Linear-response theory for the calculation of electron-phonon coupling within the LAPW method

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Abstract

Linear-response (LR) theory in combination with first-principles band structure codes allows to calculate phonons and electron-phonon interaction in an efficient way. We provide a formalism which enables us to apply LR theory within an all-electron framework utilizing the the full-potential linearized augmented plane-wave (LAPW) method. For the electron-phonon coupling matrix elements we have included all correction terms, which are either arising due to the variational solution of the Kohn-Sham equations or due to the LAPW specific basis set. The method is applied to bcc sulfur and hcp beryllium and shows excellent agreement with data obtained by the supercell approach.

INTRODUCTION

The coupling strength of the non-adiabatic interaction between electrons and lattice vibrations is an important quantity for the description of fundamental physical properties of a solid. In conjunction with the features of the phonon spectra it determines the electrical and thermal conductivity and quantifies the pairing mechanism in conventional superconductors. Therefore phonons and their interaction with the electronic subsystem have been the subject of many experimental investigations. Theoretically, the precise calculation of phonon frequencies and electron-phonon coupling constants essentially requires the knowledge of changes in the effective crystal potential upon small displacements of the atoms. This deformation potential can be obtained on an ab-initio basis using first-principles calculations based on density functional theory (DFT) [1, 2]. Within this framework two methodical procedures have been developed: In the first approach, the deformation potential is determined by interpolating potential values for at least two self-consistent calculations: one for the unperturbed system, and a second one for a unit-cell (*supercell*) which is commensurate with the $\mathbf{q}$-vector and consists of a frozen-in displacement pattern of the atoms along the eigenvector of the considered phonon. This method is very demanding in terms of computer-time, especially for complex structures (large number of atoms per unit cell) and for phonons with a non-zero, low-symmetry $\mathbf{q}$-vector. The bottle-neck lies in the determination of the Kohn-Sham states where the computational effort to solve the corresponding eigenvalue problem scales roughly with the third power of the size of the supercell. An alternative scheme is the self-consistent iterative linear-response (LR) approach, which makes use of the fact that the deformation potential is a first-order quantity in perturbation theory taking the self-consistent crystal potential as a function of the atomic positions. The main advantage of the latter scheme, which will be discussed in more detail below, lies in the fact that the required computational effort is almost independent of the $\mathbf{q}$-vector considered.

So far, electron-phonon coupling constants for a few materials have been obtained using either supercell calculations [3, 4, 5, 6, 7, 8, 9, 10] or the iterative LR-approach [11, 12, 13, 14]. Many of these calculations have been carried out within the pseudopotential method, whereas only a few works used all-electron methods, where the charge distribution in the vicinity of the nuclei is fully included in the self-consistency cycle. The crucial advantage of the latter schemes is the treatment of localized and delocalized states on the same footing. We thus have the capacity to reliably describe materials (partially) composed of heavy atoms. Due to this fact the employment of such methods is important for the theoretical study of many materials, which range from simple elemental superconductors, like Hg, Bi, or Pb, to the complex high T_c compounds. The lack of LR investigations within all-electron methods is due to the fact that they require a complex apparatus of formulas which necessitates efficient analytical and numerical tools for their evaluation. In these cases the associated programming work is also quite a tremendous and time-consuming task. The origin for the increased complexity is founded in the site-dependence of the basis sets used in all-electron methods (LMTO, LAPW, etc.). This fact introduces correction terms when a variational solution is constructed for the first-order changes in the electronic eigenstates. Furthermore, similarly to the expression for the atomic forces [15, 16, 17], the traditional electron-phonon matrix element also has to be supplemented by these incomplete-basis-set (IBS) corrections [12].

Although the LR formalism for the calculation of phonon frequencies has been worked out within the linearized augmented plane-wave (LAPW) method [18] and applied to simple materials and the high temperature superconductor La_2CuO_4 [19], it has only been used on the basis of pseudopotentials and for the determination of phonon frequencies and eigenvectors. Concerning electron-phonon matrix elements within LAPW only few data are published [4, 6]. Methodically, the deformation potential was extracted from supercell calculations and the correction terms were not included in the evaluation of the electron-phonon matrix elements [6].

In this work, we present phonon frequencies, and electron-phonon coupling constants obtained from LR theory within the LAPW method. We provide a formalism which allows us to employ LR theory within an all-electron approach.

For the electron-phonon coupling matrix elements we do not only include corrections for the matrix elements following the theoretical framework proposed by Savrasov [12] but also account for the fact that the LAPW basis functions are only continuous up to the first derivative. Our LR results are compared to data obtained by the supercell approach and show excellent agreement.

The paper is organized as follows. In the first part, the theoretical framework is provided. A short review of the variational method to obtain the single particle electronic states is presented in order to introduce the terminology of the LAPW method . In Section we first give an overview of the main ideas and equations governing the iterative linear-response scheme. We generally follow Ref. [18] but focus on the differences to that work which make the calculation easier and allow to perform all-electron calculations. We present a complete set of numerically efficient and analytically simple formulas within the LAPW-method to calculate the first-order change of the electronic states in response to an applied frozen-in phonon displacement. In a next step, we extent the LR formalism to the concept of electron-phonon coupling. In Section we formulate the expressions for the coupling constant within the LAPW basis set including all necessary correction terms to the traditional formulas. In the second part, we present selected results for some test systems. In particular, we applied the LR formalism to the study of the zone-center phonon with the displacement pattern polarized along the z-axis of hcp Be, and of the transversal phonon branch along $\mathbf{q} = [0\ 0\ \xi]$ of bcc sulfur under high pressure. A more elaborate description of the formalism can be found in Ref. [21].

Theory

Basics of the LAPW method

In bandstructure calculations based on density-functional theory [1] the single-particle electronic states $\Psi_{n\mathbf{k}}(\mathbf{r})$ and energies $\varepsilon_{n\mathbf{k}}$ are described by the solutions of the Kohn-Sham (KS) equation [2]

$$\left[-\nabla^2 + V_{eff}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r}) \tag{5}$$

with the effective potential $V_{eff}(\mathbf{r})$ being the sum of the bare Coulomb potential of the atomic nuclei $V_{nuc}(\mathbf{r})$, the Hartree potential $V_H(\mathbf{r})$ and the exchange correlation potential $V_{xc}(\mathbf{r})$. In practical calculations, Eq. (5) is solved via the Rayleigh-Ritz variational principle. In this

procedure the electronic states $\Psi_{n\mathbf{k}}(\mathbf{r})$ (KS-orbitals) are first expanded in terms of a physically appropriate finite set of basis functions $\{\phi_{\mathbf{k}+\mathbf{G}}\}$,

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G})\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \tag{6}$$

with $\mathbf{G}$ and $C_{n\mathbf{k}}(\mathbf{G})$ denoting a reciprocal space vector and the corresponding variational coefficient, respectively. To determine $C_{n\mathbf{k}}(\mathbf{G})$ the ansatz (6) is inserted into Eq. (5) followed by the minimization of the total crystal energy with respect to the variational coefficients. The eigenvectors and eigenvalues of the resulting matrix equation,

$$\sum_{\mathbf{G}'}(H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}}S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'})C_{n\mathbf{k}}(\mathbf{G}') = 0, \qquad \mathbf{k} \in \text{BZ} \tag{7}$$

with

$$H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \equiv \langle \phi_{\mathbf{k}+\mathbf{G}}| - \nabla^2 + V_{eff} |\phi_{\mathbf{k}+\mathbf{G}'}\rangle_{\Omega} \tag{8}$$

$$S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \equiv \langle \phi_{\mathbf{k}+\mathbf{G}} |\phi_{\mathbf{k}+\mathbf{G}'}\rangle_{\Omega} \tag{9}$$

denoting Hamilton and overlap matrix, respectively, finally provide the numerical values for $C_{n\mathbf{k}}(\mathbf{G})$ and $\varepsilon_{n\mathbf{k}}$. Ω is the volume of the unit cell. In the LAPW-method is partitioned into an interstitial region (Int) and non-overlapping muffin-tin spheres (MT_{α}) centered on the atomic nuclei. The corresponding basis functions are defined as,

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \ \mathbf{r} \in \text{Interstitial} \tag{10}$$

and

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_{\alpha} + \mathbf{r}) = \sum_{lm}[A_{lm}^{\alpha}(\mathbf{k} + \mathbf{G})u_l^{\alpha}(r) + B_{lm}^{\alpha}(\mathbf{k} + \mathbf{G})\dot{u}_l^{\alpha}(r)]Y_{lm}(\hat{\mathbf{r}}), \quad |\mathbf{r}| \leq R_{\alpha}, \tag{11}$$

where $\mathbf{S}_{\alpha}$ denotes the position vector of the atomic nucleus α. The radius of the corresponding muffin-tin sphere is R_{α}. The product of the spherical harmonic $Y_{lm}(\hat{\mathbf{r}})$ and the radial function $u_l^{\alpha}(r)$ is the solution of the Schrödinger equation for a spherical symmetric potential where the eigenvalue has been replaced by an appropriate energy parameter [20] . The second radial function $\dot{u}_l^{\alpha}(r)$ is the derivative of the first one with respect to the energy. The coefficients $A_{lm}^{\alpha}(\mathbf{k} + \mathbf{G})$ and $B_{lm}^{\alpha}(\mathbf{k} + \mathbf{G})$ are determined for each atom by imposing two requirements. Firstly, the values of the plane-wave (10) and the atomic-orbital like function (11) have to match each other on the surface of the muffin-tin sphere. Secondly, the same has to be true for the values of the first spatial derivatives of the two functions. For later considerations it is important to mention that the second derivative of the LAPW basis functions are discontinuous on the MT-surfaces.

Using the definitions (10) and (11), the overlap and Hamilton matrix within the LAPW formalism will schematically be calculated the following way [22]:

$$S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} = \sum_{\beta} S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}^{MT_{\beta}} + S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}^{Int} \tag{12}$$

$$H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} = \sum_{\beta} H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}^{MT_{\beta}} + H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}^{Int} \tag{13}$$

with

$$S^{MT_\beta}_{\mathbf{k+G,k+G'}} \quad = \quad \langle \phi_{\mathbf{k+G}} | \phi_{\mathbf{k+G'}} \rangle_{MT_\beta} \tag{14}$$

$$S^{Int}_{\mathbf{k+G,k+G'}} \quad = \quad \delta_{\mathbf{k+G,k+G'}} (1 - \sum_\beta \frac{4\pi}{3\Omega} R^3_\beta)$$

$$- (1 - \delta_{\mathbf{k+G,k+G'}}) \sum_\beta \langle \tilde{\phi}_{\mathbf{k+G}} | \tilde{\phi}_{\mathbf{k+G'}} \rangle_{MT_\beta} \tag{15}$$

$$H^{MT_\beta}_{\mathbf{k+G,k+G'}} \quad = \quad \langle \phi_{\mathbf{k+G}} | -\nabla^2 + V_{eff} | \phi_{\mathbf{k+G'}} \rangle_{MT_\beta} \tag{16}$$

$$H^{Int}_{\mathbf{k+G,k+G'}} \quad = \quad (\mathbf{k+G'})^2 S^{Int}_{\mathbf{k+G,k+G'}} + \sum_{\mathbf{K}} V(\mathbf{K}) S^{Int}_{\mathbf{k+K,k+G-G'}}. \tag{17}$$

For the calculation of the H- and S-matrix in the interstitial region the function $\tilde{\phi}_{\mathbf{k+G}}(\mathbf{r})$ has been introduced. It describes a plane-wave defined in the entire unit cell,

$$\tilde{\phi}_{\mathbf{k+G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k+G})\mathbf{r}}, \quad \mathbf{r} \in \Omega. \tag{18}$$

For the explicit evaluation of (16) and (17) an appropriate dual representation of the effective potential is needed. In the spheres the potential is expanded into spherical harmonics and in the interstitial it is represented by a Fourier series:

$$V_{eff}(\mathbf{S}_\alpha + \mathbf{r}) \quad = \quad \sum_{LM} V^\alpha_{LM}(r) Y_{LM}(\hat{\mathbf{r}}), \quad |\mathbf{r}| \le R_\alpha, \tag{19}$$

$$V_{eff}(\mathbf{r}) \quad = \quad \sum_{\mathbf{K}} V(\mathbf{K}) e^{i\mathbf{Kr}}, \quad \mathbf{r} \in \text{Int}. \tag{20}$$

A short review about linear-response to phonon displacements

The atomic displacement pattern representing a lattice vibration at wave vector $\mathbf{q}$, i.e.

$$\delta \mathbf{S}^{\mathbf{T}}_\alpha \quad = \quad \delta^+ \mathbf{S}_\alpha e^{i\mathbf{qT}} + \delta^- \mathbf{S}_\alpha e^{-i\mathbf{qT}}$$

$$= \quad \delta^+ \mathbf{S}_\alpha e^{i\mathbf{qT}} + [\delta^+ \mathbf{S}_\alpha]^* e^{-i\mathbf{qT}} \tag{21}$$

can be viewed as a superposition of a forward and backward travelling wave. Real-space lattice vectors are denoted by $\mathbf{T}$, and $\delta^+ \mathbf{S}_\alpha$ is a small possibly complex polarization vector. Thus the displaced position vector of an atom α in unit cell $\mathbf{T}$ will be $\mathbf{T} + \mathbf{S}_\alpha + \delta \mathbf{S}^{\mathbf{T}}_\alpha$. Within density-functional perturbation theory (DFPT) [23] this superposition of phonon displacements can be viewed as a static first-order perturbation acting on the electronic system [24, 25]. The knowledge of the corresponding first-order response of the electronic charge distribution $\delta^+ \rho(\mathbf{r})$, the effective potential $\delta^+ V_{eff}(\mathbf{r})$ and the KS-orbitals $\delta^+ \Psi_{n\mathbf{k}}(\mathbf{r})$ is essential for setting up the dynamical matrix at wavevector $\mathbf{q}$ and to determine the coupling strength for the electron-phonon interaction. To calculate these first-order quantities, a linear-response scheme has been developed [26, 27] which relies on the iterative solution of the following three equations:

$$\delta^+ V_{eff}(\mathbf{r}) = \delta^+ V_{nuc}(\mathbf{r}) + \int \frac{\delta^+ \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r'}|} d^3 r' + \delta^+ \rho(\mathbf{r}) \left. \frac{dV_{xc}}{d\rho} \right|_{\rho(\mathbf{r})} \tag{22}$$

$$(-\nabla^2 + V_{eff}(\mathbf{r}) - \varepsilon_{n\mathbf{k}})\delta^+ \Psi_{n\mathbf{k}}(\mathbf{r}) = -\delta^+ V_{eff}(\mathbf{r}) \Psi_{n\mathbf{k}}(\mathbf{r}) \qquad (23)$$

$$\delta^+ \rho(\mathbf{r}) = 2 \sum_{n\mathbf{k}} w(n, \mathbf{k}) \delta^+ \Psi_{n\mathbf{k}}(\mathbf{r}) \Psi^*_{n\mathbf{k}}(\mathbf{r}). \qquad (24)$$

In the current description the local-density approximation is assumed for the exchange-correlation potential. The orbital occupation number is denoted by $w(n, \mathbf{k})$ and the term containing $\delta\varepsilon_{n\mathbf{k}}$ has been dropped in Eq. (23). This is justified by the fact that the change in the eigenvalue is zero for non-zero $\mathbf{q}$-values [18, 28]. It is worth mentioning that in accordance with the applied lattice vibrational pattern (21) the translational behaviour of the first-order effective potential will read

$$\delta^+ V_{eff}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{qT}} \delta^+ V_{eff}(\mathbf{r}). \qquad (25)$$

It is then straightforward to see from the Sternheimer equation (23) that the first-order KS-orbital will be a Bloch wave of wave vector $\mathbf{k} + \mathbf{q}$.

When we come to the practical realization of this iterative linear-response scheme the main challenge lies in the construction of an efficient variational solution of the Sternheimer equation. The complexity of this task depends on the basis set used in the unperturbed bandstructure calculation. In the case of plane-waves the change in the wave function can entirely be traced back to the change in the variational coefficient [26], and one obtains the corresponding matrix form of the Sternheimer equation:

$$\sum_{\mathbf{G'}} (H_{\mathbf{k+q+G},\mathbf{k+q+G'}} - \varepsilon_{n\mathbf{k}} \delta_{\mathbf{G},\mathbf{G'}}) \delta^+ C_{n\mathbf{k}}(\mathbf{G'}) = -\sum_{\mathbf{G'}} \delta H_{\mathbf{k+q+G},\mathbf{k+G'}} C_{n\mathbf{k}}(\mathbf{G'}), \qquad (26)$$

with

$$\delta H_{\mathbf{k+q+G},\mathbf{k+G'}} = \left\langle \phi_{\mathbf{k+q+G}} \left| \delta^+ V_{eff} \right| \phi_{\mathbf{k+G'}} \right\rangle. \qquad (27)$$

Using position dependent basis sets (LMTO, LAPW, etc.), however, the situation is much more complicated as demonstrated by Savrasov [28] and Yu et al. [18]. To account for the change in the basis functions due to the shift of the atomic nuclei the first-order wave function has to be expanded in the original basis set supplemented by a physically appropriate ansatz for the change in the basis functions. Within this framework it can then be shown that the Sternheimer equation will read:

$$\sum_{\mathbf{G'}} (H_{\mathbf{k+q+G},\mathbf{k+q+G'}} - \varepsilon_{n\mathbf{k}} S_{\mathbf{k+q+G},\mathbf{k+q+G'}}) \delta^+ C_{n\mathbf{k}}(\mathbf{G'})$$
$$= -\sum_{\mathbf{G'}} [\delta H_{\mathbf{k+q+G},\mathbf{k+G'}} - \varepsilon_{n\mathbf{k}} \delta S_{\mathbf{k+q+G},\mathbf{k+G'}}] C_{n\mathbf{k}}(\mathbf{G'}), \qquad \mathbf{k} \in \text{BZ} \qquad (28)$$

with

$$\delta H_{\mathbf{k+q+G},\mathbf{k+G'}} = \left\langle \phi_{\mathbf{k+q+G}} \left| \delta^+ \hat{H} \right| \phi_{\mathbf{k+G'}} \right\rangle +$$
$$\left\langle \delta^- \phi_{\mathbf{k+q+G}} \left| \hat{H} \right| \phi_{\mathbf{k+G'}} \right\rangle + \left\langle \phi_{\mathbf{k+q+G}} \left| \hat{H} \right| \delta^+ \phi_{\mathbf{k+G'}} \right\rangle \qquad (29)$$
$$\delta S_{\mathbf{k+q+G},\mathbf{k+G'}} = \left\langle \delta^- \phi_{\mathbf{k+q+G}} \middle| \phi_{\mathbf{k+G'}} \right\rangle + \left\langle \phi_{\mathbf{k+q+G}} \middle| \delta^+ \phi_{\mathbf{k+G'}} \right\rangle \qquad (30)$$

Handling LAPW specific terms

We will now formulate a scheme to explicitly calculate the first-order matrices appearing on the right-hand side of Eq. (28). The scheme is particularly designed to adapt and extend the merits of available practical realizations of the LAPW method in the unperturbed case as given by Eqs. (12) and (13). To start with, we review the ansatz for the change in the basis function due to the shift of the atomic nuclei. The coordinate system refers to the unperturbed situation. As Yu et al.[18] have shown, $\delta^{\pm}\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})$ is only non-vanishing inside the MT-spheres and within the rigid-muffin tin orbital approximation will read:

$$\delta^{\pm}\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \quad \equiv \quad \frac{\partial\phi_{\mathbf{k}+\mathbf{G}}}{\partial\{\delta\mathbf{S}\}}\delta^{\pm}\mathbf{S} = -\sum_{\alpha}[\nabla\phi_{\mathbf{k}+\mathbf{G}}^{\alpha}(\mathbf{r})]\delta^{\pm}\mathbf{S}_{\alpha} +$$
$$\sum_{\alpha}i[(\mathbf{k}+\mathbf{G})\delta^{\pm}\mathbf{S}_{\alpha}]\phi_{\mathbf{k}+\mathbf{G}}^{\alpha}(\mathbf{r}) \tag{31}$$

The first term describes a rigid shift of the orbital parts of the LAPW basis function centered on the nuclei and the second term results from the fact that due to the shift of the atomic sphere the matching parameters A_{lm} and B_{lm} change by the phase factor $e^{i(\mathbf{k}+\mathbf{G})\delta^{\pm}\mathbf{S}_{\alpha}}$. In a second step, we provide an appropriate description of the change in the total effective potential again with respect to the unperturbed MT-spheres and interstitial region. Within the atomic spheres $\delta^{\pm}V_{eff}^{\alpha}(\mathbf{r})$ will read:

$$\delta^{\pm}V_{eff}^{\alpha}(\mathbf{r}) = \underbrace{\sum_{LM}\delta^{\pm}\breve{V}_{LM}^{\alpha}(r')Y_{LM}(\hat{\mathbf{r}}')}_{\equiv\delta^{\pm}\breve{V}_{eff}^{\alpha}(\mathbf{r}')} - \delta^{\pm}\mathbf{S}_{\alpha}\nabla V_{eff}^{\alpha}(\mathbf{r}) \qquad |r'| \leq R_{\alpha}, \tag{32}$$

where $\mathbf{r} = \mathbf{S}_{\alpha} + \mathbf{r}'$. The first term on the right hand side of Eq. (32) is the 'soft' contribution [6, 17] to the change in the effective potential. It represents the first-order difference between the effective potentials evaluated at point $\mathbf{r} = \mathbf{S}_{\alpha} + \delta^{\pm}\mathbf{S}_{\alpha} + \mathbf{r}'$ 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 again originates from the fact that the atomic sphere has been rigidly shifted by the position vector $\delta^{\pm}\mathbf{S}_{\alpha}$. In the interstitial region, where plane-waves are the natural choice of basis functions, $\delta^{\pm}V_{eff}^{int}(\mathbf{r})$ is:

$$\delta^{\pm}V_{eff}^{int}(\mathbf{r}) = \sum_{\mathbf{K}}\delta^{\pm}V_{eff}(\mathbf{K}+\mathbf{q})e^{i(\mathbf{K}+\mathbf{q})\mathbf{r}}. \tag{33}$$

The following should be noted: The dual representation (32) and (33) does not account for the switch of the character of basis functions in those regions of the unit cell where the interstitial region (sphere region) of the unperturbed crystal overlaps with the sphere regions (interstitial region) of the phonon-induced configuration. In fact the same is true for the ansatz (31). Nevertheless, as long as the basis sets are interchangeable in these overlapping regions (implying a small polarization vector) the accuracy of the linear-response calculation is only negligibly influenced by this approximation. When compared to the analytically complete representation [6] the advantage of (32) and (33) mainly lies in its applicability to all-electron bandstructure calculations where the Coulomb-singularity is fully taken into account.

We have now established all necessary representations of wave-functions, potentials and their respective first-order counterparts to evaluate the following matrix elements expressed in

terms of the LAPW method [18]:

$$
\begin{aligned}
&\delta H_{\mathbf{k+q+G,k+G'}} - \varepsilon_{n\mathbf{k}}\delta S_{\mathbf{k+q+G,k+G'}} \\
&= \underbrace{\left\langle \phi_{\mathbf{k+q+G}} \left| \delta^+ V_{eff}(\mathbf{r}) \right| \phi_{\mathbf{k+G'}} \right\rangle_\Omega}_{R1} \\
&\quad + \underbrace{\left\langle \frac{\partial \phi_{\mathbf{k+q+G}}}{\partial \delta \mathbf{S}}(\delta^+\mathbf{S})^* \left| \hat{H} \right| \phi_{\mathbf{k+G'}} \right\rangle_{MT}}_{R2} \\
&\quad + \underbrace{\left\langle \phi_{\mathbf{k+q+G}} \left| \hat{H} \right| \frac{\partial \phi_{\mathbf{k+G'}}}{\partial \delta \mathbf{S}}\delta^+\mathbf{S} \right\rangle_{MT}}_{R3} \\
&\quad - \varepsilon_{n\mathbf{k}} \underbrace{\left\langle \frac{\partial \phi_{\mathbf{k+q+G}}}{\partial \delta \mathbf{S}}(\delta^+\mathbf{S})^* | \phi_{\mathbf{k+G'}} \right\rangle_{MT}}_{R4} \\
&\quad - \varepsilon_{n\mathbf{k}} \underbrace{\left\langle \phi_{\mathbf{k+q+G}} | \frac{\partial \phi_{\mathbf{k+G'}}}{\partial \{\delta \mathbf{S}\}}\delta^+\mathbf{S} \right\rangle_{MT}}_{R5} \\
&\quad + \underbrace{\delta^+ \left\langle \phi_{\mathbf{k+q+G}} \left| \hat{T} \right| \phi_{\mathbf{k+G'}} \right\rangle}_{R6}
\end{aligned}
\tag{34}
$$

with

$$
\begin{aligned}
\delta^+ \left\langle \phi_{\mathbf{k+q+G}} \left| \hat{T} \right| \phi_{\mathbf{k+G'}} \right\rangle &\equiv \sum_\alpha \delta^+\mathbf{S}_\alpha \oint_{MT_\alpha} [\phi^{*\alpha}_{\mathbf{k+q+G}}(\mathbf{r})\nabla^2 \phi^\alpha_{\mathbf{k+G'}}(\mathbf{r})|_{MT_\alpha} \\
&\quad - \phi_{\mathbf{k+q+G}}(\mathbf{r})\nabla^2 \phi_{\mathbf{k+G'}}(\mathbf{r})|_{Int}]d\mathbf{A}_\alpha,
\end{aligned}
\tag{35}
$$

representing the contribution stemming from the discontinuous behaviour of the second derivative of the LAPW basis functions on the surface of the atomic sphere [15, 16]. The abbreviations MT_α and Int indicate that in the respective surface integral $(\oint_{MT_\alpha} d\mathbf{A}_\alpha)$ over the kinetic energy term the basis functions appropriate for the denoted region have to be used. Inserting (33),(32),(31),(11) and (10) into (34) immediately simplifies many of the matrix elements and in fact expresses them through formulas which are structurally very similar to the expressions describing the unperturbed H- and S-matrix:

$$
\begin{aligned}
&\delta H_{\mathbf{k+q+G,k+G'}} - \varepsilon_{n\mathbf{k}}\delta S_{\mathbf{k+q+G,k+G'}} \\
&= \sum_{\mathbf{K}} \delta^+ V_{eff}(\mathbf{K+q}) S^{Int}_{\mathbf{k+K,k+G-G'}} + \sum_\alpha \left\langle \phi_{\mathbf{k+q+G}} \left| \delta^+ \check{V}_{eff} \right| \phi_{\mathbf{k+G'}} \right\rangle_{MT_\alpha} \\
&\quad + \sum_\alpha i[(\mathbf{G'-G-q})\delta^+\mathbf{S}_\alpha][H^{MT_\alpha}_{\mathbf{k+q+G,k+G'}} - \varepsilon_{n\mathbf{k}}S^{MT_\alpha}_{\mathbf{k+q+G,k+G'}}] \\
&\quad - \sum_\alpha \delta^+\mathbf{S}_\alpha \oint_{MT_\alpha} \phi^*_{\mathbf{k+q+G}}(\mathbf{r})V_{eff}(\mathbf{r})\phi_{\mathbf{k+G'}}(\mathbf{r})|_{MT_\alpha}d\mathbf{A}_\alpha \\
&\quad - \varepsilon_{n\mathbf{k}}\sum_\alpha \delta^+\mathbf{S}_\alpha \oint_{MT_\alpha} \phi^*_{\mathbf{k+q+G}}(\mathbf{r})\phi_{\mathbf{k+G'}}(\mathbf{r})|_{MT_\alpha}d\mathbf{A}_\alpha \\
&\quad - \sum_\alpha \delta^+\mathbf{S}_\alpha \oint_{MT_\alpha} \phi^*_{\mathbf{k+q+G}}(\mathbf{r})\nabla^2 \phi_{\mathbf{k+G'}}(\mathbf{r})|_{Int}d\mathbf{A}_\alpha
\end{aligned}
\tag{36}
$$

To obtain the fourth and fifth term on the right hand side of Eq. (36) the chain rule of the gradient operator with regard to the product of the wave functions and the effective potential as well as

the Gauss theorem to transfer the volume- to a surface integral has been used. Based on a similar procedure the kinetic energy terms of the matrix elements $R2$ and $R3$ involving the gradients of the wave function have been combined with the discontinuity term $R6$ to arrive at the last term of the right hand side of Eq. (36). Utilizing the muffin-tin representations for the wave functions and the potential in term four and five on the right hand side of Eq. (36) would result in rather cumbersome summations over Gaunt-coefficients. To avoid the complexity of the corresponding formulas we exploit the fact that the wave functions and potentials are continuous in value and slope on the sphere surface. In this way we can substitute the muffin-tin representation by the plane-wave representation and then apply the Gauss theorem to back-transfer the surface to a volume integral. Thus, we obtain analytic expressions involving plane-wave integrals over the sphere volumes. These expressions already appeared in the unperturbed overlap-matrix (Eq. (15)) and are easy to program. We explicitly demonstrate the whole idea for the change in the overlap matrix appearing in the fifth term of the right hand side of Eq. (36):

$$
\begin{aligned}
&\sum_\alpha \delta^+ \mathbf{S}_\alpha \oint_{MT_\alpha} \phi^*_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{MT_\alpha} d\mathbf{A}_\alpha \\
=\ &\sum_\alpha \delta^+ \mathbf{S}_\alpha \oint_{MT_\alpha} \phi^*_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{Int} d\mathbf{A}_\alpha \\
=\ &\sum_\alpha \delta^+ \mathbf{S}_\alpha \frac{1}{\Omega} \int_{MT_\alpha} \nabla[e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}}]d^3\mathbf{r} \\
=\ &\sum_\alpha (\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta^+\mathbf{S}_\alpha \langle \tilde{\phi}_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \big| \tilde{\phi}_{\mathbf{k}+\mathbf{G}'}\rangle_{MT_\alpha} \equiv \delta S^{Int}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \quad (37)
\end{aligned}
$$

Similarly line (36) and (36) simplify to:

$$
\begin{aligned}
&\sum_\alpha \delta^+\mathbf{S}_\alpha \oint_{MT_\alpha} \phi^*_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})V_{eff}(\mathbf{r})\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{MT_\alpha} d\mathbf{A}_\alpha \\
=\ &\sum_\mathbf{K} V_{eff}(\mathbf{K})\delta S^{Int}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+(\mathbf{G}'+\mathbf{K})} \quad (38)
\end{aligned}
$$

and

$$
\begin{aligned}
&\sum_\alpha \delta^+\mathbf{S}_\alpha \oint_{MT_\alpha} \phi^*_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\nabla^2\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{Int} d\mathbf{A}_\alpha \\
=\ &|\mathbf{k}+\mathbf{G}'|^2 \delta S^{Int}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \quad (39)
\end{aligned}
$$

To reach a high efficiency in terms of computer time, formula (38) should be evaluated by the use of Fast-Fourier transforms (FFT) routines in a similar way [29] as it is done for the interstitial parts of the unperturbed matrices [22].

Electron-phonon coupling

Conventionally, the scattering process of an electron from state $\Psi_{n\mathbf{k}}$ to $\Psi_{m\mathbf{k}+\mathbf{q}}$ via a phonon of wavevector $\mathbf{q}$, frequency $\omega_{\mathbf{q}j}$ and eigenvector $\mathbf{e}_{\mathbf{q}j}$ is described by the electron-phonon matrix element

$$
g^{\mathbf{q}j}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \left\langle \Psi_{m\mathbf{k}+\mathbf{q}} \left| \sum_{\alpha=1}^{N}\sum_{x=1}^{3} \frac{e_{\mathbf{q}j}(\alpha,x)}{M_\alpha \omega_{\mathbf{q}j}} \frac{\delta V_{eff}(\mathbf{r})}{\delta S_{\alpha x}} \right| \Psi_{n\mathbf{k}} \right\rangle . \quad (40)
$$

Here we have assumed that there are N atoms in the unit cell and that the eigenvector component of atom α (atomic mass M_α) in the cartesian direction x is referenced by $e_{\mathbf{q}j}(\alpha, x)$. The essential ingredient to describe the scattering rate between the initial and final electronic state will thus be the expression

$$\left\langle \Psi_{m\mathbf{k}+\mathbf{q}} \left| \frac{\delta V_{eff}(\mathbf{r})}{\delta S_{\alpha x}} \right| \Psi_{n\mathbf{k}} \right\rangle . \tag{41}$$

In DFPT the derivative of the self-consistent effective potential with respect to the atomic displacements caused by a phonon is obtained by numerical differentiation of the finite quantity $\delta V_{eff}(\mathbf{r})$ resulting from the iterative linear-response scheme described in Section . For this reason it suffices to proceed within the terminology and definitions of the previous section and concentrate on the investigation of the matrix element:

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} \equiv \langle \Psi_{m\mathbf{k}+\mathbf{q}} | \delta V_{eff}(\mathbf{r}) | \Psi_{n\mathbf{k}} \rangle \tag{42}$$

which in the framework of a variational solution for the wave functions will read:

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \sum_{\mathbf{G},\mathbf{G}'} C_{m\mathbf{k}+\mathbf{q}}(\mathbf{G}') \delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G}',\mathbf{k}+\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) \tag{43}$$

with the change of the Hamilton matrix being described by (27). It was first shown by Savrasov [12] that the validity of expression (42) to properly describe the scattering rate of the electrons will break down when position-dependent basis sets are used to describe the wave functions. Through the rigorous application of time-dependent quantum mechanical perturbation theory he demonstrated that in such a case (42) should be supplemented by corrective terms which take account of the phonon-induced changes in the basis functions. If we apply this concept to the LAPW basis set and assume degeneracy between the initial and the final state ($\varepsilon_{n\mathbf{k}} = \varepsilon_{m\mathbf{k}+\mathbf{q}}$) we obtain:

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \sum_{\mathbf{G},\mathbf{G}'} C^{*}_{m\mathbf{k}+\mathbf{q}}(\mathbf{G})(\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} \delta S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}) C_{n\mathbf{k}}(\mathbf{G}') \tag{44}$$

with the first-order changes in the H- and S-matrix now being described by Eq. (34). Given the matrix element above, the coupling constant $\lambda_{\mathbf{q}\nu}$ for the phonon branch ν and the wavevector $\mathbf{q}$ is obtained by [6]

$$\lambda_{\mathbf{q}\nu} = \frac{1}{N(0)\omega^{2}_{\mathbf{q}\nu} \sum_{\alpha} M_{\alpha} \langle \delta u^{2}_{\alpha} \rangle} \sum_{nm\mathbf{k}} \frac{f(\epsilon_{n\mathbf{k}}) - f(\epsilon_{m\mathbf{k}+\mathbf{q}})}{\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}}} |M^{\mathbf{q}}_{mn}|^{2} \delta(\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \omega_{\mathbf{q}\nu}) \tag{45}$$

where $|M^{\mathbf{q}}_{mn}|^{2}$ stands for

$$|M^{\mathbf{q}}_{mn}|^{2} = \frac{1}{2} \left[\left| M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} \right|^{2} + \left| M^{\alpha}_{m\mathbf{k}-\mathbf{q},n\mathbf{k}} \right|^{2} \right] . \tag{46}$$

$N(0)$ is the density of states at the Fermi level per spin, $\langle \delta u^{2}_{\alpha} \rangle$ denotes the mean square displacement of all the atoms of one type with mass M_α. In case of a supercell calculation the expression on the right hand side of Eq. (45) has to be divided by the number of single cells contained in the supercell.

Table 1: Atomic displacement δz, the change of the atomic force ΔF_z with displacement δz, phonon frequency ω, and electron-phonon coupling constant for the z-axis vibration of hcp Be derived from LR and frozen-phonon calculations, respectively.

	LR			frozen-phonon		
δz [c]	ΔF_z [mRy/a.u.]	ω [meV]	λ	ΔF_z [mRy/a.u.]	ω [meV]	λ
0.002	-4.27	84.2	0.0	-4.31	84.5	0.0

Table 2: Force contributions and total force acting on the S atom in a bcc sulfur lattice under high pressure. The displacement δz is given in units of the lattice parameter (c=4.2368 a.u.).

	$F_{\delta z=0}$	$F_{\delta z=0.005}$	ΔF^{SC}	ΔF^{LR}
F_{HF}	1.30	8.73	7.43	7.47
F_{IBS}	1.08	0.57	-0.51	-0.52
F_{COR}	-2.88	-7.50	-4.62	-4.63
F_{tot}	-0.50	1.80	2.30	2.32

Results

In the following, results for atomic forces, phonon frequencies, and electron-phonon coupling constants for vibrational modes in different materials are given. All self-consistent calculations have been carried out within the LAPW code WIEN97 [30], which was also used as a basic package for the implementation of the LR scheme worked out within this work. In all cases we used well convered BZ samplings and basis sets, for the wavefuctions as well as the expansions of potential and charge density.

The first example is the z-axes vibration of hcp Be (q=0). We used the lattice parameters of $a = 4.21141$ a.u. and $c = 6.77335$ a.u. In Table 1 the atomic force and the corresponding phonon frequency of the LR calculations are compared to the data obtained by a selfconsistent calculation for the displaced atom. The results agree within 1%. Due to the absence of crossing bands at the Fermi level the electron-phonon coupling constant λ is zero.

The following results are obtained for bcc sulfur under high pressure (584 GPa) using the lattice parameter of $a = 4.2368$ a.u. (2.242 Å). This example has been chosen for comparison with detailed information available in literature [9]. Phonon frequencies and coupling constants have been computed for selected points of the transversal branch along $[0\ 0\ \xi]$ (Fig. 1). All data excellently agree with results obtained by the pseudopotential method (labelled PP) [9]. For the H-point ([001]), it can be seen from Table that all the contributions to the total force, namely the Hellman-Feynman force F_{HF}, the IBS correction F_{IBS}, and the core contribution F_{CORE} are very well reproduced be the LR scheme. For the small **k** point mesh ($10 \times 10 \times 10$ **k**-points) there is a finite remaining force for zero displacement due to the lower point symmetry used
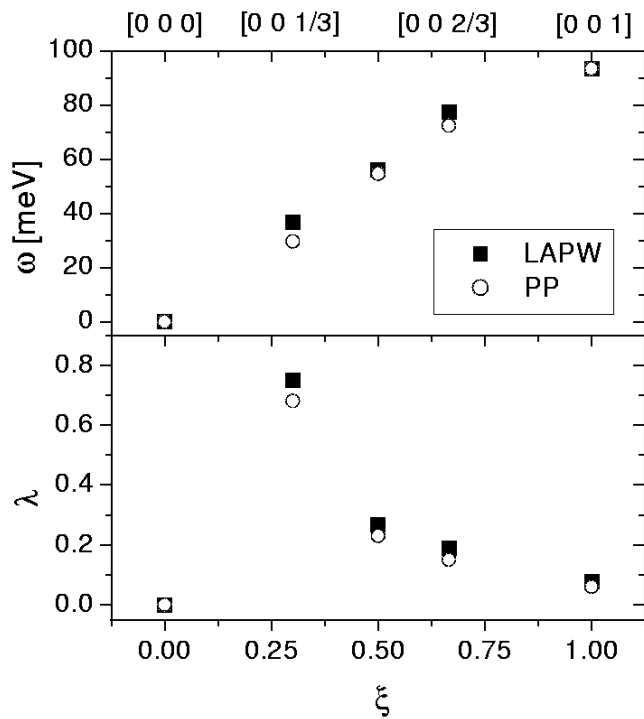
Figure 1: Phonon frequencies ω in eV (upper panel) and electron-phonon coupling constants λ (lower panel) for bcc sulfur for selected points of the transversal branch along [0 0 ξ]. The LAPW results (black squares) are compared to data from Ref. [9] (open circles).

in order to directly compare the supercell results with the LR data. These data show that the change of the force is excellently reproduced when the starting point is a configuration with a finite force. Although a rather coarse grid can lead to reasonable phonon frequencies this is not the case for the coupling constants. Since the contributions come from nearly degenerate bands at or close to the Fermi level, a very dense mesh is needed to reliably describe the electron-phonon coupling constants. For well converged values we typically used up to 300 000 points in the whole BZ. In summary, we have worked out the formalism to describe both phonons and electron-phonon coupling within the full-potential LAPW method. Our approach includes the treatment of core-states and all necessary correction terms arising due to the variational solution of the Kohn-Sham equations as well as the LAPW specific correction terms. The results obtained for different materials prove the method to be a reliable and promising tool for more complex materials.

Acknowledgments

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