alpha}[a_{lm}^{n,\mathbf{k}}u_l(r)+b_{lm}^{n,\mathbf{k}}\dot{u}_l(r)]^*[\delta\check{V}_{LM}^{\alpha}(r)][\mathbf{a}_{l'm'}^{n,\mathbf{k}}u_{l'}(r)+\mathbf{b}_{l'm'}^{n,\mathbf{k}}\dot{u}_{l'}(r)]r^2dr\\
&-\int_0^{R_\alpha}[\mathbf{a}_{lm}^{n,\mathbf{k}}u_l(r)+\mathbf{b}_{lm}^{n,\mathbf{k}}\dot{u}_l(r)]^*[\delta\check{V}_{LM}^{\alpha}(r)][a_{l'm'}^{n,\mathbf{k}}u_{l'}(r)+b_{l'm'}^{n,\mathbf{k}}\dot{u}_{l'}(r)]r^2dr\}. \qquad (1.336)
\end{aligned}
$$

To evaluate the second term we introduce the additional abbreviations:

$$
\begin{aligned}
\delta a_{lm}^{n,\mathbf{k}} &\equiv \sum_{\mathbf{G}}\delta C_{n\mathbf{k}}(\mathbf{G})A_{lm}^{\alpha}(\mathbf{k}+\mathbf{q}+\mathbf{G}), && (1.337)\\
\delta b_{lm}^{n,\mathbf{k}} &\equiv \sum_{\mathbf{G}}\delta C_{n\mathbf{k}}(\mathbf{G})B_{lm}^{\alpha}(\mathbf{k}+\mathbf{q}+\mathbf{G}), && (1.338)\\
\delta \mathbf{a}_{lm}^{n,\mathbf{k}} &\equiv \sum_{\mathbf{G}}\mathbf{G}\delta C_{n\mathbf{k}}(\mathbf{G})A_{lm}^{\alpha}(\mathbf{k}+\mathbf{q}+\mathbf{G}), && (1.339)\\
\delta \mathbf{b}_{lm}^{n,\mathbf{k}} &\equiv \sum_{\mathbf{G}}\mathbf{G}\delta C_{n\mathbf{k}}(\mathbf{G})B_{lm}^{\alpha}(\mathbf{k}+\mathbf{q}+\mathbf{G}). && (1.340)
\end{aligned}
$$

We thus obtain for the muffin-tin contributions:

$$
\begin{aligned}
&-i\mathbf{q}\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}C_{n\mathbf{k}}^*(\mathbf{G})\delta C_{n\mathbf{k}}(\mathbf{G}')\{\left\langle\phi_{\mathbf{k}+\mathbf{G}}^{\alpha}\left|\hat{T}+\hat{V}_{eff}^{s}-\varepsilon_{n\mathbf{k}}\right|\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}^{\alpha}\right\rangle_{MT_\alpha}\\
&+\left\langle\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}^{\alpha}\left|\hat{T}+\hat{V}_{eff}^{s}-\varepsilon_{n\mathbf{k}}\right|\phi_{\mathbf{k}+\mathbf{G}}^{\alpha}\right\rangle_{MT_\alpha}^{*}\}\\
=\;&-2i\mathbf{q}\sum_{n,\mathbf{k}}\sum_{lm}[a_{lm}^{n,\mathbf{k}}]^*[\delta a_{lm}^{n,\mathbf{k}}][E_l-\varepsilon_{n\mathbf{k}}]+[a_{lm}^{n,\mathbf{k}}]^*[\delta b_{lm}^{n,\mathbf{k}}]+[b_{lm}^{n,\mathbf{k}}]^*[\delta b_{lm}^{n,\mathbf{k}}][E_l-\varepsilon_{n\mathbf{k}}]N_l
\end{aligned}
$$

$$(1.341)$$

and

$$
-i\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})C_{n\mathbf{k}}^*(\mathbf{G})\delta C_{n\mathbf{k}}(\mathbf{G}')\{\left\langle\phi_{\mathbf{k}+\mathbf{G}}^{\alpha}\left|\hat{T}+\hat{V}_{eff}^{s}-\varepsilon_{n\mathbf{k}}\right|\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}^{\alpha}\right\rangle_{MT_\alpha}
$$

$$\begin{aligned} &+\left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \left| \hat{T} + \hat{V}^{s}_{eff} - \varepsilon_{n\mathbf{k}} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \right\rangle^{*}_{MT_\alpha} \} \\ = \; & -2i \sum_{n,\mathbf{k}} \sum_{lm} [a^{n,\mathbf{k}}_{lm}]^{*} [\delta \mathbf{a}^{n,\mathbf{k}}_{lm}][E_l - \varepsilon_{n\mathbf{k}}] + [a^{n,\mathbf{k}}_{lm}]^{*} [\delta \mathbf{b}^{n,\mathbf{k}}_{lm}] + [b^{n,\mathbf{k}}_{lm}]^{*} [\delta \mathbf{b}^{n,\mathbf{k}}_{lm}][E_l - \varepsilon_{n\mathbf{k}}] N_l \\ & +2i \sum_{n,\mathbf{k}} \sum_{lm} [\mathbf{a}^{n,\mathbf{k}}_{lm}]^{*} [\delta a^{n,\mathbf{k}}_{lm}][E_l - \varepsilon_{n\mathbf{k}}] + [\mathbf{a}^{n,\mathbf{k}}_{lm}]^{*} [\delta b^{n,\mathbf{k}}_{lm}] + [\mathbf{b}^{n,\mathbf{k}}_{lm}]^{*} [\delta b^{n,\mathbf{k}}_{lm}][E_l - \varepsilon_{n\mathbf{k}}] N_l . \end{aligned} \tag{1.342}$$

The contributions from the non-spherical potential are given by:

$$\begin{aligned} & -i\mathbf{q} \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} C^{*}_{n\mathbf{k}}(\mathbf{G}) \delta C_{n\mathbf{k}}(\mathbf{G}') \{ \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \left| V^{NS}_{eff} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\ & + \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \left| V^{NS}_{eff} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \right\rangle^{*}_{MT_\alpha} \} \\ = \; & -2i\mathbf{q} \sum_{n,\mathbf{k}} \sum_{l,m,,l',m'} \sum_{L>0,M} G(l,m,L,M,l',m') \\ & \times \{ \int_0^{R_\alpha} [a^{n,\mathbf{k}}_{lm} u_l(r) + b^{n,\mathbf{k}}_{lm} \dot{u}_l(r)]^{*} [V^{\alpha}_{LM}(r)][\delta a^{n,\mathbf{k}}_{l'm'} u_{l'}(r) + \delta b^{n,\mathbf{k}}_{l'm'} \dot{u}_{l'}(r)] r^2 dr \}, \end{aligned} \tag{1.343}$$

and

$$\begin{aligned} & -i \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} (\mathbf{G}' - \mathbf{G}) C^{*}_{n\mathbf{k}}(\mathbf{G}) \delta C_{n\mathbf{k}}(\mathbf{G}') \{ \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \left| V^{NS}_{eff} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \right\rangle_{MT_\alpha} \\ & + \left\langle \phi^{\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}'} \left| V^{NS}_{eff} \right| \phi^{\alpha}_{\mathbf{k}+\mathbf{G}} \right\rangle^{*}_{MT_\alpha} \} \\ = \; & -2i \sum_{n,\mathbf{k}} \sum_{l,m,,l',m'} \sum_{L>0,M} G(l,m,L,M,l',m') \\ & \times \{ \int_0^{R_\alpha} [a^{n,\mathbf{k}}_{lm} u_l(r) + b^{n,\mathbf{k}}_{lm} \dot{u}_l(r)]^{*} [V^{\alpha}_{LM}(r)][\delta \mathbf{a}^{n,\mathbf{k}}_{l'm'} u_{l'}(r) + \delta \mathbf{b}^{n,\mathbf{k}}_{l'm'} \dot{u}_{l'}(r)] r^2 dr \\ & - \int_0^{R_\alpha} [\mathbf{a}^{n,\mathbf{k}}_{lm} u_l(r) + \mathbf{b}^{n,\mathbf{k}}_{lm} \dot{u}_l(r)]^{*} [V^{\alpha}_{LM}(r)][\delta a^{n,\mathbf{k}}_{l'm'} u_{l'}(r) + \delta b^{n,\mathbf{k}}_{l'm'} \dot{u}_{l'}(r)] r^2 dr \}. \end{aligned} \tag{1.344}$$

For the third term four more abbreviations are introduced:

$$a1^{n,\mathbf{k}}_{lm} = \sum_{\mathbf{G}} [(\mathbf{k}+\mathbf{G}) \delta \mathbf{S}^{*}_{\alpha}] C_{n\mathbf{k}}(\mathbf{G}) A^{\alpha}_{lm}(\mathbf{k}+\mathbf{G}), \tag{1.345}$$

$$b1^{n,\mathbf{k}}_{lm} = \sum_{\mathbf{G}} [(\mathbf{k}+\mathbf{G}) \delta \mathbf{S}^{*}_{\alpha}] C_{n\mathbf{k}}(\mathbf{G}) B^{\alpha}_{lm}(\mathbf{k}+\mathbf{G}), \tag{1.346}$$

$$\mathbf{a1}^{n,\mathbf{k}}_{lm} = \sum_{\mathbf{G}} \mathbf{G} [(\mathbf{k}+\mathbf{G}) \delta \mathbf{S}^{*}_{\alpha}] C_{n\mathbf{k}}(\mathbf{G}) A^{\alpha}_{lm}(\mathbf{k}+\mathbf{G}), \tag{1.347}$$

$$\mathbf{b1}^{n,\mathbf{k}}_{lm} = \sum_{\mathbf{G}} \mathbf{G} [(\mathbf{k}+\mathbf{G}) \delta \mathbf{S}^{*}_{\alpha}] C_{n\mathbf{k}}(\mathbf{G}) B^{\alpha}_{lm}(\mathbf{k}+\mathbf{G}). \tag{1.348}$$

The muffin-tin contribution is then given by:

$$
\begin{aligned}
&+\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}-\mathbf{G}')[(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_\alpha]C^*_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')\{\left\langle\phi^\alpha_{\mathbf{k}+\mathbf{G}}\left|\hat{T}+\hat{V}^s_{eff}-\varepsilon_{n\mathbf{k}}\right|\phi^\alpha_{\mathbf{k}+\mathbf{G}'}\right\rangle_{MT_\alpha} \\
&+\left\langle\phi^\alpha_{\mathbf{k}+\mathbf{G}'}\left|\hat{T}+\hat{V}^s_{eff}-\varepsilon_{n\mathbf{k}}\right|\phi^\alpha_{\mathbf{k}+\mathbf{G}}\right\rangle^*_{MT_\alpha}\} \\
= \;& 2\sum_{n,\mathbf{k}}\sum_{lm}[\mathbf{a1}^{n,\mathbf{k}}_{lm}]^*[a^{n,\mathbf{k}}_{lm}][E_l-\varepsilon_{n\mathbf{k}}]+[\mathbf{a1}^{n,\mathbf{k}}_{lm}]^*[b^{n,\mathbf{k}}_{lm}]+[\mathbf{b1}^{n,\mathbf{k}}_{lm}]^*[b^{n,\mathbf{k}}_{lm}][E_l-\varepsilon_{n\mathbf{k}}]N_l \\
&-2\sum_{n,\mathbf{k}}\sum_{lm}[a1^{n,\mathbf{k}}_{lm}]^*[\mathbf{a}^{n,\mathbf{k}}_{lm}][E_l-\varepsilon_{n\mathbf{k}}]+[a1^{n,\mathbf{k}}_{lm}]^*[\mathbf{b}^{n,\mathbf{k}}_{lm}]+[b1^{n,\mathbf{k}}_{lm}]^*[\mathbf{b}^{n,\mathbf{k}}_{lm}][E_l-\varepsilon_{n\mathbf{k}}]N_l, \quad (1.349)
\end{aligned}
$$

The term related to the non-spherical potential reads:

$$
\begin{aligned}
&\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}-\mathbf{G}')[(\mathbf{k}+\mathbf{G})\delta\mathbf{S}_\alpha]C^*_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')\{\left\langle\phi^\alpha_{\mathbf{k}+\mathbf{G}}\left|\hat{V}^{NS}_{eff}\right|\phi^\alpha_{\mathbf{k}+\mathbf{G}'}\right\rangle_{MT_\alpha} \\
&+\left\langle\phi^\alpha_{\mathbf{k}+\mathbf{G}'}\left|\hat{V}^{NS}_{eff}\right|\phi^\alpha_{\mathbf{k}+\mathbf{G}}\right\rangle^*_{MT_\alpha}\} \\
= \;& 2\sum_{n,\mathbf{k}}\sum_{l,m,,l',m'}\sum_{L>0,M}G(l,m,L,M,l',m') \\
&\{\int_0^{R_\alpha}[\mathbf{a1}^{n,\mathbf{k}}_{lm}u_l(r)+\mathbf{b1}^{n,\mathbf{k}}_{lm}\dot{u}_l(r)]^*[V^\alpha_{LM}(r)][a^{n,\mathbf{k}}_{l'm'}u_{l'}(r)+b^{n,\mathbf{k}}_{l'm'}\dot{u}_{l'}(r)]r^2dr \\
&-\int_0^{R_\alpha}[a1^{n,\mathbf{k}}_{lm}u_l(r)+b1^{n,\mathbf{k}}_{lm}\dot{u}_l(r)]^*[V^\alpha_{LM}(r)][\mathbf{a}^{n,\mathbf{k}}_{l'm'}u_{l'}(r)+\mathbf{b}^{n,\mathbf{k}}_{l'm'}\dot{u}_{l'}(r)]r^2dr\}. \quad (1.350)
\end{aligned}
$$

We remember that $\sum_{n,\mathbf{k}}$ symbolizes the weighted sum over the occupied states $(n,\mathbf{k})$:

$$\sum_{n,\mathbf{k}}[...]\longrightarrow\sum_{n,\mathbf{k}}w(n,\mathbf{k})[...]. \quad (1.351)$$

The term $\mathbf{F}_{\alpha 3}$ and its first-order change $\delta\mathbf{F}_{\alpha 3}$: Due to the discontinuity of the second derivative of the wave-function at the sphere boundaries the expression,

$$\mathbf{F}_{\alpha 3}=\sum_{n,\mathbf{k}}\oint\Psi^*_{n\mathbf{k}}(\mathbf{r})(-\nabla^2-\varepsilon_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r})|_{Int}d\mathbf{A}_\alpha, \quad (1.352)$$

represents a further contribution to the total atomic force. Inserting the plane wave representation,

$$\Psi_{n\mathbf{k}}(\mathbf{r})=\frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}}C_{n\mathbf{k}}(\mathbf{G})e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \quad (1.353)$$

into expression (1.352) we obtain:

$$\mathbf{F}_{\alpha 3}=\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}C^*_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')[(\mathbf{k}+\mathbf{G}')^2-\varepsilon_{n\mathbf{k}}]\frac{1}{\Omega}\oint e^{-i(\mathbf{k}+\mathbf{G})\mathbf{r}}e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}}d\mathbf{A}_\alpha. \quad (1.354)$$

In previous works [13, 34, 39] the surface integral in Eq.(1.354) was evaluated by substituting each plane-wave by the atomic-sphere representation of its corresponding LAPW. This substitution is justified by the fact that the LAPWs are continuous in value and slope across the sphere boundaries. The essential part of the surface integral which then had to be solved was of the form,

$$\oint Y_{l'm'}(\hat{\mathbf{r}})Y_{lm}(\hat{\mathbf{r}})d\mathbf{A}_\alpha.$$

Rather tedious analytic simplifications then lead to force formulas $\mathbf{F}_{\alpha 3}$ which resembled very much the structure of the formulas describing $\mathbf{F}_{\alpha 1}$ (Eqs.(1.290)-(1.292)). In the current work we propose an alternative approach to the evaluation of

$$\frac{1}{\Omega}\oint e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}d\mathbf{A}_\alpha. \tag{1.355}$$

It is strongly oriented on ideas developed for the kinetic energy term in the Sternheimer equation and does not require the knowledge of the atomic-sphere representation of the LAPWs: Similarly as in the derivation of ΔT^{int}_{grad} (Eqs.(1.157) and (1.158)) we can apply the theorem of Gauss to the surface integral (1.355) and obtain:

$$\frac{1}{\Omega}\oint e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}d\mathbf{A}_\alpha = \frac{1}{\Omega}\int_{MT_\alpha} \nabla e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}d^3\mathbf{r} = \frac{1}{\Omega}i(\mathbf{G}'-\mathbf{G})\int_{MT_\alpha} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}d^3\mathbf{r}. \tag{1.356}$$

After inserting (1.356) into (1.354) $\mathbf{F}_{\alpha 3}$ reads:

$$\mathbf{F}_{\alpha 3} = \sum_{n,\mathbf{k},\mathbf{G},\mathbf{G}'} i(\mathbf{G}'-\mathbf{G})C^*_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')[(\mathbf{k}+\mathbf{G}')^2-\varepsilon_{n\mathbf{k}}]\frac{1}{\Omega}\int_{MT_\alpha} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}d^3\mathbf{r}, \tag{1.357}$$

with the volume integrals being explicitly given by:

$$\int_{MT_\alpha} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}d^3\mathbf{r} = \begin{cases} \frac{4\pi}{3}R_\alpha^3 & \text{for} \quad (\mathbf{G}'-\mathbf{G})=\mathbf{0} \\ \frac{4\pi}{|\mathbf{G}'-\mathbf{G}|}R_\alpha^2 j_1(R_\alpha|\mathbf{G}'-\mathbf{G}|)e^{i(\mathbf{G}'-\mathbf{G})\mathbf{S}_\alpha} & \text{for} \quad (\mathbf{G}'-\mathbf{G})\neq\mathbf{0} \end{cases}. \tag{1.358}$$

As formula (1.358) is needed for the set-up of the overlap matrix in the generalized eigenvalue problem it is already coded in LAPW band structure programs. The modifications which then have to be made to obtain $\mathbf{F}_{\alpha 3}$ are straight forward and can be implemented easily. Thus Eq.(1.357) is of considerable practical use.

We now want to evaluate $\delta\mathbf{F}_{\alpha 3}$. For this purpose we return to expression (1.352) and calculate its value after the displacement of the sphere, i.e.,

$$\mathbf{F}^{\delta\mathbf{S}_\alpha}_{\alpha 3} = \sum_{n,\mathbf{k}}\oint_{\delta\mathbf{S}_\alpha}[\Psi^{\delta\mathbf{S}_\alpha}_{n\mathbf{k}}(\mathbf{r})]^*(-\nabla^2-\varepsilon_{n\mathbf{k}})\Psi^{\delta\mathbf{S}_\alpha}_{n\mathbf{k}}(\mathbf{r})|_{Int}d\mathbf{A}_\alpha. \tag{1.359}$$

where the index $\delta\mathbf{S}_\alpha$ at the integral sign symbolizes the fact that the center of the sphere is located at $(\mathbf{S}_\alpha + \delta\mathbf{S}_\alpha)$. Additionally we have already assumed that to first-order the eigenvalue $\varepsilon_{n\mathbf{k}}$ does not change upon the phonon distortion. The interstitial wave-function $\Psi_{n\mathbf{k}}^{\delta\mathbf{S}_\alpha}(\mathbf{r})$ for the distorted crystal up to first-order in the displacement will read:

$$\Psi_{n\mathbf{k}}^{\delta\mathbf{S}_\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} [C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} + \delta C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{q}+\mathbf{G})\mathbf{r}}] \tag{1.360}$$

Inserting (1.360) into (1.359) and only keeping terms up to first-order in the variational coefficient we obtain:

$$\begin{aligned} \mathbf{F}_{\alpha 3}^{\delta\mathbf{S}_\alpha} &= \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} C_{n\mathbf{k}}^{*}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') [(\mathbf{k}+\mathbf{G}')^2 - \varepsilon_{n\mathbf{k}}] \frac{1}{\Omega} \oint_{\delta\mathbf{S}_\alpha} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} d\mathbf{A}_\alpha \\ &+ \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} \delta C_{n\mathbf{k}}^{*}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') [(\mathbf{k}+\mathbf{G}')^2 - \varepsilon_{n\mathbf{k}}] \frac{1}{\Omega} \oint_{\delta\mathbf{S}_\alpha} e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}} d\mathbf{A}_\alpha \\ &+ \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} C_{n\mathbf{k}}^{*}(\mathbf{G}) \delta C_{n\mathbf{k}}(\mathbf{G}') [(\mathbf{k}+\mathbf{q}+\mathbf{G}')^2 - \varepsilon_{n\mathbf{k}}] \frac{1}{\Omega} \oint_{\delta\mathbf{S}_\alpha} e^{i(\mathbf{G}'+\mathbf{q}-\mathbf{G})\mathbf{r}} d\mathbf{A}_\alpha . \end{aligned} \tag{1.361}$$

To connect the surface integral over the shifted sphere to the one over the undisplaced sphere we use the relation,

$$\oint_{\delta\mathbf{S}_\alpha} e^{i\mathbf{K}\mathbf{r}} d\mathbf{A}_\alpha = e^{i\mathbf{K}\delta\mathbf{S}_\alpha} \oint e^{i\mathbf{K}\mathbf{r}} d\mathbf{A}_\alpha, \tag{1.362}$$

expanded up to first-order in the displacement:

$$\oint_{\delta\mathbf{S}_\alpha} e^{i\mathbf{K}\mathbf{r}} d\mathbf{A}_\alpha = (1 + i\mathbf{K}\delta\mathbf{S}_\alpha) \oint e^{i\mathbf{K}\mathbf{r}} d\mathbf{A}_\alpha . \tag{1.363}$$

Using (1.363) in (1.361) and subtracting the force contribution $\mathbf{F}_{\alpha 3}$ given by term (1.354) we obtain for the first-order change $\delta\mathbf{F}_{\alpha 3}$:

$$\begin{aligned} \delta\mathbf{F}_{\alpha 3} &= \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} C_{n\mathbf{k}}^{*}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') [(\mathbf{k}+\mathbf{G}')^2 - \varepsilon_{n\mathbf{k}}] \frac{1}{\Omega} i[(\mathbf{G}'-\mathbf{G})\delta\mathbf{S}_\alpha] \oint e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} d\mathbf{A}_\alpha \\ &+ \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} \delta C_{n\mathbf{k}}^{*}(\mathbf{G}) C_{n\mathbf{k}}(\mathbf{G}') [(\mathbf{k}+\mathbf{G}')^2 - \varepsilon_{n\mathbf{k}}] \frac{1}{\Omega} \oint e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}} d\mathbf{A}_\alpha \\ &+ \sum_{n,\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} C_{n\mathbf{k}}^{*}(\mathbf{G}) \delta C_{n\mathbf{k}}(\mathbf{G}') [(\mathbf{k}+\mathbf{q}+\mathbf{G}')^2 - \varepsilon_{n\mathbf{k}}] \frac{1}{\Omega} \oint e^{i(\mathbf{G}'+\mathbf{q}-\mathbf{G})\mathbf{r}} d\mathbf{A}_\alpha , \end{aligned} \tag{1.364}$$

where in the second and third term the fact has been exploited that the products,

$$\delta C^*_{n\mathbf{k}}(\mathbf{G})[(\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta\mathbf{S}_\alpha] \quad \text{and} \quad \delta C_{n\mathbf{k}}(\mathbf{G}')[(\mathbf{G}'+\mathbf{q}-\mathbf{G})\delta\mathbf{S}_\alpha],$$

are second-order quantities and thus to be excluded. To arrive at the final result two more steps have to be taken: First we have to impose the right translational behaviour onto the second term in (1.364) by replacing $\mathbf{q}$ by $-\mathbf{q}$ and the variational coefficient $\delta C^*_{n\mathbf{k}}(\mathbf{G})$ by $\delta C^{-\mathbf{q}*}_{n\mathbf{k}}(\mathbf{G})$ (compare the more detailed discussion in section (1.3.7)). Second we combine the second and third term of (1.364) by exploiting the time-reversal symmetry (Kramer's theorem (1.324)) of the wave-functions. Finally using relation (1.356) we obtain:

$$\begin{aligned}
\delta\mathbf{F}_{\alpha 3} = & -\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}\{(\mathbf{G}'-\mathbf{G})C^*_{n\mathbf{k}}(\mathbf{G})C_{n\mathbf{k}}(\mathbf{G}')[(\mathbf{k}+\mathbf{G}')^2-\varepsilon_{n\mathbf{k}}] \\
& [(\mathbf{G}'-\mathbf{G})\delta\mathbf{S}_\alpha]\frac{1}{\Omega}\int_{MT_\alpha} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}d^3\mathbf{r}\} \\
& +\sum_{n,\mathbf{k}}\sum_{\mathbf{G},\mathbf{G}'}\{i(\mathbf{G}'-\mathbf{G}+\mathbf{q})C^*_{n\mathbf{k}}(\mathbf{G})\delta C_{n\mathbf{k}}(\mathbf{G}') \\
& [(\mathbf{k}+\mathbf{q}+\mathbf{G}')^2+(\mathbf{k}+\mathbf{G})^2-2\varepsilon_{n\mathbf{k}}]\frac{1}{\Omega}\int_{MT_\alpha} e^{i(\mathbf{G}'-\mathbf{G}+\mathbf{q})\mathbf{r}}d^3\mathbf{r}\}, \qquad (1.365)
\end{aligned}$$

with

$$\frac{1}{\Omega}\int_{MT_\alpha} e^{i\mathbf{K}\mathbf{r}}d^3\mathbf{r} = -\frac{4\pi}{\Omega|\mathbf{K}|}R_\alpha^2 j_1(R_\alpha|\mathbf{K}|)e^{i\mathbf{K}\mathbf{S}_\alpha} \quad \text{for} \quad \mathbf{K}\neq\mathbf{0}.$$

The first sum in (1.365) is an alternative formulation of the term described in the third and fourth line of Eq.(B9) in the publication of Yu et al. [26].

Chapter 2

Raman-active phonons in $YBa_2Cu_3O_7$

More than ten years ago, in 1986, J. G. Bednorz and K. A. Müller discovered superconductivity at ~30 K in La-Ba-Cu-O ceramics [43]. In the following years other copper-oxide based compounds where synthesized which displayed even higher transition temperatures. Two of the most prominent representatives of this new class of materials, generally termed high-temperature superconductors (HTSCs), are $YBa_2Cu_3O_7$ with T_c=92 K [44] and the layered structure $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n \leq 5$) [45]. In the case of $n = 3$ the T_c of the later compound is 136 K. The obvious technological implications of these findings – for almost all HTSCs liquid nitrogen can substitute helium as the cooling medium – triggered intensive experimental and theoretical research work all over the world. The complexity of the thus opened scientific challenge is probably best reflected in the fact that until today a universal picture of the microscopic mechanism causing these extraordinary transition temperatures has not been obtained. The nonetheless impressive amount of knowledge gained on the physical properties of HTSCs as well as the diverse efforts to develop valid theoretical models have been summarized in various review articles, e.g. by Dagotto [46], Pickett [47] and Ginsberg [48]. In the following introduction which should serve as a guideline and additional source of information for the publications of this thesis, we focus our attention mainly on aspects of zone-center phonons related to Raman spectra in $YBa_2Cu_3O_7$.

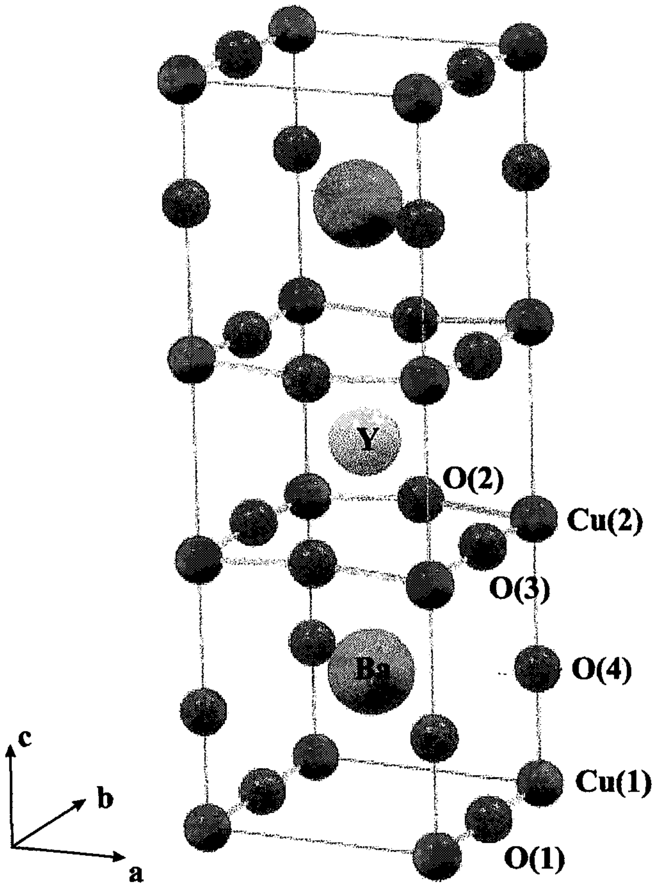

Figure 2.1: Primitive unit cell of $YBa_2Cu_3O_7$. The upper half of the cell is linked to the lower half by inversion symmetry taking the location of the Y-atom as the origin.

2.1 $YBa_2Cu_3O_7$

$YBa_2Cu_3O_7$ (from now on abbreviated YBCO7) has entered in history as the first material with a critical temperature above the boiling point of liquid nitrogen (77 K). Its structure is displayed in figure (2.1). It has an orthorhombic unit cell (space group D_{2h}) with lattice constants $a = 7.22$ a.u., $b = 7.33$ a.u., $c = 22.07$ a.u. incorporating two structural elements which are similarly found in many other copper-oxide based HTSCs and are of central importance for the physical properties of the compound. On the one hand there are copper-oxygen layers being build up of the atoms Cu(2), O(2) and O(3). They are refered to as CuO_2-planes. The copper atom is surrounded by five oxygen atoms constituting a pyramid with the apex oxygen O(4) located at its peak. This pyramid can be classified as a modified perovskite structure[1]. On the other hand there are chains of alternating copper and oxygen atoms (Cu(1) and O(1)) located along the *b*-axis of the crystal. The remaining atoms (Ba and Y) mainly serve to stabilize the structure where in particular the rare earth does not seem to play a dominant role with respect to the mobile charge carriers: The yttrium ion can be replaced with a whole series of rare earths (except Pr and Yb) with the resultant material keeping not only superconducting properties but even the same transition temperature.

The phenomenology of the metallic behaviour of YBCO7 is best described starting from the 'parent' compound $YBa_2Cu_3O_6$ (YBCO6) which is structurally similar but does not display superconductivity. In YBCO6 the chains along the *b*-axis are oxygen depleted which make the *a*- and *b*-axis equivalent and the structure thus tetragonal (space group D_{4h}). This material is an antiferromagnetic insulator. Upon increasing the oxygen concentration the empty sites in the chains are gradually filled up. The resultant compounds $YBa_2Cu_3O_{6+x}$ pass into the metallic regime at $x \sim 0.4$. For $0.4 \leq x \leq 1.0$ the material is a superconductor with T_c being a function of doping. In this latter regime certain doping levels enable the oxygen vacancies to form ordered superstructures, most prominent being the ortho-II-structure of $YBa_2Cu_3O_{6.5}$ [49] where only every second chain is fully occupied. On a microscopic level the charge transport in all these metals is assumed to be located in the quasi-two-dimensional CuO_2-plane with the oxygens in the chains functioning as a charge reservoir: Due to their negative valency the chain oxygens attract electrons from the CuO_2-planes and thus create holes which form the free charge carriers. Resistivity measurements indicate that at room temperature their mobility in *a* and *b* direction is ~100 times larger than in *c* direction. Besides the high anisotropy of the resistivity there are several other experimental results which do not conform to the behaviour expected of a conventional metal. These results range from the anomalous temperature dependence of the resistivity (at low temperatures no T^2 term behaviour) to unusual features in the optical properties (e.g. the frequency-dependent conductivity does not follow a simple Drude model). Whereas certain results can be traced back to the pronounced anisotropic structure of the material others seem to indicate that already the normal state in the YBCO compounds is partly determined by strong correlation effects between the electrons. This automatically raises the question if a conventional one-particle picture (band structure calculation within DFT) with

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[1] A typical representative in the family of full perovskites would for instance be $SrTiO_3$.

possible refinements of the ansatz for exchange and correlation effects is capable of describing the normal state of these materials correctly. The answer can be summarized as follows: The non-conductive phase YBCO6 being a Mott-Hubbard-Isolator with a very strong on-site Coulomb interaction can not be reproduced by band structure calculations based on a local approximation (LDA, GGA) for exchange and correlations. On the other hand many experimentally detectable features (e.g. Fermi surface and electric-field gradients) of the metallic phase YBCO7 are very well described within the single-particle picture [50, 51, 52, 53]. Nevertheless certain exceptions to this overall agreement could not and also should not be ignored. They are valuable indicators for possible limitations of the method. In this respect it is important to find the proper sources of the remaining deviations, offer possible methodical refinements and in this way clearly establish the area of applicability of band theory in these highly complex materials. This task was part of the underlying motivation for the work presented in the papers of this thesis.

2.2 Raman-active phonons

The unit cell of YBCO7 consists of 13 atoms. At the center of the Brillouin zone the corresponding 39 phonon branches of YBCO7 can be classified into three groups: Three acoustic modes, 15 Raman-active modes and 21 infrared (IR)-active modes. That no Raman-active mode can be IR-active and vice versa is a direct consequence of the existence of an inversion center in the crystal and implies that the Raman modes posses even and the IR modes odd parity. Consequently, atoms which are located at a center of inversion can not contribute to the eigenvector of a Raman mode. In YBCO7, the Y, Cu(1) and O(1) atoms fall into this category. The remaining elements Ba, Cu(2), O(2), O(3) and O(4) appear as pairs of equivalent atoms which are connected by inversion symmetry. According to the condition of even parity the atoms of each pair move in opposite directions. Further group theoretical analysis of the 15 Raman modes yields the following vibrational patterns: Five modes are of A_{1g}-symmetry with the five atoms moving in z-direction (c-axis). Another five modes are of B_{2g}-symmetry with vibrations along the x-direction (a-axis). The remaining five modes are of B_{3g}-symmetry with the atoms moving parallel to the y-direction (b-axis). In principle, it is possible that in each symmetry class all eigenvectors involve motions of all five pairs of atoms. No a priori assumption based on symmetry arguments can be made to decouple the contributions. Consequently, in the corresponding dynamical matrices 15 independent elements (diagonal and off-diagonal elements) have to be determined. From an experimental point of view this represents a formidable task and requires very precise spectroscopic investigations where the atoms are properly substituted by corresponding isotopes (e.g. $O^{16} \longrightarrow O^{18}$, $Ba^{138} \longrightarrow Ba^{134}$, $Cu^{63} \longrightarrow Cu^{65}$). With regard to the Raman modes, only the isotope substitution of Ba and Cu(2) within the A_{1g} modes revealed a quantitative value of the corresponding elements in the dynamical matrix [54, 55]. Raman measurements on site-selective oxygen-substituted samples have also been performed but only give a qualitative description of the admixture. The overall mode assignment obtained for the A_{1g} modes can be summarized as follows [56]: The lowest-lying frequency (115 cm^{-1}) is dominated by Ba-vibrations, the next one (150 cm^{-1}) by Cu(2)-vibrations. Both modes are strongly decoupled from the oxygen vibrations. The structure of the Raman tensor for the mode at 340 cm^{-1} revealed that it must be dominated by the out-of-phase motion of O(2) and O(3). The key to this assignment is found in the fact that this is the only mode which does not display near-tetragonal symmetry and should thus correspond to a B_{1g} mode in YBCO6 where O(2) and O(3) are equivalent atoms. The relation between certain elements of the Raman-tensor with regard to their sign is then distinctly different from the other four modes. It can thus be distinguished particularly from the two other oxygen modes at 440 cm^{-1} and 500 cm^{-1}. Although the latter one is dominated by motions of the apical oxygen O(4) and the former one by the in-phase motion of O(2) and O(3) both modes display considerable admixture of all three atoms. Turning to the B_{2g} and B_{3g} modes, the information gained from Raman scattering is very much restricted to frequency values whereas the mode assignment was basically done through a sole comparison to lattice dynamical model calculations [56]. We return to these vibrations when discussing corresponding ab-initio frozen phonon calculations. For now we only note that investigations into the B_{2g} and B_{3g} modes are very much hampered by the fact that their Raman signal is well over 100 times less intense than that observed for the typical A_{1g} modes.

The knowledge of proper mode admixture, frequencies and also possible anharmonicities in the phonon potentials are necessary ingredients in the calculation of interactions between the crystal lattice and the electronic system. The resulting electron-phonon coupling parameters could contribute to a fuller understanding of the role phonons play in the superconducting pairing mechanism. From an experimental point of view several unusual features in the Raman spectra of YBCO7 indicate the significance of a quantitative understanding of such interactions. The following examples taken from the A_{1g} modes should illustrate the situation: (i) The O(2)-O(3) phonon mode displays sharp anomalous softening when the sample passes through the transition temperature upon cooling [57]. In the region T> T_c a decrease of the temperature hardens the mode as expected from a normal metal. By the application of magnetic fields the effect of softening could be proved to be dependent on the occurrence of the superconducting phase in the material [58]. (ii) A significant phonon self-energy effect is also observable in the asymmetric line shape (Fano-lineshape) of the O(2)-O(3) as well as of the Ba mode. This effect occurs in the normal as well as in the superconducting state [56, 59]. (iii) The phonon frequency of the apex oxygen mode (~500 cm^{-1}) softens dramatically with increasing temperature [60]. Additionally the intensity of the corresponding peak in the Raman spectrum displays a pronounced decrease.

After this short detour into experimental findings we now want to return to the theoretical investigation of eigenfrequencies and eigenvectors of phonons in YBCO7. Over the last decade two main theoretical paths have been taken to obtain information on the lattice vibrations of this very complex structure. The first one is based on traditional or modified shell-model calculations and yields dispersion curves throughout the entire Brillouin zone [61, 62, 63]. The second one utilizes the ab-initio frozen phonon technique and is limited to high-symmetry phonons at the zone center and the zone boundary [64, 65]. In the shell model approach the electronic polarization is usually taken into account in the dipole approximation, the long-range interactions are described by Coulomb potentials and for the short-range forces Born-Mayer potentials are assumed. Although this model is designed to reflect lattice vibrations of purely ionic crystals it still gives a first valuable idea of the phonon dispersion also for YBCO7. To illustrate the thus obtained accuracies we list results for the 15 Raman modes in Table (2.1).

The shell model underlying the data [62] in table (2.1) is using a limited number of interaction potentials (and thus fit-parameters) to produce a 'physical picture' behind the calculated frequencies. Additionally, renormalization due to free charge carriers is not taken into account. Although these assumptions are rather crude the results are nevertheless of practical usage. This is particularly true with respect to the interpretation and mode assignment of experimentally obtained spectra. At the same time one has to notice that certain modes (e.g. oxygen dominated modes with in-plane polarization) show strong deviations from measured data. This might be attributed to metallic screening but has not been systematically investigated[2]. One also has to be aware of the general fact that when

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[2] The effect of metallic screening is particularly important in the case of LO-TO splitting of IR-active

Table 2.1: Raman-active optical phonons at **q** = **0** in cm^{-1} calculated from a shell model [62] compared to experimental data [56, 66, 67, 68].

Mode	Symm.	Theory	Exp.	Rel. deviat.
Ba	A_{1g}	115	112	+3%
Cu(2)	A_{1g}	157	154	+2%
O(2)-O(3)	A_{1g}	353	340	+4%
O(2)+O(3)	A_{1g}	377	440	-15%
O(4)	A_{1g}	509	500	+2%
Ba	B_{2g}	70	70	0%
Cu(2)	B_{2g}	142	142	0%
O(4)	B_{2g}	346	210	+65%
O(3)	B_{2g}	428	370	+16%
O(2)	B_{2g}	584	579	+1%
Ba	B_{3g}	91	83	+10%
Cu(2)	B_{3g}	137	140	-2%
O(4)	B_{3g}	411	303	+36%
O(2)	B_{3g}	490	-	-
O(3)	B_{3g}	545	526	+4%

choosing the fit-parameters in a shell model (e.g. Born-Mayer constants, ionic charge, shell charge, etc.) the point of orientation are the eigenvalues of the measured phonons. As a consequence the whole uncertainty of the model calculation is embedded in the admixture of the resulting eigenvectors. Needless to say that this is particularly relevant for complex structures. A detailed picture of mode admixture which is required for the calculation of electron-phonon coupling constants (reflected in physical quantities like life time of phonons or transition temperatures in conventional superconductors), inelastic neutron scattering intensities or Raman spectra is usually not obtainable in this approach. The method of choice to calculate eigenvectors on the same footing as eigenfrequencies is the frozen phonon technique based on first-principles band structure calculations. It not only opens the door to establish phonon potentials without adjusting parameters to experimental data but also lends itself conveniently to the investigation of possible anharmonic terms in these potentials. In YBCO7 this possibility has for instance helped to resolve the question on the existence of a double well in the apex-oxygen mode (500 cm^{-1}) proposed by certain experiments. The importance of such a scenario lay in the fact that a strong anharmonicity could

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modes. By combining an ionic shell model with an ansatz for the long-range part of the electron-phonon coupling the experimental observed suppression of this splitting in YBCO7 could be theoretically reproduced at least for the in-plane polarized modes [69].

possibly have explained the anomalously small isotope effect on the transition temperature in this compound – an experimental finding not being compatible with conventional BCS theory. In this respect frozen-phonon computations clearly indicated that although slightly anharmonic in shape the corresponding potential only exhibits one minimum [70]. This theoretical prediction was then confirmed by the majority of experiments (for a review see e.g. [71]).

At the start of this thesis a systematic approach to the Raman-active vibrations in YBCO7 via the frozen-phonon technique had already been carried out by two groups. Andersen et al. had used the LMTO method to compute the five A_{1g} modes [64, 72] whereas Cohen et al. [65, 73] utilized the LAPW method to calculate all 15 Raman modes. Both approaches had in common that they (i) used an LDA-functional to treat exchange and correlation effects, (ii) interpolated the energy surface on the sole basis of total energy values, (iii) used the experimental volume rather than the theoretically optimized one which was estimated to lie approximately 6% lower. Additionally the LAPW calculations did not fully take into account the optimized *c*-axis positions of the five atoms taking part in the vibrations. In both works, the agreement with experimental data was reasonably good. On average the calculated frequency values lay in the range of deviation of -10%. Nevertheless certain shortcomings of the results did not appear to have trivial sources of errors. This was of particular interest to us as we aimed to examine the *overall* validity of a consistent band-structure calculation for the description of vibronic properties of YBCO7. The most pronounced questionable features concerned (i) the strong deviations from experimental data in the mode admixture of the Ba- and Cu-dominated modes (A_{1g}-symmetry), (ii) the frequency value of the O(2)+O(3) mode (A_{1g}, 440 cm^{-1}) and the O(4) mode (B_{3g}, 303 cm^{-1}) which came out 18% and 15% too low, respectively, in the LAPW calculations, (iii) the generally poor agreement in the mode admixture of the A_{1g} modes between the LMTO and LAPW results.

To investigate into these problems, this thesis refocuses on the establishment of the full dynamical matrix of the Raman modes using the frozen-phonon technique within the *WIEN97* FLAPW code [31]. Several alterations to the aforementioned calculations have consecutively or simultaneously been implemented. They concern the following aspects: (i) The energy surface is established on the basis of atomic-force rather than total-energy data. The corresponding increase of information allows us to fully optimize the *c*-axis parameters of the five atoms and to investigate into possible anharmonicities of the diagonal as well as off-diagonal elements of the dynamical matrix. (ii) The LDA functional was substituted by the more sophisticated GGA (Generalized Gradient Approximation) functional. (iii) Within the LDA approach the three lattice parameters a, b, c were fully optimized prior to the set up of the dynamical matrix. As a by-product, this process of optimization enabled us to calculate the pressure dependence of the A_{1g} frequencies and the bulk modulus of YBCO7. An overall aspect in all these investigations was the careful exclusion of shortcomings due to poor convergence in the band structure calculations. The **k**-point sampling in the Brillouin zone and the number of LAPW basis functions included in the eigenvalue problem were of particular concern.

The results are published in the appended papers. The basic topics of each publication can be summarized as follows:

P1 The eigenvectors and eigenfrequencies of the five A_{1g} modes are calculated on the basis of experimental lattice constants using atomic-force data obtained within the LAPW method. Exchange and correlation effects are treated within the LDA.

P2 The improvements obtained in the calculated frequency values of the A_{1g} modes due to the employment of a GGA potential are presented.

P3 A detailed investigation into the effect of GGA on the A_{1g} modes is performed. An analysis of atomic-force data as well as a comparative study to the results based on LDA calculations is presented.

P4 Certain elements of the dynamical matrix resulting from GGA calculations are directly compared to values obtained from isotope-substitution experiments. In this context, experimentally determined mode admixtures are verified. In a second section of the paper, a model calculation for the temperature dependence of the 500 cm^{-1} mode based on an ab-initio calculation of the dielectric tensor is presented.

P5 The relation between the effect of overbinding caused by the LDA and the vibronic properties of YBCO7 is investigated. For this purpose the A_{1g} modes are calculated for a unit-cell volume which lies three percent below the experimental one.

P6 A full optimization with regard to lattice parameters and internal coordinates is performed for YBCO7. At the thus obtained equilibrium structure the A_{1g} phonons are calculated and compared to experiment. Further on, the volume coefficients of the phonons, the bulk modulus and the changes in the Fermi surface are studied for this 'LDA-consistent' structural parameters.

P7 The influence of pressure on phonons and structural parameters (bond length, lattice parameters) is investigated.

P8 The frequencies of the B_{2g} and B_{3g} modes are calculated for the optimized structural parameters and compared to experimental values. In a second section, the oxygen ordering in $YBa_2Cu_3O_{6.5}$ is studied by means of Monte-Carlo simulations based on ab-initio total energy calculations.

P9 First-principles Raman studies for the A_{1g} modes calculated for the optimized lattice parameters as well as the complete eigenvector composition of the B_{2g} and B_{3g} modes are presented.

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List of publications

1. Claudia Ambrosch-Draxl, Robert Abt, and Robert Kouba
   Optical properties of $YBa_2Cu_3O_{7-x}$ determined from full potential LAPW calculations
   Physica C 235-240, 2119 (1994)
2. R. Kouba, R. Abt and C. Ambrosch-Draxl
   Electronic and optical properties of the $YBa_2Cu_3O_{6.5}$ ortho-II structure from density functional calculations
   Physics and Material Sciences of High Temperature Superconductors III (in print)
3. R. Abt, R. Kouba, and C. Ambrosch-Draxl
   Electronic properties of $YBa_2Cu_3O_{6.5}$ compared to $YBa_2Cu_3O_7$
   Proceedings of the International Workshop on Anharmonic Properties of High-Tc Cuprates, Eds.:D. Mihailovic, G. Ruani, E. Kaldis, K. A. Müller (1994)
4. Bernd Kohler, Steffen Wilke, Matthias Scheffler, Robert Kouba, and Claudia Ambrosch-Draxl
   Force calculations and atomic-structure calculations for the full-potential linearized augmented plane-wave code WIEN
   Comp. Phys. Commun. 94, 31 (1996)
5. R. Kouba, R. Abt, and C. Ambrosch-Draxl
   A_{1g} phonons in $YBa_2Cu_3O_7$ by first-principles atomic-force calculations
   Czech. J. Phys., Suppl. 2, 46, 923 (1996)

6. R. Kouba and C. Ambrosch-Draxl
   Theoretical investigations of structural and vibronic properties of $YBa_2Cu_3O_7$ by first-principles atomic-force calculations
   Physica C 282-287, 1635 (1997)

7. R. Kouba and C. Ambrosch-Draxl
   Investigations of A_{1g} phonons in $YBa_2Cu_3O_7$ by means of linearized-augmented-plane-wave atomic-force calculations
   Phys. Rev. B 56, 14766 (1997)

8. C. Ambrosch-Draxl, R. Kouba, and P. Knoll
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   Z. Phys. B 104, 687 (1997)

9. R. Kouba and C. Ambrosch-Draxl
   Volume dependence of the A_{1g} phonons in $YBa_2Cu_3O_7$
   Z. Phys. B 104, 777 (1997)

10. R. Kouba and C. Ambrosch-Draxl
    Structure optimization of $YBa_2Cu_3O_7$ and its influence on phonons and Fermi surface
    Phys. Rev. B 60, 9321 (1999)

11. C. Ambrosch-Draxl and R. Kouba
    Pressure study of structural properties and phonons in $YBa_2Cu_3O_7$
    Journal of Low Temp. Physics, (in print)

12. R. Kouba, C. Ambrosch-Draxl, P. A. Korzhavyi, and B. Johansson
    First-principles investigations of structural properties, phonons, and vacancy ordering in $YBa_2Cu_3O_{7-x}$
    Proceedings of the *First regional conference on magnetic and superconducting materials,*Tehran 1999, (in print)

13. H. Auer, R. Kouba, and C. Ambrosch-Draxl
    First-principles Raman studies on $YBa_2Cu_3O_7$
    submitted to Physica C

14. H. Auer, C. Ambrosch-Draxl, E. Y. Sherman, and R. Kouba
    Theory of isotope effects in Raman spectra
    submitted to Physica C

Summary

This thesis is concerned with two aspects of the frozen-phonon technique – an ab-initio method to study the lattice dynamics of a crystal.

In the first part of the work a complete formulation of the iterative linear-response (ILR) scheme for crystalline solids within the framework of the linearized augmented plane-wave (LAPW) method is presented. It serves to calculate frequencies and eigenvectors of lattice vibrations (phonons). In terms of practical applications it is equally amenable to high- and low-symmetry **q**-vectors characterizing the phonon. The scheme is based on the application of first-order perturbation theory to the Kohn-Sham orbitals where the perturbing potential is the dipole field generated by the phonon-induced displacements of the nuclear point charges. The self-consistency between the charge response of the electronic system and the total change of the crystal potential is obtained via an iteration process. To link the thus obtained first-order changes of the potential, the density distribution and the Kohn-Sham orbitals to the dynamical matrix the concept of first-order atomic forces is used. The formulation of the scheme is very much designed to adapt and extend the merits of available practical realizations of the traditional LAPW method. In this respect analytical expressions are provided which are well suited for a direct implementation into existing ground-state all-electron LAPW band structure programs. The charge response of valence as well as core electrons is fully taken into account. Of particular importance is the development of efficient algorithms which reduce the complexity of specific aspects related to the calculation of the first-order Hamiltonian and overlap matrices.

In the second part of this thesis I present first-principles frozen-phonon calculations of the 15 Raman-active modes in the high temperature superconductor $YBa_2Cu_3O_7$. In order to obtain detailed and reliable information on the shape of the underlying energy surface a large number of highly converged atomic-force values is extracted from the related band

structure calculations. By employing different functionals to treat exchange and correlation effects the origins of deviations between calculated phonon quantities (frequencies and eigenvectors) and their experimentally determined counterparts are investigated. Calculations based on the traditional local-density-approximation (LDA) functional which are performed at experimental lattice constants yield frequency values approximately 10% below the experimental data. In this respect it is then found that the application of the generalized gradient approximation (GGA) particularly improves the frequencies of the Ba-Cu dominated A_{1g} modes significantly. In contrast to previous work done in this field a perfect description of the eigenvector composition of these modes is also achieved. The deviations between theory and experiment are then alternatively investigated by a full optimization of the structural parameters (internal coordinates and lattice constants) prior to the frozen-phonon calculations. In this approach an LDA functional is used. This optimization provides a theoretical framework in which an overall excellent agreement between theoretically and experimentally determined frequency values is obtainable.