Efficient Implementation of the Non-Local Exchange Potential within the FLAPW Method

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1 Introduction

Within the last decades, density-functional theory (DFT) has evolved into a powerful and widely used tool to simulate the electronic structure of matter from first principles. Its impact becomes manifest in the awarding of the Nobel prize to Walter Kohn for his pioneering work on DFT and John A. Pople for his developments of computational methods in quantum chemistry in the year 1998.

The success of DFT is based on the fact, that the electron density $n(\mathbf{r})$ is used as the independent variable to describe the electron system instead of the commonly anticipated complex N-particle wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The density depends only on 3 spatial coordinates in contrast to the many-body wave function, which depends on the 3N spatial coordinates of the electrons, leading to a significant reduction of complexity.

The fundament of DFT is laid by the Hohenberg-Kohn theorem |1|. It shows that there exists a one-to-one correspondence between the external potential and the ground-state electron density. This implies that the many-body Hamiltonian and also the N-particle wave function are uniquely defined by the ground-state density. With this all expectation values are functionals of the density. Furthermore, Hohenberg and Kohn showed that the corresponding total-energy functional becomes minimal for the true ground-state density. Since, however, the functional is unknown, we cannot apply the variational principle directly. Instead, Kohn and Sham [2] introduced a fictitious system of non-interacting particles moving in an effective local potential which is defined in such a way that the densities of the fictitious and the real system coincide. For this purpose Kohn and Sham write the total energy as the sum of the kinetic energy of the non-interacting particles, the Hartree energy, the potential energy and the exchange-correlation (xc) energy. The latter contains the energy contributions from electron exchange and correlation, but also a correction for the kinetic energy. Application of the variational principle then leads to a set of tractable one-particle equations which can be solved by standard numerical techniques. From the resulting one-particle wave functions the density is easily calculated and it is identical to the true ground-state density by construction.

Unfortunately, the xc energy functional is unknown in general. For the homogeneous electron gas, however, a functional can be fitted to very accurate Quantum Monte-Carlo calculations [3, 4]. When one applies the resulting functional also to inhomogeneous systems, it is known as the local-density approximation (LDA). In spite of its seeming crudeness the LDA yields very good results and is still often applied today. Furthermore, local-density variations are taken into account in functionals based on the generalized-gradient approximation (GGA), which generally improve on total energies leading to numerous applications in quantum chemistry [5, 6]. The latter are often called semi-local, while the former are called local.

A third generation of functionals is based on a combination of local or semi-local functionals with the explicit Hartree-Fock (HF) exchange energy, which is non-local. These functionals are called hybrid functionals. The first of its kind was a half-and-half mixing of an LDA functional with the HF exchange potential and was proposed by Becke in 1993 [7]. Since then various other semi-empirical and *ab initio* functionals have been published in literature [8–12]. The former contain parameters which are fitted to experiment (e.g. B3LYP), while the latter are derived solely from first principles (e.g. PBE0).

From a practical point of view hybrid functionals are distinguished from local or semi-local exchange-correlation functionals by

- accurate binding energies of covalently bound molecules with a root mean square deviation of 2-3 kcal/mol¹ from experimental values [8],
- an opening of the band gap in bulk semiconductors and insulators [13, 14],
- an improved description of localized *d* and *f*-electrons in transition metals and rare-earth compounds [15],
- an improved prediction of the adsorption site of small molecules on extended surfaces [16].

Thus hybrid functionals are a distinct improvement over local or semi-local xc functionals. From a theoretical point of view these functionals possess

- a reduced unphysical self-interaction compared with local or semi-local functionals,
- an additional, non-zero discontinuity of the chemical potential at integral particle numbers in contrast to local or semi-local functionals.

We will briefly describe what we mean by this. Due to the only approximate treatment of exchange, LDA or GGA xc functionals do not completely cancel the electronic self-interaction contained in the Hartree energy. As a consequence the electron partly interacts with itself. The explicit use of exact exchange in hybrid functionals reduces this unphysical self-interaction leading to an improved description of localized d- and f-electrons.

The band gap, defined by the difference of electron affinity and ionization energy, can be expressed in the framework of DFT by the sum of the band gap of the noninteracting fictitious system and an exchange-correlation discontinuity. In contrast

 $^{^11~\}mathrm{eV} = 23.06~\mathrm{kcal/mol}$

to LDA or GGA functionals the non-local exchange potential contains a non-zero discontinuity, which contributes to the band gap. Thus, the band gap, which is usually underestimated by LDA or GGA functionals, opens when hybrid functionals are used.

For the numerical realization of DFT within the KS formalism several computational schemes have been developed. In the present work we use the FLAPW method (full-potential linearized augmented plane wave method) [17, 18]. It relies on a decomposition of space into muffin-tin (MT) spheres centered at the atom position and the interstitial region (IR). Solutions of the scalar-relativistic, spherical Schrödinger equation are used as basis functions in the MT spheres and plane waves are used in the IR. The FLAPW method is an all-electron approach, which does not use any shape approximations for the potential or density, e.g. spherical averages of the potential inside the MT spheres or a constant potential in the interstitial region. Its elaborate choice of basis functions makes it universally applicable to electron systems, including d- and f-electron systems, with compact as well as open structures. It is widely considered to be one of the most precise methods in solid-state physics.

In this thesis the non-local Hartree-Fock exchange, which is an integral part in hybrid functionals, is implemented in the FLAPW method as realized in the FLEUR code [19]. Our implementation uses a mixed basis, comprising MT functions and interstitial plane waves, which is specifcally designed for representing wave-function products. As a result the exchange matrix elements can be written as Brillouin-zone (BZ) sums over vector-matrix-vector products. The long-range nature of the Coulomb interaction leads to a divergent term in the BZ sum. This divergence is separated from the sum and integrated analytically, while the non-divergent rest is integrated by standard methods. Spatial symmetry is exploited to reduce the computational effort.

The implementation is tested with HF and PBE0 calculations of bulk Si, C, GaAs, NaCl and MgO. It is found that a comparatively small mixed-basis set is sufficient to obtain converged band energies. The HF and PBE0 calculations open the band gap already after the first iteration. The HF approach, however, drastically overestimates it. The PBE0 functional overestimates the band gap for semiconductors as much as local or semi-local functionals underestimate it, whereas for insulators the band gap is still slightly underestimated, but much closer to experiment then the PBE result.

Chapter 2 gives an introduction into density-functional theory, the Kohn-Sham (KS) formalism and the construction of hybrid functionals. In practice hybrid functionals are applied within the generalized Kohn-Sham (gKS) scheme. The differences between the KS and the gKS formalism are discussed in detail. The FLAPW method is presented in detail in Chapter 3, with emphasis on algorithms and techniques, which are necessary for understanding the implementation of the non-local exchange potential. In Chapter 4 details of a practical implementation of the non-local ex-

change potential into the FLAPW code FLEUR are given. In particular, importance is attached to computational efficiency. Finally, in Chapter 5 the numerical realization is tested on prototype semiconductors and insulators. In the last chapter the main conclusions are drawn and an outlook is given.

2 Theory

A large variety of solid-state phenomena from electronic transport over magnetism to vibronic properties results from the motion of the electrons and ions under their mutual interaction. The quantum mechanical electronic and ionic motion is governed by the Schrödinger equation

$$H |\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle, \qquad (2.0.1)$$

with the many-body Hamiltonian

$$H = -\frac{1}{2} \sum_{j} \nabla_{j}^{2} - \sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2}$$
$$- \sum_{j,\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_{j} - \mathbf{R}_{\alpha}|} + \frac{1}{2} \sum_{\substack{j,k \ j \neq k}} \frac{1}{|\mathbf{r}_{j} - \mathbf{r}_{k}|} + \frac{1}{2} \sum_{\substack{\alpha,\beta \ \alpha \neq \beta}} \frac{Z_{\alpha}Z_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} \qquad (2.0.2)$$

where Z_{α} and M_{α} denote the atomic number and mass of the α -th atomic ion, \mathbf{R}_{α} its space coordinates and \mathbf{r}_{j} the coordinates of the *j*-th electron.¹ In general, equations (2.0.1) and (2.0.2) describe the whole field of non-relativistic solid-state physics. However, in practice an exact solution of the many-body Schrödinger equation is impossible.

Due to the enormous mass difference between ions and electrons their motion takes place at different time scales. On the time scale of electron motion the ions appear fixed. This justifies to define an electronic Hamiltonian

$$H = \sum_{j} \left[-\frac{1}{2} \nabla_{j}^{2} + \underbrace{\sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_{j} - \mathbf{R}_{\alpha}|}}_{V(\mathbf{r}_{j})} \right] + \frac{1}{2} \sum_{\substack{j,k\\j \neq k}} \frac{1}{|\mathbf{r}_{j} - \mathbf{r}_{k}|}, \qquad (2.0.3)$$

where the ion positions \mathbf{R}_{α} are parameters (Born-Oppenheimer approximation) [20].

A brute-force solution of the Hamiltonian (2.0.3) for an iron atom (Z = 26), by sampling each coordinate direction with 10 grid points, requires the storage of 10^{78} numbers. This already shows, that approximations are inevitable.

¹Hartree units are used throughout this work except where noted.

If the electron-electron interaction

$$V_{ee} = \frac{1}{2} \sum_{\substack{j,k \\ j \neq k}} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}$$
(2.0.4)

is neglected the stationary solution of (2.0.1) with the Hamiltonian (2.0.3) is a single Slater determinant Φ of one-particle wave functions $\{\phi_j\}$ obeying

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right]\phi_j(\mathbf{r}) = \epsilon_j\phi_j(\mathbf{r}) . \qquad (2.0.5)$$

However, this is an oversimplification, as V_{ee} represents a very important energy contribution. Instead of the Hamiltonian the wave functions can be approximated, which leads to the Hartree and Hartree-Fock approach.

In the Hartree method the many-electron wave function Ψ is written as a product of one-particle wave functions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_{\alpha_1}(\mathbf{r}_1)\phi_{\alpha_2}(\mathbf{r}_2)\dots\phi_{\alpha_N}(\mathbf{r}_N) , \qquad (2.0.6)$$

where α_i denotes a set of quantum numbers. The Pauli principle is only considered insofar as two one-particle wave functions are not allowed to agree in all quantum numbers. A conditional equation for the wave functions $\phi_{\alpha_i}(\mathbf{r}_i)$ is obtained by minimizing the total energy

$$E_{\text{Hartree}} = \langle \Psi | H | \Psi \rangle$$

$$= \sum_{i=1}^{N} \int d^3 r \, \phi^*_{\alpha_i}(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V(\mathbf{r}) \right] \phi_{\alpha_i}(\mathbf{r}) + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \iint d^3 r d^3 r' \frac{|\phi_{\alpha_i}(\mathbf{r})|^2 |\phi_{\alpha_j}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$
(2.0.7)

with respect to $\phi_{\alpha_i}^*$ (Ritz variational principle).

In contrast to the Hartree approach the Hartree-Fock (HF) method uses single Slater determinants of one-particle wave functions. With the anti-symmetrization of the wave function the Pauli principle is fully taken into account, which yields an additional energy contribution

$$E_{\rm HF} = E_{\rm Hartree} - \frac{1}{2} \sum_{\substack{i,j\\i\neq j}} \iint d^3 r d^3 r' \frac{\phi_{\alpha_i}^*(\mathbf{r})\phi_{\alpha_j}(\mathbf{r})\phi_{\alpha_j}^*(\mathbf{r}')\phi_{\alpha_i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$= \sum_{i=1}^N \int d^3 r \, \phi_{\alpha_i}^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V(\mathbf{r}) \right] \phi_{\alpha_i}(\mathbf{r}) + \frac{1}{2} \iint d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$- \frac{1}{2} \sum_{i,j} \iint d^3 r d^3 r' \frac{\phi_{\alpha_i}^*(\mathbf{r})\phi_{\alpha_j}(\mathbf{r})\phi_{\alpha_j}(\mathbf{r}')\phi_{\alpha_i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \qquad (2.0.8)$$

the so-called exchange energy. However, both approaches lead to an unsatisfying description of physical properties (e.g. in the HF method the derivative of the oneparticle energies with respect to \mathbf{k} is divergent at the Fermi vector $\mathbf{k}_{\rm F}$ leading to a vanishing density of states at $E_{\rm F}$ for metals [21]).

The Hartree-Fock Hamiltonian F, obtained by minimizing (2.0.8) with respect to $\phi^*_{\alpha_i}$, is the starting point for Møller-Plesset (MP) perturbation theory, a quantumchemical method [22, 23]. It treats correlation effects beyond Hartree-Fock theory in a perturbative manner

$$H_{\rm MP} = F + \lambda \left(H - F \right) . \tag{2.0.9}$$

Møller-Plesset perturbation theory is classified by the highest order n of λ , which is considered in the expansion of the total energy (denoted by MPn).

Density-functional theory (DFT) offers a reformulation of the many-body problem, which results in a tremendous reduction of the computational complexity in contrast to MP perturbation theory and other quantum chemical methods.

2.1 Density-functional theory (DFT)

In the last decades density-functional theory has become one of the most powerful tools to simulate the quantum-mechanical electronic structure of materials (bulk systems, thin films, surfaces and interfaces, semiconductors, magnetic materials and so on). In density-functional theory the electron system is described by the electron density $n(\mathbf{r})$, which only depends on three spacial coordinates, instead of the complex many-electron wave function Ψ .

The basis of DFT is given by the Hohenberg-Kohn theorem [1]. It states that a unique mapping exists between the external potential $V(\mathbf{r})$ and the ground-state density $n(\mathbf{r})$

$$n \leftrightarrow V$$
. (2.1.1)

Since the external potential V determines the Hamiltonian (2.0.3), the many-body wave function Ψ is a functional of V via (2.0.1) and of the ground-state density via (2.1.1). Consequently any expectation value can be regarded as a functional of the density n

$$O[n] = \langle \Psi[n] | O | \Psi[n] \rangle . \qquad (2.1.2)$$

In particular one can write

$$E[n] = \langle \Psi[n] | H | \Psi[n] \rangle$$

= $F[n] + \int d^3 r V(\mathbf{r}) n(\mathbf{r})$ (2.1.3)

for the total energy with

$$F[n] = \langle \Psi[n] | T + V_{ee} | \Psi[n] \rangle .$$
 (2.1.4)

F is a universal functional in that it is the same for each electron system and independent of the external potential.

For this total-energy functional Hohenberg and Kohn showed a variational principle: E[n] takes its minimum for the true ground-state density $n_0(\mathbf{r})$

$$\frac{\delta}{\delta n} \left[E[n] - \mu' \left(\int d^3 r \, n(\mathbf{r}) - N \right) \right] \Big|_{n=n_0} = 0 , \qquad (2.1.5)$$

where the Lagrange multiplier μ' ensures particle conservation.

The equation (2.1.3) together with the variational principle does not lead to a practicable scheme for the determination of the ground-state density, because the universal functional F[n] is unknown.

2.2 Kohn-Sham formalism

The Kohn-Sham (KS) formalism provides an ingenious and practicable reformulation of the many-body problem. It maps the interacting electron system to a system of non-interacting electrons moving in an effective, external potential V^{KS} .

The idea of Kohn and Sham [2] is to write the universal functional F as a sum of the kinetic energy T^{KS} of a non-interacting system, the Hartree energy U_{H} and the exchange-correlation energy E_{xc}

$$F[n] = T^{\text{KS}}[n] + \underbrace{\frac{1}{2} \iint d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{U_{\text{H}}[n]} + E_{\text{xc}}[n] . \qquad (2.2.1)$$

The exchange-correlation energy

$$E_{\rm xc}[n] = F[n] - U_{\rm H}[n] - T^{\rm KS}[n] \qquad (2.2.2)$$

also includes the correction for the error done by replacing the kinetic energy of the real system by the kinetic energy T^{KS} of a non-interacting system. From the stationary condition (2.1.5) the equation

$$\frac{\delta T^{\rm KS}}{\delta n(\mathbf{r})} + \int d^3 r' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})} + V(\mathbf{r}) - \mu' = 0 \qquad (2.2.3)$$

is obtained. It is formally equivalent to that obtained for a system of non-interacting

electrons, the so-called KS system, moving in the effective potential

$$V^{\rm KS}(\mathbf{r}) = V(\mathbf{r}) + \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\rm xc}(\mathbf{r}) , \qquad (2.2.4)$$

where

$$V_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})} \tag{2.2.5}$$

is the exchange-correlation potential. Consequently, the ground-state density $n_0(\mathbf{r})$ of the interacting system is found by solving the one-particle KS equations

$$\left(-\frac{1}{2}\nabla^2 + V^{\text{KS}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad (2.2.6)$$

and subsequently occupying the electron states according to the Pauli principle. The density is then given by

$$n_0(\mathbf{r}) = \sum_{i}^{\text{occ.}} |\phi_i(\mathbf{r})|^2 .$$
 (2.2.7)

Because V^{KS} itself depends on the density n, the equation must be solved selfconsistently. The true ground-state energy E_0 is then obtained by

$$E_0 = E[n_0] = T^{\text{KS}}[n_0] + U_{\text{H}}[n_0] + E_{\text{xc}}[n_0] + \int d^3 r \, n_0(\mathbf{r}) V(\mathbf{r}) \quad .$$
(2.2.8)

Theoretically this scheme is exact. However, the exact form of the exchangecorrelation energy $E_{\rm xc}$ is unknown. A simple approximation to $E_{\rm xc}$ is the so-called local-density approximation (LDA). In the LDA it is assumed, that the electrons locally act as a homogeneous electron gas. The exchange energy per electron in a homogeneous electron gas can be derived exactly with the Hartree-Fock method [24]

$$\epsilon_{\rm x}(n) = -\frac{3}{4\pi} (3\pi^2 n)^{\frac{1}{3}} , \qquad (2.2.9)$$

whereas the remaining correlation contribution is parameterized by a fit to quantum Monte-Carlo calculations [3, 4]. Finally, the exchange-correlation energy in LDA has the form

$$E_{\rm xc}^{\rm LDA}\left[n\right] = \int d^3r \, n(\mathbf{r}) \epsilon_{\rm xc}^{\rm LDA}(n(\mathbf{r})) \,. \qquad (2.2.10)$$

Surprisingly, this approximation works quite well for a wide range of systems. Its success bases on the fact, that $E_{\rm xc}^{\rm LDA}$ is the exact solution of a model system, the

homogeneous electron gas. So, it fulfills all constraints, which the exact exchangecorrelation energy must obey, like sum rules, scaling and limiting conditions [25]. Furthermore it is commonly accepted, that the error made in the exchange part partially cancels with the error made in the correlation part.

The next logical step to improve the LDA is to consider density gradients as well. This leads to the so-called generalized gradient approximation (GGA) [5, 6]

$$E_{\rm xc}^{\rm GGA}[n] = \int d^3r f(n(\mathbf{r}), \nabla n(\mathbf{r})) . \qquad (2.2.11)$$

2.3 Coupling-constant integration

In order to obtain further physical insight into the exchange-correlation energy $E_{\rm xc}$, the coupling-constant integration method or adiabatic-connection method [26–28] is discussed.

A fictitious system of N electrons is introduced with a scaled electron-electron interaction λV_{ee} and an external potential V_{λ} , which is defined such that the ground-state density n_0^{λ} is equal to the real, physical density n_0 for any $\lambda \in [0, 1]$

$$H_{\lambda} = T + V_{\lambda} + \lambda V_{ee} . \qquad (2.3.1)$$

The case $\lambda = 1$ corresponds to the interacting system with $V_{\lambda=1} = V$ and $\lambda = 0$ to the non-interacting KS system with $V_{\lambda=0} = V^{\text{KS}}$.

By subtracting the total energy of the KS system from the interacting one, an expression for the exchange-correlation energy $E_{\rm xc}$

$$E_{\rm xc}[n] = E[n] - E^{\rm KS}[n] - \frac{1}{2} \iint d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3r V(\mathbf{r})n(\mathbf{r}) + \int d^3r V^{\rm KS}(\mathbf{r})n(\mathbf{r})$$
(2.3.2)

is obtained. The energy difference of the interacting and the KS system can be evaluated alternatively by calculating the derivative of the ground-state energy of the fictitious system with respect to λ

$$\frac{dE(\lambda)}{d\lambda} = \frac{d}{d\lambda} \langle \Psi_{\lambda} | H_{\lambda} | \Psi_{\lambda} \rangle$$

$$= \langle \Psi_{\lambda} | \frac{d}{d\lambda} H_{\lambda} | \Psi_{\lambda} \rangle$$

$$= \langle \Psi_{\lambda} | V_{ee} | \Psi_{\lambda} \rangle + \frac{d}{d\lambda} \int d^{3}r V_{\lambda}(\mathbf{r}) n(\mathbf{r}) ,$$
(2.3.3)

where the Hellman-Feynman theorem has been applied and Ψ_{λ} denotes the manyelectron ground-state wave function of H_{λ} , and subsequent integration. Combining equations (2.3.2) and (2.3.3) yields an exact expression for the exchange-correlation energy

$$E_{\rm xc} = \int_0^1 d\lambda \, \langle \Psi_\lambda | \, V_{ee} \, | \Psi_\lambda \rangle - \frac{1}{2} \int d^3 r d^3 r' \, \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad (2.3.4)$$
$$= \int_0^1 d\lambda \, E_{\rm xc,\lambda}$$

where

$$E_{\mathbf{x}\mathbf{c},\lambda} = \langle \Psi_{\lambda} | V_{ee} | \Psi_{\lambda} \rangle - \frac{1}{2} \int d^3r d^3r' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,. \tag{2.3.5}$$

For a better understanding the expression (2.3.4) is represented in terms of the exchange-correlation hole $n_{\rm xc}^h(\mathbf{r}, \mathbf{r}')$ [29, 30]. For this we define the λ -dependent pairdensity $n_2^{\lambda}(\mathbf{r}, \mathbf{r}')$

$$n_{2}^{\lambda}(\mathbf{r},\mathbf{r}') = \langle \Psi_{\lambda} | \sum_{\substack{i,j\\i\neq j}} \delta(\mathbf{r}-\mathbf{r}_{i}) \delta(\mathbf{r}'-\mathbf{r}_{j}) | \Psi_{\lambda} \rangle$$
(2.3.6)

and the λ -dependent exchange-correlation hole

$$n_{\mathrm{xc},\lambda}^{h}(\mathbf{r},\mathbf{r}') = \frac{n_{2}^{\lambda}(\mathbf{r},\mathbf{r}') - n(\mathbf{r})n(\mathbf{r}')}{n(\mathbf{r})} . \qquad (2.3.7)$$

The exchange-correlation hole $n_{\rm xc}^h({f r},{f r}')$ itself is a coupling-constant average

$$n_{\rm xc}^{h}(\mathbf{r},\mathbf{r}') = \int_{0}^{1} d\lambda \, n_{{\rm xc},\lambda}^{h}(\mathbf{r},\mathbf{r}') \qquad (2.3.8)$$

and it fulfills the sum-rule

$$\int d^3r' n_{\rm xc}^h(\mathbf{r}, \mathbf{r}') = \int d^3r' n_{\rm xc,\lambda}^h(\mathbf{r}, \mathbf{r}') = -1 . \qquad (2.3.9)$$

With these definitions we can write

$$E_{\rm xc} = \frac{1}{2} \iint d^3 r d^3 r' \frac{n(\mathbf{r}) n_{\rm xc}^h(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$= \frac{1}{2} \iint d^3 r d^3 r' \frac{n(\mathbf{r}) n_{\rm xc}^h(\mathbf{r}, \mathbf{r} - \mathbf{r}')}{|\mathbf{r}'|} .$$
(2.3.10)

Thus $E_{\rm xc}$ results from the interaction of the electrons with their exchange-correlation hole. The hole is created on the one hand by the Coulomb repulsion and on the other hand by the Pauli principle, which separates electrons of the same spin in space.

Both equivalent representations of the exchange-correlation energy $E_{\rm xc}$, equation (2.3.4) and (2.3.10), are the basis to construct approximate expressions.

2.4 Hybrid functionals

The construction of hybrid functionals is motivated by expression (2.3.4). The integrand $E_{\text{xc},\lambda}$ at $\lambda = 0$ corresponds to the Hartree-Fock exchange-energy expression

$$E_{\rm x} = -\frac{1}{2} \sum_{i,j} \iint d^3 r d^3 r' \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(2.4.1)

evaluated with KS orbitals, because the many-electron wave function $\Psi_{\lambda=0}$ is a single Slater determinant Φ of KS orbitals $\{\phi_i\}$. As a consequence exact exchange is a fundamental ingredient of the exchange-correlation functional. The class of functionals, which are combinations of a local or a semi-local and an exact-exchange part, are called hybrid functionals.

The simplest way to approximate the integrand (2.3.5) is a linear interpolation

$$E_{\mathrm{xc},\lambda} = E_{\mathrm{xc},\lambda=0} + \lambda \left(E_{\mathrm{xc},\lambda=1} - E_{\mathrm{xc},\lambda=0} \right) , \qquad (2.4.2)$$

which gives

$$E_{\rm xc} = \frac{1}{2} (E_{\rm xc,\lambda=1} + E_{\rm xc,\lambda=0}) = \frac{1}{2} (E_{\rm xc,\lambda=1} + E_{\rm x}) . \qquad (2.4.3)$$

At or near $\lambda = 1$ the exchange-correlation hole $n_{\mathrm{xc},\lambda}^h$ is deeper because of the full electron-electron interaction strength and thus more localized. It has been shown in Ref. 31, that local or semi-local approximations for the exchange-correlation energy describe the exchange-correlation hole $n_{\mathrm{xc}}^h(\mathbf{r}, \mathbf{r} - \mathbf{r}')$ accurately for small $\mathbf{r} - \mathbf{r}'$. Consequently, they are especially suited for the $\lambda = 1$ end of the integral and one obtains

$$E_{\rm xc} = \frac{1}{2} (E_{\rm xc}^{\rm DF} + E_{\rm x}) , \qquad (2.4.4)$$

where DF denotes any local or semi-local density functional. This approximation has been proposed by Becke [7] with $E_{\rm xc}^{\rm DF} = E_{\rm xc}^{\rm LDA}$ and it is known as 'half-and-half mixing'.

In order to further improve the approximation for $E_{\rm xc}$, a detailed understanding of the λ dependence of the integrand $E_{{\rm xc},\lambda}$ is necessary. For the homogeneous electron gas it can be calculated exactly (s. Fig. 2.1). For high densities the curve is nearly linear in λ . Its curvature becomes larger for smaller densities.

Perdew et al. [32] interpolate the λ dependence of the integrand between $\lambda = 0$



Figure 2.1: The λ dependence of the exchange-correlation energy per particle for the uniform electron gas, where r_s denotes the Wigner-Seitz radius $\left(r_s = \left(\frac{3}{4\pi n}\right)^{1/3}\right)$. Graphs are taken from Ref. 29.

and $\lambda = 1$ by

$$E_{\mathrm{xc},\lambda} = E_{\mathrm{xc},\lambda}^{\mathrm{DF}} + \left(E_{\mathrm{x}} - E_{\mathrm{x}}^{\mathrm{DF}}\right) \left(1 - \lambda\right)^{n-1}$$
(2.4.5)

with

$$E_{\rm x}^{\rm DF} = E_{{\rm xc},\lambda=0}^{\rm DF} . \qquad (2.4.6)$$

By reformulating the scaling of the electron-electron interaction as a scaling of the space coordinates of the many-electron system [33–35], one obtains

$$E_{\mathrm{xc},\lambda}\left[n\right] = \frac{d}{d\lambda} \left\{ \lambda^2 E_{\mathrm{xc}}\left[\frac{n(\frac{\mathbf{r}}{\lambda})}{\lambda^3}\right] \right\} . \tag{2.4.7}$$

With the consequence that for any density functional $E_{\rm xc}^{\rm DF}$ there exists a couplingconstant representation $E_{{\rm xc},\lambda}^{\rm DF}$. The functional form (2.4.5) guarantees, that the integrand is identical to its exact expression $E_{\rm x}$ at $\lambda = 0$ and to the density-functional approximation $E_{{\rm xc},\lambda}^{\rm DF}$ at $\lambda = 1$, where it is supposed to be accurate. The integer *n* determines how rapid $E_{{\rm xc},\lambda}$ tends to $E_{{\rm xc},\lambda}^{\rm DF}$ for $\lambda \to 1$. It is argued, that the integer *n* should be the lowest order of Møller-Plesset (MP) perturbation theory, which provides a realistic description of the many-electron system. For a large class of materials Møller-Plesset perturbation theory of fourth order (MP4) gives very accurate results. Thus, one obtains

$$E_{\rm xc} = E_{\rm xc}^{\rm DF} + \frac{1}{4} \left(E_{\rm x} - E_{\rm x}^{\rm DF} \right) .$$
 (2.4.8)

With $E_{\rm xc}^{\rm DF} = E_{\rm xc}^{\rm PBE}$ this defines the PBE0 functional. Becke [8] further proposed a generalized, semi-empirical approximation for $E_{\rm xc}$ of the form

$$E_{\rm xc}^{\rm LDA} + a_0 (E_{\rm x} - E_{\rm x}^{\rm LDA}) + a_{\rm x} \Delta E_{\rm x}^{\rm B88} + a_{\rm c} \Delta E_{\rm c} . \qquad (2.4.9)$$

Here, in contrast to equation (2.4.4) also gradient corrections for correlation ΔE_c and exchange $\Delta E_{\rm x}^{\rm B88}$, in particular the Becke88 exchange functional [36], are taken into account. The three parameters a_0 , a_x and a_c are determined by a fit to the 56 atomization energies, 42 ionization energies, 8 proton affinities and the 10 first-row total atomic energies of the molecules of the G1 database [37]. Equation (2.4.9)fulfills the homogeneous electron-gas limit, if the same applies for the correlation functional.

Originally, Becke proposed to use the PW91-functional [38] for $\Delta E_{\rm c}$. Another variant is the famous B3LYP functional, which uses the Lee-Yang-Parr functional 39.

In practice, hybrid functionals are typically not applied within the KS densityfunctional formalism. Instead, a Hartree-Fock density-functional or generalized KS (gKS) formalism is applied (s. Sec. 2.5). This leads to Hartree-Fock-like equations for the orbitals $\{\phi_i\}$

$$\left[-\frac{1}{2}\Delta + V^{\text{gKS}}(\mathbf{r})\right]\phi_i(\mathbf{r}) - a\sum_k \int d^3r' \,\frac{\phi_k^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\phi_k(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) , \quad (2.4.10)$$

where V^{gKS} is the effective potential of the gKS system and

$$a = 1/2 \quad \text{for equation (2.4.4)} a = 1/4 \quad \text{for equation (2.4.8)} a = a_0 \quad \text{for equation (2.4.9)}.$$

For the treatment of hybrid functionals within the KS formalism a local effective potential $V^{\rm KS}(\mathbf{r})$ is required. In the framework of the optimized-effective-potential (OEP) [40, 41] method a local effective potential is generated from an orbitaldependent exchange-correlation functional, e.g. $E_{\rm x}$. However, this scheme is rather complex mathematically and numerically.

2.5 Generalized Kohn-Sham scheme

It is sometimes argued, that the treatment of hybrid functionals according to (2.4.10) is outside the realm of density-functional theory at all. This is not correct. It is outside the KS formalism. In the KS formalism the universal functional is written as a sum of the Hartree energy, the exchange-correlation energy and the kinetic energy of a non-interacting electron system

$$T^{\text{KS}}[n] = \min_{\Phi \to n} \langle \Phi | T | \Phi \rangle , \qquad (2.5.1)$$

which finally leads to tractable one-particle equations. The minimization $\Phi \to n$ is over single Slater determinants Φ yielding the density n. As the separation (2.2.1) is arbitrary, one can define a different partitioning of the universal functional F, leading to the gKS system² [42]. For hybrid functionals we write

$$F[n] = \min_{\Phi \to n} \langle \Phi | T + aV_{ee} | \Phi \rangle + (1 - a)U_{\rm H}[n] + E_{\rm xc}^{\rm gKS}[n] \\ = \underbrace{\min_{\Phi \to n} [\langle \Phi | T | \Phi \rangle + aE_{\rm x} + aU_{\rm H}[n]]}_{:=S[n]} + (1 - a)U[n] + E_{\rm xc}^{\rm gKS}[n], (2.5.2)$$

where $a \in [0, 1]$ is a parameter, $U_{\rm H}[n]$ denotes the Hartree energy and $E_{\rm xc}^{\rm gKS}[n]$ subsumes missing exchange-correlation effects, that are not already contained in S[n]. Application of the Hohenberg-Kohn variational principle to (2.5.2) yields

$$\frac{\delta S}{\delta n} + (1-a)V_{\rm H} + \frac{\delta E_{\rm xc}^{\rm gKS}}{\delta n} + V(\mathbf{r}) - \mu' = 0. \qquad (2.5.3)$$

This Euler-Lagrange equation is formally equivalent to that obtained for a system, with an external potential

$$V^{\rm gKS}(\mathbf{r}) = V_{\rm H}(\mathbf{r}) + V_{\rm xc}^{\rm gKS}(\mathbf{r}) + V(\mathbf{r}),$$
 (2.5.4)

where

$$V_{\rm xc}^{\rm gKS}(\mathbf{r}) = \frac{\delta E_{\rm xc}^{\rm gKS}}{\delta n(\mathbf{r})} , \qquad (2.5.5)$$

and an orbital-dependent exact-exchange potential. Thus the one-particle wave functions, building up the Slater determinant, are solutions of Hartree-Fock-like equations

$$\left[-\frac{1}{2}\Delta + V^{\text{gKS}}(\mathbf{r})\right]\phi_i(\mathbf{r}) - a\sum_k \int d^3r' \frac{\phi_k^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\phi_k(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \quad (2.5.6)$$

²Note that in contrast to the KS system the gKS system is not defined uniquely.

and the density is obtained by (2.2.7).

If one chooses a = 0, the gKS scheme corresponds to the KS formalism. For a = 1 a HF scheme with DFT correlation is obtained. Any value in-between defines a hybrid functional.

Strictly speaking the treatment of hybrid functionals in the above defined gKS system contains an inconsistency, because the KS coupling-constant integration expression for $E_{\rm xc}$ is used to find the parameter *a* and the local exchange-correlation functional of the gKS system. However, an analogous calculation (s. Appendix A) as in the coupling-constant integration method for the KS system yields a corresponding expression for the gKS system

$$E_{\rm xc}^{\rm gKS} = \int_0^1 d\lambda E_{\rm xc,\lambda} - aE_{\rm x}^{\rm gKS} + \left\langle \Phi^{\rm KS} \right| T \left| \Phi^{\rm KS} \right\rangle - \left\langle \Phi^{\rm gKS} \right| T \left| \Phi^{\rm gKS} \right\rangle , \quad (2.5.7)$$

where $E_{\text{xc},\lambda}$ is defined as in equation (2.3.5) and $E_{\text{x}}^{\text{gKS}}$ denotes the exact-exchange energy evaluated with the gKS Slater determinant Φ^{gKS} . In fact, this expression should be the basis for approximations to $E_{\text{xc}}^{\text{gKS}}$. If the difference between the KS and the gKS Slater determinant is neglected, (2.5.7) becomes

$$E_{\rm xc}^{\rm gKS} = \int_0^1 d\lambda E_{{\rm xc},\lambda} - aE_{\rm x} , \qquad (2.5.8)$$

which justifies the above described treatment.

2.6 Self-interaction and discontinuity of $E_{\rm xc}$

Hybrid functionals, that contain exact exchange explicitly, are especially suited to describe the electronic structure of molecules, semiconductors and localized d- and f-electrons [8, 13–15]. Two special features of the exchange term distinguish them from local or semi-local functionals: a partial compensation of the electronic self-interaction and the non-vanishing discontinuity of the exchange-correlation potential at integral particle numbers.

Due to the separation of the Hartree energy $U_{\rm H}[n]$ (s. Eq. (2.2.1)) and the only approximate treatment of exchange in local or semi-local exchange-correlation functionals the total energy E[n] contains an unphysical self-interaction. This means that the electron wave function ϕ_i is determined by an electrostatic potential which is partly created by itself. The usage of exact exchange $E_x[n]$ in hybrid functionals partially compensates the unphysical self-interaction

$$V_{\mathbf{x}}(\mathbf{r}) := -\sum_{j} \int d^{3}r' \frac{\phi_{j}^{*}(\mathbf{r}')\phi_{i}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_{j}(\mathbf{r})$$

$$= -\int d^{3}r' \frac{\phi_{i}^{*}(\mathbf{r}')\phi_{i}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_{i}(\mathbf{r}) - \sum_{j\neq i} \int d^{3}r' \frac{\phi_{j}^{*}(\mathbf{r}')\phi_{i}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_{j}(\mathbf{r}) . \quad (2.6.1)$$

Furthermore, the functional $E_x[n]$ is discontinuous at integral particle numbers, which is necessary for an improved determination of band gaps in semiconductors or insulators. This fact is discussed in the following.

In principle, the energy spectrum of the Kohn-Sham system has no physical meaning, because it is the spectrum of an auxiliary non-interacting system. But the band structure is often qualitatively similar to the band structure of the real material. Quantitatively LDA and GGA band gaps for semiconductors calculated by the energy difference of the lowest unoccupied KS state and highest occupied state are roughly 50% too small.

The band gap of a semiconductor or an insulator can be expressed by the groundstate energies of the N - 1, N and N + 1 electron systems

$$E_{\text{gap}} = E(N-1) - E(N) - (E(N) - E(N+1))$$

= $\frac{E(N-1) - E(N)}{N-1 - N} + \frac{E(N+1) - E(N)}{N+1 - N}$, (2.6.2)

which is the energy difference between ionization energy and electron affinity. Since systems with $N \gg 1$ are regarded, the fractions in (2.6.2) can be understood as the right- and left-hand side derivatives of E with respect to N. By using the definition of the chemical potential $\mu(N) = \frac{\partial E(N)}{\partial N}$ the band gap can be expressed in terms of μ

$$E_{\text{gap}} = -\mu(N-0) + \mu(N+0) ,$$
 (2.6.3)

where ± 0 denote the derivatives from the right and left, respectively. Furthermore, the Lagrange parameter μ' introduced in (2.1.5) is identical to the chemical potential

$$\mu(N) = \frac{\partial E(N)}{\partial N} = \int d^3r \underbrace{\frac{\delta E[n]}{\delta n(\mathbf{r})}}_{\mu'(N)} \frac{\partial n(\mathbf{r})}{\partial N} = \mu'(N) . \qquad (2.6.4)$$

Hence the band gap results from the discontinuity of the functional derivative of E with respect to n

$$E_{\text{gap}} = \frac{\delta E[n]}{\delta n(\mathbf{r})} \bigg|_{n=n_0, N+0} - \frac{\delta E[n]}{\delta n(\mathbf{r})} \bigg|_{n=n_0, N-0} .$$
(2.6.5)

The addition of an electron to the N electron system $(N \gg 1)$ only leads to an infinitesimal change in the density. So the changes in the total energy

$$E = T^{\rm KS} + \frac{1}{2} \iint d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r' V(\mathbf{r}')n(\mathbf{r}') + E_{\rm xc} \qquad (2.6.6)$$

can only arise from a discontinuity in T^{KS} and E_{xc} .

This argumentation is also valid for the KS system. However, the band gap in the KS system with the total energy

$$E^{\rm KS} = T^{\rm KS} + \int d^3 r' V^{\rm KS}(\mathbf{r}') n(\mathbf{r}') \qquad (2.6.7)$$

can only be caused by the discontinuity of T^{KS} at integral particle numbers, which results from the different shape of the KS wave function of the highest occupied and lowest unoccupied state in band-gap materials

$$\epsilon_{N+1}^{\rm KS} - \epsilon_N^{\rm KS} = \left. \frac{\delta T^{\rm KS}}{\delta n} \right|_{N+0} - \left. \frac{\delta T^{\rm KS}}{\delta n} \right|_{N-0} \,. \tag{2.6.8}$$

Finally, the band gap of the physical system can be expressed in terms of the KS band gap and the discontinuity Δ_{xc} of the exchange-correlation energy

$$E_{\text{gap}} = \epsilon_{N+1}^{\text{KS}} - \epsilon_{N}^{\text{KS}} + \Delta_{\text{xc}} . \qquad (2.6.9)$$

Thus the underestimation of the band gap calculated by the difference of the lowest unoccupied and highest occupied KS state can be attributed on the one hand to the approximations for $E_{\rm xc}$ and on the other hand to the neglect of the discontinuity $\Delta_{\rm xc}$. LDA and GGA functionals do not contain a discontinuity $\Delta_{\rm xc}$, because they are analytic functionals of the density.

The exact-exchange expression E_x is orbital-dependent as the kinetic energy T^{KS} and so it also exhibits a discontinuity, which adds to the gKS band gap

$$E_{\text{gap}}^{\text{gKS}} = \frac{\delta T^{\text{KS}}}{\delta n} \Big|_{N+0} - \frac{\delta T^{\text{KS}}}{\delta n} \Big|_{N-0} + a \left. \frac{\delta E_{\text{x}}}{\delta n} \right|_{N+0} - a \left. \frac{\delta E_{\text{x}}}{\delta n} \right|_{N-0}$$
$$= \epsilon_{N+1}^{\text{KS}} - \epsilon_{N}^{\text{KS}} + a \left. \frac{\delta E_{\text{x}}}{\delta n} \right|_{N+0} - a \left. \frac{\delta E_{\text{x}}}{\delta n} \right|_{N-0} .$$
(2.6.10)

It must be noted that although it is expected that the gKS scheme should provide better band gaps, the gKS eigenspectrum is still the spectrum of an artificial system.

3 Electronic-structure methods

There is a variety of numerical methods to solve the KS equations (2.2.6). Most methods rely on the representation of the KS wave functions in a basis set $\{\chi\}$, which is adapted to the physical problem. In this way the differential KS equation is cast into an algebraic one

$$\sum_{\mathbf{G}} H_{\mathbf{G}'\mathbf{G}}(\mathbf{k}) z_{\mathbf{G}}(n, \mathbf{k}) = \epsilon_{n, \mathbf{k}} \sum_{\mathbf{G}} S_{\mathbf{G}'\mathbf{G}}(\mathbf{k}) z_{\mathbf{G}}(n, \mathbf{k})$$
(3.0.1)

where

$$H_{\mathbf{G'G}}(\mathbf{k}) = \int d^3 r \, \chi^*_{\mathbf{k},\mathbf{G'}}(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V^{\mathrm{KS}}(\mathbf{r}) \right] \chi_{\mathbf{k},\mathbf{G}}(\mathbf{r}) \qquad (3.0.2)$$

$$S_{\mathbf{G'G}}(\mathbf{k}) = \int d^3 r \, \chi^*_{\mathbf{k},\mathbf{G'}}(\mathbf{r}) \chi_{\mathbf{k},\mathbf{G}}(\mathbf{r})$$
(3.0.3)

$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} z_{\mathbf{G}}(n,\mathbf{k})\chi_{\mathbf{k},\mathbf{G}}(\mathbf{r})$$
(3.0.4)

and **k** denotes the k point and n the band index. In general the overlap matrix $S_{\mathbf{G'G}}$ is not diagonal and therefore equation (3.0.1) represents a generalized eigenvalue problem

$$Hz = \epsilon Sz. \tag{3.0.5}$$

From the large spectrum of electronic-structure methods we describe the linearized augmented-plane-wave (LAPW) method, which has been used in this work, and its precursor, the APW method, as well as numerical aspects of a practical implementation.

3.1 APW method

The basis set $\{\chi\}$ should be chosen according to the system at hand. Since our main interest is in periodic systems, one could, inspired by the Bloch theorem, choose plane waves. In this basis each power of the momentum operator is diagonal, in particular the kinetic energy. The Hartree potential is obtained by a simple algebraic expression. However, near the atom cores the wave functions vary rapidly. Consequently, its accurate representation requires a large number of plane waves. This can be avoided



Figure 3.1: Division of space into muffin-tin (MT) spheres and the interstitial region (IR) .

by using so-called pseudo-potentials, i.e., effective potentials created by the atomic nuclei and the core electrons. In a full-potential approach, where core electrons are treated on the same footing as valence electrons, the use of a plane-wave basis set is impractical due to the large number of basis functions needed to achieve convergence.

Taking into account that the potential is nearly spherical around the atomic nucleus and relatively smooth between the atoms, it is natural to divide the space into two regions, the muffin-tin (MT) spheres, that are centered at the atom positions, and the interstitial region (s. Fig. 3.1). In the APW method solutions of the scalarrelativistic, spherical Schrödinger equation are used as basis functions in the MT spheres and plane waves are used in the IR. For a non-spin-polarized system with a single-atom basis the APW basis in the unit cell can be written as

$$\chi_{\mathbf{k},\mathbf{G}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{N\Omega}} \exp\left[i\left(\mathbf{k}+\mathbf{G}\right)\mathbf{r}\right] & \mathbf{r} \in \mathrm{IR} \\ \frac{1}{\sqrt{N}} \sum_{lm} a_{lm}(\mathbf{k},\mathbf{G})u_l(r)Y_{lm}(\mathbf{r}) & \mathbf{r} \in \mathrm{MT} \end{cases}, \quad (3.1.1)$$

where Ω is the unit-cell volume, N the number of unit cells, u_l the radial solution of the spherical Schrödinger equation¹

$$\left\{-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l\right\} r u_l(r) = 0$$
(3.1.2)

¹For simplicity we give the non-relativistic equations here.

to the energy parameter E_l . The coefficients $a_{lm}(\mathbf{k}, \mathbf{G})$ are determined by requiring continuity of the basis function on the sphere boundary yielding the coefficients

$$a_{lm}(\mathbf{k}, \mathbf{G}) = \frac{4\pi i^l}{\sqrt{\Omega} u_l(R_{\mathrm{MT}})} j_l \left(|\mathbf{k} + \mathbf{G}| R_{\mathrm{MT}} \right) Y_{lm}^*(\mathbf{k} + \mathbf{G}) , \qquad (3.1.3)$$

where the Rayleigh expansion

$$\exp\left[i\left(\mathbf{k}+\mathbf{G}\right)\mathbf{r}\right] = 4\pi \sum_{lm} i^{l} j_{l}(|\mathbf{k}+\mathbf{G}|r) Y_{lm}^{*}(\mathbf{k}+\mathbf{G}) Y_{lm}(\mathbf{r}) \qquad (3.1.4)$$

has been used and $R_{\rm MT}$ denotes the sphere radius.

If the denominator of (3.1.3) vanishes, numerical problems can occur (asymptote problem). A further difficulty of the APW method is caused by the lack of variational freedom of the $\chi_{\mathbf{k},\mathbf{G}}$ in the MT region, which leads to the requirement that the energy parameter E_l must equal the band energies. With this, equation (3.0.5) becomes a non-linear equation in the energies. This makes the APW method difficult to implement and computationally demanding.

3.2 LAPW method

The LAPW method solves the above mentioned essential problems of the APW approach. The basis functions $\{\chi\}$ are modified in the MT region by adding a second radial function, the energy derivative $\dot{u}_l(r)$ of the radial function $u_l(r)$. So, the basis functions in the unit cell take the form

$$\chi_{\mathbf{k},\mathbf{G}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{N\Omega}} \exp\left[i\left(\mathbf{k}+\mathbf{G}\right)\mathbf{r}\right] & \mathbf{r} \in \mathrm{IR} \\ \frac{1}{\sqrt{N}} \sum_{lm} \left[a_{lm}(\mathbf{k},\mathbf{G})u_l(r) + b_{lm}(\mathbf{k},\mathbf{G})\dot{u}_l(r)\right] Y_{lm}(\mathbf{r}) & \mathbf{r} \in \mathrm{MT} \end{cases}, (3.2.1)$$

where the energy derivative is obtained from

$$\left\{-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l\right\} r\dot{u}_l(r) = ru_l(r).$$
(3.2.2)

By requiring continuity of the basis functions (3.2.1) and their radial derivatives on the MT sphere boundary the coefficients $a_{lm}(\mathbf{k}, \mathbf{G})$, $b_{lm}(\mathbf{k}, \mathbf{G})$ are fixed

$$a_{lm}(\mathbf{k}, \mathbf{G})$$

$$= 4\pi i^{l} \frac{\left(\frac{d}{dr} \dot{u}_{l}(R_{\rm MT}) - i\left(\mathbf{k} + \mathbf{G}\right) \dot{u}_{l}(R_{\rm MT})\right)}{u_{l}(R_{\rm MT}) \frac{d}{dr} \dot{u}_{l}(R_{\rm MT}) - \dot{u}_{l}(R_{\rm MT}) \frac{d}{dr} u_{l}(R_{\rm MT})} j_{l} \left(|\mathbf{k} + \mathbf{G}|R_{\rm MT}\right) Y_{lm}^{*}(\mathbf{k} + \mathbf{G})$$
(3.2.3)

$$b_{lm}(\mathbf{k}, \mathbf{G})$$

$$= 4\pi i^{l} \frac{\left(\frac{d}{dr}u_{l}(R_{\rm MT}) - i\left(\mathbf{k} + \mathbf{G}\right)u_{l}(R_{\rm MT})\right)}{\dot{u}_{l}(R_{\rm MT})\frac{d}{dr}u_{l}(R_{\rm MT}) - u_{l}(R_{\rm MT})\frac{d}{dr}\dot{u}_{l}(R_{\rm MT})}j_{l}\left(|\mathbf{k} + \mathbf{G}|R_{\rm MT}\right)Y_{lm}^{*}(\mathbf{k} + \mathbf{G}).$$
(3.2.4)

The addition of the energy derivative $\dot{u}_l(r)$ in the MT region improves the flexibility of the basis. With the consequence that solutions of the radial Schrödinger equation (3.1.2) with energy ϵ can be synthesized up to an error of the order O $[(\epsilon - E_l)^2]$

$$u_{l}(\epsilon, r) = u(E_{l}, r) + \dot{u}_{l}(E_{l}, r)(\epsilon - E_{l}) + O\left[(\epsilon - E_{l})^{2}\right].$$
(3.2.5)

With this increased flexibility the energy parameters need not equal the band energies, which are then obtained from a linear generalized eigenvalue equation by a single diagonalization. This is an enormous simplification compared to the APW method.

Furthermore there is no asymptote problem in the LAPW approach. This can be shown by using the equations (3.1.2), (3.2.2) and the normalization of u_l $\left(\int dr r^2 u_l^2(r) = 1\right)$

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] f(r) = 0 \left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] g(r) = f(r) \Rightarrow -g \frac{d^2}{dr^2} f + f \frac{d^2}{dr^2} g = -f^2 \Rightarrow \int_0^{R_{\rm MT}} dr \left[-g \frac{d^2}{dr^2} f + f \frac{d^2}{dr^2} g \right] = -\int_0^{R_{\rm MT}} dr f^2 \Rightarrow f(r) \frac{d}{dr} g(r) - g(r) \frac{d}{dr} f(r) \Big|_{R_{\rm MT}} = -1 \Rightarrow r^2 \left(u_l(r) \frac{d}{dr} \dot{u}_l(r) - \dot{u}_l(r) \frac{d}{dr} u_l(r) \right) \Big|_{R_{\rm MT}} = -1 , \qquad (3.2.6)$$

where

$$f(r) = ru_l(r)$$

 $g(r) = r\dot{u}_l(r)$. (3.2.7)

Equation (3.2.6) shows, that the denominator in (3.2.3) and (3.2.4) does not vanish.

The basis-set size can be controlled by the parameters **G**-cutoff g_{max} and *l*-cutoff l_{max} . All **G** vectors inside a sphere around **k** with radius g_{max} and all contributions in the MT region of angular momentum smaller than or equal l_{max} are taken into account. Due to the matching conditions at the MT sphere there exists a connection

between l_{max} , g_{max} and the MT radius R_{MT} . Since a *l*-cutoff of l_{max} allows to represent functions with maximum $2l_{\text{max}}$ nodes along a great circle around the MT sphere (s. Fig. 3.2), i.e. $l_{\text{max}}/\pi R_{\text{MT}}$ nodes per distance, and a **G**-cutoff of g_{max} functions with g_{max}/π nodes per distance, it makes sense to choose g_{max} , l_{max} and R_{MT} such, that the maximal number of nodes per distance is the same in the MT and IR. This leads to the criterion

$$R_{\rm MT}g_{\rm max} = l_{\rm max} . \tag{3.2.8}$$

3.2.1 Representation of density and potential

The rapid variations of the wave functions in the vicinity of the atoms are also seen in the density $n(\mathbf{r}) = \sum_{n,\mathbf{k}}^{\text{occ.}} |\phi_{n,k}(\mathbf{r})|^2$. In order to cope with them a dual representation for the density similar to that for the wave functions is necessary. Furthermore, the fact that the density is invariant under symmetry operations can be exploited to reduce the computational effort. This is achieved by choosing a symmetry-adapted basis set: symmetrized plane waves in the IR, so-called stars, and symmetrized spherical harmonics in the MT spheres, so-called lattice harmonics. The same applies for the potential.

3.2.1.1 Stars

The stars [17] are symmetrized plane waves

$$\phi_s(\mathbf{r}) = \frac{1}{N_{\text{op}}} \sum_{\{R,\tau\}} \exp\left[iR\mathbf{G}\left(\mathbf{r}-\boldsymbol{\tau}\right)\right] , \qquad (3.2.9)$$

where $N_{\rm op}$ denotes the number of space-group elements $\{R, \tau\}$, R denotes the rotational part, τ the translational part. The so-defined stars are invariant under any symmetry operation. All components of a star have the same $|\mathbf{G}|$.

The stars can be constructed by calculating all **G** within the sphere of radius $g_{\text{max}}^{\text{s}}$, where the exact representation of the density $n(\mathbf{r})$ within the IR requires a $g_{\text{max}}^{\text{s}}$ twice as large as the g_{max} for the basis functions. Then the **G**'s are ordered according to their length and those **G**'s of the same length are determined, which can be mapped onto each other by symmetry operations. The number of stars is normally much smaller than the number of plane waves.

3.2.1.2 Lattice harmonics

Inside the MT spheres an expansion in spherical harmonics multiplied by radial functions is used. Symmetry adapted spherical harmonics, so-called lattice harmonics L



Figure 3.2: Number of nodes of a spherical harmonic along a great circle. Figure taken from Ref. 43.

are generated by exploiting the site symmetry of the corresponding atom [17]. As the application of a rotation does not change the l quantum number of the spherical harmonic, the *i*-th lattice harmonics centered at atom \mathbf{R}_a can be written as

$$L_{i,a}(\mathbf{r} - \mathbf{R}_a) = \sum_m c^a_{im} Y_{lm}(\mathbf{r} - \mathbf{R}_a) .$$
 (3.2.10)

The coefficients c_{im}^a are determined by requiring invariance under all symmetry operations of the site symmetry and orthogonality of the lattice harmonics.

Symmetry-equivalent MT spheres exhibit the same charge density (potential) inside (except for a rotation). So, the representation for only one atom of a group of equivalent atoms, the so-called representative atom, has to be calculated. The representations for the other members of the group are either obtained by rotating the representation of the representative atom explicitly. Or, if a local reference frame in each MT sphere is defined, which rotates according to the symmetry operation, which maps the representative atom to the atom under consideration, the expansion coefficients are the same for all atoms of a group.

3.2.2 Poisson solver

The electrostatic potential $V(\mathbf{r})$ consists of the Hartree potential

$$V_{\rm H}(\mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(3.2.11)

and the nuclear potential. It can be determined by integrating the Poisson equation

$$\Delta V(\mathbf{r}) = -4\pi n_{\text{total}}(\mathbf{r}) , \qquad (3.2.12)$$

where $n_{\text{total}}(\mathbf{r})$ subsumes electronic and nuclear charge

$$n_{\text{total}}(\mathbf{r}) = n(\mathbf{r}) + \sum_{\alpha} Z_{\alpha} \delta(\mathbf{r} - \mathbf{R}_{\alpha}) .$$
 (3.2.13)

In the case of a pure plane-wave basis the solution is trivial

$$V(\mathbf{G}) = \frac{4\pi n_{\text{total}}(\mathbf{G})}{\mathbf{G}^2}.$$
 (3.2.14)

In order to determine the electrostatic potential $V(\mathbf{r})$ in the FLAPW method, where space is divided into MT spheres and the interstitial region, the density in the latter is extended over the whole space

$$n_{\text{total}}(\mathbf{r}) = n_{\text{total}}^{\text{IR}}(\mathbf{r})\Theta(\mathbf{r}) + n_{\text{total}}^{\text{MT}}(\mathbf{r}) (1 - \Theta(\mathbf{r}))$$

= $n^{\text{IR}}(\mathbf{r}) + \tilde{n}^{\text{MT}}(\mathbf{r}) (1 - \Theta(\mathbf{r}))$, (3.2.15)

where

$$\tilde{n}^{\mathrm{MT}}(\mathbf{r}) = n_{\mathrm{total}}^{\mathrm{MT}}(\mathbf{r}) - n^{\mathrm{IR}}(\mathbf{r}) \qquad (3.2.16)$$

$$\Theta(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in \mathrm{IR} \\ 0, & \mathbf{r} \in \mathrm{MT} \end{cases} .$$
 (3.2.17)

The electrostatic potential in the IR is created by the interstitial charge but also by the MT multipole moments. Weinert [44] proposed to replace the charge in the MT spheres by a smoother one, the so-called pseudo-charge, which has the same multipole moments as \tilde{n}^{MT} and a convergent Fourier transformation. Otherwise the choice of the pseudo-charge distribution is arbitrary. Usually the polynomial form

$$\tilde{n}_{\text{pseudo}}^{\text{MT}}(\mathbf{r}) = \sum_{lm} Q_{lm} \frac{1}{R_{\text{MT}}^{l+3}} \left(\frac{r}{R_{\text{MT}}}\right)^l \left(1 - \frac{r^2}{R_{\text{MT}}^2}\right)^N Y_{lm}(\mathbf{r}) \qquad (3.2.18)$$

is chosen with a parameter N (typically $N = \frac{1}{2}R_{\rm MT}g_{\rm max}$). The multipole moments of the pseudo-charge are

$$q_{lm}^{\text{pseudo}} = \sqrt{\frac{4\pi}{2l+1}} \int d^3 r \, \tilde{n}_{\text{MT}}^{\text{pseudo}}(\mathbf{r}) r^l Y_{lm}^*(\mathbf{r}) = \sqrt{\frac{4\pi}{2l+1}} \frac{Q_{lm}}{R_{\text{MT}}^{l+3}} \int_0^{R_{\text{MT}}} dr \, r^{l+2} \left(\frac{r}{R_{\text{MT}}}\right)^l \left(1 - \frac{r^2}{R_{\text{MT}}^2}\right)^N = \sqrt{\frac{4\pi}{2l+1}} Q_{lm} \int_0^1 dx \, x^{2l+2} \left(1 - x^2\right)^N = Q_{lm} \frac{2^N N! \, (2l+1)!!}{(2l+2N+3)!!} \,.$$
(3.2.19)

The coefficients Q_{lm} are chosen in such a way that the multipole moments of the pseudo-charge q_{lm}^{pseudo} are identical to the moments q_{lm} of the charge $\tilde{n}^{\text{MT}}(\mathbf{r})$. Thus the potential V in the IR can be computed via (3.2.14) for the density $n_{\text{IR}}(\mathbf{r}) + \tilde{n}_{\text{MT}}^{\text{pseudo}}(\mathbf{r})\Theta(\mathbf{r} \in \text{MT})$.

As the IR potential is now given on the sphere boundary, the determination of the potential in the MT spheres constitutes a spherical boundary problem in each sphere for the true electronic charge density. This problem is solved by using the Green-function approach [45]

$$V^{\rm MT}(\mathbf{r}) = \int_{\rm MT} d^3 r' \, n^{\rm MT}(\mathbf{r}') G(\mathbf{r}, \mathbf{r}') - \frac{R_{\rm MT}^2}{4\pi} \oint_{\rm MT} d\Omega \, V(\mathbf{r}') \frac{\partial G}{\partial n'}, \quad (3.2.20)$$

where the Green function $G(\mathbf{r}, \mathbf{r}')$ for the spherical geometry is given by

$$G(\mathbf{r}, \mathbf{r}') = 4\pi \sum_{lm} \frac{Y_{lm}(\mathbf{r}')Y_{lm}(\mathbf{r})}{2l+1} \frac{\min(r, r')^l}{\max(r, r')^{l+1}} \left(1 - \left(\frac{\max(r, r')}{R_{MT}}\right)^{2l+1}\right) . (3.2.21)$$

Finally, the MT potential is expanded into lattice harmonics

$$V^{\mathrm{MT}}(\mathbf{r}) = \sum_{i} V_{\mathrm{MT},i}(r) L_i(\mathbf{r}) \qquad (3.2.22)$$

and the potential of the nucleus Z_{α}/r is added to the spherical component.

3.2.3 Exchange-correlation potential

The computation of the local or semi-local part of the exchange-correlation potential $V_{\rm xc}$ must be performed in real space, because it is in general a non-linear function of the density. The calculation principally consists of three steps

- calculation of the density at the points of a real-space grid
- evaluation of the exchange-correlation potential at the real-space grid points
- representation of $V_{\rm xc}$ in stars and lattice harmonics.

In the IR the transformation of the density from a plane-wave basis to a real space grid and vice-versa is performed by a fast Fourier transformation [46].

In the MT spheres the radial part of the density is already stored on a radial mesh. However, the lattice harmonics must be evaluated at each mesh point. Then $V_{\rm xc}$ is computed at each discrete point and its representation in radial functions multiplied by lattice harmonics is determined [17].

3.2.4 Core electrons

The radial functions u_l and \dot{u}_l of the LAPW basis set are orthogonal to any other radial solution u of (3.1.2) with a different energy parameter and with a vanishing value on the MT sphere boundary and beyond as it is approximatively the case for core electrons. This can be shown by subtracting the radial Schrödinger equations for u and u_l as well as for u and \dot{u}_l , respectively

$$(E - E_l) r^2 u u_l = r u \frac{d^2}{dr^2} r u_l - r u_l \frac{d^2}{dr^2} r u$$
$$(E - E_l) \int_0^{MT} dr r^2 u u_l = r u \frac{d}{dr} r u_l \Big|_0^{MT} - r u_l \frac{d}{dr} r u \Big|_0^{MT} = 0 \qquad (3.2.23)$$

$$(E - E_l) r^2 u \dot{u}_l = r^2 u u_l + r u \frac{d^2}{dr^2} r \dot{u}_l - r \dot{u}_l \frac{d^2}{dr^2} r u$$
$$(E - E_l) \int_0^{\text{MT}} dr r^2 u \dot{u}_l = \int_0^{\text{MT}} dr r^2 u u_l + r u \frac{d}{dr} r \dot{u}_l \Big|_0^{\text{MT}} - r \dot{u}_l \frac{d}{dr} r u \Big|_0^{\text{MT}} = 0. (3.2.24)$$

Because of this orthogonality the LAPW basis cannot describe the core electrons. Due to their spatial confinement it is justified to treat them atomic-like, by solving the fully relativistic Dirac equation with the spherical part (l = 0) of the potential. For example for Silicon the $1s^{1/2}$, $2s^{1/2}$, $2p^{1/2}$ and $2p^{3/2}$ electrons are considered as core electrons.

However, high-lying core states (e.g. 3*d* electrons in GaAs), so-called semi-core states, whose wave functions extend considerably over the MT sphere boundary cannot be described well neither as core nor as valence electrons in a normal LAPW approach. In order to make an accurate description of these states possible, local orbitals (lo) are added to the LAPW basis set.

3.2.5 Local Orbitals

As discussed in the previous section for the correct treatment of semi-core states additional basis functions, local orbitals (lo), are needed in the corresponding MT sphere [47]. Their radial part is constructed by linear combinations of $u_l(E_l)$, $\dot{u}_l(E_l)$ and a third radial function $u_l(E_l^{\text{lo}})$ with an additional energy parameter E_l^{lo}

$$u_l^{\rm lo}(r) = a_l^{\rm lo} u_l(r, E_l) + b_l^{\rm lo} \dot{u}_l(r, E_l) + c_l^{\rm lo} u_l(r, E_l^{\rm lo}), \qquad (3.2.25)$$

so that u_l^{lo} and du_l^{lo}/dr vanish on the MT boundary and u_l^{lo} is normalized. These three conditions determine the coefficients a_l^{lo} , b_l^{lo} and c_l^{lo} uniquely. Finally, the basis functions added to the LAPW basis at atom a have the form

$$\chi_{\mathbf{k},lm}^{\mathrm{lo},a}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} u_l^{\mathrm{lo}}(|\mathbf{r} - \mathbf{R}_a - \mathbf{T}|) Y_{lm}(\mathbf{r} - \mathbf{R}_a - \mathbf{T}) \exp\left[i\mathbf{kT}\right] . (3.2.26)$$

The local orbitals $\chi_{\mathbf{k},lm}^{\mathrm{lo},a}$ can be used very specifically, e.g., if one wants to describe the 3d semi-core states of Ga in GaAs correctly only local orbitals with d character at the Gallium atom must be added to the basis set. As a result the number of LAPW

basis functions only increases by 2l + 1 local orbitals per equivalent atom.

In the case of a system with inversion symmetry local orbitals are desirable, which obey the relation

$$\chi^{\rm lo}(-\mathbf{r}) = \chi^{\rm lo}(\mathbf{r})^*, \qquad (3.2.27)$$

in order to obtain a real Hamiltonian². This can be achieved by constructing linear combinations over all local orbitals of the same atom type α

$$\chi_{\mathbf{k},\mathbf{G}^{\mathrm{lo}}}^{\mathrm{lo},\alpha}(\mathbf{r}) = \sum_{a\in\alpha} \sum_{\mathbf{T}} \sum_{m} c_{lm}^{\mathrm{lo},a} u_{l}^{\mathrm{lo}}(|\mathbf{r}-\mathbf{R}_{a}-\mathbf{T}|) Y_{lm}(\mathbf{r}-\mathbf{R}_{a}-\mathbf{T}) \exp\left[i\mathbf{kT}\right], \quad (3.2.28)$$

and matching these to virtual plane waves which have zero amplitude

$$c_{lm}^{\text{lo},a} = \frac{1}{\sqrt{V}} 4\pi \exp\left[i(\mathbf{k} + \mathbf{G}^{\text{lo}})\mathbf{R}_{a}\right] i^{l} j_{l}(|\mathbf{k} + \mathbf{G}^{\text{lo}}|R_{\text{MT}}) Y_{lm}^{*}(R(\mathbf{k} + \mathbf{G}^{\text{lo}})). \quad (3.2.29)$$

R denotes the rotation which maps the global frame to the local one attached to the MT centered at \mathbf{R}_a (cf. Eq. (3.1.3)). The Bessel function does not influence the angular behavior and can be omitted. The \mathbf{G}^{lo} are chosen in such a way that the local orbitals are linearly independent.

3.2.6 Brillouin-zone integration

Summing up all occupied states is necessary for the calculation of several quantities, e.g. the density $n(\mathbf{r}) = \sum_{\mathbf{k},\epsilon_n(\mathbf{k}) \leq E_F} |\phi_{n,\mathbf{k}}(\mathbf{r})|^2$ or the eigenvalue sum $\sum_{\mathbf{k},\epsilon_n(\mathbf{k}) \leq E_F} \epsilon_{n,\mathbf{k}}$. In an infinite system these sums involve an integral over the Brillouin zone (BZ)

$$\sum_{\mathbf{k},\epsilon_n(\mathbf{k})\leq E_F} f_n(\mathbf{k}) \to \frac{1}{V_{\mathrm{BZ}}} \int_{\epsilon_n(\mathbf{k})\leq E_F} d^3k f_n(\mathbf{k}) . \qquad (3.2.30)$$

The integration over the reciprocal space can be calculated numerically by using for example the tetrahedron [48] or the special points method [49]. In both approaches the integral is replaced by a weighted sum $\sum_{n,\mathbf{k}} w(n,\mathbf{k}) f_n(\mathbf{k})$.

$$\begin{aligned} \langle \chi_{\mathbf{k},\mathbf{G}} | H | \chi_{\mathbf{k},\mathbf{G}'} \rangle &= \langle \chi_{\mathbf{k},\mathbf{G}} | H I | \chi_{\mathbf{k},\mathbf{G}'} \rangle \\ &= \langle \chi_{\mathbf{k},\mathbf{G}}^* | H | \chi_{\mathbf{k},\mathbf{G}'}^* \rangle \\ &= \langle \chi_{\mathbf{k},\mathbf{G}'} | H | \chi_{\mathbf{k},\mathbf{G}} \rangle \\ &= (\langle \chi_{\mathbf{k},\mathbf{G}} | H | \chi_{\mathbf{k},\mathbf{G}} \rangle)^* \end{aligned}$$

² Let *I* be the inversion operator, *H* be the Hamiltonian of a system with inversion symmetry and $\chi_{\mathbf{k},\mathbf{G}}(-\mathbf{r}) = \chi^*_{\mathbf{k},\mathbf{G}}(\mathbf{r})$ be valid. Then *I* commutes with *H* and the matrix elements of *H* in the basis $\{\chi_{\mathbf{k},\mathbf{G}}\}$ are real symmetric:

3.2.7 Self-consistency

Since the local potential of the KS system depends on the density itself the KS equations must be solved self-consistently. That means, starting with a suitably chosen density n_1 , for example a superposition of atomic densities, the potential is set up, the KS equations are solved and a new density $n_2(\mathbf{r}) = \sum_{n,\mathbf{k}}^{\text{occ.}} |\phi_{n,\mathbf{k}}(\mathbf{r})|$ is constructed. These steps formally define a mapping

$$n_{m+1}(\mathbf{r}) = F[n_m(\mathbf{r})]$$
 (3.2.31)

It is iterated until the integrated square of the difference between output and input densities is smaller than a given threshold (usually $10^{-4} - 10^{-6} \text{me/Bohr}^3$).

However in practice this scheme is often divergent. In order to achieve convergence the output density has to be mixed with the input density. Different mixing schemes are available, like simple mixing and Broyden mixing of first and second kind. In the first case the new density is constructed by a linear combination of the input and output density

$$n_{m+1}(\mathbf{r}) = (1-\alpha)n_m(\mathbf{r}) + \alpha F[n_m(\mathbf{r})]$$
(3.2.32)

with the mixing parameter α . Simple mixing provides a linear convergence, that means

$$\frac{|\delta n_{m+1}|}{|\delta n_m|} \leq \text{ const.} , \qquad (3.2.33)$$

where δn_m denotes the distance of the density of the *m*-th iteration from the unknown fix-point n_0

$$\delta n_m = n_m - n_0 . (3.2.34)$$

The Broyden mixing schemes belong to the so-called quasi-Newton methods. They base on the idea to find the zero point of the mapping

$$\ddot{F}[n] = F[n] - n$$
. (3.2.35)

When the density is expanded into a set of basis functions, it can be represented by a coefficient vector. So, equation (3.2.35) can be regarded as a function mapping from \mathbb{C}^N to \mathbb{C}^N , where N denotes the number of basis functions. In order to find the zero point of the mapping it is expanded around the approximate solution n_m

$$\tilde{F}[n] = \tilde{F}[n_m] + J(n - n_m) ,$$
 (3.2.36)

where J denotes the Jacobian. In analogy to the Newton method in one dimension



Figure 3.3: Schematic program process

the approximation n_{m+1} is obtained by the condition

$$\hat{F}[n_{m+1}] = 0$$

 $\Rightarrow n_{m+1} = n_m - J^{-1} \tilde{F}[n_m] .$
(3.2.37)

The difficulty in this method arises in the setting up and inversion of the Jacobian J. In the quasi-Newton methods it is set up approximately and improved in each iteration step. Quasi-Newton methods converge super-linearly

$$\frac{|\delta n_{m+1}|}{|\delta n_m|} \to 0.$$
(3.2.38)

A detailed discussion of the different methods can be found in [50].

Finally the numerical process of the self-consistency loop is schematically illustrated in Figure 3.3.
4 Evaluation of the exchange potential

As discussed in chapter 2 the non-local exchange potential is an important ingredient in hybrid functionals, which in the gKS scheme lead to one-particle equations of the form

$$\left(-\frac{1}{2}\nabla^2 + V_{\rm gKS}^{\sigma}(\mathbf{r})\right)\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) - a\sum_{n',\mathbf{q}}^{\rm occ.}\int d^3r' \,\frac{\phi_{n',\mathbf{q}}^{\sigma*}(\mathbf{r}')\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\phi_{n',\mathbf{q}}^{\sigma}(\mathbf{r}) = \epsilon_{n,\mathbf{k}}^{\sigma}\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) \,, \, (4.0.1)$$

where from now on we also take into account the electron spin σ . In the LAPW basis $\{\chi_{\mathbf{k},\mathbf{G}}^{\sigma}\}$ the differential equation becomes an algebraic one

$$\sum_{\mathbf{G}} \left[H^{\sigma}_{\mathbf{G}'\mathbf{G}}(\mathbf{k}) + aV^{\sigma}_{\mathbf{x},\mathbf{G}'\mathbf{G}}(\mathbf{k}) \right] z^{\sigma}_{\mathbf{G}}(n,\mathbf{k}) = \epsilon^{\sigma}_{n,\mathbf{k}} \sum_{\mathbf{G}} S^{\sigma}_{\mathbf{G}'\mathbf{G}}(\mathbf{k}) z^{\sigma}_{\mathbf{G}}(n,\mathbf{k}) \quad (4.0.2)$$

with the exact-exchange matrix

$$V_{\mathbf{x},\mathbf{G'G}}^{\sigma}(\mathbf{k}) = -\sum_{n',\mathbf{q}}^{\text{occ.}} \iint d^3r d^3r' \frac{\chi_{\mathbf{k},\mathbf{G'}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{q}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{q}}^{\sigma*}(\mathbf{r}')\chi_{\mathbf{k},\mathbf{G}}^{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} . \quad (4.0.3)$$

While straightforward in Gaussian and plane-wave basis sets, its efficient implementation in the highly accurate LAPW method is still a challenge. In order to illustrate the effort for the computation of one matrix element $V_{\mathbf{x},\mathbf{G}'\mathbf{G}}^{\sigma}(\mathbf{k})$ within the LAPW method, the number of double integrals, which must be evaluated, is estimated. The double integral (4.0.3) can be decomposed into

$$\int_{\rm MT} d^3r \int_{\rm MT} d^3r' \dots + \int_{\rm MT} d^3r \int_{\rm IR} d^3r' \dots + \int_{\rm IR} d^3r \int_{\rm MT} d^3r' \dots + \int_{\rm IR} d^3r \int_{\rm IR} d^3r' \dots + \int_{\rm IR} d^3r' \dots + \int_{\rm IR} d^3r' \int_{\rm IR} d^3r' \dots + \int_{\rm IR} d^3r' \dots$$

For Silicon with $l_{\text{max}} = 8$, $g_{\text{max}} = 3.6$ Htr and a lattice constant of 5.43Å the basis set $\{\chi^{\sigma}_{\mathbf{k},\mathbf{G}}\}$ consists of 222 elements. The number of double integrals for the different combinations split up into

- $\int_{\mathrm{MT}} d^3r \int_{\mathrm{MT}} d^3r' \dots 162^4$ integrals
- $\int_{\mathrm{MT}} d^3r \int_{\mathrm{IR}} d^3r' \dots \& \int_{\mathrm{IR}} d^3r \int_{\mathrm{MT}} d^3r' \dots : 162^2 \cdot 222$ integrals

• $\int_{\mathrm{IR}} d^3r \int_{\mathrm{IR}} d^3r' \dots$: 222² integrals .

In total 700.449.156 integrals must be evaluated to obtain one matrix element $V_{\mathbf{x},\mathbf{G'G}}^{\sigma}(\mathbf{k})$ not including the summation over the Brillouin zone (BZ).

Therefore an efficient algorithm is needed to reduce the effort for computing the exchange term. One possibility is to generalize the Poisson solver (s. Sec. 3.2.2), since the product $\phi_{n',\mathbf{q}}^{\sigma*}(\mathbf{r}')\chi_{\mathbf{k},\mathbf{G}}^{\sigma}(\mathbf{r}')$ can be regarded as an artificial density $\hat{n}(\mathbf{r}')$, which is in general complex and does not show the symmetry of the crystal. A generalization of the Poisson solver permits to calculate the integral

$$\int d^3 r' \, \frac{\phi_{n',\mathbf{q}}^{\sigma*}(\mathbf{r}')\chi_{\mathbf{k},\mathbf{G}}^{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \,. \tag{4.0.4}$$

A detailed discussion of this approach can be found in Ref. 51.

We use a different approach. It is based on the representation of the product $\phi_{n',\mathbf{q}}^{\sigma}(\mathbf{r})\chi_{\mathbf{k},\mathbf{G}}^{\sigma*}(\mathbf{r})$ in a specifically designed basis $\{M\}$. In this way, the computation of the exchange potential $V_{\mathbf{x},\mathbf{G}'\mathbf{G}}^{\sigma}$ becomes a BZ sum over vector-matrix-vector products

$$V_{\mathbf{x},\mathbf{G'G}}^{\sigma}(\mathbf{k})$$

$$= -\sum_{n',\mathbf{q}}\sum_{IJ} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \left| \chi_{\mathbf{k},\mathbf{G}}^{\sigma} \tilde{M}_{\mathbf{q},I} \right\rangle \left\langle M_{\mathbf{q},I} \left| \frac{1}{|\mathbf{r}-\mathbf{r'}|} \right| M_{\mathbf{q},J} \right\rangle \left\langle \tilde{M}_{\mathbf{q},J} \chi_{\mathbf{k},\mathbf{G'}}^{\sigma} \right| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$(4.0.5)$$

where $\left\{\tilde{M}\right\}$ is the biorthogonal basis. The Coulomb matrix [52]

$$C_{IJ}(\mathbf{q}) = \left\langle M_{\mathbf{q},I} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| M_{\mathbf{q},J} \right\rangle$$
$$= \iint d^3 r d^3 r' \frac{M_{\mathbf{q},I}^*(\mathbf{r}) M_{\mathbf{q},J}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} , \qquad (4.0.6)$$

has to be calculated only once at the beginning of a calculation: instead of calculating the double integral (4.0.3) in each self-consistency step for all combinations of **G**, **G'**, **k**, **q** and n' only the projection $\langle \tilde{M}_{\mathbf{q},J}\chi^{\sigma}_{\mathbf{k},\mathbf{G}} | \phi^{\sigma}_{n',\mathbf{k}+\mathbf{q}} \rangle$, a single integral, has to be evaluated.

We compute the exchange potential (4.0.3) in the space of the wave functions and subsequently transform it to the LAPW basis. This procedure simplifies the treatment of the Γ point (s. Sec. 4.3) and permits to eliminate negligible contributions to the exchange matrix, which will speed up calculations considerably (s. Ch. 5).

For the transformation a relation between basis and wave functions is needed.

Equation (3.0.4) can be formally written as

$$\phi^{\sigma}(\mathbf{k}) = T^{\sigma^{T}}(\mathbf{k}) \chi^{\sigma}(\mathbf{k})$$
(4.0.7)

with

$$T^{\sigma}(\mathbf{k}) = \begin{pmatrix} z^{\sigma}_{\mathbf{G}_{1}}(n_{1}, \mathbf{k}) & \dots & z^{\sigma}_{\mathbf{G}_{1}}(n_{N}, \mathbf{k}) \\ \vdots & \ddots & \\ z^{\sigma}_{\mathbf{G}_{N}}(n_{1}, \mathbf{k}) & z^{\sigma}_{\mathbf{G}_{N}}(n_{N}, \mathbf{k}) \end{pmatrix}$$
(4.0.8)

$$\chi^{\sigma}(\mathbf{k}) = \begin{pmatrix} \chi^{\sigma}_{\mathbf{G}_{1}}(\mathbf{k}) \\ \vdots \\ \chi^{\sigma}_{\mathbf{G}_{N}}(\mathbf{k}) \end{pmatrix} \phi^{\sigma}(\mathbf{k}) = \begin{pmatrix} \phi^{\sigma}_{n_{1},\mathbf{k}} \\ \vdots \\ \phi^{\sigma}_{n_{N},\mathbf{k}} \end{pmatrix} .$$
(4.0.9)

Due to the orthogonality of the wave functions

$$T^{\sigma^{T^*}}S^{\sigma}T^{\sigma} = 1 \tag{4.0.10}$$

the inverse of T is

$$T^{\sigma^{-1}} = T^{\sigma^{T^*}} S^{\sigma} . (4.0.11)$$

Thus, the transformation is given by

$$V_{\mathbf{x},\mathbf{G'G}}^{\sigma}(\mathbf{k}) = -\sum_{n',\mathbf{q}}^{\text{occ.}} \iint d^3 r d^3 r' \frac{\chi_{\mathbf{k},\mathbf{G}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}')\chi_{\mathbf{k},\mathbf{G'}}^{\sigma*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$= -\sum_{n_1,n_2} T_{n_1,\mathbf{G}}^{\sigma^{-1}}(\mathbf{k}) \sum_{n',\mathbf{q}}^{\text{occ.}} \iint d^3 r d^3 r' \frac{\phi_{n_1,\mathbf{k}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma*}(\mathbf{r}')\phi_{n_2,\mathbf{k}}^{\sigma*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} T_{n_2,\mathbf{G'}}^{\sigma^{-1*}}(\mathbf{k})$$

and (4.0.5) becomes

$$V_{\mathbf{x},n_{1}n_{2}}^{\sigma}(\mathbf{k})$$

$$= -\sum_{n',\mathbf{q}}^{\text{occ.}} \sum_{IJ} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} \tilde{M}_{\mathbf{q},I} \right\rangle \left\langle M_{\mathbf{q},I} \middle| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \middle| M_{\mathbf{q},J} \right\rangle \left\langle \tilde{M}_{\mathbf{q},J} \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle.$$

$$(4.0.13)$$

It should be noted, that the transformation maps the exchange potential on the LAPW basis functions of the previous self-consistency cycle instead of on the current basis. In the limit of convergence this inconsistency vanishes. Its influence on the convergence behavior has been examined by inserting a projector

$$\sum_{\mathbf{G}} |\chi_{\mathbf{k},\mathbf{G}}\rangle \langle \chi_{\mathbf{k},\mathbf{G}}| \tag{4.0.14}$$

on the actual basis set. With this the exchange potential is approximately transformed on the current basis set. However, we have observed only little changes in the convergence behavior or in the converged results.

4.1 Construction of the mixed basis

A good basis set $\{M\}$ for representing the products of wave functions should be provided by MT and interstitial functions, each constructed from products of the corresponding parts in the LAPW basis functions. In contrast to the LAPW basis set the interstitial functions are not combined with those in the MT spheres to build continuous functions all over the space. Instead, they are simply grouped together in a mixed basis [53].

4.1.1 Muffin-tin region

Within the MT region of a given atom a the product of two LAPW basis functions consists of terms

$$u_{pl}^{a\sigma}(r)u_{p'l'}^{a\sigma}(r)Y_{lm}^{*}(\mathbf{r})Y_{l'm'}(\mathbf{r}) = u_{pl}^{a\sigma}(r)u_{p'l'}^{a\sigma}(r)\sum_{LM}G_{lm,l'm',LM}Y_{LM}(\mathbf{r}) , \quad (4.1.1)$$

where p and p' distinguish between radial function u_l , energy derivative \dot{u}_l and local orbital u_l^{lo} , and

$$G_{lm,l'm',LM} = \int d\Omega Y_{lm}^*(\mathbf{r}) Y_{l'm'}(\mathbf{r}) Y_{LM}^*(\mathbf{r}) \qquad (4.1.2)$$

are the Gaunt coefficients, which are non-zero only if $L \in \{|l - l'|, \dots, l + l'\}, M = m' - m$ or |M| < L.

The product of two radial functions

$$\varphi_{iL}^{a\sigma}(r) = u_{pl}^{a\sigma}(r)u_{p'l'}^{a\sigma}(r) \tag{4.1.3}$$

multiplied by a corresponding spherical harmonic is defined as a preliminary basis in the MT sphere at atom a

$$\hat{M}_{iLM}^{a\sigma}(\mathbf{r}) = \varphi_{iL}^{a\sigma}(r)Y_{LM}(\mathbf{r}) . \qquad (4.1.4)$$

To each L there are several combinations of pl and p'l'. These combinations are counted with the index *i*.

The so-defined set $\{\hat{M}\}$ consists of several hundred functions (s. Table 4.2). In order to reduce the MT basis-set size several additional parameters are introduced into the FLEUR input file (s. Fig. 4.1):

lcutm: Only basis functions \hat{M} up to $L \leq$ lcutm are constructed.

- **select:** The keyword select is used to restrict the radial functions u_{pl} , which are used to set up $\{\hat{M}\}$. As an example the choice select = 3, 2; 4, 4 restricts the radial functions in equation (4.1.3) to $l \leq 3$ for p = 1, $l \leq 2$ for p = 2, $l' \leq 4$ for p' = 1 and p' = 2. The radial part of a local orbital (p > 2, p' > 2) is always used to construct $\{\tilde{M}\}$.
- **mtol**: In order to get rid of those functions \hat{M} for a fixed L, which do not significantly improve the flexibility of the basis set, the overlap matrix between the different radial functions $\varphi_{iL}^{a\sigma}$

$$O_{(i\sigma)(i'\sigma')}^{L} = \int_{0}^{R_{\rm MT(a)}} dr r^{2} \varphi_{iL}^{a\sigma}(r) \varphi_{i'L}^{a\sigma'}(r) \qquad (4.1.5)$$

is diagonalized and only those eigenvectors with an eigenvalue, which is greater then the threshold mtol (typical value 10^{-4}), are retained. As a side effect the basis set is orthogonalized and becomes spin-independent, because products of both spin-up as well as spin-down basis functions are included in (4.1.5).

Table 4.2 shows the number of MT basis functions for different choices of these parameters.

As the product of two Bloch functions is again a Bloch function, the final form of the MT basis functions is obtained by constructing Bloch functions explicitly

$$M^{a}_{\mathbf{k},iLM}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} \hat{M}_{iLM}(\mathbf{r} - \mathbf{T} - \mathbf{R}_{a}) \exp\left[i\mathbf{k}(\mathbf{T} + \mathbf{R}_{a})\right]$$
$$M^{a}_{\mathbf{k},iLM}(\mathbf{r} + \mathbf{T}') = \exp\left[i\mathbf{k}\mathbf{T}'\right] M^{a}_{\mathbf{k},iLM}(\mathbf{r}) . \qquad (4.1.6)$$

The factor $\exp[i\mathbf{kR}_a]$ has been added to obtain a simple expression for the Coulombmatrix expansion.

4.1.2 Interstitial region

The product of two plane waves is again a plane wave. Consequently the basis M in the IR is simply defined by

$$M_{\mathbf{k},I}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} \exp\left[i(\mathbf{k} + \mathbf{G}_I)\mathbf{r}\right] & \text{for } \mathbf{r} \in \mathrm{IR} \\ 0 & \text{for } \mathbf{r} \in \mathrm{MT} \end{cases}$$
(4.1.7)

These functions are not orthogonal, because they are non-zero only in the interstitial region. Therefore the set of biorthogonal functions

$$\tilde{M}_{\mathbf{k},I}(\mathbf{r}) = \sum_{J} O_{JI}^{-1}(\mathbf{k}) M_{\mathbf{k},J}(\mathbf{r})$$
(4.1.8)

is used in conjunction with $\{M\}$ with the k-dependent overlap matrix

$$O_{IJ}(\mathbf{k}) = \langle M_{\mathbf{k},I} | M_{\mathbf{k},J} \rangle , \qquad (4.1.9)$$

but must never be constructed explicitly. The overlap matrix is **k**-dependent, since the number of basis functions can vary at different **k** points. $\{M_{\mathbf{k},J}\}$ and $\{\tilde{M}_{\mathbf{k},I}\}$ form a pairwise orthonormal set of functions

$$\left\langle M_{\mathbf{k},I} \left| \tilde{M}_{\mathbf{k},J} \right\rangle = \delta_{IJ} \right.$$

The size of the interstitial basis set can be controlled by a G cutoff gcutm (s. Fig. 4.1).

The complete mixed basis is a combination of the two sets $\{M^a_{\mathbf{k},iLM}, M_{\mathbf{k},\mathbf{G}}\} = \{M_{\mathbf{k},I}\}$. The MT function $M_{\mathbf{k},I}$ are zero in the IR and vice-versa.

In Figure 4.2 the MT representation of selected wave-function products in the mixed basis $\{M_{\mathbf{k},I}\}$ is compared with the exact product. With higher cutoff values leutm convergence with the exact curve is achieved.

In the IR the representation becomes exact when a gcutm twice as large as the **G** cutoff g_{max} of the LAPW basis is chosen.

If the basis is sufficiently complete it is justified to use the completeness relation

$$\sum_{I} \left| \tilde{M}_{\mathbf{k},I} \right\rangle \left\langle M_{\mathbf{k},I} \right| = 1 \tag{4.1.10}$$

in the space of wave-functions products.

\mathbf{L}	mtol = 0	mtol = 0.0001	mtol = 0.0001	mtol = 0.0001
	select = 8, 8; 8, 8	select = 8, 8; 8, 8	select = 4, 4; 4, 4	select = 4, 4; 4, 4
	lcutm = 16	lcutm = 16	lcutm = 16	lcutm = 4
0	27	12	10	10
1	48	10	8	8
2	66	10	8	8
3	78	9	7	7
4	87	8	7	7
5	90	7	6	
6	90	7	5	
7	84	7	4	
8	75	6	3	
9	60	6		
10	48	5		
11	36	5		
12	27	5		
13	18	5		
14	12	4		
15	6	4		
16	3	3		
Sum	11295	1535	428	186

Table 4.2: The number of radial basis functions with angular-momentum quantum number L for different choices of the parameters mtol, select and lcutm. The last row shows the total number of MT functions taking into account the multiplicity $M = -L, \ldots, L$. The results are obtained for Silicon with $l_{\text{max}} = 8$.

```
strho=F,fifm=F,dos=F,isec1=99,ndir= 0,secvar=F
C (diamond) {exp lattice constant, 2 atoms unit cell}
any any ,invs=T,zrfs=F,invs2=F,jspins=1,l_noco=F,l_J=F
  0.00000000 \quad 3.37150000 \quad 3.37150000
  3.37150000 0.00000000 3.37150000
  3.37150000 - 3.37150000 - 0.000000000
                                        0.00000000
                                                     1.00000000
hf non-relativi
gcutm= 5.50000,mtol=0.00010000,Iambda= 8.radius=15,15,lexp=16,bands=100
 1
*****
C 6 1 6 343 1.420000 0.029000
2,force =F,lcutm= 4,select= 4, 2; 4, 4,nlo= 0,llo=
 1,000000 1,000000 1,000000 8,000000
-1.000000 -1.000000 -1.000000 8.000000
********************************
12.600000 10.500000
vchk=F,cdinf=F,pot8=T,gw=0,gw_neigd=_0
lpr=0,form66=F,l_f=F,eonly=F,eig66=F
6
 10
Window #1
 -2.00000 20.00000 8.00000
 4.20000
gauss=F 0.00100tria=F
 0.00000 0.00000,1_soc=F
frcor=T,slice=F,ctail=F,disp=F,kcrel=0,u2f=F,f2u=F
itmax=99,maxiter= 15,imix= 7,alpha= 0.05,spinf= 2.00
swsp=F 0.00
Iflip=F 1
vacdos=F,layers=0,integ=F,star=F,nstars=0 0.00 0.00 0.00 0.00,nstm=0,tworkf=
0.000000
iplot=F,score=F,plpot=F,band=F
0 0.000000 0.000000,nnne= 0,pallst=F
xa= 2.00000,thetad= 330.00000,epsdisp= 0.00001,epsforce= 0.00001
relax 001
emin_dos= -0.50000,emax_dos= 0.50000,sig_dos= 0.01500
nkpt= 59
```

Figure 4.1: Additional parameters in the input file that control the size of the mixed basis: gcutm, mtol, lcutm and select.



Figure 4.2: Comparison of the exact wave-function product $\phi_{n_1,\mathbf{k}}^*\phi_{n_2,\mathbf{k}+\mathbf{q}}$ with its mixed-basis representation for different lcutm inside a MT sphere for Silicon.

4.2 Calculation of $\left\langle \tilde{M}_{\mathbf{q},I}\phi_{n,\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$

For a given **k** point the representation of the product $\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})$ in the biorthogonal set $\{\tilde{M}\}$ must be calculated for all occupied bands n', for all bands n and for all \mathbf{q} . Due to the different basis functions in the MT spheres and the IR, the evaluation is discussed separately for each region.

4.2.1 Muffin-tin region

In the MT region the biorthogonal functions $\tilde{M}_{\mathbf{q},I}$ are identical to the functions $M_{\mathbf{q},I}$ (I = aiLM) and non-zero only in the MT sphere a

$$\int d^{3}r M_{\mathbf{q},I}^{*}(\mathbf{r})\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})$$

$$= \frac{1}{N^{\frac{1}{2}}} \exp\left[-i\mathbf{q}\mathbf{R}_{a}\right] \sum_{plm} \sum_{p'l'm'} c_{plm}^{a\sigma*}(n,\mathbf{k}) c_{p'l'm'}^{a\sigma}(n',\mathbf{k}+\mathbf{q})$$

$$\int_{0}^{R_{\mathrm{MT}(a)}} dr r^{2} \varphi_{iL}^{a}(r) u_{pl}^{a\sigma}(r) u_{p'l'}^{a\sigma}(r) \underbrace{\int d\Omega Y_{LM}^{*}(\mathbf{r}) Y_{l'm'}(\mathbf{r}) Y_{lm}^{*}(\mathbf{r})}_{\mathbf{G}_{LM,l'm',lm}} . \quad (4.2.1)$$

The sum over m' cancels, if the property of the Gaunt coefficients $G_{LM,l'm',lm} = 0$ if $m' \neq m + M$ is exploited. Furthermore, the radial integral remains identical if pl and p'l' are exchanged, which can be used to restrict the sum over p'l' and we can write

$$\int d^{3}r \, M_{\mathbf{q},I}^{*}(\mathbf{r})\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})$$

$$= \frac{1}{N^{\frac{1}{2}}} \exp\left[-i\mathbf{q}\mathbf{R}_{a}\right] \sum_{plm} \sum_{p'=1}^{p} \sum_{l'=0}^{l} \int_{0}^{R_{\mathrm{MT}(a)}} dr \, r^{2}\varphi_{iL}^{a}(r)u_{pl}^{a}(r)u_{p'l'}^{a}(r)$$

$$\left[c_{plm}^{a\sigma*}(n,\mathbf{k})c_{p'l'm+M}^{a\sigma}(n',\mathbf{k}+\mathbf{q})G_{lm,l'm+M,LM}\right.$$

$$\left.+c_{p'l'(m-M)}^{a\sigma*}(n,\mathbf{k})c_{plm}^{a\sigma}(n',\mathbf{k}+\mathbf{q})G_{l'm-M,lm,LM}\right] . \qquad (4.2.2)$$

The vector $\mathbf{k} + \mathbf{q}$ can fall outside the first Brillouin zone (1. BZ). Then we must replace $\mathbf{k} + \mathbf{q}$ by $\mathbf{k} + \mathbf{q} + \mathbf{G}'$ in (4.2.2), where \mathbf{G}' maps $\mathbf{k} + \mathbf{q}$ back into the 1. BZ.

4.2.2 Interstitial region

Now the computation of $\left\langle \tilde{M}_{\mathbf{q},I}\phi_{n,\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$ for an interstitial basis function $\tilde{M}_{\mathbf{q},I}$ with $I = \mathbf{G}_{I}$ is discussed. The product of two wave functions $\phi_{n,\mathbf{k}}^{\sigma*}\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}$ in the IR is

$$\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}) = \sum_{\mathbf{GG}'} z_{\mathbf{G}}^{*}(n,\mathbf{k})z_{\mathbf{G}'}(n',\mathbf{k}+\mathbf{q})\frac{1}{V}\exp\left[i\left(\mathbf{q}+\mathbf{G}'-\mathbf{G}\right)\mathbf{r}\right], \quad (4.2.3)$$

where the exponential function can be regarded as an interstitial basis function $M_{\mathbf{q},\mathbf{G}'-\mathbf{G}}$

$$\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}) = \sum_{\mathbf{GG}'} z_{\mathbf{G}}^{*}(n,\mathbf{k}) z_{\mathbf{G}'}(n',\mathbf{k}+\mathbf{q}) \frac{1}{\sqrt{V}} M_{\mathbf{q},\mathbf{G}'-\mathbf{G}}(\mathbf{r}) . \quad (4.2.4)$$

By exploiting the pairwise orthogonality of $\{M, \tilde{M}\}$ the representation is easily obtained

$$\int d^{3}r \, \tilde{M}_{\mathbf{q},\mathbf{G}_{I}}^{*}(\mathbf{r}) \phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r}) \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}$$

$$= \sum_{\mathbf{G}\mathbf{G}'} z_{\mathbf{G}}^{*}(n,\mathbf{k}) z_{\mathbf{G}'}(n',\mathbf{k}+\mathbf{q}) \frac{1}{\sqrt{V}} \underbrace{\int d^{3}r \, \tilde{M}_{\mathbf{q},\mathbf{G}_{I}}(\mathbf{r}) M_{\mathbf{q},\mathbf{G}'-\mathbf{G}}(\mathbf{r})}_{\delta_{\mathbf{G}_{I},\mathbf{G}'-\mathbf{G}}}$$

$$= \frac{1}{\sqrt{N}} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} z_{\mathbf{G}}^{*}(n,\mathbf{k}) z_{\mathbf{G}+\mathbf{G}_{I}}(n',\mathbf{k}+\mathbf{q}) . \qquad (4.2.5)$$

The factor $\frac{1}{\sqrt{N}}$ in (4.2.2) and (4.2.5) combine to a factor $\frac{1}{N}$ in (4.0.13), which cancels with the factor N from the sum over the BZ.

4.3 Treatment of the Γ point

Due to the long-range nature of the Coulomb interaction the Coulomb matrix $C_{IJ}(\mathbf{q})$ diverges for $\mathbf{q} \to 0$. The 3-dimensional BZ integration over this divergence (~ $1/q^2$) yields a finite value. However, numerically the BZ integral is evaluated by a weighted sum over a discrete **k**-point mesh (s. Sec. 3.2.6), which contains the Γ point, where the integrand is infinite. In order to integrate over the divergence properly we separate the divergent part from the non-divergent one and integrate it analytically.

For this the Coulomb matrix (4.0.6) is diagonalized around the Γ point. In a complete basis the exact eigenvectors and -values of the Coulomb matrix would be plane waves $\frac{1}{\sqrt{V}} \exp \left[i\left(\mathbf{q} + \mathbf{G}_I\right)\mathbf{r}\right]$ with eigenvalues $4\pi/|\mathbf{q} + \mathbf{G}_I|^2$. However, the mixed basis is only complete in the space spanned by the products of wave functions. Thus

the resulting eigenvectors $E_{\mathbf{q},I}$ with eigenvalues $e_{\mathbf{q},I}$ are similar but not identical to plane waves. As a constant function is added to the basis $\{M\}$, the plane wave with $\mathbf{G}_{I=1} = 0$ is represented exactly in the limit $\mathbf{q} \to 0$. The remaining eigenvalues $e_{\mathbf{q},I}$ and -vectors $E_{\mathbf{q},I}$ are calculated numerically. After the transformation into the basis of eigenvectors $\{E_{\mathbf{q},I}\}$, one obtains for small \mathbf{q}

$$\sum_{IJ} \sum_{n'}^{\text{occ.}} w_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} \tilde{M}_{\mathbf{q},I} \right\rangle C_{IJ}(\mathbf{q}) \left\langle \tilde{M}_{\mathbf{q},J} \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$
$$= \sum_{n'}^{\text{occ.}} w_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} \frac{1}{\sqrt{V}} \exp\left[i\mathbf{q}\mathbf{r}\right] \right\rangle \frac{4\pi}{q^{2}} \left\langle \frac{1}{\sqrt{V}} \exp\left[i\mathbf{q}\mathbf{r}\right] \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$
$$+ \sum_{I \neq 1} \sum_{n'}^{\text{occ.}} w_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} E_{\mathbf{q},I} \right\rangle e_{\mathbf{q},I} \left\langle E_{\mathbf{q},I} \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle , \qquad (4.3.1)$$

where V denotes the crystal volume and $w_{n,\mathbf{k}}^{\sigma}$ the integration weight of band n and point **k**. The two terms correspond to the divergent and the non-divergent term, respectively. The former contains additional **q**-dependent terms. In order to obtain the analytic behavior of the divergent term around the Γ point, the projections of the wave-function products $\phi_{n,\mathbf{k}}^{\sigma*}\phi_{n',\mathbf{k+q}}^{\sigma}$ on the plane wave $\frac{1}{\sqrt{V}} \exp[i\mathbf{qr}]$ have to be expanded around $\mathbf{q} = 0$. For this the Bloch property of the wave functions $\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) = u_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) \exp[i\mathbf{kr}]$ is employed and $u_{n,\mathbf{k+q}}^{\sigma}$ is expanded around $\mathbf{q} = 0$

$$\left\langle \frac{1}{\sqrt{V}} \exp\left[i\mathbf{q}\mathbf{r}\right] \phi_{n,\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \frac{1}{\sqrt{V}} \left\langle u_{n,\mathbf{k}}^{\sigma} \middle| u_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \frac{1}{\sqrt{V}} \left[\left\langle u_{n,\mathbf{k}}^{\sigma} \middle| u_{n',\mathbf{k}}^{\sigma} \right\rangle + \left\langle u_{n,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{T} u_{n',\mathbf{k}}^{\sigma} \right\rangle \mathbf{q} + \frac{1}{2} \mathbf{q}^{T} \left\langle u_{n,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{2} u_{n',\mathbf{k}}^{\sigma} \right\rangle \mathbf{q} + O\left(q^{3}\right) \right]$$

$$= \frac{1}{\sqrt{V}} \left\{ \begin{array}{c} 1 + \frac{1}{2} \mathbf{q}^{T} \left\langle u_{n,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{2} u_{n',\mathbf{k}}^{\sigma} \right\rangle \mathbf{q} + O\left(q^{3}\right) & \text{for } n = n' \\ \left\langle u_{n,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{T} u_{n',\mathbf{k}}^{\sigma} \right\rangle \mathbf{q} + \frac{1}{2} \mathbf{q}^{T} \left\langle u_{n,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{2} u_{n',\mathbf{k}}^{\sigma} \right\rangle \mathbf{q} + O\left(q^{3}\right) & \text{for } n \neq n' \end{array} \right.$$

where $\nabla_{\mathbf{k}}^2$ abbreviates the Hesse matrix $\nabla_{\mathbf{k}} \nabla_{\mathbf{k}}^T$.

If the transformation from the LAPW basis $\{\chi\}$ to the wave functions $\{\phi\}$ had not been performed, the term $\left\langle \frac{1}{\sqrt{V}} \exp\left[i\mathbf{q}\mathbf{r}\right] \chi^{\sigma}_{\mathbf{k},\mathbf{G}} \middle| \phi^{\sigma}_{n,\mathbf{k}+\mathbf{q}} \right\rangle$ would have to be evaluated instead of (4.3.2). The evaluation of this term is much more complex, because no orthogonality between $u_{n,\mathbf{k}}$ and $\chi_{\mathbf{k},\mathbf{G}}$ can be exploited.

Inserting (4.3.2) into (4.3.1) leads to an analytic expression for the divergence around the Γ point

$$A(\mathbf{q}) \coloneqq \sum_{n'}^{\text{occ.}} w_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} \frac{1}{\sqrt{V}} \exp\left[i\mathbf{q}\mathbf{r}\right] \right\rangle \frac{1}{q^{2}} \left\langle \frac{1}{\sqrt{V}} \exp\left[i\mathbf{q}\mathbf{r}\right] \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$
$$= \frac{4\pi}{V} \left\{ w_{n_{1},\mathbf{k}}^{\sigma} \delta_{n_{1},n_{2}} \left[\frac{1}{q^{2}} + \frac{1}{2} \hat{\mathbf{q}}^{T} \left(\left\langle \nabla_{\mathbf{k}}^{2} u_{n_{1},\mathbf{k}}^{\sigma} \middle| u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle + \left\langle u_{n_{1},\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{2} u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle \right) \hat{\mathbf{q}} \right]$$
$$+ (1 - \delta_{n_{1},n_{2}}) \frac{1}{q} \left(w_{n_{2},\mathbf{k}}^{\sigma} \left\langle \nabla_{\mathbf{k}}^{T} u_{n_{2},\mathbf{k}}^{\sigma} \middle| u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle + w_{n_{1},\mathbf{k}}^{\sigma} \left\langle u_{n_{2},\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{T} u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle \right) \hat{\mathbf{q}}$$
$$+ \frac{1}{2} (1 - \delta_{n_{1},n_{2}}) \hat{\mathbf{q}}^{T} \left(w_{n_{2},\mathbf{k}}^{\sigma} \left\langle \nabla_{\mathbf{k}}^{2} u_{n_{2},\mathbf{k}}^{\sigma} \middle| u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle + w_{n_{1},\mathbf{k}}^{\sigma} \left\langle u_{n_{2},\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{2} u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle \hat{\mathbf{q}}$$
$$+ \sum_{n' \neq n_{1},n_{2}}^{\text{occ.}} w_{n',\mathbf{k}}^{\sigma} \hat{\mathbf{q}}^{T} \left\langle \nabla_{\mathbf{k}} u_{n',\mathbf{k}}^{\sigma} \middle| u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle \left\langle u_{n_{2},\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{T} u_{n',\mathbf{k}}^{\sigma} \right\rangle \hat{\mathbf{q}} \right\}$$
(4.3.3)

where $\hat{\mathbf{q}}$ denotes the unit vector.

The terms containing $\nabla_{\bf k}$ are evaluated by ${\bf k}\cdot {\bf p}$ perturbation theory (s. Sec. 4.3.1)

$$\left\langle u_{n,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}} u_{n',\mathbf{k}}^{\sigma} \right\rangle = \begin{cases} -i \frac{\left\langle \phi_{n,\mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle}{\epsilon_{n',\mathbf{k}}^{\sigma} - \epsilon_{n,\mathbf{k}}^{\sigma}} & \text{if } \epsilon_{n',\mathbf{k}}^{\sigma} \neq \epsilon_{n,\mathbf{k}}^{\sigma} \\ 0 & \text{otherwise} \end{cases}$$
(4.3.4)

$$\operatorname{Re}\left(\left\langle u_{n,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{2} u_{n,\mathbf{k}}^{\sigma} \right\rangle\right) = \sum_{n' \neq n}^{\operatorname{all}} \frac{\left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle \left\langle \phi_{n,\mathbf{k}}^{\sigma} \middle| \nabla^{T} \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle}{(\epsilon_{n',\mathbf{k}}^{\sigma} - \epsilon_{n,\mathbf{k}}^{\sigma})^{2}} \quad (4.3.5)$$

$$\left\langle \nabla_{\mathbf{k}}^{2} u_{n_{2},\mathbf{k}}^{\sigma} \middle| u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle + \left\langle u_{n_{2},\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^{2} u_{n_{1},\mathbf{k}}^{\sigma} \right\rangle = 2 \sum_{n' \neq n_{1},n_{2}}^{\text{all}} \frac{\left\langle \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \nabla \left| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle \left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| \nabla^{T} \left| \phi_{n_{1},\mathbf{k}}^{\sigma} \right\rangle}{(\epsilon_{n_{2},\mathbf{k}}^{\sigma} - \epsilon_{n',\mathbf{k}}^{\sigma})(\epsilon_{n_{1},\mathbf{k}}^{\sigma} - \epsilon_{n',\mathbf{k}}^{\sigma})}$$
(4.3.6)

For clarity expressions for occupied and unoccupied states n_1 and n_2 are given for a band-gap material:

• n_1 and n_2 occupied

$$A(\mathbf{q}) = \frac{4\pi}{V} \frac{1}{N_k} \left\{ \delta_{n_1, n_2} \frac{1}{q^2} + \hat{\mathbf{q}}^T \left[\sum_{n' \neq n_1, n_2}^{\text{all}} (\delta_{n_1, n_2} - f_{n', \mathbf{k}}) \frac{\left\langle \phi_{n', \mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n_1, \mathbf{k}}^{\sigma} \right\rangle \left\langle \phi_{n_2, \mathbf{k}}^{\sigma} \middle| \nabla^T \middle| \phi_{n', \mathbf{k}}^{\sigma} \right\rangle}{(\epsilon_{n', \mathbf{k}}^{\sigma} - \epsilon_{n_1, \mathbf{k}}^{\sigma})(\epsilon_{n', \mathbf{k}}^{\sigma} - \epsilon_{n_2, \mathbf{k}}^{\sigma})} \right] \hat{\mathbf{q}} + (1 - \delta_{n_1, n_2}) \hat{\mathbf{q}}^T \sum_{n' \neq n_1, n_2}^{\text{all}} \frac{\left\langle \phi_{n_2, \mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n', \mathbf{k}}^{\sigma} \right\rangle \left\langle \phi_{n', \mathbf{k}}^{\sigma} \middle| \nabla^T \middle| \phi_{n_1, \mathbf{k}}^{\sigma} \right\rangle}{(\epsilon_{n_2, \mathbf{k}}^{\sigma} - \epsilon_{n', \mathbf{k}}^{\sigma})(\epsilon_{n_1, \mathbf{k}}^{\sigma} - \epsilon_{n', \mathbf{k}}^{\sigma})} \hat{\mathbf{q}} \right\}$$

• n_1 and n_2 unoccupied

$$A(\mathbf{q}) = -\frac{4\pi}{V} \frac{1}{N_k} \left\{ \hat{\mathbf{q}}^T \left[\sum_{n' \neq n_1, n_2}^{\text{occ.}} \frac{\left\langle \phi_{n', \mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n_1, \mathbf{k}}^{\sigma} \right\rangle \left\langle \phi_{n_2, \mathbf{k}}^{\sigma} \middle| \nabla^T \middle| \phi_{n', \mathbf{k}}^{\sigma} \right\rangle}{(\epsilon_{n', \mathbf{k}}^{\sigma} - \epsilon_{n_1, \mathbf{k}}^{\sigma})(\epsilon_{n', \mathbf{k}}^{\sigma} - \epsilon_{n_2, \mathbf{k}}^{\sigma})} \right] \hat{\mathbf{q}} \right\} (4.3.8)$$

• n_1 occupied and n_2 unoccupied or vice versa

$$A(\mathbf{q}) = \frac{4\pi}{V} \frac{1}{N_k} \left\{ -\hat{\mathbf{q}}^T \left[\sum_{n'\neq n_1, n_2}^{\text{occ.}} \frac{\left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n_1,\mathbf{k}}^{\sigma} \right\rangle \left\langle \phi_{n_2,\mathbf{k}}^{\sigma} \middle| \nabla^T \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle}{(\epsilon_{n',\mathbf{k}}^{\sigma} - \epsilon_{n_1,\mathbf{k}}^{\sigma})(\epsilon_{n',\mathbf{k}}^{\sigma} - \epsilon_{n_2,\mathbf{k}}^{\sigma})} \right] \hat{\mathbf{q}} + \frac{1}{q} (-i) \frac{\left\langle \phi_{n_2,\mathbf{k}}^{\sigma} \middle| \nabla^T \middle| \phi_{n_1,\mathbf{k}}^{\sigma} \right\rangle}{\epsilon_{n_1,\mathbf{k}}^{\sigma} - \epsilon_{n_2,\mathbf{k}}^{\sigma}} (f_{n_1,\mathbf{k}} - f_{n_2,\mathbf{k}}) \hat{\mathbf{q}} + \frac{1}{2} \hat{\mathbf{q}}^T \left(f_{n_1,\mathbf{k}} \left\langle u_{n_2,\mathbf{k}}^{\sigma} \middle| \nabla_{\mathbf{k}}^2 u_{n_1,\mathbf{k}}^{\sigma} \right\rangle + f_{n_2,\mathbf{k}} \left\langle \nabla_{\mathbf{k}}^2 u_{n_2,\mathbf{k}}^{\sigma} \middle| u_{n_1,\mathbf{k}}^{\sigma} \right\rangle) \hat{\mathbf{q}} \right\}$$

$$(4.3.9)$$

where $f_{n,\mathbf{k}}$ is the occupation number defined by

$$f_{n,\mathbf{k}} = \begin{cases} 1 & \text{if the state } (n,\mathbf{k}) & \text{is occupied} \\ 0 & \text{else} \end{cases}$$
(4.3.10)

and N_k denotes the total number of **k** points. We neglect the second-order term $\langle u_{n_2,\mathbf{k}}^{\sigma} | \nabla_{\mathbf{k}}^2 u_{n_1,\mathbf{k}}^{\sigma} \rangle$ or $\langle \nabla_{\mathbf{k}}^2 u_{n_2,\mathbf{k}}^{\sigma} | u_{n_1,\mathbf{k}}^{\sigma} \rangle$ in equation (4.3.9).

Thus, analytic expressions for the divergent term around $\mathbf{q} = 0$ have been found. The expansion of the integrand is tested with the **k**-point set $1 \times 1 \times 100$, which is dense in one direction. In the long-wavelength limit the exact integrand

$$\sum_{n'}\sum_{I,J}\left\langle\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}\left|\phi_{n_{1},\mathbf{k}}^{\sigma}\tilde{M}_{\mathbf{q},I}\right\rangle C_{IJ}(\mathbf{q})\left\langle\tilde{M}_{\mathbf{q},J}\phi_{n_{2},\mathbf{k}}^{\sigma}\right|\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}\right\rangle$$
(4.3.11)

is compared with the expansion

$$A(\mathbf{q}) + \sum_{n'} \sum_{I \neq 1} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_1,\mathbf{k}}^{\sigma} E_{\mathbf{0},I} \right\rangle e_{\mathbf{0},I} \left\langle E_{\mathbf{0},I} \phi_{n_2,\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle .$$
(4.3.12)

Figure 4.3 shows, that for the different combinations of n_1 and n_2 the exact integrand and the expansion always become identical for $q \to 0$.

Finally, the BZ integration is decomposed into a numerical integration of the nondivergent part and an analytical integration of the divergent part $A(\mathbf{q})$. Figure 4.4 illustrates this approach schematically. The red curve represents the exact integrand and the black one its expansion around the Γ point, which is integrated analytically. The difference between expansion and exact integrand is integrated numerically (red area).



Figure 4.3: For selected combinations of n_1 and n_2 the expansion around the Γ point is compared with the exact integrand.

We finally obtain

$$\sum_{n',\mathbf{q}} \sum_{IJ} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} \tilde{M}_{\mathbf{q},I} \right\rangle C_{IJ}(\mathbf{q}) \left\langle \tilde{M}_{\mathbf{q},J} \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \underbrace{\frac{V}{8\pi^{3}} \int_{BZ} d^{3}q A(\mathbf{q})}_{\text{analytic integration}} \\ + \underbrace{\sum_{n',\mathbf{q}\neq 0} w_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \sum_{IJ} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} \tilde{M}_{\mathbf{q},I} \right\rangle C_{IJ}(\mathbf{q}) \left\langle \tilde{M}_{\mathbf{q},J} \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle - \sum_{\mathbf{q}\neq 0} A(\mathbf{q})}_{\text{numerical integration } \mathbf{q}\neq 0} \\ + \underbrace{\sum_{n'} w_{n',\mathbf{k}}^{\sigma} \sum_{I\neq 1} \left\langle \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n_{1},\mathbf{k}}^{\sigma} E_{\mathbf{0},I} \right\rangle e_{\mathbf{0},I}(\mathbf{0}) \left\langle E_{\mathbf{0},I} \phi_{n_{2},\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle .$$
(4.3.13)

numerical integration of non-divergent part at q=0

Since our aim is to obtain the value of the integral rather than the integrand itself, as exact as possible, we can spherically average the terms of the type

$$-\hat{\mathbf{q}}^{T}\left[\sum_{n'\neq n_{1},n_{2}}\frac{\left\langle\phi_{n',\mathbf{k}}^{\sigma}\left|\nabla\right|\phi_{n_{1},\mathbf{k}}^{\sigma}\right\rangle\left\langle\phi_{n_{2},\mathbf{k}}^{\sigma}\left|\nabla^{T}\right|\phi_{n',\mathbf{k}}^{\sigma}\right\rangle}{(\epsilon_{n',\mathbf{k}}^{\sigma}-\epsilon_{n_{1},\mathbf{k}}^{\sigma})(\epsilon_{n',\mathbf{k}}^{\sigma}-\epsilon_{n_{2},\mathbf{k}}^{\sigma})}\right]\hat{\mathbf{q}}$$
(4.3.14)

in equations (4.3.7), (4.3.8) and (4.3.9), which gives

$$-\frac{4\pi}{3}\sum_{i=1}^{3}\sum_{n'\neq n_1,n_2}\frac{\left\langle\phi_{n',\mathbf{k}}^{\sigma}|\partial_{x_i}|\phi_{n_1,\mathbf{k}}^{\sigma}\right\rangle\left\langle\phi_{n_2,\mathbf{k}}^{\sigma}|\partial_{x_i}|\phi_{n',\mathbf{k}}^{\sigma}\right\rangle}{(\epsilon_{n',\mathbf{k}}^{\sigma}-\epsilon_{n_1,\mathbf{k}}^{\sigma})(\epsilon_{n',\mathbf{k}}^{\sigma}-\epsilon_{n_2,\mathbf{k}}^{\sigma})}$$
(4.3.15)

and add them to the numerical integration.

The analytic integration over the divergence of $A(\mathbf{q})$ is simplified by introducing a switching-off function g(q)

$$g(q) = \begin{cases} 1 - \frac{q^3}{q_0^3} \left(4 - 3\frac{q}{q_0}\right) & \text{for } 0 \le q \le q_0 \\ 0 & q > q_0 \end{cases}$$
(4.3.16)

with the properties g(0) = 1, g(q) = 0 for $q \ge q_0$ and $g'(0) = g'(q_0) = 0$, where q_0 denotes the radius of the largest sphere, that fits into the 1. BZ. By replacing $A(\mathbf{q})$ with $g(q)A(\mathbf{q})$ the integration region becomes spherical, and we use

$$\int_{BZ} d^3 q \, g(q) \frac{1}{q^2} = 4\pi \int_0^{q_0} \left[1 - \frac{q^3}{q_0^3} \left(4 - 3\frac{q}{q_0} \right) \right] \frac{1}{q^2} dq = \frac{12}{5}\pi q_0 \quad (4.3.17)$$

$$\int_{BZ} d^3 q \, g(q) \frac{1}{q} \hat{\mathbf{q}} = \mathbf{0} \,. \tag{4.3.18}$$

It must be noted that $A(\mathbf{q})$ must also be substituted by $g(q)A(\mathbf{q})$ in the numerical integration.



Figure 4.4: Decomposition of the integration into an analytic (dark grey) and a numerical part (light red).

4.3.1 $\mathbf{k} \cdot \mathbf{p}$ perturbation theory

The $\mathbf{k} \cdot \mathbf{p}$ perturbation theory allows to expand $\phi_{n,\mathbf{k}+\mathbf{q}}^{\sigma}$ around $\phi_{n,\mathbf{k}}^{\sigma}$. For this the wave function $\phi_{n,\mathbf{k}+\mathbf{q}}^{\sigma}$ is written as

$$\phi_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}) = \tilde{u}_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}) \exp\left[i(\mathbf{k}+\mathbf{q})\mathbf{r}\right] \\ = \underbrace{\tilde{u}_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}) \exp\left[i\mathbf{k}\mathbf{r}\right]}_{=:u_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})} \exp\left[i\mathbf{q}\mathbf{r}\right], \qquad (4.3.19)$$

where $\tilde{u}_{n,\mathbf{k}+\mathbf{q}}^{\sigma}$ is the periodic part of the wave function. For $\mathbf{q} = 0$ $u_{n,\mathbf{k}+\mathbf{q}}^{\sigma}$ corresponds to the wave function $\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r})$.

By applying the gKS differential equation to (4.3.19), an equation for $u_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})$ is obtained, where terms of order q^2 are neglected (a detailed calculation can be found in the Appendix B)

$$\begin{bmatrix} -\frac{\nabla^2}{2} + V^{\text{gKS}}(\mathbf{r}) \end{bmatrix} u_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}) - \sum_{n',\mathbf{b}} \int d^3 r' \, \frac{u_{n',\mathbf{b}}^{\sigma*}(\mathbf{r}') u_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} u_{n',\mathbf{b}}^{\sigma}(\mathbf{r}) + \mathbf{q} \mathbf{p} u_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})$$
$$= \epsilon_{n,\mathbf{k}+\mathbf{q}} u_{n,\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})$$
(4.3.20)

Obviously, $\mathbf{q}\mathbf{p} = \mathbf{q}(-i\nabla)$ can be treated as a perturbation. First order Rayleigh-Schrödinger perturbation theory yields

$$\left\langle u_{n',\mathbf{k}}^{\sigma} \middle| \underline{u_{n,\mathbf{k}}^{\sigma}} \right\rangle = \frac{\left\langle u_{n',\mathbf{k}}^{\sigma} \middle| \mathbf{p} \middle| u_{n,\mathbf{k}}^{\sigma} \right\rangle}{\epsilon_{n,\mathbf{k}}^{\sigma} - \epsilon_{n',\mathbf{k}}^{\sigma}} = \frac{\left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| \mathbf{p} \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle}{\epsilon_{n,\mathbf{k}}^{\sigma} - \epsilon_{n',\mathbf{k}}^{\sigma}}$$
(4.3.21)

if $\epsilon_{n,\mathbf{k}}^{\sigma} \neq \epsilon_{n',\mathbf{k}}^{\sigma}$ and

$$\left\langle u_{n',\mathbf{k}}^{\sigma} \middle| \underline{u_{n,\mathbf{k}}^{\sigma}} \right\rangle = 0 \tag{4.3.22}$$

if $\epsilon_{n,\mathbf{k}}^{\sigma} = \epsilon_{n',\mathbf{k}}^{\sigma}$.

Comparing the coefficients of the quadratic order in

$$0 = \left\langle \phi_{n,\mathbf{k}+\mathbf{q}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \left\langle u_{n,\mathbf{k}+\mathbf{q}} \middle| u_{n',\mathbf{k}+\mathbf{q}} \right\rangle$$

$$= \left\langle u_{n,\mathbf{k}} \middle| u_{n',\mathbf{k}} \right\rangle + \left[\left\langle \underline{u}_{n,\mathbf{k}}^{1} \middle| u_{n',\mathbf{k}} \right\rangle + \left\langle u_{n,\mathbf{k}} \middle| \underline{u}_{n',\mathbf{k}}^{1} \right\rangle \right] \mathbf{q}$$

$$+ \frac{1}{2} \mathbf{q}^{T} \left[\left\langle \underline{u}_{n,\mathbf{k}}^{2} \middle| u_{n',\mathbf{k}} \right\rangle + \left\langle u_{n,\mathbf{k}} \middle| \underline{u}_{n',\mathbf{k}}^{2} \right\rangle + 2 \left\langle \underline{u}_{n,\mathbf{k}}^{1} \middle| \underline{u}_{n',\mathbf{k}}^{1} \right\rangle \right] \mathbf{q} + O(q^{3}) \quad (4.3.23)$$

gives equation (4.3.6).

4.3.2 Calculation of the momentum matrix

The calculation of the MT contribution to the momentum matrix

$$\left\langle \phi_{n,\mathbf{k}}^{\sigma} \middle| \mathbf{p} \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle = -i \left\langle \phi_{n,\mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle$$
(4.3.24)

is performed by applying the nabla operator in the so-called 'natural' coordinates, which are defined by

$$z_{-1} = \frac{1}{\sqrt{2}}(x - iy) \tag{4.3.25}$$

$$z_1 = \frac{1}{\sqrt{2}}(-x - iy) \tag{4.3.26}$$

$$z_0 = z$$
, (4.3.27)

and afterwards transforming back to Cartesian coordinates. In the natural coordinates the ∇ operator is

$$\partial_{z_{-1}} = \frac{1}{\sqrt{2}} (\partial_x + i\partial_y)$$

$$= \frac{1}{\sqrt{2}} \left[\sin\theta \exp\left(-i\varphi\right) \partial_r + \frac{1}{r} \exp\left(-i\varphi\right) \left(\cos\theta \partial_\theta + \frac{i}{\sin\theta} \partial_\varphi\right) \right] (4.3.28)$$

$$\partial_{z_1} = \frac{1}{\sqrt{2}} (-\partial_x + i\partial_y)$$

$$= -\frac{1}{\sqrt{2}} \left[\sin\theta \exp\left(-i\varphi\right) \partial_r + \frac{1}{r} \exp\left(-i\varphi\right) \left(\cos\theta \partial_\theta - \frac{i}{\sin\theta} \partial_\varphi\right) \right] (4.3.29)$$

$$\partial_{z_0} = \partial_z = \cos\theta \partial_r - \frac{\sin\theta}{r} \partial_\theta . \qquad (4.3.30)$$

By using recursion relations for Legendre polynomials and spherical harmonics [54] one obtains

$$\frac{1}{\sqrt{2}}\exp(i\varphi)\sin\theta Y_{lm}(\mathbf{r}) = F_{lm}^{-1}Y_{l+1,m+1}(\mathbf{r}) + G_{lm}^{-1}Y_{l-1,m+1}(\mathbf{r}) \quad (4.3.31)$$

$$-\frac{1}{\sqrt{2}}\exp(-i\varphi)\sin\theta Y_{lm}(\mathbf{r}) = F_{lm}^{1}Y_{l+1,m-1}(\mathbf{r}) + G_{lm}^{1}Y_{l-1,m-1}(\mathbf{r}) \quad (4.3.32)$$

$$\cos\theta Y_{lm}(\mathbf{r}) = F_{lm}^0 Y_{l+1,m}(\mathbf{r}) + G_{lm}^0 Y_{l-1,m}(\mathbf{r})$$
(4.3.33)

and

$$\frac{1}{\sqrt{2}} \exp\left(i\varphi\right) \left[\cos\theta\partial_{\theta} + \frac{i}{\sin\theta}\partial_{\varphi}\right] Y_{lm}(\mathbf{r}) = -l F_{lm}^{-1} Y_{l+1,m+1}(\mathbf{r}) + (l+1) G_{lm}^{-1} Y_{l-1,m+1}(\mathbf{r})$$
(4.3.34)
$$-\frac{1}{2} \exp\left(-i\varphi\right) \left[\cos\theta\partial_{\theta} - \frac{i}{2}\partial_{z}\right] Y_{lm}(\mathbf{r})$$

$$-\frac{1}{\sqrt{2}} \exp\left(-l\varphi\right) \left[\cos l\partial_{\theta} - \frac{1}{\sin \theta} \partial_{\varphi}\right] T_{lm}(\mathbf{r})$$

$$= -l F_{lm}^{1} Y_{l+1,m-1}(\mathbf{r}) + (l+1) G_{lm}^{1} Y_{l-1,m-1}(\mathbf{r})$$

$$-\sin \theta \partial_{\theta} Y_{lm}(\mathbf{r})$$

$$(4.3.35)$$

$$= -l F_{lm}^{0} Y_{l+1,m}(\mathbf{r}) + (l+1) G_{lm}^{0} Y_{l-1,m}(\mathbf{r})$$
(4.3.36)

where

$$F_{lm}^{-1} = -\sqrt{\frac{(l+m+1)(l+m+2)}{2(2l+1)(2l+3)}} \qquad G_{lm}^{-1} = \sqrt{\frac{(l-m)(l-m-1)}{2(2l-1)(2l+1)}} \\F_{lm}^{1} = -\sqrt{\frac{(l-m+1)(l-m+2)}{2(2l+1)(2l+3)}} \qquad G_{lm}^{1} = \sqrt{\frac{(l+m)(l+m-1)}{2(2l-1)(2l+1)}} \\F_{lm}^{0} = \sqrt{\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}} \qquad G_{lm}^{0} = \sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}}$$
(4.3.37)

With these expressions the matrix element $\left\langle \phi_{n,\mathbf{k}}^{\sigma} \middle| \partial_{z_i} \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle$ can be easily calculated

$$\left\langle \phi_{n,\mathbf{k}}^{\sigma} \middle| \partial_{z_{i}} \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle_{\mathrm{MT}} = \sum_{a} \sum_{plm} \sum_{p'l'm'} c_{plm}^{a\sigma*}(n,\mathbf{k}) A_{plm,p'l'm'}^{aa,\sigma}(\partial_{z_{i}}) c_{p'l'm'}^{a\sigma}(n',\mathbf{k})$$
(4.3.38)

with

$$\begin{aligned} A^{aa,\sigma}_{plm,p'l'm'}(\partial_{z_{i}}) &:= \int_{\mathrm{MT}(a)} d^{3}r \, u^{a\sigma}_{pl}(r) Y^{*}_{lm}(\mathbf{r}) \partial_{z_{i}} \left(u^{a\sigma}_{p'l'} Y_{l'm'}(\mathbf{r}) \right) & (4.3.39) \\ &= F^{i}_{l'm'} \delta_{l,l'+1} \delta_{m,m'-i} \left(\int dr \, r^{2} u^{a\sigma}_{pl}(r) \partial_{r} u^{a\sigma}_{p'l'}(r) - l' \int dr \, r u^{a\sigma}_{pl}(r) u^{a\sigma}_{p'l'}(r) \right) \\ &+ G^{i}_{l'm'} \delta_{l,l'-1} \delta_{m,m'-i} \left(\int dr \, r^{2} u^{a\sigma}_{pl}(r) \partial_{r} u^{a\sigma}_{p'l'}(r) + (l'+1) \int dr \, r u^{a\sigma}_{pl}(r) u^{a\sigma}_{p'l'}(r) \right) .
\end{aligned}$$

For the interstitial contribution one directly obtains

$$\left\langle \phi_{n,\mathbf{k}}^{\sigma} \middle| \nabla \middle| \phi_{n',\mathbf{k}}^{\sigma} \right\rangle_{\mathrm{IR}}$$

$$= \sum_{\mathbf{G}} \sum_{\mathbf{G}'} z_{\mathbf{G}}^{\sigma*}(n,\mathbf{k}) z_{\mathbf{G}'}^{\sigma}(n',\mathbf{k}) \int_{\mathrm{IR}} d^{3}r \exp\left[-i\left(\mathbf{k}+\mathbf{G}\right)\mathbf{r}\right] \nabla \exp\left[i\left(\mathbf{k}+\mathbf{G}'\right)\mathbf{r}\right]$$

$$= i \sum_{\mathbf{G}} \sum_{\mathbf{G}'} z_{\mathbf{G}}^{\sigma*}(n,\mathbf{k}) z_{\mathbf{G}'}^{\sigma}(n',\mathbf{k}) \left(\mathbf{k}+\mathbf{G}'\right) O_{\mathbf{GG}'}$$

$$(4.3.40)$$

with

$$O_{\mathbf{GG'}} = \int_{\mathrm{IR}} d^3 r \exp\left[i\left(\mathbf{G'} - \mathbf{G}\right)\mathbf{r}\right]$$

= $\delta_{\mathbf{GG'}} - \frac{4\pi}{\Omega} \sum_{a} I\left(\mathbf{G'} - \mathbf{G}, R_{\mathrm{MT}(a)}\right) \exp\left[i\left(\mathbf{G'} - \mathbf{G}\right)\mathbf{R}_{a}\right]$ (4.3.41)

and

$$I(\mathbf{k}, R) = \frac{\sin\left(|\mathbf{k}|R\right) - |\mathbf{k}|R\cos\left(|\mathbf{k}|R\right)}{|\mathbf{k}|^3} .$$

$$(4.3.42)$$

We use the fact that the momentum operator is Hermitian to test the implementation. Hence

$$\langle \phi_{n,\mathbf{k}} | \nabla | \phi_{n',\mathbf{k}} \rangle = - \langle \phi_{n',\mathbf{k}} | \nabla | \phi_{n,\mathbf{k}} \rangle^*$$
(4.3.43)

should be valid. For the Hermiticity it is necessary that the wave functions $\phi_{n,\mathbf{k}}$ and $\phi_{n',\mathbf{k}}$ are continuous and differentiable. However, it exists a slight discontinuity of the LAPW basis set at the MT sphere boundary. Thus also the wave functions exhibits this discontinuity. As a result equation (4.3.43) is only fulfilled for the first three digits in practice.

4.4 Spatial symmetry

4.4.1 Irreducible Brillouin zone

A spatial symmetry operation is denoted by $P(R, \boldsymbol{\tau})$. Its action on a function f is defined by

$$P(R, \boldsymbol{\tau}) f(\mathbf{r}) = f \left[R^{-1}(\mathbf{r} - \boldsymbol{\tau}) \right] .$$

$$(4.4.1)$$

A symmetry operation maps each atom of the system onto itself or an equivalent atom, so that the system after applying the operation is indistinguishable from the original one. Consequently the Hamiltonian H commutes with any symmetry operation P

$$[P,H] = 0. (4.4.2)$$

From this follows that $P(R, \tau)\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r})$ is an eigenfunction of H with eigenvalue $\epsilon_{n,\mathbf{k}}^{\sigma}$

$$H P(R, \boldsymbol{\tau}) \phi_{n, \mathbf{k}}^{\sigma}(\mathbf{r}) = P(R, \boldsymbol{\tau}) H \phi_{n, \mathbf{k}}^{\sigma}(\mathbf{r})$$

= $\epsilon_{n, \mathbf{k}}^{\sigma} P(R, \boldsymbol{\tau}) \phi_{n, \mathbf{k}}^{\sigma}(\mathbf{r})$. (4.4.3)

Using the Bloch theorem

$$\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) = u_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) \exp\left[i\mathbf{k}\mathbf{r}\right]$$
$$= \sum_{\mathbf{G}} \beta_{\mathbf{G}}^{\sigma}(n,\mathbf{k}) \exp\left[i(\mathbf{k}+\mathbf{G})\mathbf{r}\right]$$
(4.4.4)

P acts on $\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r})$ according to

$$P(R, \boldsymbol{\tau})\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) = \sum_{\mathbf{G}} \beta_{n\mathbf{k},\mathbf{G}}^{\sigma} \exp\left[i(\mathbf{k}+\mathbf{G})R^{-1}(\mathbf{r}-\boldsymbol{\tau})\right]$$
(4.4.5)
$$= \underbrace{\sum_{\tilde{\mathbf{G}}} \beta_{R^{-1}(\tilde{\mathbf{G}}-\mathbf{G}')}^{\sigma}(n, R^{-1}(\mathbf{k}'+\mathbf{G}')) \exp\left[-i(\mathbf{k}'+\tilde{\mathbf{G}})\boldsymbol{\tau}\right] \exp\left[i\tilde{\mathbf{G}}\mathbf{r}\right]}_{u_{n\mathbf{k}'}^{\sigma}(\mathbf{r})} \exp\left[i\mathbf{k}'\mathbf{r}\right]$$

where \mathbf{G}' maps $R\mathbf{k}$ back into the BZ

$$R\mathbf{k} = \mathbf{k}' + \mathbf{G}' . \tag{4.4.6}$$

As a consequence the eigenspectra at ${\bf k}$ and ${\bf k}'$ are equivalent.

Thus, it is sufficient to know the wave functions $\phi_{n,\mathbf{k}}^{\sigma}$ and eigenvalues $\epsilon_{n,\mathbf{k}}^{\sigma}$ at those \mathbf{k} points, from which all other \mathbf{k} points can be generated by symmetry operations. This minimal set is called irreducible Brillouin zone (IBZ). The wave functions (eigenvalues) at $\mathbf{k} \notin$ IBZ can be constructed from its parent \mathbf{k} point in the IBZ.

4.4.2 Extended irreducible Brillouin zone

The exchange term

$$-\sum_{n',\mathbf{q}}^{\text{occ.}} \iint d^3r d^3r' \frac{\phi_{n_1,\mathbf{k}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}')\phi_{n_2,\mathbf{k}}^{\sigma*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
(4.4.7)

contains the point \mathbf{k} , at which the Hamiltonian is set up and diagonalized, and the summation \mathbf{q} points. In general, both points cannot be restricted to the IBZ simultaneously. While we can restrict the \mathbf{k} points to the IBZ, we must use an extended irreducible Brillouin zone (EIBZ(\mathbf{k})) for the summation \mathbf{q} points, which depends on \mathbf{k} . The EIBZ(\mathbf{k}) contains those points, from which the whole BZ can be generated by applying the subset of symmetry operations, which keep \mathbf{k} invariant. This subset is called little group of \mathbf{k} .

By applying the symmetry operation P of the little group of \mathbf{k} , which maps \mathbf{q}'

on \mathbf{q} , on the exchange term (4.4.7) at \mathbf{q}' , the value of the double integral does not change, because the symmetry operation is equivalent to a rotation and translation of the coordinate system

$$-\sum_{n'}^{\text{occ.}} \iint d^3 r d^3 r' \frac{\phi_{n_1,\mathbf{k}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}'}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}'}^{\sigma}(\mathbf{r}')\phi_{n_2,\mathbf{k}}^{\sigma*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$= -\sum_{n'}^{\text{occ.}} \iint d^3 r d^3 r' \frac{P\phi_{n_1,\mathbf{k}}^{\sigma}(\mathbf{r})P\phi_{n',\mathbf{k}+\mathbf{q}'}^{\sigma*}(\mathbf{r})P\phi_{n',\mathbf{k}+\mathbf{q}'}^{\sigma*}(\mathbf{r}')P\phi_{n_2,\mathbf{k}}^{\sigma*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} . \quad (4.4.8)$$

The action of P on $\phi_{n,\mathbf{k}}^{\sigma}$ generates a wave function belonging to the eigenspace of $\epsilon_{n,\mathbf{k}}^{\sigma}$. Consequently $P\phi_{n,\mathbf{k}}^{\sigma}$ can be expressed as a linear combination of the wave functions in that eigenspace

$$P\phi_{n,\mathbf{k}}^{\sigma} = \sum_{\substack{\alpha'\\ \epsilon_{n',\mathbf{k}}^{\sigma} = \epsilon_{n,\mathbf{k}}^{\sigma}}} \left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| P \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle \phi_{n',\mathbf{k}}^{\sigma}$$
(4.4.9)

If n is not degenerate, $P\phi_{n,\mathbf{k}}^{\sigma}$ equals to $\phi_{n,\mathbf{k}}^{\sigma}$ except for a phase factor. With an analogous equation for the inner wave functions we can show

$$\sum_{\substack{n'\\\epsilon^{\sigma}_{n',\mathbf{k}+\mathbf{q}'}=\epsilon^{\sigma}_{n,\mathbf{k}+\mathbf{q}'}}} P\phi^{\sigma*}_{n',\mathbf{k}+\mathbf{q}'}(\mathbf{r}) P\phi^{\sigma}_{n',\mathbf{k}+\mathbf{q}'}(\mathbf{r}') = \sum_{\substack{n''\\\epsilon^{\sigma}_{n'',\mathbf{k}+\mathbf{q}}=\epsilon^{\sigma}_{n,\mathbf{k}+\mathbf{q}}}} \phi^{\sigma*}_{n'',\mathbf{k}+\mathbf{q}}\phi^{\sigma}_{n'',\mathbf{k}+\mathbf{q}} . \quad (4.4.10)$$

Finally, the exchange term at $\mathbf{q}' \notin \text{EIBZ}(\mathbf{k})$ can be calculated from the corresponding exchange term at $\mathbf{q} \in \text{EIBZ}(\mathbf{k})$ by the following transformation

$$-\sum_{n'}^{\text{occ.}} \iint d^{3}r d^{3}r' \frac{\phi_{n_{1},\mathbf{k}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}'}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}'}^{\sigma}(\mathbf{r}')\phi_{n_{2},\mathbf{k}}^{n}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$= -\sum_{\substack{\epsilon_{n_{3}}}} \sum_{\substack{n_{4} \\ \epsilon_{n_{4},\mathbf{k}}}} \sum_{\substack{\epsilon_{n_{4}}}} \left\langle \phi_{n_{3},\mathbf{k}}^{\sigma} \right| P \left| \phi_{n_{1},\mathbf{k}}^{\sigma} \right\rangle \left\langle \phi_{n_{4},\mathbf{k}}^{\sigma} \right| P \left| \phi_{n_{2},\mathbf{k}}^{\sigma} \right\rangle^{*}$$

$$\sum_{n'}^{\text{occ.}} \iint d^{3}r d^{3}r' \frac{\phi_{n_{3},\mathbf{k}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r}')\phi_{n_{4},\mathbf{k}}^{\sigma*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (4.4.11)$$

4.4.3 Calculation of $\left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| P(R, \boldsymbol{\tau}) \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle$

Due to the different representation of the wave functions in the MT spheres and the IR the term $\langle \phi_{n',\mathbf{k}}^{\sigma} | P(R, \boldsymbol{\tau}) | \phi_{n,\mathbf{k}}^{\sigma} \rangle$ is evaluated separately in both regions

$$\left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| P(R,\boldsymbol{\tau}) \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle = \left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| P(R,\boldsymbol{\tau}) \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle_{\mathrm{MT}} + \left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| P(R,\boldsymbol{\tau}) \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle_{\mathrm{IR}}. (4.4.12)$$

The action of $P(R, \tau)$ on $\phi_{n,\mathbf{k}}^{\sigma}$ in the MT spheres is analyzed by using its formal definition (4.4.1)

$$P(R, \boldsymbol{\tau})\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{a,\mathbf{T}} \sum_{plm} c_{plm}^{a\sigma}(n, \mathbf{k}) u_{pl}^{a\sigma} \left(|R^{-1}(\mathbf{r} - \boldsymbol{\tau} - R\mathbf{T} - R\mathbf{R}_{a})| \right)$$

$$Y_{lm} \left(R^{-1}(\mathbf{r} - \boldsymbol{\tau} - R\mathbf{T} - R\mathbf{R}_{a}) \right) \exp \left[i\mathbf{kT} \right] \qquad (4.4.13)$$

$$= \frac{1}{\sqrt{N}} \sum_{a,\mathbf{T}} \sum_{plm'} \left[\sum_{m} D_{m'm}^{l}(R) c_{plm}^{(P^{-1}a)\sigma}(n, \mathbf{k}) \exp \left[iR\mathbf{kT'} \right] \right]$$

$$u_{pl}^{a\sigma} \left(|\mathbf{r} - \mathbf{T} - \mathbf{R}_{a}| \right) Y_{lm'} \left(\mathbf{r} - \mathbf{T} - \mathbf{R}_{a} \right) \exp \left[iR\mathbf{kT} \right] , \quad (4.4.14)$$

where it has been used that $P(R, \tau)$ maps atom *a* onto itself or a symmetry-equivalent atom, which does not necessarily lie inside the first unit cell. The translation \mathbf{T}' maps it back into the first unit cell

$$R\mathbf{R}_a + \boldsymbol{\tau} + \mathbf{T}' = \mathbf{R}_{a'} . \tag{4.4.15}$$

 $D_{mm'}^l(R)$ denotes the Wigner rotation matrices

$$Y_{lm}(R\mathbf{r}) = \sum_{m'} D^{l}_{m'm}(R^{-1})Y_{lm'}(\mathbf{r})$$
(4.4.16)

with the properties

$$\sum_{m} D_{m'm}^{l}(R) D_{mm''}^{l}(R^{-1}) = \delta_{m'm''} \quad , \quad D_{mm'}^{l}(R^{-1}) = D_{mm'}^{l*}(R) \quad (4.4.17)$$

and P^{-1} the inverse symmetry operation. So far we have not exploited, that $P(R, \tau)$ belongs to the little group of **k**

$$P(R, \boldsymbol{\tau})\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{a,\mathbf{T}} \sum_{plm'} \left[\sum_{m} D_{m'm}^{l}(R) c_{plm}^{(P^{-1}a)\sigma}(n, \mathbf{k}) \exp\left[i\mathbf{kT'}\right] \right]$$
$$u_{pl}^{a\sigma} \left(|\mathbf{r} - \mathbf{T} - \mathbf{R}_{a}|\right) Y_{lm'} \left(\mathbf{r} - \mathbf{T} - \mathbf{R}_{a}\right) \exp\left[i\mathbf{kT}\right] , \quad (4.4.18)$$

from which follows the MT contribution

$$\left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| P(R,\boldsymbol{\tau}) \left| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle_{\mathrm{MT}} = \sum_{a} \sum_{lm} \sum_{pp'} c_{p'lm}^{a\sigma*}(n',\mathbf{k}) \int_{0}^{R_{\mathrm{MT}(a)}} dr \, r^{2} u_{p'l}^{a\sigma}(r) u_{pl}^{a\sigma}(r) \\ \left[\sum_{m''} D_{mm''}^{l}(R) c_{plm''}^{(P^{-1}a)\sigma}(n,\mathbf{k}) \exp\left[i\mathbf{kT'}\right] \right].$$
(4.4.19)

For $\mathbf{r} \in \mathrm{IR}$ we have

$$P(R, \boldsymbol{\tau})\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}} z_{\mathbf{G}}^{\sigma}(n, \mathbf{k}) \exp\left[i(\mathbf{k} + \mathbf{G})R^{-1}(\mathbf{r} - \boldsymbol{\tau})\right] \\ = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}} z_{R^{-1}(\mathbf{G} + \tilde{\mathbf{G}})}^{\sigma}(n, \mathbf{k}) \exp\left[-i\left(\mathbf{k} + \mathbf{G}\right)\boldsymbol{\tau}\right] \exp\left[i(\mathbf{k} + \mathbf{G})\mathbf{r}\right], \quad (4.4.20)$$

where $\tilde{\mathbf{G}}$ maps $R\mathbf{k}$ back into the BZ

$$R\mathbf{k} + \tilde{\mathbf{G}} = \mathbf{k}. \tag{4.4.21}$$

Consequently the interstitial contribution to the matrix elements is

$$\left\langle \phi_{n',\mathbf{k}}^{\sigma} \middle| P(R,\boldsymbol{\tau}) \middle| \phi_{n,\mathbf{k}}^{\sigma} \right\rangle_{\mathrm{IR}} = \sum_{\mathbf{G}'} \sum_{\mathbf{G}} z_{\mathbf{G}'}^{\sigma*}(n',\mathbf{k}) z_{R^{-1}(\mathbf{G}+\tilde{\mathbf{G}})}^{\sigma}(n,\mathbf{k}) \exp\left[-i\left(\mathbf{k}+\mathbf{G}\right)\boldsymbol{\tau}\right] \\ \frac{1}{V} \int_{\mathrm{IR}} d^{3}r \exp\left[i(\mathbf{G}-\mathbf{G}')\mathbf{r}\right] .$$
(4.4.22)

4.4.4 Restriction of the Coulomb matrix to the IBZ

In order to reduce the effort for calculating and storing the Coulomb matrix $C_{IJ}(\mathbf{q})$, it is only evaluated at $\mathbf{q} \in \text{IBZ}$. If the Coulomb matrix is needed at $\mathbf{q}' \notin \text{IBZ}$, it can be transformed from its parent $\mathbf{q} \in \text{IBZ}$ to \mathbf{q}' . However, instead of transforming the Coulomb matrix it is much faster to transform the scalar products $\left\langle \tilde{M}_{\mathbf{q}',I}\phi_{n,\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$ in the vector-matrix-vector product.

In order to calculate the transformation the behavior of M under a symmetry operation P is needed. In analogy to the transformation of the wave functions under P one obtains

$$P(R, \boldsymbol{\tau}) M_{\mathbf{q}, PLM}^{a}(\mathbf{r})$$

$$= \exp\left[-i(\mathbf{q}'+\mathbf{G})\boldsymbol{\tau}\right] \exp\left[i\mathbf{GR}_{a'}\right] \sum_{M'} D_{M'M}^{L}(R) M_{\mathbf{q}', PLM'}^{a'}(\mathbf{r}) \qquad (4.4.23)$$

$$\Rightarrow M_{\mathbf{q}', PLM'}^{a}(\mathbf{r})$$

$$= \exp\left[i(\mathbf{q}'+\mathbf{G})\boldsymbol{\tau}\right] \exp\left[-i\mathbf{GR}_{a'}\right] \sum_{M} D_{M'M}^{L*}(R) P(R, \boldsymbol{\tau}) M_{\mathbf{q}, PLM}^{a}(\mathbf{r}) \qquad (4.4.24)$$

$$P(R, \boldsymbol{\tau})M_{\mathbf{q}, \mathbf{G}_{J}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp\left[i(\mathbf{q} + \mathbf{G}_{J})R^{-1}(\mathbf{r} - \boldsymbol{\tau})\right]$$

$$= \exp\left[-i(\mathbf{q}' + \mathbf{G}')\boldsymbol{\tau}\right]M_{\mathbf{q}', \mathbf{G}' = R\mathbf{G}_{J} + \mathbf{G}}(\mathbf{r}) \qquad (4.4.25)$$

$$\Rightarrow M_{\mathbf{q}',\mathbf{G}'}(\mathbf{r}) = \exp\left[i(\mathbf{q}'+\mathbf{G}')\boldsymbol{\tau}\right]P(R,\boldsymbol{\tau})M_{\mathbf{q},R^{-1}(\mathbf{G}'-\mathbf{G})}(\mathbf{r}) \quad (4.4.26)$$

where **G** maps R**q** back into the first BZ

$$R\mathbf{q} = \mathbf{q}' + \mathbf{G} \tag{4.4.27}$$

and atom a' is symmetry-equivalent to atom a under the symmetry operation P. To derive the corresponding equations the exchange term is regarded at $\mathbf{q}' \notin \text{IBZ}$. For clarity only the right-hand side of equation (4.0.13) is considered for a IR and MT mixed-basis function M

$$\sum_{I} \left\langle M_{\mathbf{q}',J} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| M_{\mathbf{q}',I=\mathbf{G}'} \right\rangle \left\langle \tilde{M}_{\mathbf{q}',I=\mathbf{G}'} \phi_{n_{2},\mathbf{k}}^{\sigma} \right| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \sum_{\mathbf{G}'} \left\langle M_{\mathbf{q}',J} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \exp\left[i(\mathbf{q}' + \mathbf{G}')\tau\right] P(R, \boldsymbol{\tau}) M_{\mathbf{q},\mathbf{G}''(\mathbf{G}')} \right\rangle$$

$$\left\langle \tilde{M}_{\mathbf{q}',\mathbf{G}'} \phi_{n_{2},\mathbf{k}}^{\sigma} \right| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \sum_{\mathbf{G}''} \left\langle M_{\mathbf{q}',J} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| P(R, \boldsymbol{\tau}) M_{\mathbf{q},\mathbf{G}''} \right\rangle$$

$$\exp\left[i(\mathbf{q}' + \mathbf{G} + R\mathbf{G}'')\tau\right] \left\langle \tilde{M}_{\mathbf{q}',R\mathbf{G}''+\mathbf{G}} \phi_{n_{2},\mathbf{k}}^{\sigma} \right| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$
(4.4.28)

$$\sum_{I} \left\langle M_{\mathbf{q}',J} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| M_{\mathbf{q}',I=aPLM} \right\rangle \left\langle \tilde{M}_{\mathbf{q}',I=aPLM} \phi_{n_{2},\mathbf{k}}^{\sigma} \right| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \sum_{aPLM} \left\langle M_{\mathbf{q}',J} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \sum_{M'} D_{MM'}^{L*}(R) P(R, \boldsymbol{\tau}) M_{\mathbf{q},PLM'}^{a} \right\rangle \exp\left[i(\mathbf{q}' + \mathbf{G})\boldsymbol{\tau}\right]$$

$$\exp\left[-i\mathbf{GR}_{a'}\right] \left\langle \tilde{M}_{\mathbf{q}',PLM}^{a} \phi_{n_{2},\mathbf{k}}^{\sigma} \right| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$

$$= \sum_{aPLM'} \left\langle M_{\mathbf{q}',J} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| P(R, \boldsymbol{\tau}) M_{\mathbf{q},PLM'}^{a} \right\rangle \exp\left[i(\mathbf{q}' + \mathbf{G})\boldsymbol{\tau}\right]$$

$$\exp\left[-i\mathbf{GR}_{a'}\right] \sum_{M} D_{MM'}^{L*}(R) \left\langle \tilde{M}_{\mathbf{q}',PLM}^{a} \phi_{n_{2},\mathbf{k}}^{\sigma} \right| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$$
(4.4.29)

The action of the symmetry operation on $M_{\mathbf{q},\mathbf{G}''}$ or $M^a_{\mathbf{q},PLM'}$ within the Coulomb

matrix cancels by applying the same scheme for the left side.

4.4.5 Inversion symmetry

So far the spatial symmetry operations are not specified. However, if the physical system under consideration possesses inversion symmetry in particular, the evaluation of the exchange term can be further simplified.

Since in a system with inversion symmetry the inversion operator I commutes with the Hamiltonian and the LAPW basis functions $\chi_{\mathbf{k},\mathbf{G}}$ become the complex conjugates of themselves under the action of I

$$I \chi_{\mathbf{k},\mathbf{G}}(\mathbf{r}) = \chi_{\mathbf{k},\mathbf{G}}(-\mathbf{r}) = \chi^*_{\mathbf{k},\mathbf{G}}(\mathbf{r}), \qquad (4.4.30)$$

the corresponding Hamiltonian is real symmetric

$$\langle \chi_{\mathbf{k},\mathbf{G}} | H | \chi_{\mathbf{k},\mathbf{G}'} \rangle = \langle \chi_{\mathbf{k},\mathbf{G}} | I^{\dagger} H I | \chi_{\mathbf{k},\mathbf{G}'} \rangle$$

$$= \langle \chi_{\mathbf{k},\mathbf{G}'} | H | \chi_{\mathbf{k},\mathbf{G}} \rangle$$

$$= \langle \chi_{\mathbf{k},\mathbf{G}} | H | \chi_{\mathbf{k},\mathbf{G}'} \rangle^* .$$

$$(4.4.31)$$

This fact is already exploited for the set-up of the Hamiltonian in the FLEUR code.

The MT functions of the mixed basis M, as defined in Section 4.1.1, do not fulfill the corresponding equation to (4.4.30). However, we can modify them such that they obey the analogous equation:

$$M_{\mathbf{q},PLM}^{'a}(\mathbf{r}) = \frac{1}{\sqrt{2N}} \sum_{\mathbf{T}} \left[\varphi_{PL}^{a}(|\mathbf{r} - \mathbf{R}_{a} - \mathbf{T}|) Y_{LM}(\mathbf{r} - \mathbf{R}_{a} - \mathbf{T}) \exp\left[i\mathbf{q}\mathbf{R}_{a}\right] + (-1)^{L+M} \varphi_{PL}^{a}(|\mathbf{r} + \mathbf{R}_{a} - \mathbf{T}|) Y_{L-M}(\mathbf{r} + \mathbf{R}_{a} - \mathbf{T}) \exp\left[-i\mathbf{q}\mathbf{R}_{a}\right] \right] \exp\left[i\mathbf{q}\mathbf{T}\right]$$

$$M_{\mathbf{q},PLM}^{''a}(\mathbf{r}) = \frac{1}{\sqrt{2N}} \sum_{\mathbf{T}} i \left[\varphi_{PL}^{a}(|\mathbf{r} - \mathbf{R}_{a} - \mathbf{T}|) Y_{LM}(\mathbf{r} - \mathbf{R}_{a} - \mathbf{T}) \exp\left[i\mathbf{q}\mathbf{R}_{a}\right] - (-1)^{L+M} \varphi_{PL}^{a}(|\mathbf{r} + \mathbf{R}_{a} - \mathbf{T}|) Y_{L-M}(\mathbf{r} + \mathbf{R}_{a} - \mathbf{T}) \exp\left[-i\mathbf{q}\mathbf{R}_{a}\right] \right] \exp\left[i\mathbf{q}\mathbf{T}\right].$$

In the particular case, that an atom is placed at the origin $(\mathbf{R}_a = \mathbf{0})$ and m = 0, one sets

$$M_{\mathbf{q},PLM=0}^{a=0}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} \varphi_{PL}^{a}(|\mathbf{r}-\mathbf{T}|) Y_{LM=0}(\mathbf{r}-\mathbf{T}) \exp\left[i\mathbf{q}\mathbf{T}\right] & \text{l even} \\ \frac{i}{\sqrt{N}} \sum_{\mathbf{T}} \varphi_{PL}^{a}(|\mathbf{r}-\mathbf{T}|) Y_{LM=0}(\mathbf{r}-\mathbf{T}) \exp\left[i\mathbf{q}\mathbf{T}\right] & \text{l odd} \end{cases} (4.4.34)$$

With this the Coulomb matrix $C_{IJ}(\mathbf{q})$ and $\left\langle \tilde{M}_{\mathbf{q},I}\phi_{n,\mathbf{k}}^{\sigma} \middle| \phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma} \right\rangle$ become real-valued and the computation of the vector-matrix-vector product more efficient.

4.5 Core electrons

The exchange potential for the valence electrons contains a sum over all occupied states $\phi_{n',\mathbf{k}+\mathbf{q}}^{\sigma}(\mathbf{r})$ including core electrons. For the core electrons the fully relativistic Dirac equation with the spherical component of the local effective potential is solved. The radial functions belonging to the set of quantum numbers $\{n, l, j = l + \frac{1}{2}\}$ and $\{n, l, j = l - \frac{1}{2}\}$ (principal quantum and angular-momentum quantum number n and l) differ only very little. Hence we can average over the two radial functions, which gives a single radial function $u_{nl}^{c,a\sigma}$. With this the core wave functions are given by

$$\phi_{n'=(nlm),\mathbf{k}}^{c,\sigma}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{a,\mathbf{T}} u_{nl}^{c,a\sigma}(|\mathbf{r}-\mathbf{T}-\mathbf{R}_a|) Y_{lm}(\mathbf{r}-\mathbf{T}-\mathbf{R}_a) \exp\left[i\mathbf{kT}\right], \quad (4.5.1)$$

whose contribution to the exchange potential

$$V_{\mathbf{x},n_{1}n_{2}}^{\sigma,\text{core}}(\mathbf{k}) = -\sum_{n'}^{\text{core}} \sum_{\mathbf{q}} \iint d^{3}r d^{3}r' \frac{\phi_{n_{1},\mathbf{k}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{c,\sigma*}(\mathbf{r})\phi_{n',\mathbf{k}+\mathbf{q}}^{c,\sigma}(\mathbf{r}')\phi_{n_{2},\mathbf{k}}^{\sigma*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
(4.5.2)

can be evaluated directly without employing the mixed basis. The product

$$\phi_{n',\mathbf{k}+\mathbf{q}}^{c,\sigma}(\mathbf{r})\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r}) = \frac{1}{N} \sum_{a,\mathbf{T}} \sum_{p'l'm'} c_{p'l'm'}^{a\sigma*}(n,\mathbf{k}) u_{pl}^{c,a\sigma}(|\mathbf{r}-\mathbf{T}-\mathbf{R}_a|) u_{p'l'}^{a\sigma}(|\mathbf{r}-\mathbf{T}-\mathbf{R}_a|) Y_{lm}(\mathbf{r}-\mathbf{T}-\mathbf{R}_a) Y_{l'm'}^{*}(\mathbf{r}-\mathbf{T}-\mathbf{R}_a) \exp\left[i\mathbf{q}\mathbf{T}\right] (4.5.3)$$

is reformulated as a sum over radial functions multiplied by spherical harmonics. With the Gaunt coefficients (4.1.2) and denoting the products $u_{pl}^{c,a\sigma}u_{p'l'}^{a\sigma}$ by $\varphi_{PL}^{a\sigma}$, where P again distinguishes between different combinations of pl and p'l' with $|l-l'| \leq L \leq l+l'$, one obtains

$$\phi_{n',\mathbf{k}+\mathbf{q}}^{c,\sigma}(\mathbf{r})\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r}) = \frac{1}{N} \sum_{a,\mathbf{T}} \sum_{PLM} c_{p'l'm-M}^{a\sigma*}(n,\mathbf{k}) G_{l'm-M,lm,LM} \varphi_{PL}^{a\sigma}(|\mathbf{r}-\mathbf{T}-\mathbf{R}_a|)$$

$$Y_{LM}(\mathbf{r}-\mathbf{T}-\mathbf{R}_a) \exp[i\mathbf{q}\mathbf{T}]. \qquad (4.5.4)$$

Hence the core contribution to the exchange term involves double integrals of the form

$$\iint d^3r d^3r' \frac{\varphi_{P'L'}^{a'\sigma}(|\mathbf{r}-\mathbf{T}'-\mathbf{R}_{a'}|)Y_{L'M'}^*(\mathbf{r}-\mathbf{T}'-\mathbf{R}_{a'})\varphi_{PL}^{a\sigma}(|\mathbf{r}-\mathbf{T}-\mathbf{R}_{a}|)Y_{LM}(\mathbf{r}-\mathbf{T}-\mathbf{R}_{a})}{|\mathbf{r}-\mathbf{r}'|}.$$
 (4.5.5)

This type of integrals must be evaluated in the calculation of the Coulomb matrix [52] and can be written as the sum of three terms, of which two are periodic in reciprocal space and therefore vanish in the BZ integration and one survives

$$V_{\mathbf{x},n_{1}n_{2}}^{\sigma,\text{core}}(\mathbf{k}) = -\sum_{n'}^{\text{core}} \sum_{a} \sum_{PLM} \sum_{P'} \frac{4\pi}{2L+1} G_{l'(L,P)m-M,lm,LM} G_{l'(L,P')m-M,lm,LM} \\ c_{p'(P,L),l'(P,L),m-M}^{a\sigma}(n_{1},\mathbf{k}) c_{p'(P',L)l'(P',L)m-M}^{a\sigma*}(n_{2},\mathbf{k})$$

$$\int_{0}^{R_{\text{MT}(a)}} dr \, r^{2} \varphi_{LP}^{a\sigma}(r) \left[\frac{1}{r^{L+1}} \int_{0}^{r} dr' \, r'^{L+2} \varphi_{LP'}^{a\sigma}(r') + r^{L} \int_{r}^{R_{\text{MT}(a)}} dr' \, \frac{\varphi_{LP'}^{a\sigma}(r')}{r'^{L-1}} \right].$$
(4.5.6)

A direct treatment of the core electrons with the non-local exchange potential is not implemented, so far. However, if the core states are described by local orbitals, they are formally treated as valence electrons and experience the full non-local exchange potential.

4.6 Total energy

In the gKS scheme the total energy consists of

- kinetic energy T
- Hartree energy $U_{\rm H}$
- exchange correlation energy $E_{\rm xc}^{\rm gKS}$
- electron-nuclear energy $E_{\rm ne}$
- nuclear-nuclear interaction energy E_{nn}
- electron exchange energy $a \cdot E_x$

$$E = T + U_{\rm H} + E_{\rm xc}^{\rm gKS} + E_{\rm ne} + E_{nn} + a \cdot E_{\rm x}, \qquad (4.6.1)$$

where

$$T = \sum_{n,\mathbf{k},\sigma}^{\text{occ.}} \int d^3 r \phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r})$$
(4.6.2)

$$U_{\rm H} = \frac{1}{2} \iint d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(4.6.3)

$$E_{\mathbf{x}} = -\frac{1}{2} \sum_{n,\mathbf{k},\sigma}^{\text{occ.}} \sum_{n',\mathbf{k'}}^{\text{occ.}} \iint d^3r d^3r' \frac{\phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r})\phi_{n',\mathbf{k'}}^{\sigma}(\mathbf{r})\phi_{n',\mathbf{k'}}^{\sigma*}(\mathbf{r'})\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|} .$$
(4.6.4)

In order to avoid numerical instabilities arising from the evaluation of the Laplace operator within the kinetic energy part, the gKS equation (2.2.6) is used to find an expression for the kinetic energy

$$T = \sum_{n,\mathbf{k},\sigma}^{\text{occ.}} \epsilon_{n,\mathbf{k}}^{\sigma} - \sum_{\sigma} \int d^3 r \, n^{\sigma}(\mathbf{r}) \left[V(\mathbf{r}) + V_{\text{xc}}^{\text{gKS},\sigma}(\mathbf{r}) \right] - 2U_{\text{H}} - 2aE_{\text{x}} \quad (4.6.5)$$

with

$$n(\mathbf{r}) = \sum_{\sigma} n^{\sigma}(\mathbf{r}) . \qquad (4.6.6)$$

With this the total energy is given by

$$E = \sum_{n,\mathbf{k},\sigma}^{\text{occ.}} \epsilon_{n,\mathbf{k}}^{\sigma} - \sum_{\sigma} \int d^3 r \, n^{\sigma}(\mathbf{r}) \left[V(\mathbf{r}) + V_{\text{xc}}^{\text{gKS},\sigma}(\mathbf{r}) \right] - U_{\text{H}} + E_{\text{xc}}^{\text{gKS}} + E_{\text{ne}} + E_{\text{nn}} - aE_{\text{x}}$$
$$= \sum_{n,\mathbf{k},\sigma}^{\text{occ.}} \epsilon_{n,\mathbf{k}}^{\sigma} - \sum_{\sigma} \int d^3 r \, n^{\sigma}(\mathbf{r}) V_{\text{xc}}^{\text{gKS},\sigma}(\mathbf{r}) - U_{\text{H}} + E_{\text{xc}}^{\text{gKS}} + E_{\text{nn}} - aE_{\text{x}}$$
(4.6.7)

In the case $E_{\rm xc}^{\rm gKS} = V_{\rm xc}^{\rm gKS,\sigma} = 0$ the total-energy expression coincides with the HF total energy.

4.7 Adding and subtracting an additional potential

The radial functions $u_{pl}^{\sigma}(r)$ of the LAPW basis set are determined by the spherical component of the local potential. In a pure Hartree-Fock calculation ($V_{\rm xc}^{\rm gKS} = 0$, a = 1) the local potential consists of the external and Hartree potential. By adding the X_{\alpha} potential, a local form of the Hartree-Fock exchange term, we hope to create radial functions, which are suited for the representation of the HF wave functions. Later the X_{\alpha} potential is again subtracted from the total Hamiltonian.

Moreover, we perform a HF or hybrid functional calculation starting from a converged



Figure 4.5: Process flow of a HF (a = 1) or hybrid-functional calculation (0 < a < 1) (cf. Fig. 3.3).

DFT calculation employing a local or semi-local functional (s. Fig. 4.5), because the computation of the exchange term requires wave functions at each \mathbf{k} point. For the first iteration the local potential must be adopted from the converged DFT calculation. With the consequence that this local effective potential is used together with the non-local exchange potential. Therefore it is desirable to subtract some amount of the adopted exchange correlation potential in the first iteration. For example for a PBE0 calculation starting from a PBE calculation, we subtract 25% of the PBE exchange-correlation potential in the first iteration.

Consequently, we have to evaluate matrix elements of the local or semi-local exchange-correlation potential, which is a standard problem in the FLAPW method [17].

5 First calculations

The implementation of the non-local exchange potential discussed in the previous chapter is tested on selected prototype semiconductors and insulators. The aim is to assess the influence of the convergence parameters on the accuracy and the computational cost.

5.1 Hartree-Fock calculation for Diamond (C)

Diamond crystallizes in a face-centered cubic (fcc) structure with the experimental lattice constant a = 6.743 a.u. and is a system with inversion symmetry. Starting from a converged DFT calculation with the X_{α} potential and the basis-set parameters $g_{\text{max}} = 4.2$ Htr and $l_{\text{max}} = 6$, a Hartree-Fock (HF) calculation ($V_{\text{xc}}^{\text{gKS}} = 0, a = 1$) is started. In the first iteration the converged X_{α} orbitals are used to evaluate the exchange term. Since the X_{α} potential is the local form of the exchange potential for a homogeneous electron gas, it should be a reasonable starting point for a HF calculation.

In a pure HF calculation the local potential (s. Eq. (2.5.6)) is given by the sum of Hartree potential $V_{\rm H}$ and external potential V. The radial functions u and \dot{u} of the LAPW basis are determined by the spherical component of this local potential (cf. Eq. (3.1.2) and (3.2.2)). In order to include the exchange approximately in this step we add the X_{α} potential to the local potential before generating the radial functions and subtract it later.

The core electrons, i.e., the two $1s_{1/2}$ electrons of Diamond, are treated in the frozen-core approximation, where the core wave functions are kept fixed during the self-consistence cycle.

Already after the first HF iteration the opening of the band gap is observed. A selfconsistent density is achieved after about 40 - 60 iterations with a Broyden mixing scheme (s. Fig. 5.1). In comparison with the X_{α} calculation for Diamond it needs roughly 5 times more iterations to converge. We assume this fact is caused by using a mixing scheme only for the density but not for the wave functions. As the input density for a new iteration is a mixture of several densities of previous iterations, it is never consistent with the wave functions used to build up the exchange potential before convergence is achieved. This inconsistency leads to a finite self-interaction contribution.

The convergence of the eigenspectrum with respect to the basis-set parameters of $\{M\}$ is examined by varying one parameter and keeping the others fixed. Ta-



Figure 5.1: Convergence behavior of the density and the total energy of a Diamond calculation with a Broyden mixing scheme. The density distance is defined as the integrated square of the difference between input and output density and the distance in the total energy is measured with respect to the converged total energy.

gcutm [Htr]	4.20	4.50	5.00	5.50	6.00	6.50	7.50
$\Gamma_{1v} [\text{eV}]$	-28.70	-28.86	-29.04	-29.08	-29.08	-29.07	-29.06
$\Gamma_{25v} [\text{eV}]$	0	0	0	0	0	0	0
$\Gamma_{15c} [\text{eV}]$	15.32	15.23	15.12	15.10	15.10	15.10	15.11
$\Gamma_{2'c} \left[\text{eV} \right]$	25.46	25.28	25.06	25.01	25.01	25.02	25.03
$X_{1c} \left[\text{eV} \right]$	13.87	13.72	13.57	13.53	13.54	13.54	13.55
$L_{1c} \left[\text{eV} \right]$	18.87	18.76	18.64	18.62	18.62	18.63	18.63
$X_{4v} \to X_{1c} [\text{eV}]$	22.02	21.90	21.78	21.76	21.76	21.77	21.77
$L_{3'v} \to L_{1c}[eV]$	22.48	22.39	22.28	22.27	22.28	22.28	22.28

Table 5.1: Convergence of band energies for Diamond at high-symmetry points in the BZ with respect to the parameter gcutm (lcutm = 4).

lcutm	2	4	6	8
$\Gamma_{1v} [\mathrm{eV}]$	-29.26	-29.08	-29.08	-29.08
$\Gamma_{25v} [\mathrm{eV}]$	0	0	0	0
$\Gamma_{15c} [\mathrm{eV}]$	15.06	15.10	15.10	15.10
$\Gamma_{2'c} [\mathrm{eV}]$	24.82	25.01	25.01	25.01
$X_{1c} \left[\text{eV} \right]$	13.55	13.53	13.54	13.54
$L_{1c} \left[\text{eV} \right]$	18.62	18.62	18.62	18.62
$X_{4v} \to X_{1c} [\text{eV}]$	21.87	21.76	21.76	21.76
$L_{3'v} \to L_{1c}[eV]$	22.33	22.27	22.27	22.27

Table 5.2: Convergence of band energies for Diamond with respect to lcutm (gcutm = 5.5 Htr).

ble 5.1 shows the dependence of selected band energies on the parameter gcutm. Energies are measured with respect to the valence-band maximum. We can conclude that for Diamond already gcutm = $5.5 \text{ Htr} (1.31 \cdot g_{\text{max}})$ ensures convergence of the band structure. Convergence of the band energies in terms of the maximal angular momentum is achieved with lcutm = 4 (s. Table 5.2).

In order to analyze the ability of M to represent the wave-function products in spite of the changes of the radial functions of the FLAPW basis set in each self-consistence step, we have compared the results above, where the mixed basis M is generated once at the beginning of the calculation, with that obtained from a calculation, where the mixed basis M and the Coulomb matrix $C_{IJ}(\mathbf{q})$ is build up in each iteration step. The differences in the converged results between both approaches are negligible, which justifies to generate M once at the beginning of a calculation and keep it fixed.

The computation of the non-local exchange term is by far the most expensive

number of bands	0	10	20	30	40	60	100
$\Gamma_{1v} [\text{eV}]$	-22.38	-28.93	-28.94	-29.05	-29.07	-29.08	-29.08
$\Gamma_{25v} [\mathrm{eV}]$	0	0	0	0	0	0	0
$\Gamma_{15c} [\mathrm{eV}]$	4.72	15.05	15.14	15.10	15.10	15.10	15.10
$\Gamma_{2'c} \left[\text{eV} \right]$	14.74	25.88	25.14	25.07	25.07	25.02	25.01
$X_{1c} \left[\text{eV} \right]$	2.80	13.89	13.79	13.59	13.55	13.55	13.53
$L_{1c} [\mathrm{eV}]$	7.23	18.72	18.73	18.63	18.62	18.62	18.62
$\begin{array}{l} X_{4v} \to X_{1c} [\text{eV}] \\ L_{3'v} \to L_{1c} [\text{eV}] \end{array}$	$9.89 \\ 10.30$	$21.94 \\ 22.30$	$21.90 \\ 22.39$	$21.81 \\ 22.28$	21.77 22.28	21.77 22.28	$21.76 \\ 22.27$
time per it. $[s]$	10.86	24.1	39.1	56.7	74.0	116.5	185.8

Table 5.3: Convergence of the band energies for Diamond with respect to the exchange-matrix size given by the number of bands and corresponding timings for a single iteration (lcutm = 4, gcutm = 5.5 Htr). Calculations are performed on a single CPU.

step in the build-up of the Hamiltonian. For an efficient implementation further approximations are necessary. The off-diagonal elements of the exchange matrix in the space of the wave functions decrease with increasing band number. This can be understood, if the exchange term is regarded as a small perturbation. In perturbation theory of first order a state n' contributes to a state n with a weight proportional to $\frac{1}{\epsilon_n - \epsilon_{n'}}$. So we can restrict the number of bands for which the exchange term in the space of wave functions is evaluated without loosing too much accuracy. Table 5.3 shows that already with 30 - 40 bands the error is well below 0.1 eV for the band energies and the computational cost for each iteration is reduced by a factor of 3.

Figure 5.2 shows a detailed chart, how much time is spent in the different program routines, which are needed to calculate the exchange potential, in a single iteration. Nearly 2/3 of the time for one iteration is spent in the subroutine 'wavefunction products', which calculates the representation of the wave-function product in the mixed basis, 1/3 is needed to set up the exchange matrix ('valence exchange'). The time spent in the other routines, which calculate the valence-core exchange, the irreducible representation and generate the wave functions at all **k** points from the irreducible one, is much smaller. While the computation of the wave-function products scales linearly with the number of bands, the time needed to set up the exchange matrix elements splits up into the time for the computation of the Γ point decomposition and the time for the calculation of the vector-matrix-vector products leading to a scaling of the form

$$a_0 + a_1 n^2$$
, (5.1.1)


Figure 5.2: Detailed analysis of the time spent in each routine per iteration on a single CPU.

where n denotes the number of bands.

Finally, we examine the convergence with respect to the number of **k** points. So far all calculations have been performed with a $4 \times 4 \times 4$ **k**-point set, corresponding to 8 **k** points in the IBZ. Since the Hamiltonian is built up at the irreducible points of the BZ and each matrix element of the non-local exchange potential contains a sum over occupied states, the time needed for one iteration scales not linearly with the number of **k** points. For example in the case of a $8 \times 8 \times 8$ **k**-point mesh the exchange matrix must be set-up at 29 irreducible points and each exchange matrix element contains a sum over 512 **k** points. For a $6 \times 6 \times 6$ **k**-point mesh the irreducible wedge consists of 16 points and for each matrix element a sum over 216 **k** points must be performed. Consequently the computation time scales as

$$aN_k N_{\text{IBZ}}$$
, (5.1.2)

where N_k denotes the total number of **k** points and N_{IBZ} the number of irreducible points. However, for small **k**-point sets the restriction of the sum over the occupied states to the EIBZ(**k**) leads to a significant reduction in computation time.

We check the convergence for a $2 \times 2 \times 2$, $4 \times 4 \times 4$, $6 \times 6 \times 6$ and $8 \times 8 \times 8$ mesh (s. Table 5.4). On the basis of these calculations we can conclude that relative dense **k**-point sets are needed to achieve convergence. This agrees with findings by Paier et. al [55], who conclude in a projector augmented wave (PAW) approach that for converged PBE0 calculations of semiconductors at least a $12 \times 12 \times 12$ **k**-point mesh is needed.

In Table 5.4 the results are compared with a FLAPW HF calculation by Massidda

	$2 \times 2 \times 2$	$4 \times 4 \times 4$	$6 \times 6 \times 6$	$8 \times 8 \times 8$		Exp.
$\Gamma_{1v} [\mathrm{eV}]$	-28.13	-29.07	-29.23	-29.27	-29.4^{a}	-24.2^{b}
$\Gamma_{15c} [\text{eV}]$	15.43	15.10	14.84	14.78	14.7^{a}	7.3^{b}
$\Gamma_{2'c} [\text{eV}]$	25.39	25.07	24.83	24.79	24.5^{a}	15.3^{b}
X_{1c} [eV]	13.73	13.55	13.31	13.26	13.2^{a}	
$L_{1c} [\mathrm{eV}]$	18.84	18.62	18.42	18.37	18.3^{a}	
$\begin{array}{l} X_{4v} \to X_{1c} [\text{eV}] \\ L_{3'v} \to L_{1c} [\text{eV}] \end{array}$	21.40 22.28	21.77 22.28	$21.61 \\ 22.12$	$21.58 \\ 22.09$	21.5^a 22.0^a	12.5^b 12.5^b
time pro it. $[s]$	24.0	74.1	550.7	2516.8		

^{*a*} Ref. 51 (FLAPW calculation)

^b Ref. 56

Table 5.4: Convergence of the Hartree-Fock band energies of Diamond with respect to the k-point set (lcutm = 4, gcutm = 5.5, number of bands = 40). The calculated band energies are compared with theoretical and experimental values from the literature.

et. al [51]. They only use 2 special Chadi-Cohen \mathbf{k} points [57]. A comparison with the experimental results shows, that pure HF calculations overestimate the experimental band gap and transition energies by about a factor of 2. This can be attributed to the fact that the HF method only considers static correlation between electrons of the same spin, but no dynamic correlation. It gives a practical hint, that a scaled exchange operator should give better results.

5.2 Hartree-Fock calculation for Silicon (Si)

Analogous tests have been performed with bulk Silicon (experimental lattice constant a = 10.26 a.u.) starting from converged X_{α} calculations with the basis parameters $l_{\text{max}} = 8$ and $g_{\text{max}} = 3.6$ Htr.

We conclude that 40 bands, a gcutm of $4.5 \text{ Htr } (1.25 \cdot g_{\text{max}})$ and an lcutm of 4 are sufficient to obtain band energies with an accuracy of 0.1eV employing a $4 \times 4 \times 4$ **k**-point set (s. Tables 5.5, 5.6 and 5.7). The results for Silicon are in agreement with Ref. 51. The small deviations we attribute to the use of different **k**-point sets.

5.3 PBE0 functional

Once the non-local exchange potential is implemented, the PBE0 functional is simply obtained by scaling the non-local exchange potential down to 25% and adding 75%

number of bands	0	10	30	40	50	60	120
$\Gamma_{1v} [\mathrm{eV}]$	-12.65	-16.34	-16.90	-16.95	-16.90	-16.89	-16.90
$\Gamma_{25v} [\mathrm{eV}]$	0	0	0	0	0	0	0
$\Gamma_{15c} [\mathrm{eV}]$	1.65	9.34	9.33	9.27	9.32	9.32	9.31
$\Gamma_{2'c} \left[\text{eV} \right]$	4.46	11.62	11.08	11.03	11.09	10.99	10.99
$X_{1c} \left[\text{eV} \right]$	-1.12	7.20	6.92	6.80	6.83	6.84	6.82
$L_{1c} \left[\text{eV} \right]$	1.18	8.30	8.24	8.07	8.12	8.13	8.11
$X_{4v} \to X_{1c} [\text{eV}]$	2.27	11.10	10.72	10.65	10.63	10.61	10.61
$L_{3'v} \to L_{1c}[eV]$	2.49	10.05	9.82	9.71	9.69	9.69	9.67
time pro it. $[s]$	143.89	167.38	239.00	260.16	294.55	325.81	528.74

Table 5.5: Convergence of the band and transition energies of Silicon with respect to the exchange-matrix size given by the number of bands with corresponding timings for a single iteration (gcutm = 5 Htr,lcutm = 4).

$\operatorname{gcutm}\left[\operatorname{Htr}\right]$	3.60	4.00	4.50	5.00	5.50	6.00
$\Gamma_{1v} \left[\text{eV} \right]$	-16.96	-16.96	-16.95	-16.95	-16.95	-16.95
$\Gamma_{25v} [\mathrm{eV}]$	0	0	0	0	0	0
$\Gamma_{15c} [\mathrm{eV}]$	9.30	9.29	9.28	9.27	9.27	9.27
$\Gamma_{2'c} \left[\text{eV} \right]$	11.09	11.06	11.04	11.03	11.03	11.03
$X_{1c} \left[\text{eV} \right]$	6.84	6.82	6.81	6.80	6.80	6.80
$L_{1c} \left[\text{eV} \right]$	8.12	8.09	8.08	8.07	8.07	8.07
$X_{4v} \to X_{1c} [\text{eV}]$	10.68	10.67	10.65	10.65	10.65	10.65
$L_{3'v} \to L_{1c}[eV]$	9.75	9.72	9.71	9.71	9.71	9.71

Table 5.6: Convergence with respect to the parameter gcutm for Silicon (lcutm = 4, number of bands = 40).

lcutm	2	4	6	8		Exp.
$\Gamma_{1v} [\mathrm{eV}]$	-17.20	-16.95	-16.95	-16.95	-17.1^{a}	-12.5^{b}
$\Gamma_{25v} [\mathrm{eV}]$	0	0	0	0		
$\Gamma_{15c} [\text{eV}]$	9.16	9.28	9.27	9.27	9.0^{a}	3.4^{b}
$\Gamma_{2'c} \left[\text{eV} \right]$	10.74	11.04	11.04	11.04	10.6^{a}	4.2^{b}
X_{1c} [eV]	6.73	6.81	6.81	6.81	6.6^{a}	1.3^{c}
$L_{1c} \left[\text{eV} \right]$	7.96	8.08	8.07	8.07	7.8^{a}	2.4^{c}
$X_{4v} \to X_{1c} [\text{eV}]$	10.73	10.65	10.65	10.65	10.5^{a}	$4.2^{c} - 4.5^{b}$
$L_{3'v} \to L_{1c}[eV]$	9.67	9.71	9.71	9.71	9.4^{a}	$3.5^b - 3.9^c$

^a Ref. 51 (FLAPW calculation)

^b Ref. 58

 c Ref. 59

Table 5.7: Convergence of selected band energies of Silicon with respect to the parameter lcutm (number of bands = 40, gcutm = 4.5 Htr). The calculated values are compared with theoretical and experimental values.

of PBE exchange and 100% of PBE correlation. The latter semi-local functionals are already implemented in the FLEUR code.

The local potential for the PBE0 hybrid functional (s. Eq. (2.5.6)) is given by

$$V^{\text{gKS}}(\mathbf{r}) = V(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + \underbrace{0.75V_{\text{x}}^{\text{PBE}} + V_{\text{c}}^{\text{PBE}}}_{V_{\text{xc}}^{\text{gKS}}}.$$
(5.3.1)

We assume that this is already a reasonable potential for the generation of the radial functions and do not add any X_{α} contribution.

Using the converged parameters of the HF calculations for C and Si, we examine the performance of the PBE0 functional for these materials. Self-consistency is achieved after 30 - 40 iterations with a Broyden mixing scheme. Selected PBE and PBE0 band energies and experimental values are shown in Tables 5.8 and 5.9.

As anticipated in Section 2.6 the opening of the band gap with respect to the PBE calculation can be observed for both materials. The description of Diamond with the PBE0 functional agrees well with the experimental results. In the case of Silicon the PBE0 functional overestimates the band gap by about the same amount as PBE underestimates it. The results for both materials are in good agreement with the results of Paier et. al [55], who use a larger **k**-point set $(12 \times 12 \times 12)$.

We analyze the influence of the frozen-core approximation for Silicon by describing its 2p electrons with local orbitals. Thus, the 2p electrons are treated as valence electrons and experience the full non-local exchange potential. Here, we must fix the energy parameter for the local orbital. Otherwise small oscillations in the band energies of the 2p electrons prevent convergence. The changes in the band energies

Si	PBE	PBE0		Exp.
$\Gamma_{1v} [\mathrm{eV}]$	-11.98	-13.36		-12.5^{b}
$\Gamma_{15c} [\text{eV}]$	2.54	4.02	3.97^{a}	3.4^{b}
$\Gamma_{2'c} \left[\text{eV} \right]$	3.38	5.13		4.2^{b}
$X_{1c} \left[\text{eV} \right]$	0.69	2.02	1.93^{a}	1.3^{c}
$L_{1c} \left[\text{eV} \right]$	1.53	2.98	2.88^{a}	2.4^{c}
$X_{4v} \to X_{1c} [\text{eV}]$	3.56	5.22		$4.2^{c}-4.5^{b}$
$L_{3'v} \to L_{1c}[eV]$	2.74	4.33		$3.5^{b} - 3.9^{c}$

- a Ref. 55: PAW calculation
- ^b Ref. 58
- c Ref. 59
- Table 5.8: PBE, PBE0 and experimental results for Silicon (gcutm = 4.5, lcutm = 4, number of bands=40 and $4 \times 4 \times 4$ k-point set). Energies are measured with respect to the valence-band maximum.

С	PBE	PE	BE0	Exp
$\Gamma_{1v} [\mathrm{eV}]$	-21.46	-23.51		-24.2^{b}
$\Gamma_{15c} [\text{eV}]$	5.63	7.82	7.69^{a}	7.3^{b}
$\Gamma_{2'c} \left[\text{eV} \right]$	13.33	16.20		15.3^{b}
$X_{1c} \left[\text{eV} \right]$	4.78	6.78	6.66^{a}	
$L_{1c} [\mathrm{eV}]$	8.57	10.98	10.77^{a}	
$X_{4v} \to X_{1c} [\text{eV}]$	11.03	13.62		12.5^{b}
$L_{3'v} \to L_{1c}[eV]$	11.33	14.02		12.5^{b}

 a Ref. 55: PAW calculation

 b Ref. 56

Table 5.9: PBE, PBE0 and experimental band energies for Diamond (gcutm = $4.5 \,\text{Htr}$, lcutm = 4, number of bands=40 and $4 \times 4 \times 4$ k-point set). Energies are measured with respect to the valence-band maximum. between PBE0 calculations with and without local orbitals are in the same order of magnitude as corresponding changes in PBE calculations, where the core wave functions are not fixed. We conclude that the difference is caused by the non-relativistic description of the 2p electrons when local orbitals are employed and that the frozen-core approximation affects the results only very little.

So far systems with inversion symmetry have been calculated. The implementation for systems without inversion symmetry is tested by computing the electronic structure of GaAs at the experimental lattice constant of a = 10.68 a.u. with the PBE0 functional.

The 3*d* electrons of Ga are loosely bound (~ -0.3 Htr) and extend considerably over the MT boundary. Thus, they must be described by local orbitals. Because of the higher atomic number of As its 3*d* electrons are bound more strongly and can be treated as core electrons.

The integrand (4.3.11) of the non-local exchange term for GaAs is shown for the diagonal element $n_1 = n_2 = 10$ with a one dimensional, dense **k**-point set in Figure 5.3. It shows a steep, nearly δ -like behavior close to $q_x = 0$. This behavior is caused by the terms of the form

$$\frac{\langle \phi_{n_1,\mathbf{k}} | \nabla | \phi_{n_2,\mathbf{k}} \rangle}{\epsilon_{n_2,\mathbf{k}} - \epsilon_{n_1,\mathbf{k}}} \tag{5.3.2}$$

in the Γ decomposition. Since the PBE calculation ($l_{\text{max}} = 8$, $g_{\text{max}} = 3.5$) of GaAs yields a semiconductor with a small direct band gap of ~ 0.5eV, the energy denominator in (4.3.8) causes a relative large value at $\mathbf{q} = 0$ for the diagonal element $n_1 = n_2 = 10$. As a result the numerical integration converges badly with the **k**-point sampling. With a $4 \times 4 \times 4$ **k**-point mesh GaAs becomes a metal after the first iteration. Unfortunately, using finer **k**-point meshes increases the computational cost drastically. An alternative is to avoid the evaluation of these terms in the first iteration altogether. Then the band gap opens after the first iteration as it should and as a consequence the integrand becomes smoother and a finer **k**-point mesh is not needed anymore.

This approach is at first applied to a GaAs calculation without local orbitals. Therefore the 3d electrons of Ga are artificially restricted to the MT region, by applying an additional electric field for the calculation of the core states. Consequently also the loosely bound Gallium 3d states possess a nearly vanishing probability on the MT sphere and do not occur in the valence spectrum. The self-consistent results obtained with this approach are shown in Table 5.10.

The treatment of the 3d electrons of Ga with local orbitals causes convergence problems with a Broyden mixing scheme. The band energies of the 3d electrons oscillate which prevents the system to converge. Even with a fixed energy parameter for the local orbitals the calculation does not converge. If one employs a linear



Figure 5.3: Integrand (4.3.11) of GaAs along a line in the BZ from the Γ point to $\frac{2\pi}{a}(0.25, 0, 0)$. The steep increase close to $q_x = 0$ is caused by small denominators in (4.3.8).

GaAs	PBE	PI	BE0	Exp.
$\Gamma_{1c} \left[\text{eV} \right]$	0.56	2.23	2.01^{a}	1.52^{b}
$X_{1c} \left[\text{eV} \right]$	1.48	2.90	2.67^{a}	
$L_{1c} \left[\text{eV} \right]$	1.02	2.58	2.37^{a}	

^a Ref. 55: PAW calculation

^b Ref. 60

Table 5.10: Selected PBE, PBE0 and experimental band energies for GaAs. The PBE0 results are obtained without local orbitals (gcutm = 4.5 Htr, lcutm = 4, number of bands=40 and a $4 \times 4 \times 4$ k-point set). Energies are given with respect to the valence-band maximum.

GaAs	PBE	PBE0	Exp.
$\Gamma_{1c} \left[\text{eV} \right]$	0.56	$2.23 2.01^a$	1.52^{b}
$X_{1c} \left[\mathrm{eV} \right]$	1.48	2.83 2.67^a	
$L_{1c} \left[\text{eV} \right]$	1.02	2.54 2.37^{a}	

 a Ref. 55: PAW calculation

^b Ref. 60

Table 5.11: PBE0 results for GaAs with local orbitals (gcutm = 4.5 Htr, lcutm = 4, number of bands=40 and a $4 \times 4 \times 4$ k-point set). Energies are given with respect to the valence-band maximum.

MgO	PBE	PBE0		Exp.
$\Gamma_{15} [\mathrm{eV}]$	4.84	7.67	7.24^{a}	7.8^{b}
$X_{4'}$ [eV]	9.14	12.01	11.67^{a}	
$L_1 [\mathrm{eV}]$	7.91	10.79	10.38^{a}	

^a Ref. 55: PAW calculation

^b Ref. 61

Table 5.12: PBE0 results for MgO (gcutm = 5.0 Htr, lcutm = 4, number of bands=40 and a $4 \times 4 \times 4$ k-point set). The PBE calculation is performed with the basis parameters $l_{\text{max}} = 8$ and $g_{\text{max}} = 4.1$ Htr. Energies are given with respect to the valence-band maximum.

mixing scheme in analogy to (3.2.32) for the densities with $\alpha = 0.05$ and for the energy parameters, the calculation converges steadily, but very slowly. After 200 iterations a distance in the density of $0.0005 \frac{\text{me}}{\text{Bohr}^3}$ is achieved. A comparison of the calculations with and without local orbitals shows (s. Tables 5.10 and 5.11), that the treatment of the 3*d* electrons with local orbitals affects the excitation energies only very little. The slight discrepancies to the PAW calculations from Ref. 55 is attributed to the use of different **k**-point sets.

After applying the PBE0 implementation to covalently-bound materials with and without inversion symmetry, we calculate the band gap of the ionically bound systems MgO and NaCl. Both materials crystallize in the Rocksalt structure. The calculations are performed at the experimental lattice constants (MgO: a = 7.99 a.u., NaCl: a = 10.87 a.u.). We find, that the opening of the band gap brings it in good agreement to the experimental value (s. Tables 5.12 and 5.13).

In all cases starting from a converged PBE calculation the admixture of exact exchange opens the band gap. It seems, that the PBE0 functional overestimates the band gaps for semiconductors and still underestimates it for large gap insulators,

NaCl	PBE	PBE0	Exp.
$\Gamma_{15} [\mathrm{eV}]$	5.08	7.49 7.26^a	8.5^{b}
$X_{4'}$ [eV]	7.39	9.88 9.66^a	
$L_1 [\mathrm{eV}]$	7.29	9.61 9.41^a	

 a Ref. 55: PAW calculation

^b Ref. 62

Table 5.13: Converged PBE0 results for NaCl with parameters gcutm = 4.0 Htr, lcutm = 4, number of bands=40 and a $4 \times 4 \times 4$ k-point set. The PBE results are obtained with $l_{\text{max}} = 10$ and $g_{\text{max}} = 3.7$ Htr. Energies are given with respect to the valence-band maximum.

where the underestimation is reduced drastically in comparison to a PBE calculation.

5.4 Generation of band structures

KS band structures are usually generated by

- choosing a moderate **k**-point set to converge the calculation
- generating a fine, one dimensional **k**-point mesh, which samples the high symmetry directions ($\Gamma \rightarrow L, X \rightarrow \Gamma$ etc.)
- starting from the converged calculation a single iteration with the fine, one dimensional \mathbf{k} -point set.

This scheme is not practicable for calculations with the non-local exchange potential, since its evaluation at a certain \mathbf{k} point involves the wave functions at all other \mathbf{k} points.

In order to approximate the band structures, we use the $4 \times 4 \times 4$ k-point set, which contains five k points on a line $X \to \Gamma \to L$ and interpolate between them with polynomials. Furthermore, we consider in the interpolation whether the band under consideration possesses extrema at the high symmetry points or not. For this we have oriented on a LDA or GGA band structure of the same material. In the case of band-crossing the energy eigenvalues must be rearranged according to the bands. Otherwise the interpolation does not work.

By applying this scheme the band structures for the above discussed materials along $X \to \Gamma \to L$ are obtained (s. Fig. 5.4, 5.5, 5.6 and 5.7).



Figure 5.4: Band structure of Diamond obtained from a PBE, HF and PBE0 calculation.



Figure 5.5: Band structure of Silicon obtained from a PBE, HF and PBE0 calculation.



Figure 5.6: PBE and PBE0 band structure for MgO.



Figure 5.7: Band structure of NaCl obtained from a PBE and PBE0 calculation.

6 Conclusion & Outlook

In the present work we have implemented the Hartree-Fock-type exchange in the context of density-functional theory (DFT) into the full-potential linearized augmented plane-wave method (FLAPW) [17, 18] as realized in the FLEUR program [19]. This provides the essential basis for the further implementation of hybrid functionals for the exchange-correlation energy of density-functional theory. Hybrid functionals are currently explored as a practical approach to functionals with chemical accuracy for molecules, with improved band gaps in bulk semiconductors and insulators and with an improved description of strongly correlated systems. Several of these functionals have been developed. We have implemented and worked with the PBE0 functional first published by Perdew, Burke and Ernzerhof [10].

The Hartree-Fock-type exchange is non-local in nature. As compared to the local potential which is central to the Kohn-Sham theory, the non-local potential provides a much wider class of potentials to search for the optimal density, but meets the challenge that the implementation into an all-electron method with a numerical basis set for the wave functions is a non-trivial task and the computational cost becomes an issue.

In this thesis we have chosen a mixed basis set for the representation of wave-function products consisting of muffin-tin and interstitial plane-wave functions as explored first by Kotani [53] to describe the non-local exchange with sufficient accuracy and efficiency. In this basis the non-local exchange potential becomes a Brillouin-zone (BZ) sum over vector-matrix-vector products. Due to the long-range nature of the Coulomb interaction the matrix diverges at the Γ -point. Therefore, we separate the divergent term from the non-divergent rest and integrate it analytically. The integration of the remaining non-divergent part is performed with standard techniques. Furthermore, spatial symmetry is exploited to reduce considerably the effort for calculating the exchange term.

The efficiency of the basis set was investigated in detail. It was found that already moderate basis-set parameters of the mixed-basis set are sufficient to obtain converged results. The main parameters are gcutm and lcutm, as they are called in the input file of FLEUR, and specify the reciprocal cutoff radius for the plane waves and the maximal angular-momentum quantum number of the muffin-tin functions, respectively. Further parameters include a tolerance value (mtol) for eliminating linear dependencies from the basis as well as a set of numbers (select) defining from which FLAPW radial functions the mixed basis is to be generated.

It was found that a truncation of the exchange matrix in the space of the wave functions to only 30-40 bands is possible without compromising the accuracy. This reduces the computational effort drastically.

We have applied the non-local exchange in Hartree-Fock and PBE0 calculations to Si, C, GaAs, MgO and NaCl. We found that the opening of the band gap in the first iteration already brings it close to the converged result. However, full selfconsistency of the electron density is achieved only after 40-50 iterations. For the semiconductors the PBE0 functional overestimates the band gap about as much as the semi-local PBE functionals underestimates it. In the case of large-gap insulators the PBE0 functional still slightly underestimates the experimental band gap and is in much better agreement with experiment than the PBE functional.

Due to the enormous computational effort to evaluate the exchange potential compared with DFT calculations employing local or semi-local functionals an efficient and massive parallelization of the program code is desirable and it is indispensable for applications to larger systems. Furthermore, an efficient mixing scheme for density and wave functions (e.g. the direct inversion of iterative space method [63, 64]) might reduce the number of iterations to achieve self-consistence.

Recently, a novel hybrid functional has been published by Heyd, Scuseria and Ernzerhof [65], which is known as the HSE functional. It is based on the PBE0 functional and divides the exact exchange as well as the DFT exchange part in a shortand long-range part. The long-range part of the exact exchange term is replaced by a suitable local density functional. With this, the evaluation of the exchange term in real-space codes or codes, which rely on a local basis set, becomes much faster, because the non-locality of the exchange interaction in space is reduced. On the other hand this partitioning can also be beneficial in a reciprocal-space description, because the short-range exchange potential is not divergent at the Γ point and should therefore converge faster with respect to the number of **k** points [55].

In conclusion with this work the fundament for the implementation of further hybrid functionals (B3LYP, B3PW91, B1B91 etc.) within the FLEUR program has been laid. They are a distinct improvement over local or semi-local exchange-correlation potentials and present a further step on the 'Jacob's ladder' towards the universal functional.



Figure 6.1: Jacob's ladder towards the 'divine' functional.

A Coupling-constant integration for gKS

In analogy to the coupling-constant integration method for the KS system an expression for the exchange-correlation energy of the gKS system can be derived

$$E_{\rm xc}^{\rm gKS}[n] = E[n] - E^{\rm gKS}[n] - (1-a)U[n] + \int d^3r \left[V^{\rm gKS}(\mathbf{r}) - V(\mathbf{r}) \right] n(\mathbf{r}) \,. \quad (A.0.1)$$

The energy difference of the fully interacting system $E\left[n\right]$ and the gKS system $E^{\rm gKS}\left[n\right]$ is written as

$$E[n] - E^{\text{gKS}}[n] = E[n] - E^{\text{KS}}[n] + E^{\text{KS}}[n] - E^{\text{gKS}}[n] .$$
 (A.0.2)

By using the coupling-constant integration expression

$$E[n] - E^{\text{KS}}[n] = \int_0^1 d\lambda \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle + \int d^3 r \left[V(\mathbf{r}) - V^{\text{KS}}(\mathbf{r}) \right] n(\mathbf{r}) \quad (A.0.3)$$

one obtains

$$E_{\rm xc}^{\rm gKS}[n] = \int_0^1 d\lambda \left\langle \Psi_\lambda \left| V_{ee} \right| \Psi_\lambda \right\rangle + E^{\rm KS}[n] - E^{\rm gKS}[n] - (1-a)U[n] + \int d^3r \left[V^{\rm gKS}(\mathbf{r}) - V^{\rm KS}(\mathbf{r}) \right] n(\mathbf{r}) .$$
(A.0.4)

With

$$E^{\text{KS}}[n] = \langle \Phi^{\text{KS}} | T | \Phi^{\text{KS}} \rangle + \int d^3 r \, V^{\text{KS}}(\mathbf{r}) n(\mathbf{r})$$
(A.0.5)

and

$$E^{\text{gKS}}[n] = \left\langle \Phi^{\text{gKS}} | T | \Phi^{\text{gKS}} \right\rangle + \int d^3 r \, V^{\text{gKS}}(\mathbf{r}) n(\mathbf{r}) \tag{A.0.6}$$

we finally get

$$E_{\rm xc}^{\rm gKS}\left[n\right] = \int_{0}^{1} d\lambda E_{{\rm xc},\lambda} - aE_{\rm xc}^{\rm gKS} + \left\langle \Phi^{\rm KS} \mid T \mid \Phi^{\rm KS} \right\rangle - \left\langle \Phi^{\rm gKS} \mid T \mid \Phi^{\rm gKS} \right\rangle \quad (A.0.7)$$

where

$$E_{\mathrm{xc},\lambda} = \langle \Psi_{\lambda} | V_{ee} | \Psi_{\lambda} \rangle - U[n]$$
(A.0.8)

$$E_{\rm xc}^{\rm gKS} = \left\langle \Phi^{\rm gKS} \left| V_{ee} \right| \Phi^{\rm gKS} \right\rangle - U[n] . \qquad (A.0.9)$$

B kp perturbation theory

We apply the non-local gKS equation (4.0.1) to the wave function (4.3.19) and obtain with

$$\begin{bmatrix} -\frac{\nabla^2}{2} + V^{\mathrm{gKS}}(\mathbf{r}) \end{bmatrix} u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) \exp\left[i\mathbf{q}\mathbf{r}\right] - \sum_{n',\mathbf{b}} \int d^3 r' \frac{\phi_{n',\mathbf{b}}^*(\mathbf{r}')u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}') \exp\left[i\mathbf{q}\mathbf{r}'\right]}{|\mathbf{r}-\mathbf{r}'|} \phi_{n',\mathbf{b}}(\mathbf{r})$$

$$= \epsilon_{n,\mathbf{k}+\mathbf{q}}u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) \exp\left[i\mathbf{q}\mathbf{r}\right]$$

$$\Leftrightarrow \quad \exp\left[i\mathbf{q}\mathbf{r}\right] \left[-\frac{\nabla^2}{2} - i\mathbf{q}\nabla + V^{\mathrm{gKS}}(\mathbf{r}) - q^2 \right] u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) - \sum_{n',\mathbf{b}} \int d^3 r' \frac{\phi_{n',\mathbf{b}+\mathbf{q}}^*(\mathbf{r}')u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}') \exp\left[i\mathbf{q}\mathbf{r}'\right]}{|\mathbf{r}-\mathbf{r}'|} \phi_{n',\mathbf{b}+\mathbf{q}}(\mathbf{r})$$

$$= \epsilon_{n,\mathbf{k}+\mathbf{q}}u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) \exp\left[i\mathbf{q}\mathbf{r}\right]$$

$$\Leftrightarrow \quad \left\{ \left[-\frac{\nabla^2}{2} - i\mathbf{q}\nabla + V^{\mathrm{gKS}}(\mathbf{r}) - q^2 \right] u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) - \sum_{n',\mathbf{b}} \int d^3 r' \frac{u_{n',\mathbf{b}+\mathbf{q}}(\mathbf{r}')u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} u_{n',\mathbf{b}+\mathbf{q}}(\mathbf{r}) \right\} \exp\left[i\mathbf{q}\mathbf{r}\right]$$

$$= \epsilon_{n,\mathbf{k}+\mathbf{q}}u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) \left[u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) - \sum_{n',\mathbf{b}} \int d^3 r' \frac{u_{n',\mathbf{b}}^*(\mathbf{r}')u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} u_{n',\mathbf{b}}(\mathbf{r}) + -i\mathbf{q}\nabla u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}) + q^2u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

$$= \epsilon_{n,\mathbf{k}+\mathbf{q}}u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

$$(B.0.1)$$

a differential equation for $u_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r})$. For $\mathbf{q} = 0$ this equation is identical to the gKS equation for $\phi_{n,\mathbf{k}}$. Thus we can treat $\mathbf{q}\mathbf{p} = -i\mathbf{q}\nabla$ as a small perturbation, where the term q^2 can be omitted in first order perturbation theory.

For the non-local potential we get the same relations in first order perturbation theory as for a local potential

$$\sum_{n''} \left\langle u_{n'',\mathbf{k}} | \underline{u}_{n,\mathbf{k}}^{1} \right\rangle \int d^{3}r u_{n',\mathbf{k}}^{*}(\mathbf{r}) \underbrace{\left[\left(-\frac{\nabla^{2}}{2} + V^{\mathrm{gKS}}(\mathbf{r}) \right) u_{n'',\mathbf{k}}(\mathbf{r}) - \sum_{n''',\mathbf{b}} \int d^{3}r' \frac{u_{n'',\mathbf{b}}^{*}(\mathbf{r}') u_{n'',\mathbf{k}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} u_{n''',\mathbf{b}}(\mathbf{r}) \right]}_{\epsilon_{n'',\mathbf{k}} u_{n'',\mathbf{k}}(\mathbf{r})} + \left\langle u_{n',\mathbf{k}} | \underline{u}_{n',\mathbf{k}}^{1} \right\rangle \left\langle u_{n',\mathbf{k}} | u_{n'',\mathbf{k}} \right\rangle + \left\langle u_{n',\mathbf{k}} | W | u_{n,\mathbf{k}} \right\rangle}_{\epsilon_{n'',\mathbf{k}} u_{n'',\mathbf{k}}(\mathbf{r})} = \sum_{n''} \epsilon_{n',\mathbf{k}} \left\langle u_{n',\mathbf{k}} | \underline{u}_{n,\mathbf{k}}^{1} \right\rangle \left\langle u_{n',\mathbf{k}} | u_{n'',\mathbf{k}} \right\rangle + \left\langle u_{n',\mathbf{k}} | W | u_{n,\mathbf{k}} \right\rangle}_{\epsilon_{n'',\mathbf{k}} u_{n',\mathbf{k}}(\mathbf{r})}$$

$$= \epsilon_{n',\mathbf{k}} \left\langle u_{n',\mathbf{k}} | \underline{u}_{n,\mathbf{k}}^{1} \right\rangle + \left\langle u_{n',\mathbf{k}} | W | u_{n,\mathbf{k}} \right\rangle$$

$$= \underline{\epsilon}_{n,\mathbf{k}}^{1} \left\langle u_{n',\mathbf{k}} | u_{n,\mathbf{k}} \right\rangle + \epsilon_{n,\mathbf{k}} \left\langle u_{n',\mathbf{k}} | \underline{u}_{n,\mathbf{k}}^{1} \right\rangle.$$
(B.0.2)

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Selbstständigkeitserklärung

Hiermit versichere ich, die vorliegende Arbeit selbständig und nur unter Zuhilfenahme der angegebenen Quellen und Hilfsmittel angefertigt zu haben.

Jülich im September 2007

Markus Betzinger